



Colloid particle deposition on heterogeneous surfaces produced by polyelectrolyte adsorption

Zbigniew Adamczyk^{a,*}, Anna Bratek^a, Ewa Szeląg^b, Anna Bastrzyk^b, Aneta Michna^a, Jakub Barbasz^a

^a Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Cracow, Poland

^b Wrocław University of Technology, Faculty of Chemical Engineering, ul. Norwida 4/6, 50-373 Wrocław, Poland

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ABSTRACT

The kinetics of polystyrene latex deposition on mica surface covered by mono- and bilayers of polyelectrolytes has been studied using the optical microscopy and the AFM methods. In these investigations the cationic poly(ethylene imine) (PEI) having an averaged molecular weight of 70 kD was used and the anionic poly(acrylic acid) (PAA) having a linear structure and an average molecular weights of 12 and 70 kD. Formation and stability of polyelectrolyte layers on mica was characterized in terms of streaming potential measurements carried out using a parallel-plate channel arrangement. These polyelectrolyte layers have been exploited as substrates of controlled heterogeneity and charge density for deposition of colloid particles. Positively charged polystyrene latex particles having an average size of 450 nm (determined by laser diffractometry, PCS and AFM) were used in these experiments. Latex deposition kinetics was studied under convection-controlled transport conditions using the impinging-jet cell and the optical microscopy method. The AFM method was also used to confirm maximum coverage of latex particles. The dependence of the initial deposition rate of particles on the coverage of PAA in the PEI/PAA bilayer was systematically studied. It was found that the initial deposition rate increased monotonically with the density of the adsorbed polyelectrolyte layer. These experimental results, deviating from the DLVO theory predictions, were successfully interpreted in terms of a theoretical model, which considered charge fluctuations within the adsorbed polyelectrolyte layers. It was concluded that the particle deposition method can be applied as a sensitive tool for quantitatively determining the presence of polyelectrolyte layers on solid surfaces, at a coverage degree inaccessible for other methods.

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1. Introduction

Polyelectrolytes (ionic macromolecules) are widely used in the paper [1,2], food [3,4], and pharmaceutical industries, in ternary oil recovery, in life sciences [5], for gene transfer in molecular medicine [6–8] and so forth. Another important field of polyelectrolyte applications is preparing multilayered films at solid substrates, having a controlled architecture and functionality, which is often realized using the layer-by-layer deposition method [9]. Such films can be used as convenient supports for protein and nanoparticles, which can be embedded into the growing multilayer.

In order to understand physicochemical aspects of the polyelectrolyte multilayer structure, it is essential to learn about the fundamental mechanisms of polyelectrolyte adsorption. However, despite numerous theoretical [10–12] and experimental [13–15] studies devoted to this subject little quantitative data have been collected concerning the influence of the first few layers on the

properties of the entire film. This is mainly due to the lack of sensitive experimental techniques capable of detecting polyelectrolyte layers at low density and determine their local properties, e.g., charge distribution.

In this respect, one of the most sensitive is the streaming potential technique, exploiting channel flows. This method has been successfully applied for detecting the formation of polyelectrolyte mono- and multilayers on mica [16].

The impact of experimental data acquired from electrokinetic measurements can significantly be enhanced by using complementary colloid particle deposition studies. Particle deposition can furnish relevant information on polyelectrolyte adsorption, especially on the local density (coverage) of the film and surface charge distribution [17–19]. In this way, polyelectrolyte coverage in the range of 1% can be detected by applying well-defined particle transport conditions, like the impinging-jet method.

Despite its significance, few systematic studies were performed with the aim of elucidating the mechanism and kinetics of particle deposition on heterogeneous surfaces formed by polyelectrolyte adsorption. Boluk and van de Ven [20] applied the impinging-jet technique to study the deposition kinetics of titanium particles

* Corresponding author. Tel.: +48 12 6395104; fax: +48 12 4251923.

E-mail address: ncadamcz@cyf-kr.edu.pl (Z. Adamczyk).

on cellophane modified by adsorption of cationic polyacrylamide (PAM). The same method was used by van de Ven and Kelemen [21] to study a simultaneous deposition of colloid titanium and adsorption of poly(ethylene imine) on covered glass slides. It was demonstrated that this method can be used as a sensitive tool for detecting the presence of polyelectrolyte (PE) in solution at very low concentrations, in the range of 1 ppm and below. However, no quantitative analysis of the kinetics of this phenomenon was carried out.

Kinetic studies of silica particle deposition on silicon surfaces modified by adsorption of cationic poly(vinylimidazole) (mPVI) were carried out using the optical reflectometry and have been reported in Refs. [22,23]. Mono- and multilayers of polyelectrolyte/silica particles have been produced using the stagnation point flow cell which indicated that particles did not penetrate into the polyelectrolyte layers.

Another interesting work of this type was performed by Kozlova and Santore [24] who produced, in a controlled way, patchy surfaces by adsorbing poly(dimethylaminoethyl methacrylate) (pDMAEMA) on glass slides. Then, the kinetics of silica particle deposition, as a function of polyelectrolyte coverage, was studied systematically, using the direct microscope observation technique. A non-linear dependence of the initial flux on the coverage of polyelectrolyte was found, which was interpreted theoretically in terms of polyelectrolyte density fluctuations.

A similar theoretical approach was used previously to interpret deposition kinetics of polystyrene latex particles on mica modified by adsorption of a monolayer of poly(allylamine chloride), PAH [17] and PEI [18] a cationic polyelectrolyte, which is not only important in industrial applications, but has also extensively been used in various basic studies of the stability of colloid suspensions.

The aim of this work is to characterize in terms of the streaming potential and to the particle deposition methods, the more complicated case of polyelectrolyte bilayer formed by PEI and poly(acrylic acid) (PAA), whose physicochemical characteristics have been precisely determined before. In particular we are interested in determining the applicability of the theoretical model based on the charge fluctuation concept developed before [18].

2. Experimental

2.1. Materials

Natural ruby mica sheets supplied by Continental Trade Ltd., Poland were used as a substrate for polyelectrolyte adsorption. Thin sheets were freshly cleaved and used in experiments without any pre-treatment.

The polyelectrolyte used in our measurements was poly(ethylene imine) of a cationic type. This polymer, having

an average molecular mass of 70,000 and a rather broad size distribution, was purchased from Polysciences, Inc. For sake of convenience, the physicochemical data of PEI are collected in Table 1.

Another polyelectrolyte applied in our studies was the poly(acrylic acid), of an anionic type, having an averaged molecular weight $M_w = 12,000$ (PAA12) and $M_w = 70,000$ (PAA70), kindly supplied of Coatex, France. The stock polymer solution had a concentration of 35% and a density of $1.23 \times 10^3 \text{ kg m}^{-3}$. Other physicochemical characteristics of these PAA samples are presented in Table 1.

Sodium chloride was supplied by Fluka. Ultrapure water (Elix & Simplicity 185 system, Millipore SA Molsheim, France) was used for the preparation of all solutions. PEI solutions of appropriate concentrations were prepared in 10^{-3} or 10^{-2} M NaCl.

Working with solutions of very low polyelectrolyte concentrations requires special care to avoid PEI depletion caused by adsorption at cell and glassware walls. This was achieved by conditioning three times all the glassware in PEI solutions prior to the adsorption step.

A model suspension of polystyrene latex particles was used. The positively charged latex suspensions were synthesized according to the polymerization procedure using the *N,N'*-dimethyl-4,4'-azobis-4-cyano-1-methyl piperidine dinitrate (DACMP·DiN) [25,26] and purified by steam distillation and prolonged ultrafiltration. This latex possesses a spherical shape and low polydispersity. Particle size distribution of samples used in experiments was determined by a laser diffractometer (Particle Size Analyzer LS 13 320 Beckman Coulter) with an accuracy of a few percent. The average size of the latex was equal to $0.46 \mu\text{m}$ with the standard deviation of 40 nm. The zeta potential obtained by microelectrophoresis (Zeta-Pals Brookhaven Instruments) in 10^{-3} M NaCl, pH 5.5 was equal to $\zeta = +50 \text{ mV}$.

2.2. Streaming potential measurements

Streaming potential was determined using a home-made apparatus previously described in detail [16–18]. Due to a hydrostatic pressure gradient ΔP between the in- and outlet compartments, the studied solutions were driven through the parallel-plate channel of dimensions $2b_c \times 2c_c \times L = 0.027 \times 0.29 \times 6.2 \text{ cm}$ (where b_c , c_c , L are the width, the height and the length of the channel) formed by mica sheets separated by a tetrafluoroethylene spacer. Streaming potential was measured for each applied pressure to obtain the slope of the E_s vs. ΔP dependence. Knowing the E_s vs. ΔP dependence one can calculate the apparent zeta potential of the channel using Smoluchowski's formula [16].

Table 1
Physicochemical characteristics of the polyelectrolytes studied.

Property	Sample		
	PAA12	PAA70	PEI70
Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	3.7×10^{-7}	0.98×10^{-7}	4.0×10^{-7}
Molecular weight (kg mol^{-1})	1.2×10^4	7×10^4	7×10^4
Number of monomers, N_m	167	972	603
Volume of molecule (nm^3)	16.2	94.5	111
Bare chain diameter, d_c (nm)	0.71	0.71	–
Extended length, L_{ext} (nm)	41	239	–
Bare cross-section area, S_g (nm^2)	29.0	170	88.2
Hydrated chain diameter d_h (nm)	1.0	1.0	–
Aspect ratio, $L = L_{\text{ext}}/d_h$ (nm)	41	239	–
Hydrodynamic radius, R_h (nm) experimental data	4.8	19.7	5.3
Radius of gyration, R_g (nm)	11.8	69	–
Equivalent sphere radius, R_s (nm)	1.6	2.8	3.0

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