



Adsorption of cationic polyacrylamide at the cellulose–liquid interface: A neutron reflectometry study



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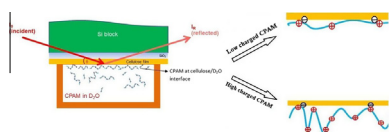
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GRAPHICAL ABSTRACT



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ABSTRACT

The layer thickness and density of high molecular weight cationic polyacrylamide (CPAM) adsorbed at the cellulose–water interface was quantified by neutron reflectometry. The thickness of a full monolayer of CPAM of constant molecular weight (13 MD) but different charge densities, adsorbed with or without NaCl (10^{-3} M), was studied. Thin cellulose films (40 ± 7 Å) of roughness <10 Å were produced by spin coating a cellulose acetate–acetone solution and regenerating by alkaline hydrolysis. Film smoothness was greatly improved by controlling the concentration of cellulose acetate (0.13 wt%) and the hydrolysis time in sodium methoxide. The adsorption thickness of CPAM (40% charge 13 MD) at the solid–D₂O interface was 43 ± 4 Å on cellulose and 13 ± 2 Å on silicon, an order of magnitude smaller than the CPAM radius of gyration. At constant molecular weight, the thickness of the CPAM layer adsorbed on cellulose increases with polymer charge density (10 ± 1 Å at 5%). Addition of 10^{-3} M NaCl decreased the thickness of CPAM layer already adsorbed on cellulose. However, the adsorption layer on cellulose of a CPAM solution equilibrated in 10^{-3} M NaCl is much thicker (89 ± 11 Å for 40% CPAM). For high molecular weight CPAMs adsorbed from solution under constant conditions, the adsorption layer can be varied by 1 order of magnitude via control of the variables affecting electrostatic intra- and inter-polymer chain interactions.

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1. Introduction

Polyelectrolytes are widely used in industrial and research settings to control the stability of colloids and the interaction properties of surfaces. In papermaking, polyelectrolytes are commonly used as retention aids for process colloids (filler and fines) and as

drainage additives. In wastewater treatment, polyelectrolytes coagulate dissolved solids, suspended matter and control the flocculation of sludge; in mining and oil industries, polyelectrolytes improve recovery through selective adsorption. Recent research applications of polyelectrolytes include the retention of enzymes, antibodies and nanoparticles on surfaces for paper bionanotechnology [1,2], the development of functional materials, and control of biomolecule activity [3,4].

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Cationic polyacrylamides copolymers (CPAMs) are among the most commonly used polyelectrolytes and are important for industry, because of their efficiency, low cost and availability in a wide range of polymer compositions and structures. CPAM is commercially available with molecular weight and charge densities up to 15 MD and 100%, respectively. The linear charge density of CPAM is defined as the percentage of monomers bearing a formal charge, typically a quaternary amine. However, in spite of their economic and technological importance, the adsorption behavior of CPAM and the effect of the adsorbed layer morphology on the dynamic stability of colloids are still poorly quantified and understood [5–7], where separate trials are usually needed for each application.

Typically, a polyelectrolyte is adsorbed from solution onto a surface and remains at the liquid–solid interface. The variables affecting the morphology of the adsorbed layer are dictated by the polymer (composition, charge, molecular weight), its affinity for the solvent and surface (Flory–Huggins factor χ), the concentration at which it is adsorbed, solvent properties (temperature, pH, salt concentration and type), surface coverage and kinetics. The theory predicting the basic behavior of polyelectrolytes in solutions and at interfaces is a topic of active research, and can be expressed mathematically as reviewed by Dobrynin and Rubinstein [8] and Fleer et al. [5]; however, the practical behavior is not well characterized. For polyelectrolytes adsorbed at the interface, Dobrynin and Rubinstein [8] identified 2 regimes. At lower surface charge densities, polyelectrolytes adsorb as two-dimensional layers. For this regime, the balance of the electrostatic attraction between the polymer and charged surface and the electrostatic repulsion between the adsorbed chains control the adsorbed morphology. At high surface charge densities, polyelectrolytes adsorb as three dimensional chains with electrostatic attractions governing the phenomenon [8].

Experimental information on the structure and thickness of adsorbed polyelectrolyte layers remains scarce [5]. The structural features of polyelectrolytes adsorbed at the solid–liquid interface have been quantified by ellipsometry, neutron reflectometry, atomic force microscopy and the surface forces apparatus. Three key issues remain poorly understood: (1) the morphology of polymers on surfaces, (2) the link between the morphology of the polymer in solution and at the solid–liquid interface, especially under the kinetically controlled conditions used in industry, and (3) the effect of polymer morphology at the solid–liquid interface and colloid stability/surface functionality. This study focuses on the first issue with a special emphasis on CPAM adsorbed onto cellulosic surfaces. Cellulose is an important surface for paper biondiagnostics in which polyelectrolytes can be used to retain biomolecules (antibodies, enzymes, cell) and nanoparticles used to amplify signal. The CPAM–cellulose interaction also plays an important role in industrial processes such as papermaking, painting and coating.

Lindstrom and Soremark measured the adsorption and surface coverage of CPAM on cellulose fibers under the high shear conditions relevant to papermaking [9]. The variables investigated were CPAM charge density, molecular weight and concentration as well as the ionic strength and temperature of the solution. The quantity of polymer adsorbed on fibers was calculated from the CPAM concentration measured in the supernatant by refractive index. An increase in CPAM molecular weight and charge density was found to decrease the amount of CPAM adsorbed on cellulose fibers [9]. The charge stoichiometry was found to be a governing factor [10]. Wagberg et al. also measured the kinetics of polyelectrolyte adsorption on cellulosic fibers, finding a strong correlation with key polymer properties (MW, charge, concentration) [11].

The hydrodynamic thickness (δ) of cationic polyacrylamides on silica is reported to increase as an increasing amount of polymer is adsorbed (Γ) until a plateau is reached. Small cations

compete with polymer for surface adsorption and decrease both δ and Γ [5,12], which represents the typical behavior of electro-sorption of weakly charged polymer chains. A different behavior was reported for hydrolysed polyacrylamides on cationic polystyrene latex with the amount of polymer adsorbed and its layer thickness both increasing with the ionic strength of the solution [13]. This was apparently due to non-electrostatic affinity of the polymer for the surface [5,13], in contrast to the observation that electrolytes strongly affect electrostatically-driven CPAM adsorption [6,7,14–16]. Shubin and Linse reported yet a different behavior for the adsorption of CPAM on silica in which Γ and δ both decreased as a function of the electrolyte concentration. Moreover, Γ was a function of the type of cation, while δ was mostly independent of this [16]. This was explained by the change in the ratio of adsorbed polymer trains–ends and loops. By competing for the surface, the cations dislodged or prevented trains of polymer from effectively adsorbing on the surface, resulting in a lower adsorbed amount but an increased layer thickness. Solberg and Wagberg reported a similar behavior for the adsorption of CPAM on silica as a function of NaCl concentration using ellipsometry [17].

These previous studies highlight the complex and poorly understood effect of surface chemistry, polymer charge, molecular weight and concentration as well as salt concentration on the morphology of adsorbed polymer. Little is known about the effect of the surface crystallinity, swelling and porosity on the adsorption morphology of polyelectrolyte. Cellulose is the ideal surface to investigate these important variables.

It is the objective of this study to quantify the layer thickness of high molecular weight cationic polyacrylamide (CPAM) adsorbed at the cellulose–water interface using a well-defined system. The thickness of CPAM of different charge densities, but constant molecular weight (13MD) adsorbed with or without NaCl (10^{-3} M), was measured by neutron reflectometry on smooth cellulose films under conditions of full surface coverage. Smooth cellulose films were prepared by spin coating either a nanocellulose crystal suspension or a cellulose acetate solution subsequently regenerated into cellulose by alkaline hydrolysis. The cellulose films were fully characterized and their smoothness and chemical homogeneity were optimized for neutron reflectometry characterization of their interfaces. In this study, we aim at quantifying how the interaction between cellulose and CPAM can affect the adsorbed polymer morphology, with a view to better understanding the surface interactions involved.

2. Experimental section

2.1. Materials

Cellulose acetate ($M_n \sim 29,000$, acetyl groups substitution $\sim 40\%$), sodium methoxide (purum, $\geq 97.0\%$), methanol (anhydrous, 99.8%) and sodium chloride were purchased from Sigma–Aldrich. Cellulose nanocrystals were graciously provided by U.S. Department of Agriculture in dry powder form. The cationic polyacrylamides (CPAMs) were kindly supplied by AQUA + TECH (Switzerland) and used as received. The specific polymer formulations were copolymers of uncharged acrylamide with cationic dimethylaminoethylacrylate methyl chloride (Table 1 and Fig. 1a). The charge of CPAM was determined by polyelectrolyte titration from sodium poly(ethylenesulfonate) (Pes-Na, 0.001 N, BTG Australia). Polished silicon blocks (50.8 mm diameter, 12 mm and 0.5 mm height, n-type Si:P, [100], El-Cat, Inc. US.) were cleaned for 20 min by UV ozonolysis (UVO cleaner[®], model 144AX), and used as substrates for spin coating.

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