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POLYELECTROLYTE MONOLAYERS FOR BIOACTIVE SURFACES

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INTRODUCTION: Polyelectrolyte brushes are promising candidates for the generation of surfaces with specific biocompatibility requirements, such as to template and coordinate protein or cell adhesion. In these biological systems, a mix of monovalent and multivalent ions is necessary for their proper function. The presence of these ions, however, also modifies the polyelctrolyte brush structure, which in turn modifies its function. The current challenge is to quantify the influence of the complex aqueous environment on the swelling behavior of charged, water-soluble brushes.

METHODS: Poly(methacrylic acid) (PMAA) brushes were synthesized via the "grafting from" technique as described in the literature.[1]

The swelling behavior of these brushes was investigated by multiple angle nulling ellipsometry and the volume fraction profiles were modelled by using a complementary error function.[2]

RESULTS: We report on the swelling behavior of PMAA brushes in contact with aqueous solutions of monovalent, bivalent and trivalent counterions at neutral pH. A fundamentally different behavior was found for the three types of ions. **Figure. 1** shows the evolution of the brush thickness with increasing ionic strength for each of the sodium, calcium and aluminum nitrate solutions.

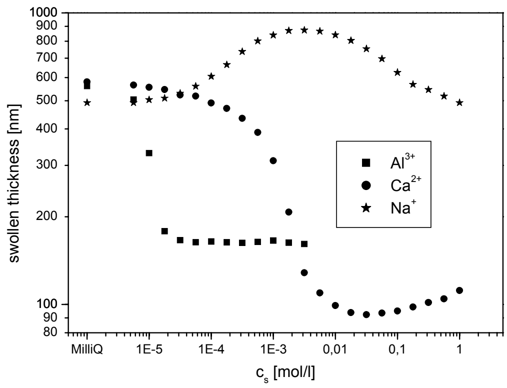

Fig. 1: Swollen thickness of PMAA brushes as a function of the external salt concentration. The respective dry thicknesses were 42 nm (star), 45 nm (circle) and 46 nm (square).

The brush thickness passes through a maximum only for the monovalent sodium ion. With respect to the bivalent alkaline earth metal, calcium, we find that the brush collapses at intermediate concentrations (around 10^{-3} mol/l) and exhibits no maximum in brush thickness. Lastly, PMAA brushes in contact with aluminum solutions show a behavior similar to the calcium case; however, the collapse concentration is found to be lower by roughly 2 orders of magnitude and the collapse already starts at concentrations $<10^{-5}$ mol/l.

DISCUSSION & CONCLUSIONS: Theoretical studies based on ionic interactions alone show that the brush will display a maximum in its thickness with increasing ionic strength. This behavior is predicted for both monovalent and multivalent ions. In contrast to theory[3] we only find such a situation for monovalent ions. The lack of such behavior for the bivalent calcium and trivalent aluminum counterions leads us to believe that ionic interactions alone do not govern the brush structure. Indeed, there have been experimental investigations on the interaction of weak polyacids in different topologies with multivalent cations in the literature that support our findings.[4-6]

We conclude that the swelling behavior of weak polyacid brushes is indeed very sensitive to the presence of bivalent and trivalent cations and that specific interactions must be taken into account. Therefore, as a basis for a predictable engineering of interface properties in biological environments it is crucial to understand the relationship between the structure of weak polyacid brushes and their specific environment.

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