

## P10 – Single Molecule Force Measurements Delineate Co-Solute and Interfacial Effects on Biopolymer Adhesion

Tobias Pirzer

Zentralinstitut fuer Medizintechnik IMETUM  
Boltzmannstr. 11, D-85748 Garching  
Email: pirzer@tum.de  
Tel.: +49 89 289-16783

The adhesion of polypeptides and proteins onto interfaces is important for a wide variety of systems from the adhesion onto vessels during their production process over functional coatings to protein-membrane interactions in single cells. We use an atomic force microscopy based single molecule method and various biopolymers to determine the adhesion strength [1,2] and the location of polypeptides at interfaces.

We observe a linear dependence of the adhesion force on the concentration of three selected salts and a Hofmeister series both for anions and cations [3]. Surprisingly, the support (solid, liquid or gas) does hardly influence the adhesion in aqueous environment. These findings allow us to propose the location of the biopolymer at the interface and a compensation mechanism between dispersive and hydration forces.

Publications:

[1] M. Geisler, T. Pirzer, C. Ackerschott, S. Lud, J. Garrido, T. Scheibel, T. Hugel, *Langmuir*, 24, 1350 (2008)


Influence of Hofmeister Salts on the adhesion of spider silk proteins onto hydrophobic substrates: an AFM-based single molecule study

[2] D. Horinek, A. Serr, M. Geisler, T. Pirzer, U. Slotta, S. Q. Lud, J. A. Garrido, T. Scheibel, T. Hugel, R. R. Netz, *PNAS*, 105, 2842 (2008)

Peptide adsorption on a hydrophobic surface results from an interplay of solvation, surface, and intrapeptide forces

[3] T. Pirzer, M. Geisler, T. Scheibel, T. Hugel, *Phys. Biol.*, 6, 025004 (2009)

Single molecule force measurements delineate salt, pH and surface effects on biopolymer adhesion




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## Single molecule force measurements delineate co-solute and interfacial affects on biopolymer adhesion

Tobias Pirzer and Thorsten Hugel

Physics Department, IMETUM, CeNS and CIPSM, TU München, Garching, Germany  
Email: Pirzer@tum.de



Physik  
Department



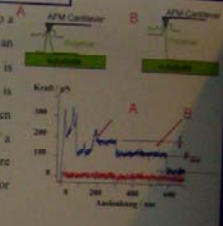
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### Introduction

The adhesion of polypeptides and proteins onto interfaces is important for a wide variety of systems from the adhesion onto vessels during their production process over functional coatings to protein-membrane interactions in single cells. We use an atomic force microscopy based single molecule method and various biopolymers to determine the adhesion strength [1,2] and the location of polypeptides at interfaces. We observe a linear dependence of the adhesion force on the concentration of three selected salts and a Hofmeister series [3]. Surprisingly, the support (solid, liquid or gas) does hardly influence the adhesion in aqueous environment. These findings allow us to propose the location of the biopolymer at the interface and a compensation mechanism between dispersive and hydration forces [4].

### Method

Few polymers are covalently attached onto a cantilever and brought into contact with an interface (red trace). Then the cantilever is retracted and the desorption force is measured (blue trace). The distance between the two plateaus is the desorption force of a single polymer ( $F_{des}$ ). The plateaus are loading rate independent (steady-state) for the typical loading rates of an AFM [2].



### Results

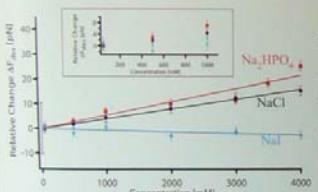


Figure 1 shows this relative change of the desorption force of spider silk protein; it is normalized to zero force in pure water. A clear linear dependence is observed with slopes that are qualitatively consistent with the concentration dependent Hofmeister series. Each salt series itself was carried out with one and the same cantilever, and the relative error within one salt has therefore a uncertainty of only 2% [3].

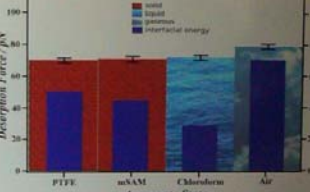


Figure 2 shows the desorption forces of poly-D-tyrosine on various hydrophobic interfaces in water. All interfaces are stable and the components do not mix. It clearly demonstrates that the desorption forces (pictured bars) do not follow the trend of the interfacial energy of the used interfaces (dark blue bars). Even the aggregate state of the components has only little effect on the desorption force [4].

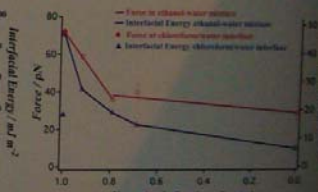
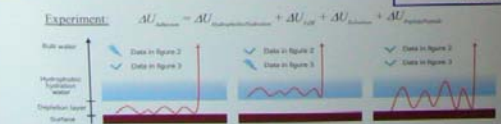


Figure 3 shows the desorption force on a hydrophobic mSAM again for poly-D-tyrosin, but this time in dependence on the mole fraction of water in ethanol (open circles). When 20% of water is replaced by ethanol the desorption force already decrease to about 30% of the initial value. We added the desorption force at the chloroform/water interface, with its interfacial energy of 28 mJ/m<sup>2</sup> (solid circle and solid triangle for the force and interfacial energy, respectively) [4].

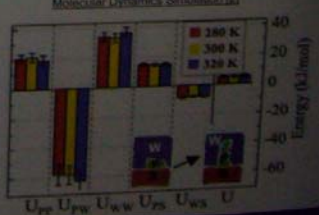
### Discussion

**Experiment:**  $\Delta U_{des} = \Delta U_{interfacial} + \Delta U_{des} + \Delta U_{hydration} + \Delta U_{dispersion}$



- $\Delta U_{interfacial} = const.$  &  $\Delta U_{des} = const.$ , but  $\Delta U_{des}$  depends on substrate
- The hydrophobic hydration layer acts like a mask  $\Rightarrow \Delta U_{interfacial}, \Delta U_{des}$  are const. With ethanol poly-D-tyrosin is less soluble and the amount of hydrophobic hydration water decreases
- Compensation mechanism: water-structure effects and dispersive interactions give contributions of comparable magnitude that largely cancel out [2,3].

### Molecular Dynamics Simulation [2]



Energy components:  $U_{PP}, U_{PW}, U_{WW}, U_{PS}, U_{WS}, U$

### Summary

- Salt can influence the adhesion of single polypeptides, but only at non physiol. conditions
- There's no influence of completely different surfaces/interfaces  $\rightarrow$  elasticity, density & even aggregate state: no influence
- Hydration water is essential for high adhesion forces  $\rightarrow$  Hydrophobic Effect
- Only a compensation mechanism can explain the data
- Polypeptides are located at both the (solid) support and the hydration water

### References

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- T. Pirzer et al., *Advances in Protein Chemistry and Structural Biology*, 2008, 78, 1-15