Comprehensive Control of Molecular Self-Assembly at the Calcite(10.4)-Water Interface

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Water-soluble, organic molecules at the mineral-water interface are known to exhibit a decisive influence on additive-controlled crystallization processes like, for example, dissolution, growth, surface restructuring, mineral replacement and molecular self-assembly [1].

In-situ atomic force microscopy (AFM) has proven to provide high-resolution insights into the interfacial morphology, especially for imaging mineral surfaces [2] as well as the self-assembly of organic molecules in liquid environments [3, 4].

Here, we study the interaction of the azo dye Benzopurpurine (BPP) with the calcite(10.4) surface using *in-situ* high-resolution AFM. We find that BPP forms well-ordered structures wetting the calcite(10.4) substrate. Additionally, BPP induces a restructuring of the surface morphology during calcite dissolution. For the first time we will show and discuss in detail how controlling parameters such as the initial pH, the initial BPP concentration and the initial concentration of calcium ions significantly affects the coverage of BPP molecules. In addition, the quantitative analysis of the coverage for different initial BPP concentration allows us for calculating a pseudo-equilibrium constant for the adsorption of BPP from solution on the calcite(10.4.) surface. Moreover, we illustrate how to steer the nucleation and growth process of the molecular structures by varying the initial pH and the initial concentration of calcium ions including the complete inhibition under well-defined condition.

Our findings demonstrate the capability of a comprehensive control of molecular self-assembly at the calcite(10.4)-water interface and therefore, enable qualitative and quantitative molecular-scale insights on the adsorption behavior of organic molecules onto mineral surfaces in aqueous solution.

[1] Song *et al*. (2011) *CrystEngComm* **13**, 1249-1276. [2] Rode *et al*. (2009) *Langmuir* **25**, 2850-2853. [3] Momper *et al*. (2015) *Langmuir* **31**, 7283-7287. [4] Nalbach *et al*. (2016) *Langmuir* **32**, 9975-9981.