Supporting Information for

Surface charge density and diffuse layer properties of highly-defined 2:1 layered silicate platelets

Volodymyr Kuznetsov[a#], Katharina Ottermann[a#], Nicolas Helfricht[a,b], Daniel Kunz[c], Patrick Loch[c], Hussein Kalo[c], Josef Breu[b,c]*, Georg Papastavrou[a,b]*

[a] Physical Chemistry II, University of Bayreuth, Universitätsstr. 30, 95440, Bayreuth, Germany

[b] Bavarian Polymer Institute, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

[c] Inorganic Chemistry I, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

# both authors contributed equally

* Corresponding authors: Josef.Breu@uni-bayreuth.de, Georg.Papastavrou@uni-bayreuth.de

Quantitative Evaluation of Interaction Force Profiles

The interaction forces have been quantitatively evaluated by means of full solutions to the Poisson-Boltzmann equation including charge regulation. [1, 2]

Generally, charge regulation falls between the boundary conditions of constant charge (CC) and constant potential (CP). Here, charge regulation has been implemented by means of the constant regulation approximation (CR) where the surface chemistry is summarized by means of the so-called regulation parameter p defined by:

$$p = \frac{C^D}{C^I + C^D}$$

where C^D is the diffuse layer capacitance and C^I is the inner layer capacitance, respectively.[3-6]

The boundary conditions of constant charge and constant potential correspond to p = 1 and p = 0, respectively. However, charge regulation has only to be taken into account for separation distances smaller than the Debye-length κ^{-1}. This parameter is defined by

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2 N_A e^2 I}}$$

where $\varepsilon\varepsilon_0$ is the total permittivity, $k_B T$ is the thermal energy, N_A is the Avogadro's number, e is the elementary charge and I is the total ionic strength of the electrolyte solution, respectively. [1, 2]

Here, fits have been performed for separation distances $\kappa^{-1} < D < 5\,\kappa^{-1}$, thus the regulation parameter has not a significant influence on the diffuse layer potentials as obtained from the fits. The regulation parameter for the silica colloidal probe has been determined in a symmetric set of experiments in the sphere-sphere geometry between two silica particles.

The diffuse layer charge density σ, which is not directly related to interlayer charge, is given by the so-called Grahame equation

$$\sigma = \sqrt{8c_0 \varepsilon\varepsilon_0 k_B T} \sinh\left(\frac{e\psi_0}{2k_B T}\right)$$

where c_0 is the electrolyte concentration and ψ_0 is the surface potential, respectively.[1, 2]

References

1. Israelachvili JN Intermolecular and surface forces, 8 ed. Academic Press Limited, London

2. Butt H-J, Graf K, Kappl M (2003) Physics and Chemistry of Interfaces. Wiley-VCH Verlag

3. Pericet-Camara R, Papastavrou G, Behrens SH, Borkovec M (2004) Interaction between Charged Surfaces on the Poisson–Boltzmann Level: The Constant Regulation Approximation. J Phys Chem B 108:19467–19475. doi: 10.1021/jp0473063

4. Rentsch S, Siegenthaler H, Papastavrou G (2007) Diffuse Layer Properties of Thiol-Modified Gold Electrodes Probed by Direct Force Measurements. Langmuir 23:9083–9091. doi: 10.1021/la700987u

5. Kuznetsov V, Papastavrou G (2014) Ion Adsorption on Modified Electrodes as Determined by Direct Force Measurements under Potentiostatic Control. J Phys Chem C 118:2673–2685. doi: 10.1021/jp500425g

6. Helfricht N, Mark A, Dorwling-Carter L, et al (2017) Extending the limits of direct force measurements: colloidal probes from sub-micron particles. Nanoscale 9:9491–9501. doi: 10.1039/C7NR02226C