Stepwise collapse of highly overlapping electrical double layers

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Supplementary information

In our experiments, the K^+ / H_3O^+ surface excess balance is tuned by varying the pH of the solution in the range $3.3 - 9.69$, while the co-ionic strength is maintained constant by adding either HNO_3 or KOH under concurrent reduction of KNO_3. Since it has been observed that the proton has a 1000 fold higher probability to occupy the mica surface site as compared to alkali metal ions due to its ability to penetrate the space between the three oxygen atoms of the Si-O tetrahedron [1, 2], H_3O^+ is essentially the surface potential determining ion. The mass action equation of the surface is then given by:

$$SH \overset{K_d}{\rightleftharpoons} S^- + H^+ \qquad (1)$$

where SH is the concentration of the neutralized sites on the mica surface, S^- is the concentration of the negative surface sites available for ion exchange and H^+ is the concentration of the protons, where K_d is surface dissociation constant. The surface charge, σ, can be determined from the dissociation constant, the surface potential ψ_0 and the pH according to [3] :

$$\sigma = \alpha\sigma_0 = \frac{K_d}{K_d + [HNO_3]_\infty \, e^{-\psi_0/25.7}}\sigma_0 \qquad (2)$$

The surface charge of mica σ_0 is independent of bulk pH and it remains constant [4, 5]. The Grahame equation relates surface charge and surface potential at a single surface as a function of the electrolyte concentration:

$$\sigma = 0.117\sinh\left(\frac{\psi_0}{51.4}\right)\sqrt{[KNO_3]_\infty + [HNO_3]_\infty} \qquad (3)$$

Thus, knowing that the maximum surface charge density of mica σ_0 is 1 charge per 47 A^2 (i.e. 0.33 C/m^2 [6]) and the surface dissociation constant, which remains constant with pH, is 10^{-2} M (since the pK of mica is approximately 2 and the K_d can be directly related to the pK), we obtain the surface potential ψ_0 and the surface coverage α. The contact values of K^+ at the surface can finally be estimated from the Boltzmann distribution of ions near a charged surface in electrolyte solutions as

$$\left[K^+ \right]_0 = \left[K^+ \right]_\infty e^{-e\psi_0/kT} \tag{4}$$

We can use this contact value to display the π-transition in terms of interfacial K^+ ion concentration in Figure 6.
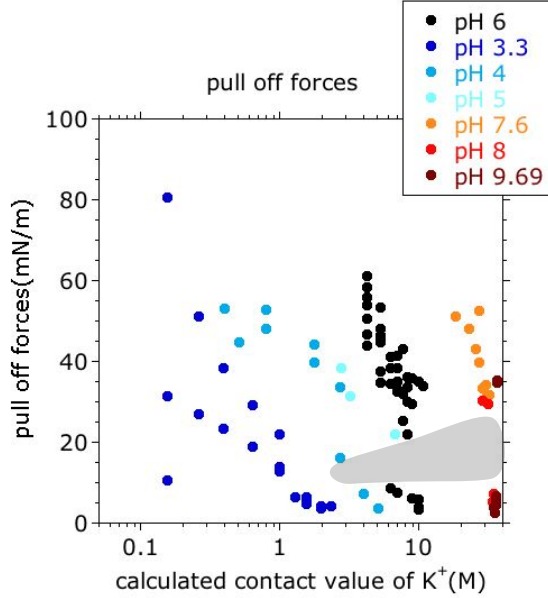

Figure S1. *Measured pull-off forces as a function of the contact values of K^+ calculated from Graham's equation for a single surface for different pH values. For the reader's convenience, the striped area highlights absence of measured points, which is characteristic for the π-transition.*

The effect of pH on the critical interface concentration for K^+ is shown in Figure S1, with the limitation, of course, that the calculated contact values of K^+ are for a single surface. The striped region highlights the area of inexistent data points, which marks the location of the π-instability. The critical interfacial K^+ concentration at the π-instability is strongly dependent on pH. At the lowest investigated pH-values (pH 3.3), the contact value of K^+ remains so low that there are no clear traces of a π-instability. The gray area in Figure 1S indicates that the π-instability first occurs at a critical K^+ contact value somewhere around 3±1M; this is when layering forces start to play a role.

Note that although the above equations are only valid for single surfaces, Pashley found a good agreement between measured force-distance curves and DLVO prediction with constant charge regulation as boundary condition, assuming the dissociation constants for single surfaces [7]. Thus, although better models are needed, this points out that surface population equilibria alone cannot explain the abrupt nature of the observed Π-instability.

References

1. Pashley, R.M., *Hydration Forces between Mica Surfaces in Aqueous-Electrolyte Solutions.* Journal of Colloid and Interface Science, 1981. **80**(1): p. 153-162.
2. Quirk, J.P. and R.M. Pashley, *The Nature of Contact in Measuring the Forces between Muscovite Surfaces.* Journal of Physical Chemistry, 1991. **95**(8): p. 3300-3301.
3. Israelachvili, J.N., *Intermolecular and Surface Forces, 3rd Edition.* Intermolecular and Surface Forces, 3rd Edition, 2011: p. 1-674.
4. Lee, S.S., et al., *Monovalent Ion Adsorption at the Muscovite (001)-Solution Interface: Relationships among Ion Coverage and Speciation, Interfacial Water Structure, and Substrate Relaxation.* Langmuir, 2012. **28**(23): p. 8637-8650.
5. Bowers, G.M., D.L. Bish, and R.J. Kirkpatrick, *Cation exchange at the mineral-water interface: H3O+/K+ competition at the surface of nano-muscovite.* Langmuir, 2008. **24**(18): p. 10240-10244.
6. Schlegel, M.L., et al., *Cation sorption on the muscovite (001) surface in chloride solutions using high-resolution X-ray reflectivity.* Geochimica Et Cosmochimica Acta, 2006. **70**(14): p. 3549-3565.
7. Pashley, R.M., *DLVO and hydration forces between mica surfaces in Li+, Na+, K+, and Cs+ electrolyte solutions: A correlation of double-layer and hydration forces with surface cation exchange properties.* Journal of Colloid and Interface Science, 1981. **83**(2): p. 531-546.