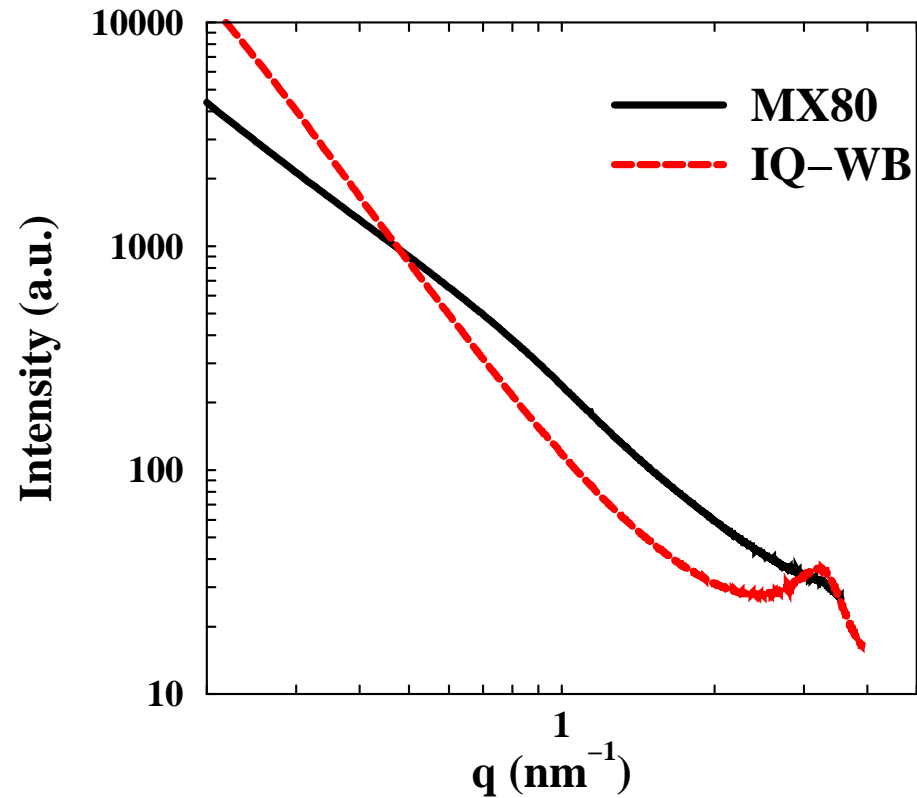


SAXS and Monte Carlo Studies of Montmorillonite in Mixed Salt Solution

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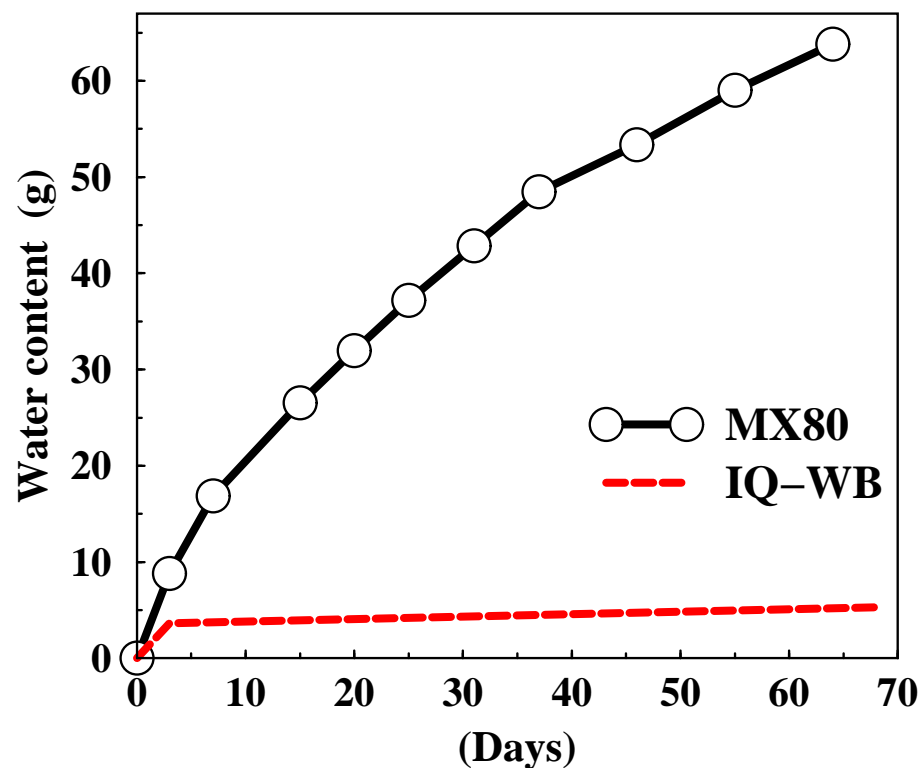
Two Natural Clays - MX80 and IR-WB



SAXS spectra with a peak indicating tactoid formation. MX80 is dominated by Na⁺ counterions while the Iraqi bentonite is dominated by Ca⁺² ions.

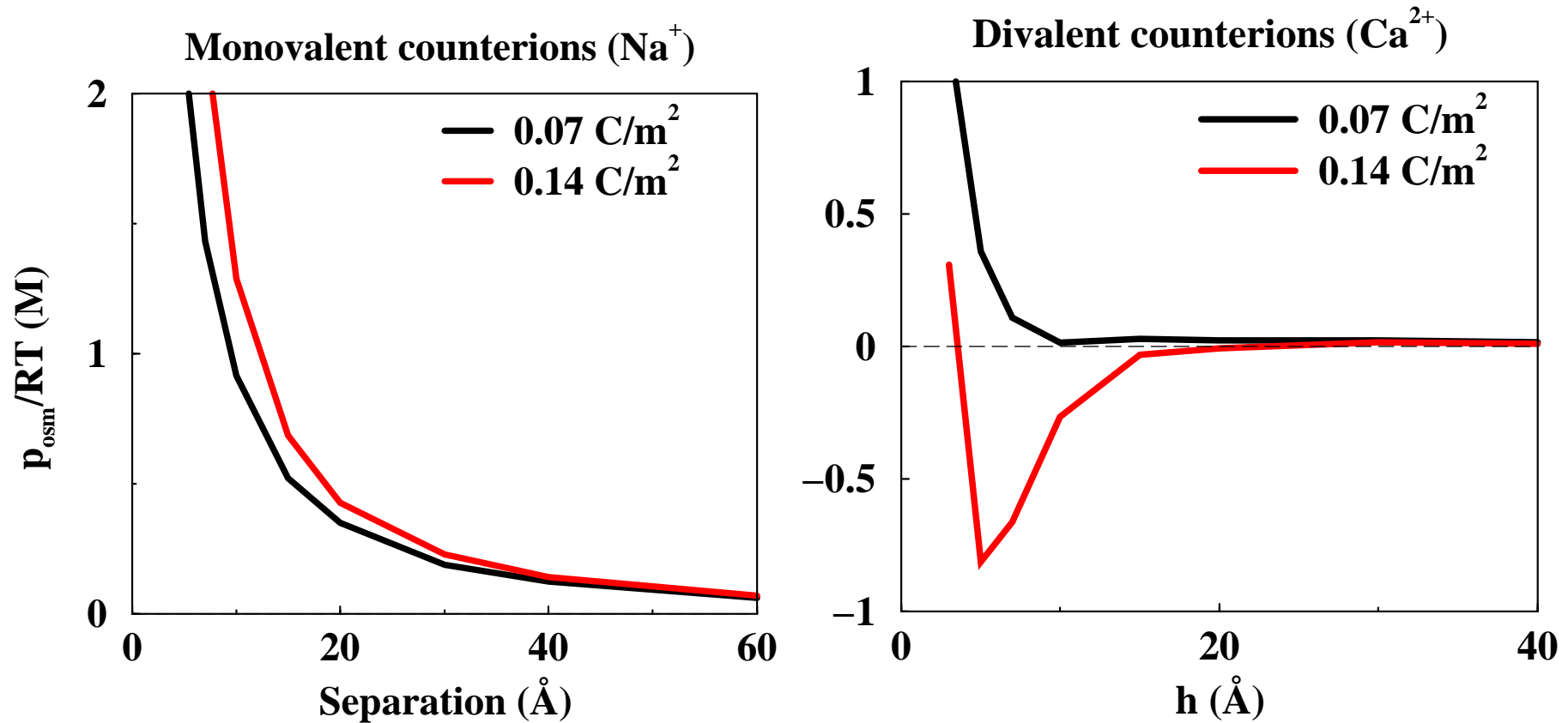
Swelling of MX80 and IR-WB

(b)



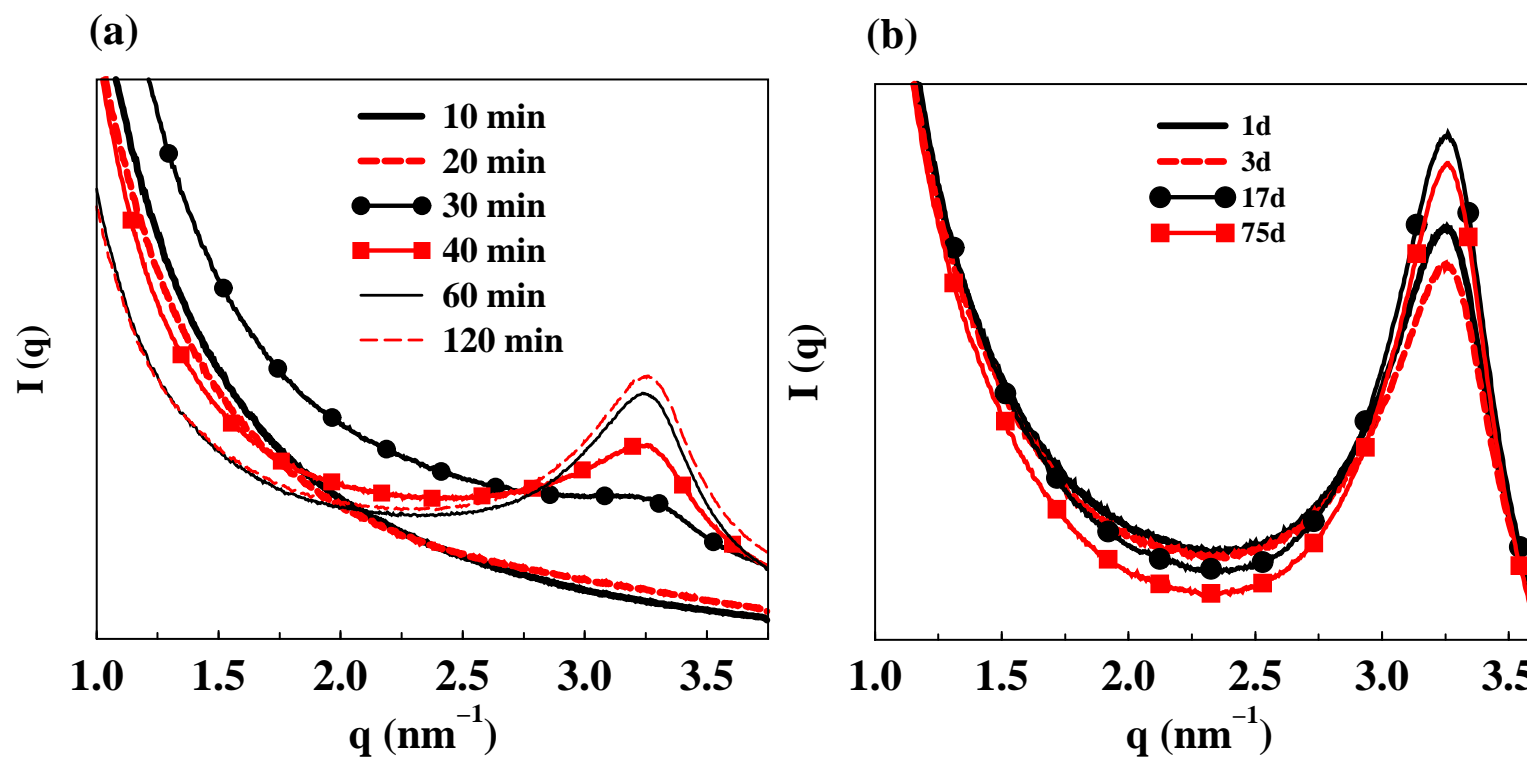
MX80 shows a much larger swelling due to monovalent Na^+ counterions. Note that the Iraqi clay swells much more than the intralamellar swelling of the tactoids.

Ion-Ion Correlations



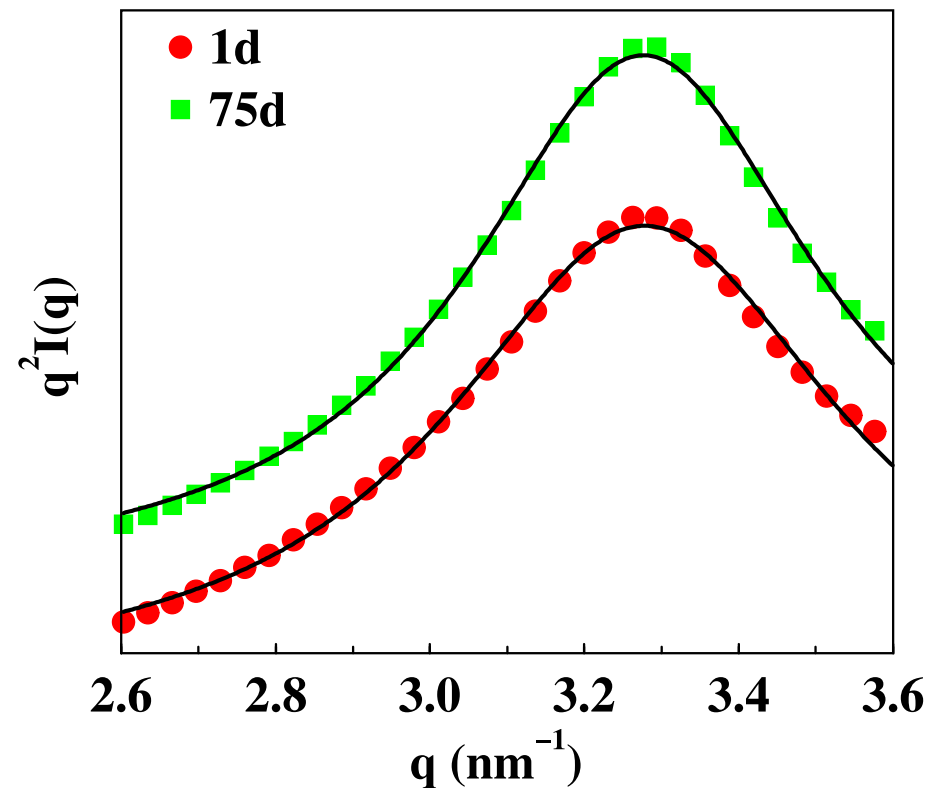
Attraction at increased surface charge and divalent counterions.

Tactoid Kinetics

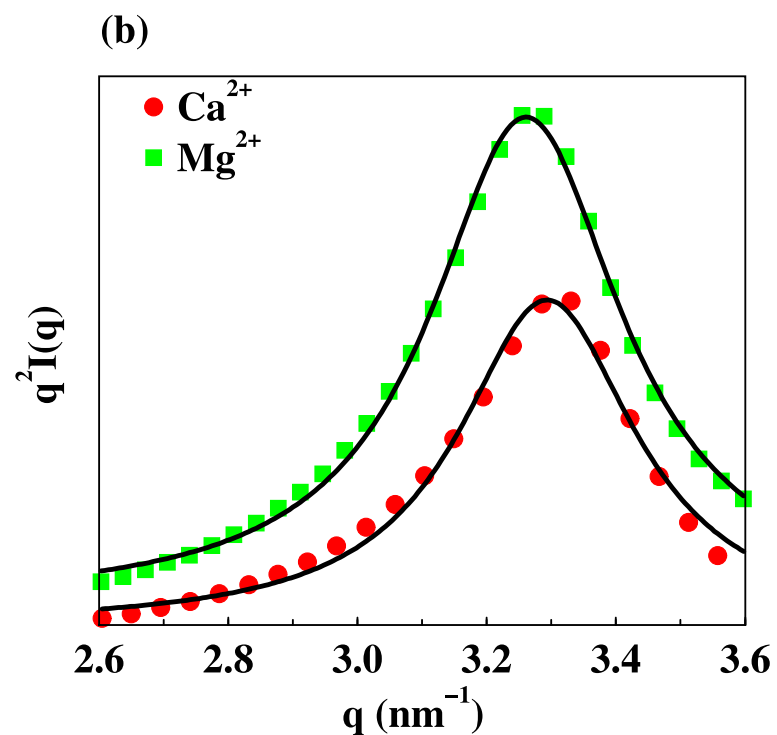


SAXS spectra from Na montmorillonite dispersions equilibrated with a 5 mM CaCl₂ solution for increasing time intervals indicated in the graphs. Note the peak appearing after 30 minutes of cation exchange.

Tactoid Size

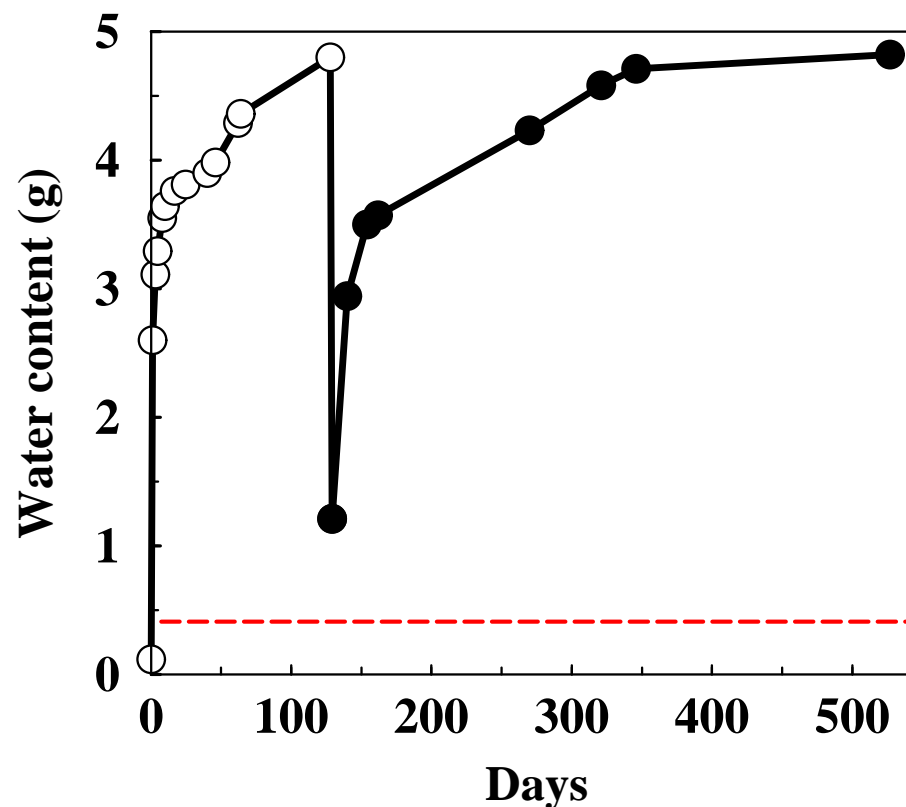


SAXS spectra from Na montmorillonite dispersions equilibrated in a dialysis pocket with 5 mM CaCl_2 . After one day (red circles) the fitting procedure gives $\langle N \rangle \simeq 10$ and after 75 days (green squares) $\langle N \rangle \simeq 12$.

Mg^{2+} or Ca^{2+} 

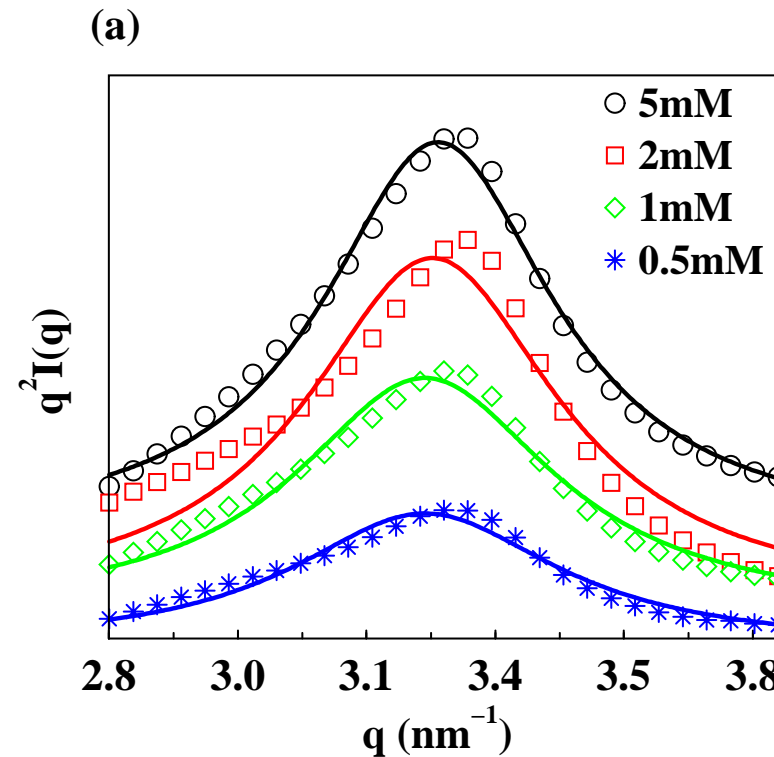
Dispersions of Ca and Mg montmorillonite have been equilibrated in a dialysis pocket during three months. The average numbers of platelets per tactoid, calculated from the SAXS peak widths, are $\langle N \rangle = 19$ (Ca) and $\langle N \rangle = 18$ (Mg).

Swelling Reversibility



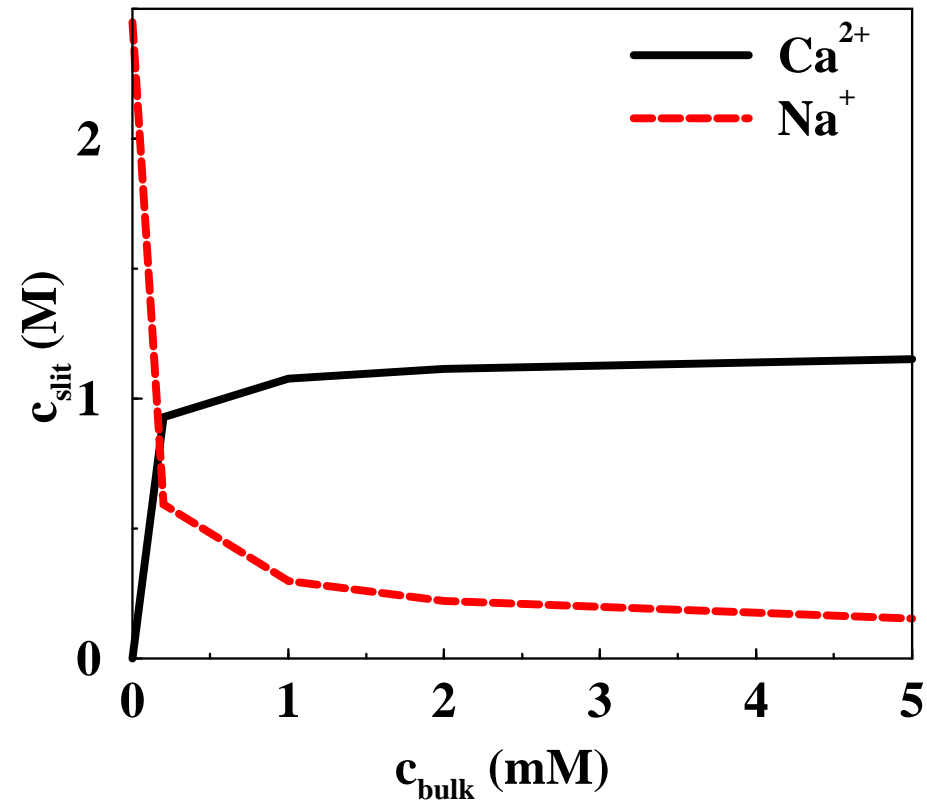
Dry Ca montmorillonite was placed in a dialysis pocket and immersed in millipore water. After 128 days the pocket was immersed for one day in a 16% wt solution of poly(ethylene glycol). Second swelling (closed circles): the pocket was immersed again in millipore water. The dashed line indicates the repeat distance to 1.9 nm.

Counterion Competition



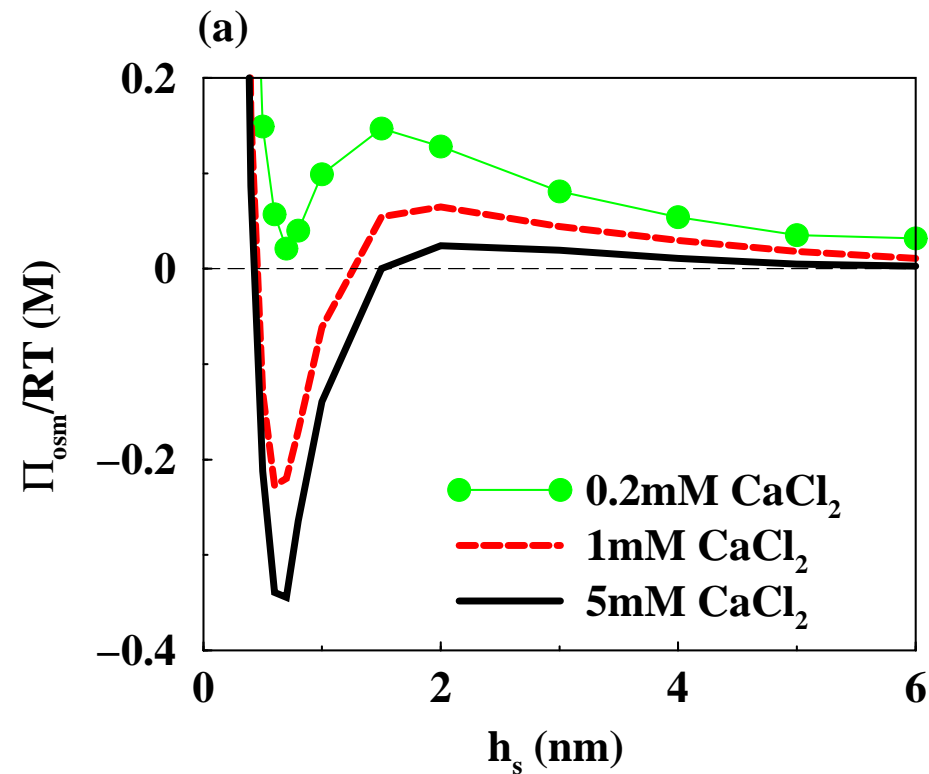
The NaCl concentration is kept fixed at 20 mM, while the CaCl_2 concentration is varied. Dispersions of MX-80 have been equilibrated in a dialysis pocket during three months. The tactoid size is from top to bottom 14.1, 13.4, 13.0 and 12.4.

Competition - Simulation Results



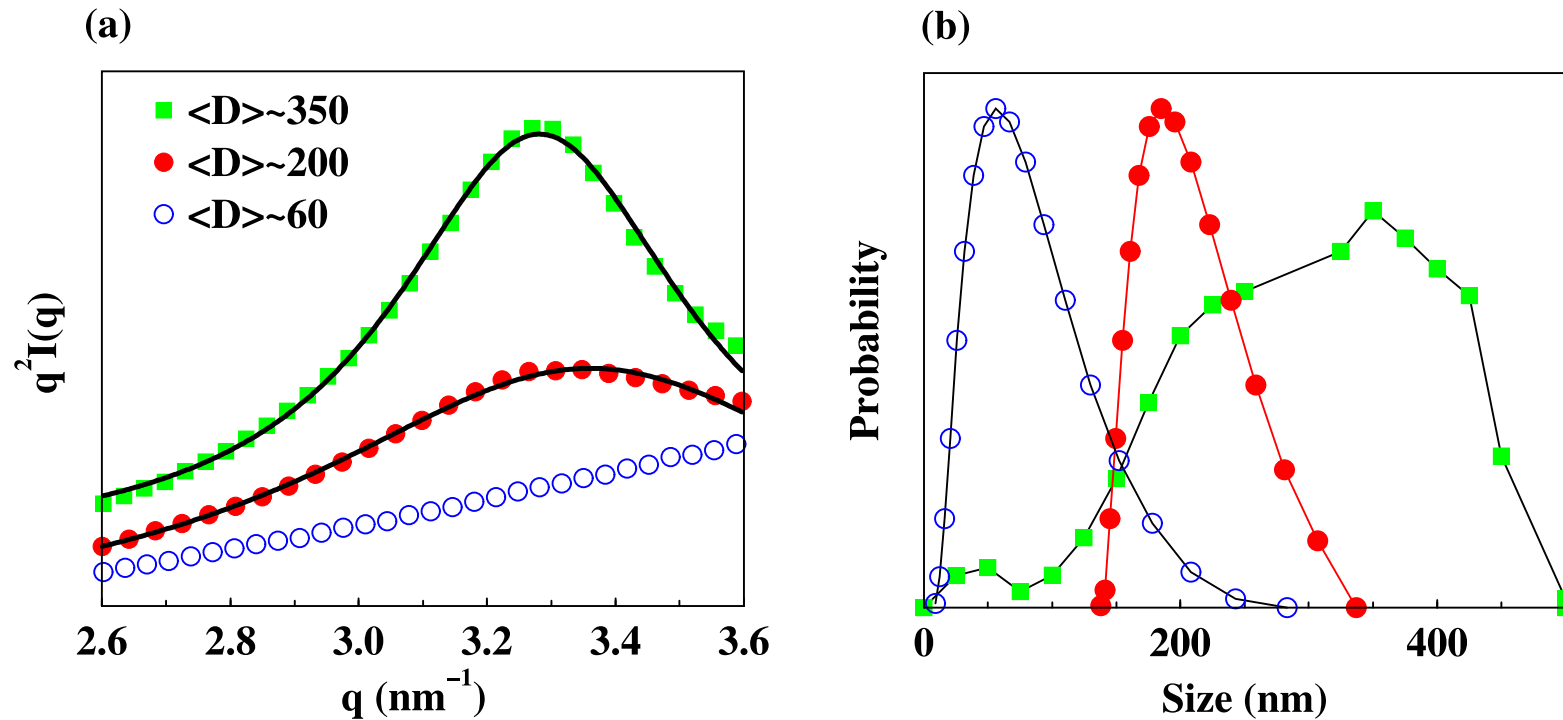
Counterion competition - the bulk contains 20 mM of NaCl.

Monte Carlo Simulations



Monte Carlo simulation results for the net osmotic pressure between two negatively charged walls. The slit is in equilibrium with a salt reservoir containing a mix of CaCl_2 and NaCl salt. The CaCl_2 concentration is indicated in the graph. The surface charge density, $\sigma = 0.737 \text{ e/nm}^2$, is taken from a cation exchange capacity measurement.

Platelet vs Tactoid Size



(a) SAXS spectra of Na montmorillonite equilibrated in dialysis pockets during 60 min with 50 mM CaCl_2 solutions. Particle diameters are indicated in figure - $\langle N \rangle = 12, 7$ and 0. (b) The corresponding platelet size distributions of centrifuged clay fractions obtained through dynamic light scattering.

Conclusions

- Divalent counterions lead to tactoid formation - MC+SAXS.
- The tactoid formation is fast (\approx one day).
- The tactoids grow with platelet size - MC+SAXS.
- The bulk composition is important - MC.
- We do not understand the extralamellar swelling.
- The Poisson-Boltzmann equation is not valid for divalent ions.