

THE POLYELECTROLYTE GEL-LIKE MODEL OF CLAY SWELLING

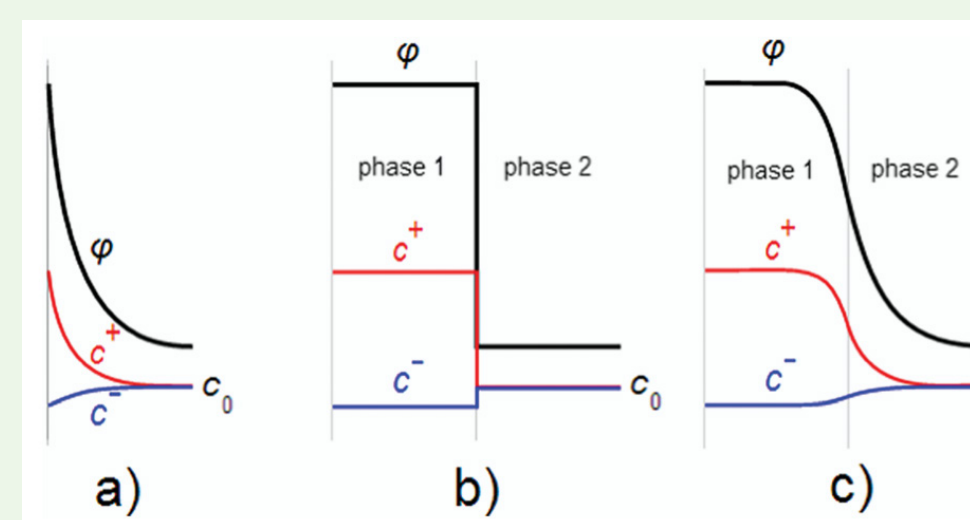
Ing. Anna Girová, PhD. and prof. Ing. Jirí Škvarla, CSC.

Department of Mineral Processing, Institute of Earth Resources, Faculty of Mining, Ecology, Process Control and Geotechnologies (BERG), Technical University of Košice, Park Komenského 19, 04200, Košice, Slovak Republic, anna.girova@tuke.sk, jiri.skvarla@tuke.sk



Motivation: Donnan or Gouy-Chapman ?

The fundamental physico-chemical (electrostatic) mechanism of osmotic swelling of clays is traditionally thought known to be governed by two different concepts of ionic distribution rendering the neutralization of the surface charge of clay platelets in aqueous solutions – Donnan (D) and Poisson-Boltzmann (P-B).



(a) *Gouy-Chapman or diffuse layer model.* In this fundamental model of two-dimensional interface, the thermal motion and electric forces of ions (Boltzmann law) are combined with the electrostatic potential ϕ (Poisson equation) to give rise to a decaying equilibrium distribution of counterions c^+ and co-ions c^- present at unequal concentrations.

(b) *Macroscopic Donnan model.* In this two-phase model, it is assumed that a constant Donnan potential is established between an uniform surface phase ("polyion domain") and external solution. The step-like distribution of ions between these phases is characterized by a simple rule (the law of equality of products).

(c) *Microscopic Donnan model.* It accounts also for the thermal motion of ions that causes the electric potential to distribute across the two-phase interface. The distribution is obtainable by solving the composite Poisson-Boltzmann (P-B) equation for both phases.

For more details, see: Škvarla, J., Kaňuchová, M., Shchukarev, A., Brežáni, I., & Škvarla, J. (2017). *Accumulation of counterions and coions evaluated by cryogenic XPS as a new tool for describing the structure of electric double layer at the silica/water interface.* *Physical Chemistry Chemical Physics*, 19(43), 29047–29052. doi:10.1039/c7cp0643

Neither of these models has been proven to express clay swelling satisfactorily and, consequently, a main question whether they function individually or combined with each other or with another possible effect, especially the elasticity of the polyion phase, remains to be answered.

Strategy: A simplest test – comparison of simplest experiments with the simplest theory.

A confrontation of free swelling of bentonite, devoid in an ideal case of any competitive mutual force of opposing platelets, as an analytical function of concentration (activity) of simple ions in an aquatic solution with the prediction based on the Donnan and Poisson-Boltzmann theory. There are two possibilities:

1. **Poisson-Boltzmann.** The Debye-Hückel screening length (thickness of the diffuse Gouy-Chapman double layer)

$$\kappa^{-1} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2e^2 I} \right)^{1/2}$$

and because the ionic strength $I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$, for a symmetrical 1:1 electrolyte such as NaCl, I equals the bulk concentration c and κ^{-1} , reflecting a free swelling degree, is in proportion with $c^{-1/2}$

$$\kappa^{-1} \propto c^{-1/2}$$

2. **Donnan. ???**

The statistical thermodynamic theory for elasticity of individual, electrically neutral polymers was worked out in the Flory-Huggins theory of polymer solutions in 1941. In this theory, a statistical mean-field distribution of polymer segments was used to express their Gibbs free energy change of mixing with the solvent (hydration by the solvent molecules), expressed via the polymer-solvent interaction parameter χ_1 , depending on the nature of both the polymer segments and the solvent molecules. In 1943, the combination of the semi-quantitative Flory-Huggins theory of polymer solutions with the theory of deformable polymer networks and rubber elasticity resulted in the Flory-Rehner theory of swelling of crosslinked polymer gels. In 1953, in the final Flory theory, swelling of a homogeneous and unstrained (isotropic) macroscopic ionic polymer network (polyelectrolyte gel) of low degree cross-linking is in the state of equilibrium when three osmotic pressure contributions compensate: (i) the mixing contribution due to the mixing of water molecules with the polymer segments (entropy of dilution) which depends on the Flory-Huggins parameter χ_1 ; (ii) the rubber-like elastic contribution due to the retractive forces of the polymer network; (iii) ionic contribution due to the intramolecular repulsion between charged segments (due to ionizing functional groups) and to the osmotic pressure of mobile ions (Donnan effect). Because an explicit general solution of the equilibrium is difficult, only special cases can be solved analytically. When the concentration of ions in the solution is large compared to the charge bound to this gel, the first ionic contribution is greatly reduced and the equilibrium swelling degree q_m (a ratio of the volume of swollen and unswollen gel, $q_m = V/V_0$) to the five thirds power is proportional to a reciprocal of the ionic strength I , i. e., since $I \equiv c$ by definition, of the concentration or, better, activity of monovalent ions in the external solution:

$$q_m^{5/3} \approx \left[\left(\frac{i}{2v_1} \right) I^{1/2} \right]^2 + (1/2 - \chi_1) / v_1 \left[V_0 / v_1 \right]$$

$$\text{or} \\ q_m \propto c^{-3/5}$$

In the above equation, v_1 is the effective number of chains in the gel network, v_1 is the molar volume of the solvent and i/v_1 is the concentration of the fixed charge referred to the unswollen or relaxed polymer network of volume V_0 (i is the degree of ionization of the groups). For planar geometries, q_m is proportional to the interlayer distance obtainable from the X-ray diffraction as well as the sediment volume of clays V_s .

Experiments

Macroscopic

1. Equilibrium sediment volume (V_s) of highly concentrated clay dispersions and intrinsic viscosity (K) of extremely diluted clay dispersions

The sedimentation volume as a measure of free swelling of clays was determined by placing 0.1, 0.25, 0.5 and 1.0 g of dry mineral powder in 10 ml graduated test tubes containing aqueous solutions of alkali metal chlorides of varying concentration (0.01 to 0.5 M), providing 1, 2.5, 5 and 10 % w/v suspensions, respectively. The test tubes were mixed to provide homogeneous clay dispersions that were remained undisturbed to settle and the equilibrium volume of the sediment was read after at least 24 hours (see Fig. 2 for the illustration of the inhibitory effect of ions in a series of test tubes with final sediments formed at an increasing salt concentration). The determined sedimentation volume was corrected for the curvature of the rounded-bottom of the test tubes, providing finally $V_{s,eq}$ in cm^3 . This method of evaluating free swelling has been found capable to give comparable results if various clay samples were prepared in pure water under uniform conditions of room temperature and humidity. Moreover, especially for the fine clay powder dispersed in presence of salts, inducing the formation of visually sharp sediment-water interface, the method was found reliable to such an extent that even corrections could have been made to refine the readouts of the final volume of sediments in individual test tubes due to their inner diameter variations within a batch. The relative equilibrium swelling volume $V_{s,rel}$ was calculated as a ratio of $V_{s,eq}$ to that at a critical mean activity of ions a_c .



A series of test tubes with sediments equilibrated in the presence of increasing KCl concentrations

For the viscosity of dispersions of colloids in a liquid, Einstein derived in 1906 the following formula:

$$\eta = \eta_m (1 + K\phi)$$

where η is the viscosity of the dispersion, η_m is the viscosity of the liquid medium and ϕ is the total volume fraction of the colloidal particles. For irregular platelet-like colloid particles, at very low volume fraction, numerous studies have shown that the factor K is much higher than 2.5. We expect that the specific viscosity $(\eta/\eta_m - 1)$ for a given irregular particle with its characteristic K is still proportional to the volume fraction of dry particles, as Einstein's equation predicts, i. e. that K and ϕ remain multiplicative in their effect. It can also be assumed that the individual (dry) clay particles have such a high geometrical aspect ratio ($\text{nm} \times \mu\text{m}$) that changes in K obtained from fits of viscosity experiments in salts (using the dry mass-based ϕ) will reflect proportionally the swollen volume, whatever is the water-induced reason of its enlargement, but not the shape of the particles. We adopted the capillary viscometry to determine K . A glass micro Ubbelohde capillary viscometer in a glass jacket was used to measure the dynamic viscosity of very dilute dispersions of clay minerals in water or in presence of added electrolyte ions. The temperature of water in the jacket and so in the capillary was maintained at 25 °C using a circulation thermostat (Alpha, Lauda). The calibrated capillary constant of the viscometer was 0.0321. The efflux time of the dispersion was measured manually using a stopwatch.

A setup for measuring the viscosity of clay dispersions

Microscopic

A survey of available data on the interlayer spacing of clay platelets, determined as a function of concentration of simple ions by the X-ray diffraction, has been made.

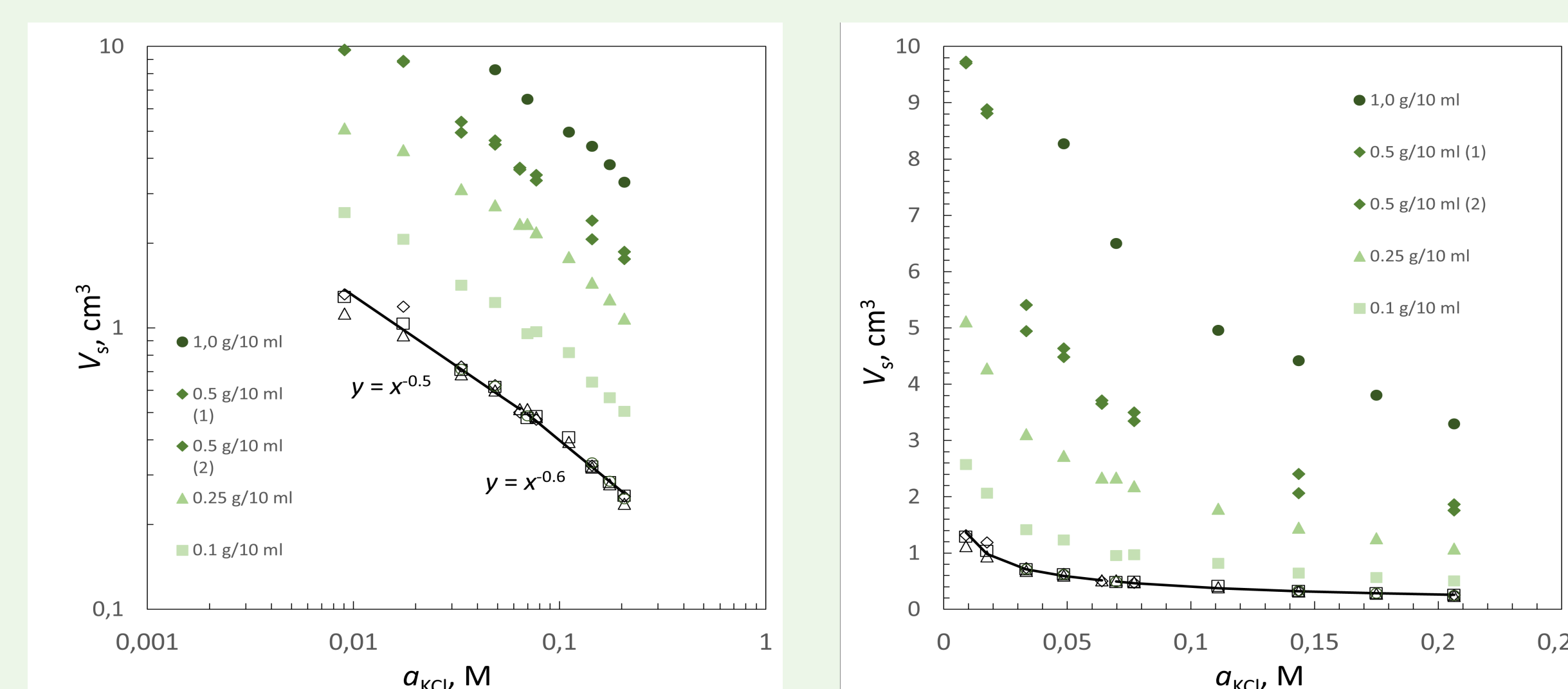
Material

The Redmond bentonite clay (Utah, USA) that is prevalently a K,Na,Ca-form of montmorillonite was purchased from Redmond Trading Company, L. C. The sample in the form of very fine powder was used as received. The result of screening multi-elemental analysis of the air dry powder performed with the ED-XRF spectrometer Spectro Xepos (XEPO5) provided the following chemical composition expressed as the weight percent of major oxides: SiO₂ (56.33 %), Al₂O₃ (19.47 %), Fe₂O₃ (3.84 %), MgO (2.20), Na₂O (1.63 %), CaO (2.77 %), K₂O (2.50 %). The loss of ignition (12.1 %) was determined as the total TG mass loss (≤ 1000 °C) using the simultaneous thermal analyzer Netzsch STA 449F3. A preliminary calculation provided the following unit cell formula: $\text{Na}_{0.218}\text{K}_{0.222}\text{Ca}_{0.205}(\text{Al}_{1.406}\text{Fe}_{0.199}\text{Mg}_{0.228})_2(\text{Si}_{3.822}\text{Al}_{0.177})_4$. Aside from montmorillonite, X-ray diffraction identified illite-montmorillonite, gypsum, muscovite, feldspar, tridymite, quartz, cristobalite, albite, illite, kaolinite, and calcite as mineral impurities. Since the first endothermic peak in the DTA pattern is singular and sharp, typical for monovalent cationic forms of montmorillonite (instead of double peak for divalent cations), we think that the apparently higher content of Ca is a result of the presence of gypsum, as also indicates the presence of sulphur in the XRF analysis (0.0895 wt %).

Results

Sedimentation – Clay content

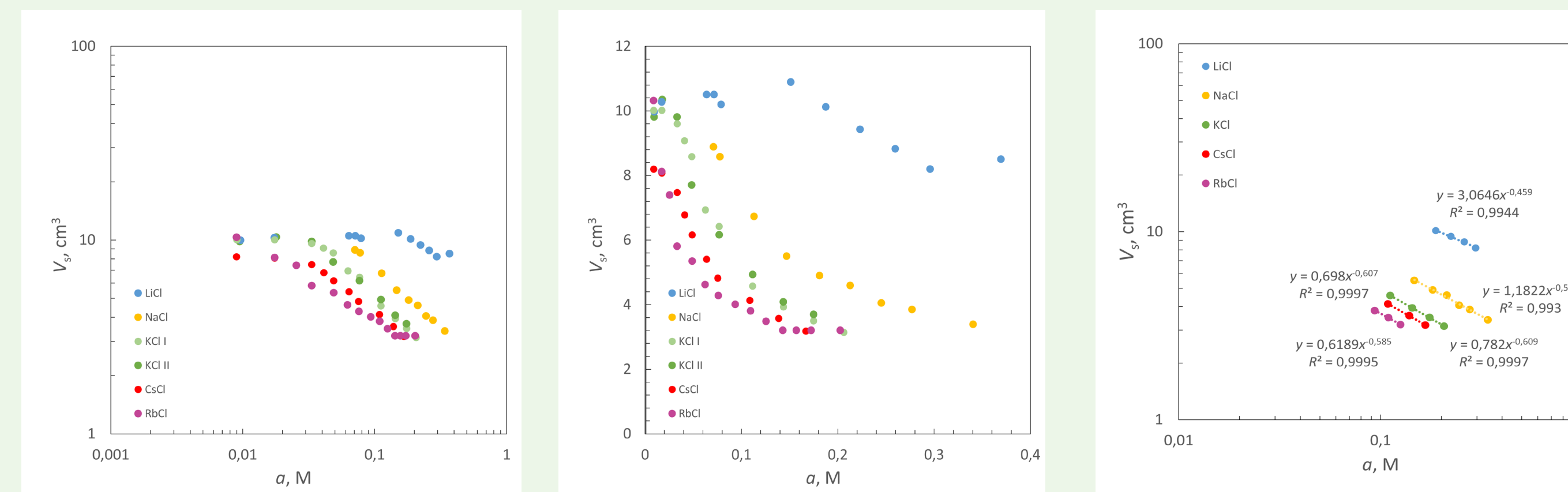
- A General trend of equilibrium sediment volume changing with an increasing activity of KCl electrolyte is sigmoidal.
- The descending part of the sigmoids due to shrinkage of clay platelets, when drawn in the log-log coordinates, is shifted proportionally with the clay load in the initial dispersion, with its course unchanged, and manifests distinctly a double-decay at lower and higher KCl activities, respectively.
- The former decay seems to follow a power law with the exponent of -0.5 , while the latter decays with the exponent of -0.6 .



Dependences of the equilibrium sediment volume on the activity of KCl for various dry mass of clay in its initial dispersion (g/10 ml). Log-log (left) and linear (right) coordinates. Two experimental data sets for 0.5 g/10 ml are shown to illustrate the repeatability of the measurements. Theoretical power law with selected exponents are indicated to guide eye.

Sedimentation – Cation type

- The descending part of the sigmoidal dependences is apparently unchanged but shifted proportionally to higher electrolyte activities with changing from most chaotropic (least hydrated) cations (RbCl) to most kosmotropic (most hydrated) cations (LiCl), according to Hofmeister series for monovalent cations
- All the dependences approach asymptotically a power law with the exponent of -0.6

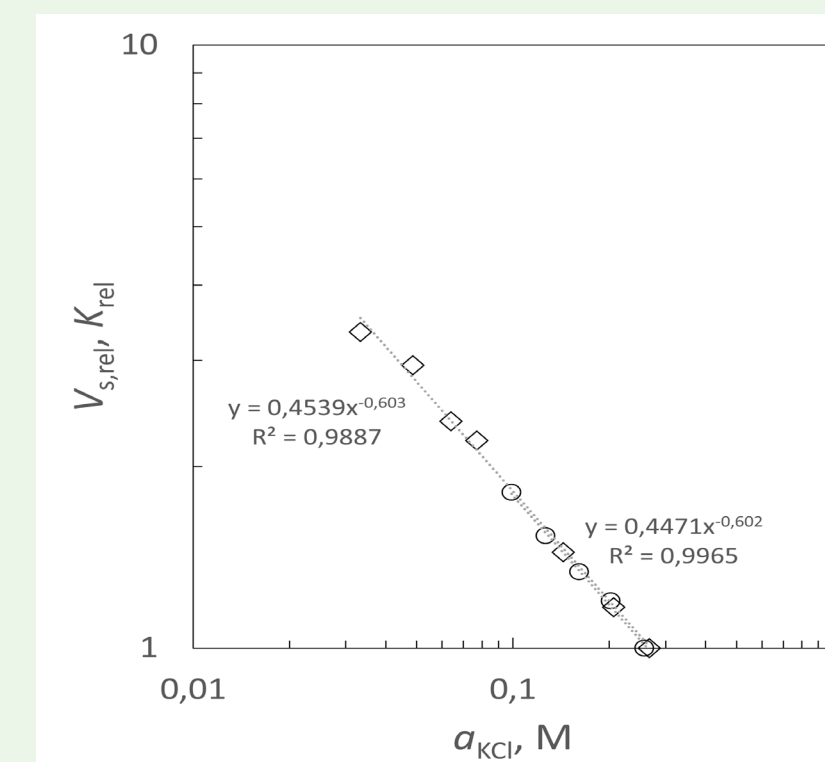


Complete dependences of the equilibrium sediment volume on the activity of alkali metal chlorides at 1 g of clay in 10 ml of solution in the log-log coordinates (left) and linear (middle) coordinates and limit parts of dependences (log-log coordinates) fitted with power law functions.

Viscosity

- The intrinsic viscosity coefficient of Einstein equation, a measure of the volume of individual clay platelets, descends with the increasing KCl activity by a power law with the exponent of -0.6 , in the same way as for the equilibrium sediment volume.
- The equilibrium sediment volume-KCl activity and the intrinsic viscosity-KCl activity, both related to the same (critical) reference KCl activity, can be shown identical.

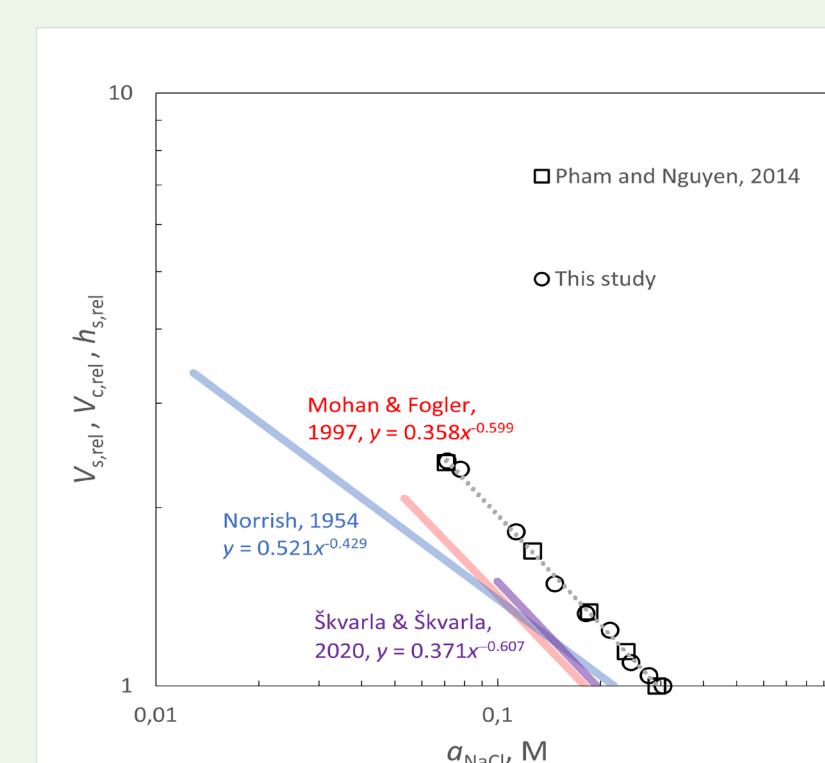
Relative dependences of the equilibrium sediment volume (rhombus) and the intrinsic viscosity (circles) factor on the activity of KCl. Log-log coordinates.



X-ray diffraction (re-evaluations of former experiments by others)

- The distance between clay platelets, published by various authors as a function of NaCl, has been found to vary according to the power law with the exponent in the range of -0.5 to -0.6 , depending probably on the preparation of clay specimens (see Norrish vs. Mohan and Fogler data).

Relative dependences of the equilibrium sediment volume (circles) in this study and from others' experiments and the relative dependence of the interlayer distance from X-ray diffraction experiments on the activity of NaCl. Log-log coordinates.



Conclusions

- There is a coincidence between the normalized dependence of the macroscopic measures of swelling (equilibrium sediment volume and intrinsic viscosity) and the microscopic measure of swelling (X-ray diffraction interlayer distance) on the activity of monovalent electrolytes, when the activity is high enough. This confirms the swelling in effect with no external constraints (free swelling).
- The dependence can be well fitted with a power law function with the exponent of -0.6 . This can be considered to indicate the presence and manifestation of a polyelectrolyte-like gel layer formed on the surface of clay platelets. The identical power law decay has been derived in polymer physics for the swelling degree of polyelectrolyte gels in presence of electrolytes, assuming the Donnan equilibrium of ions and the rubber-like elasticity of the charged gel network.
- The dependence is preserved irrespective of the type of monovalent cations, meaning a role of yet another effect.
- The latter fact holds seemingly true for the dependence at lower electrolyte activities, fittable by a power law exponent of -0.5 , reflecting the Gouy-Chapman electric double layer. The question remains if the diffuse layers of ions are the only factor in this low-ionic activity domain, or they are superimposed on the Donnanian elastic polyelectrolyte gel-like layers. Because the analytical solution of the combined effect of ions is not yet available, the question remains open.

Further references on the topic:

Škvarla, J. (2013). Quantitative interpretation of anomalous coagulation behavior of colloidal silica using a swellable polyelectrolyte gel model of electrical double layer. *Langmuir*, 29, 8809–8824. <https://doi.org/10.1021/la401502f>

Škvarla (2023). On the gel layer interpretation of anomalous viscosity of colloidal silica dispersions. *Colloid Polymer Sci.*, 301, 1539–1546. <https://doi.org/10.1007/s00396-023-05167-1>

Škvarla, J., & Škvarla, J. (2017). A swellable polyelectrolyte gel-like layer on the surface of hydrous metal oxides in simple electrolyte solutions: Hematite vs. silica colloids. *Colloids and Surfaces A: Phys. Eng. Aspects*, 513, 463–467. <https://doi.org/10.1016/j.colsurfa.2016.11.018>

Škvarla, J., & Škvarla, J. (2017). An identification of the soft polyelectrolyte gel-like layer on silica colloids using atomic force and electron microscopy. *Ultramicroscopy*, 181, 97–106. <https://doi.org/10.1016/j.ultramic.2017.05.011>

Škvarla, J., & Škvarla, J. (2020). A unified analysis of the coagulation behaviour of silica hydrosols—when the colloid and polymer science meet. *Colloid and Polymer Sci.*, 298, 123–138. <https://doi.org/10.1007/s00396-019-04582-7>

Škvarla, J., Kaňuchová, M., Shchukarev, A., Girová, A., & Brežáni, I. (2020). Cryo-XPS – A new technique for the quantitative analysis of the structure of electric double layer at colloidal particles. *Colloids and Surfaces A: Phys. Eng. Aspects*, 586, 124234. <https://doi.org/10.1016/j.colsurfa.2019.124234>