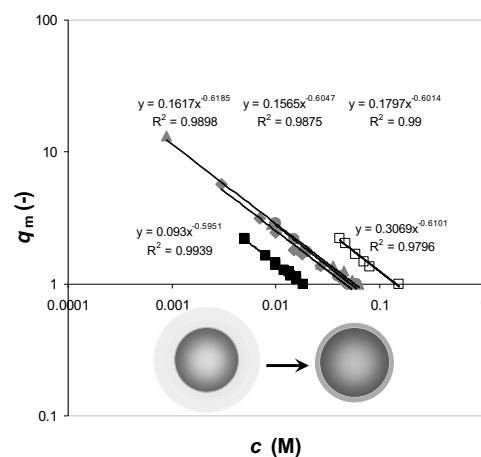




A swellable polyelectrolyte gel-like layer on the surface of hydrous metal oxides in simple electrolyte solutions: Hematite vs. silica colloids



GRAPHICAL ABSTRACT



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ABSTRACT

To elucidate the puzzling surface structure of hydrophilic colloidal particles of metal oxides dispersed in aqueous solutions, we reanalysed seemingly anomalous coagulation kinetics experiments carried out by various authors on nonporous as well as porous near-spherical iron oxide–hematite colloids synthesized by forced hydrolysis. The swelling degree of the shell (mimicking a loose gel layer of uniform fixed charge due to the ionization of functional groups) of the core-shell – modelled crystalline colloids was found to scale with the concentration of coagulating uni–univalent electrolyte according to the simple power law with the exponent of $-3/5$. In polymer physics, this scaling law was derived for swellable polyelectrolyte gels with a low degree of crosslinking, in which a delicate balance between competing thermodynamic forces is established. The same scaling law has recently been found by us to apply in colloidal systems of amorphous silica, indicating a more generalizable appearance of the swelling gel phase at the metal oxide/solution interface than previously thought.

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In colloid chemistry, the traditional comprehension of the electric double layer (EDL) and all associated phenomena are based on the idea of electric charge homogeneously spread across an ideal two-dimensional surface, regulated by potential determining ions and neutralized by other ions distributed between the compact Helmholtz (Stern) and diffuse (Gouy–Chapman) layer in an adjacent solution. The repulsive electrostatic double layer (EDL) interaction of such interfaces together with the attractive van der Waals interaction is then a footing of the celebrated DLVO [1–3]

and aggregation theory of thermally encountering colloids [4–6] expressed by the stability ratio W of the fast (diffusion-limited) to the slow (reaction-limited) aggregation rate. In aggregation stimulated by an increasing addition of electrolyte it is assumed that the transition between the two regimes occurs at $W = 1$ when the electrolyte concentration c is critical (ccc) and the maximum of the net DLVO interaction drops to a value close to the thermal energy.

The correctness of the DLVO theory has recently been proved by analysing the kinetics of the electrolytic coagulation of well-defined

colloid systems of weakly charged PS latexes using explicitly determined parameters of both the interaction types, i.e., the surface electrostatic potential and the Hamaker constant [7,8]. However, the same quantitative analysis failed when applied to hydrophilic colloidal particles of inorganic oxides such as silica [9,10] and hematite [11] in conditions rendering their high or even near-zero surface charge (i.e., at pH distant from or close to the pH_{PZC}). Consequently, their behaviour is still perceived as anomalous.

One may presume that the way out is nothing less than to abandon the basic assumption of the DLVO theory, i.e., the idealized solid/solution interface. In fact, many studies scattered throughout last decades and based on viscosity [12,13], coagulation [14], surface charge [15–17], electrophoretic [18,19], and other [20,21] measurements of hydrated silica particles have amassed, resulting in the concept of a rigid or elastic porous shell layer encircling the solid core. In none of these studies, however, the physically justified, systematic variation in the shell layer thickness or volume with the electrolyte concentration, if any, was found. On other hand, an ion-exchange [22,23] or even Donnan [24] (ion-selective permeable membrane) [25–27] feature of such a layer was noticed. Moreover, experimental stability ratios of well-defined nonporous silica colloids brought into equality with those calculated ones [28] yielded the so-called swelling ratio q_m of the layer to scale with c in a strict agreement with the power law derived from the Flory-Huggins thermodynamic theory of unstrained isotropic swelling of polyelectrolyte gels [29–31], that is $q_m \sim c^{-3/5}$.

In the coagulation analysis [28], the shell was assumed to be formed by a homogeneous, loose, ion- and water molecule-permeable polyelectrolyte network of fixed charge density ρ_{fix} that was used as the main parameter in the Donnan potential-governed electrosteric interaction between the core-shells or “soft” spheres [32]. Contrary to the surface electrostatic potential in the classical EDL interaction between “hard” spheres that can hardly be evaluated directly, ρ_{fix} can be quantified by dividing the surface charge density σ_0 (unique for a given oxide and electrolyte and obtainable experimentally by the acid-base titration) with the shell thickness d . The latter thus remains to be the only fitting parameter of the electrosteric interaction from which q_m is directly calculable (see the next text).

This simple “trick” opens up a possibility of re-analysing aggregation kinetics experiments of any colloidal metal oxide, not only silica, from the standpoint of the core-shell model and of confirming or refuting the contemplation of the more general existence of the gel layer within metal oxides family or even beyond. In this communication we analyse stability ratios obtained independently by various authors for model synthetic colloidal particles of $\alpha\text{-Fe}_2\text{O}_3$ iron oxide (hematite) of a near-spherical shape and a narrow size distribution. In fact, this oxide is, in the colloid form, probably the second most frequently studied one for its coagulation kinetics. Yet, its particles differ from the colloids of amorphous silica in that they are crystalline and moderately basic so that they acquire a positive or negative surface charge reflected by the existence of both sides of titration isotherms around $\text{pH}_{\text{PZC}} \approx 9$.

There are indeed numerous aggregation studies on hematite in the literature but only few of them are usable for our purpose [33–46]. First, coagulation experiments with almost entirely nonporous colloidal particles of hematite [34], were subjected to our analysis using original surface charge data at six concentrations of NaCl, ranging from 0.0415 M to 0.1552 M at pH 4.7, i.e., about 4 pH units below pH_{PZC} . The (positive) values of σ_0 for these concentrations were calculated by interpolating the data points (at pH 5.1, the lowest available) for 0.0025, 0.012 and 0.1 M NaCl with no correction for porosity (the specific surface area calculated from the spherical geometry was almost identical with that determined actually by the BET method for these particles). All relevant parameters of the analysis are summarized in Table 1.

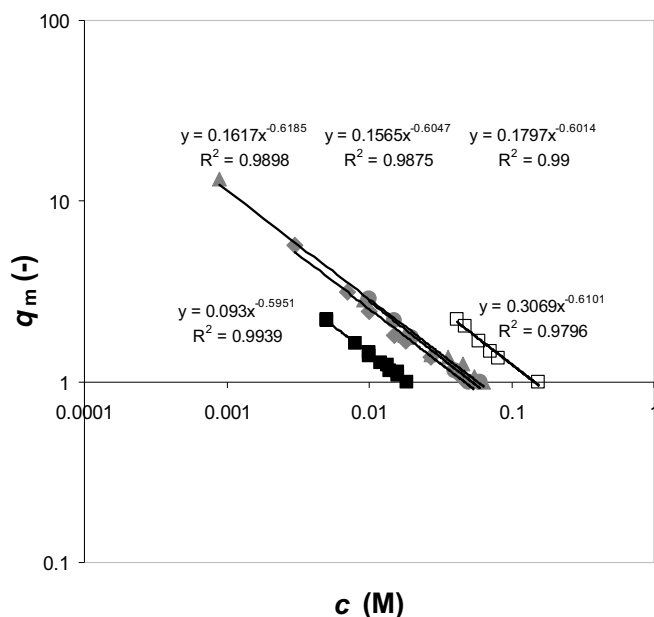


Fig. 1. Swelling degree-vs-electrolyte concentration (log-log) dependences extracted from coagulation kinetics of Liang et al. [32,33], (open squares), He et al., [45] for hematite particles of 12 nm (grey triangles), 32 nm (grey rhombs) and 65 nm (grey circles) diameter, and Tiller and OñMelía [46] (black squares). The lines are fits by power law functions with the description included.

Then, we analysed aggregation measurements for disperse systems of hematite nanoparticles with a uniform size of 12, 32 and 65 nm in the presence of 1 to 200 mM of the same electrolyte (NaCl) at pH 5.7 [45]. Coagulation experiments published in ref. 46 were tested at the end. Since the electrolyte (NaNO_3) contained nitrate anions instead of chloride ones, we interpolated titration curves (corrected for the porosity) presented in Ref. [47] for an electrolyte with the same anion (KNO_3) at pH of the coagulation experiments (6.3).

For any σ_0 value obtained for a given coagulating electrolyte concentration, the corresponding shell thickness was determined iteratively by comparing the theoretical with the experimental stability ratio until their equalization. The swelling degree, which is the ratio of the swollen to the unswollen shell volume, V and V_0 respectively, was finally calculated according to the geometric formula:

$$q_m = \frac{V}{V_0} = \frac{(D + 2d)^3 - D^3}{(D + 2d_0)^3 - D^3}, \quad (1)$$

where D is the core diameter given as the diameter of “plain” hematite spheres in absence of the shell layer (taken as the diameter of the spheres with a collapsed layer, as determined by the electron microscopy in vacuum), d is the swollen shell thickness obtained for the coagulating electrolyte concentration and d_0 is the deswollen shell thickness obtained at the c.c.c. of this electrolyte (the highest c value of the pertinent data sets).

In Table 1 we can see that the swelling degree extracted from Liang’s data [34] scales with the NaCl concentration as $q_m \cong c^{-0.6101}$ ($R^2 = 0.9796$), with the exponent being very close to that predicted by the Flory–Huggins theory (-0.6) and in agreement with our previously published observations of silica. [28] Similarly, coagulations by Ho et al. [45] provided again power laws with exponents -0.6185 , -0.6047 and -0.6014 , all with R^2 above 0.99. And to the third place, experiments by Tiller and OñMelía [46] also have confirmed scaling with the exponent very close to -0.6 (-0.5951).

These scalings are visualized in Fig. 1, where dependences of the calculated swelling degree on the electrolyte concentration are

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