

Theoretical study of the amphoteric oxide nanoparticle surface charge during multi-particle interactions in aqueous solutions

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Abstract. Nanoparticle surface charge plays an important role in many biological applications. In this study, an analytical surface charging model for the amphoteric oxide nanoparticles has been presented. The model accounts for the particle's electric double layer self-action on the charging process and the charge regulation during multi-particle interactions in aqueous solutions. The employment of the model allows to explicitly describe the nanoparticle agglomeration process and the accompanying agglomerate surface charge variation.

1. Introduction

Recent studies in the fields of nanotoxicology, nanobiotechnology and drug delivery suggest that the surface charge of a nanoparticle can significantly influence its interactions with biological matter. It has been shown that the cellular uptake, cytotoxicity and overall reactivity of amphoteric oxide nanoparticles are highly dependent on their charge [1, 2]. In the presence of agglomeration, the interparticle interaction and morphology of the agglomerates are also governed by the nanoparticle surface charge [3].

The present study proposes an analytical model for the amphoteric oxide nanoparticle surface charging mechanism which accounts for the charge regulation during the multi-particle interaction in aqueous solutions. This allows for the explicit description of the nanoparticle agglomeration process and the accompanying agglomerate surface charge variation.

2. Methods

The suggested colloid nanoparticle interaction and agglomeration model has been developed in the framework of the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory. This theory assumes that the interaction between colloid particles can be represented using the attractive van der Waals term and the repulsive electrostatic term. The latter arises due to the overlap of particles' electric double layers (EDLs).

We use a system of Debye-Hückel equations for the electrostatic potential φ to describe the ion atmosphere of a single spherical nanoparticle suspended in electrolyte solution:

$$\begin{aligned}\Delta\varphi_I &= 0, \quad a < r < b \\ \Delta\varphi_{II} &= \kappa^2\varphi_{II}, \quad r > b\end{aligned}\quad (1)$$

with boundary conditions:

$$\begin{aligned}\left.\frac{d}{dr}\varphi_I\right|_{r=a} &= -\frac{\sigma}{\varepsilon_h\varepsilon_0} & \varepsilon_h\left.\frac{d}{dr}\varphi_I\right|_{r=b-} &= \varepsilon\left.\frac{d}{dr}\varphi_{II}\right|_{r=b+} \\ \varphi_I(b) &= \varphi_{II}(b) = \varphi_0 & \varphi_{II}\big|_{r\rightarrow\infty} &= 0\end{aligned}\quad (2)$$



where r - radial coordinate of the spherical coordinate system; a - particle radius; b - effective radius of the hydrated particle; φ_1 , φ_{II} - potential in the hydration layer and the diffuse ion layer correspondingly; κ - reciprocal of the Debye screening length; σ - nanoparticle surface charge density ε_h , ε - effective dielectric permittivity in the hydration layer and the diffuse ion layer correspondingly; ε_0 - dielectric constant; φ_0 - zeta potential.

Solving (1) with (2) we can show that the zeta-potential expression is given by:

$$\varphi_0 = \frac{1}{4\pi\varepsilon\varepsilon_0} \cdot \frac{4\pi a^2 \cdot \sigma}{b(1 + \kappa b)} \quad (3)$$

We also introduce the original surface charge model for amphoteric oxide nanoparticles that accounts for a number of charging mechanisms including competitive protonation and deprotonation of the $[-OH]$ surface groups, chemical adsorption of H^+ and OH^- ions and van der Waals adsorption onto the particle surface and operates in the limit of non-saturated adsorption and desorption. The model also accounts for the external electric field effect and the nanoparticle's electric double layer self-action on the surface charging process.

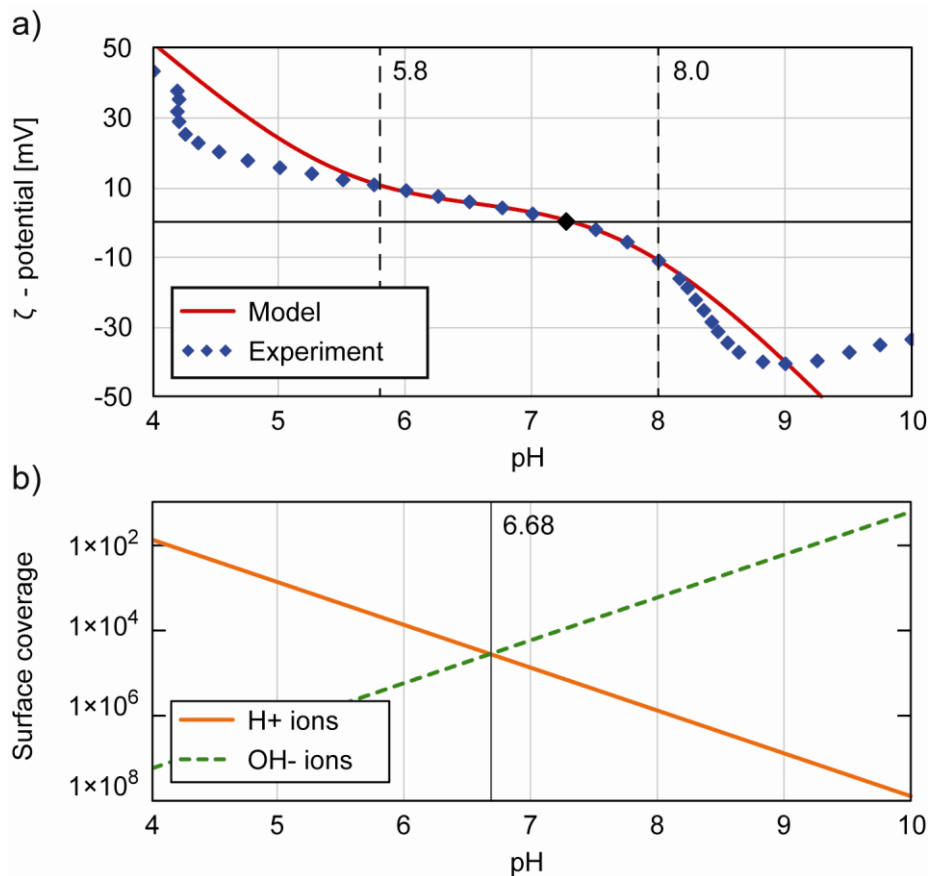


Figure 1. Nanoparticle surface charge model. a) – fitting of the experimental zeta potential dependency on pH [2] with the suggested model; dashed vertical lines indicate the limits of applicability of the model. b) – fraction of the nanoparticle surface covered with H^+ and OH^- ions as a function of pH for the suggested model.

Linearization of the potential-dependent H^+ and OH^- concentrations at the particle surface yields a simple expression for the nanoparticle surface charge density σ :

$$\sigma = \left\{ \sigma_0 + e \left[\beta_+ n_H \left(1 - \frac{e\varphi_\Sigma}{kT} \right) - \beta_- n_{OH} \left(1 + \frac{e\varphi_\Sigma}{kT} \right) \right] \right\} \cdot \left\{ 1 + \frac{e^2 [\beta_+ n_H + \beta_- n_{OH}]}{4\pi\epsilon\epsilon_0 \cdot kT} \left[\frac{1}{b(1+\kappa b)} + \frac{b-a}{ab} \right] \right\}^{-1}, \quad (4)$$

where σ_0 - constant portion of charge; n_H, n_{OH} - bulk H^+ and OH^- concentrations; a, b - physical and hydrodynamic particle radii; β_+, β_- - coefficients proportional to the sums of the rate constants for the adsorption processes involved; φ_Σ - potential of the external field; e - elementary charge.

By substituting (4) into (3) we obtain the model expression for the nanoparticle zeta-potential as a function of pH (H^+ and OH^- concentrations). By fitting the experimental zeta potential versus pH dependency for ZnO 30 nm colloid particles taken from [2] with the obtained theoretical expression we can find the model parameters σ_0 and β_+, β_- . The results of such data fitting are represented in figure 1. It can be seen that the model provides good agreement with the experiment except for the adsorption saturation effects at low and high pH-values.

The surface charge model can be implemented into the many-body nanoparticle interaction model, first introduced by the authors in [4]. Using the monopole in the framework of the classic the monopole approximation, we substitute each particle with its equivalent screened point-charge [5]:

$$Q = 4\pi\epsilon\epsilon_0 \cdot \varphi_0 \cdot b e^{\kappa b}. \quad (5)$$

As it has been shown in [4], the equivalent screened point-charges of multiple interacting particles can be than found by solving the following linear system of algebraic equations:

$$Q_\alpha + \sum_{\beta \neq \alpha} \theta_{\alpha,\beta} \cdot Q_\beta = Q_0 \quad (6)$$

with the coefficient given by:

$$\theta_{\alpha,\beta} = \frac{1}{4\pi\epsilon\epsilon_0} \cdot \frac{e^2}{kT} \cdot \frac{1}{R_{\alpha,\beta}(1+\kappa b)} \cdot \frac{(\beta_+ n_H + \beta_- n_{OH}) \cdot \exp[-\kappa(R_{\alpha,\beta} - b)]}{1 + \frac{e^2 [\beta_+ n_H + \beta_- n_{OH}]}{4\pi\epsilon\epsilon_0 \cdot kT} \left[\frac{1}{b(1+\kappa b)} + \frac{b-a}{ab} \right]} \quad (7)$$

Q_0 - the equivalent charge of an isolated particle; α, β - particle numbers; $R_{\alpha,\beta}$ - centre-to-centre separation between particles α and β .

3. Results and discussion

The presented colloid nanoparticle interaction and charge regulation model allows us to calculate the equivalent effective charges of multiple interacting particles using (6) and (7). The model also allows to study the multi-particle interaction potential energy, which was previously discussed in [4]. It has been shown that the electroosmotic repulsion between nanoparticles can give rise to orientation effects during their agglomeration. Namely, depending on the primary particle concentration and pH the most energetically favourable agglomerate configuration might be either compact, or dendritic (fractal-like).

In the present work the proposed interaction and charge regulation model was used to study the effective charge and surface charge density transformations during nanoparticle agglomeration process. To account for the agglomerate morphology differences mentioned above we have considered both compact and linear (as a limiting case of dendritic) agglomerates of varied sizes.

The limits of applicability for the presented model are illustrated on figure 2 and figure 1a. Figure 1a illustrates the limits of applicability of the non-saturated adsorption and desorption assumption for pH. Figure 2a demonstrates the limitations on the primary particle size and pH arising from the monopole approximation. Finally, figure 2b shows the maximum electrostatic potential in the agglomerate's ion atmosphere as a function of the number of it's constituent particles and pH. The Debye-Huckel equations (1) are only applicable when the potential in the system less or equal 10 mV at 283 K. Therefore, figure 2a provides another set of limitations for the possible agglomerate sizes and pH values.

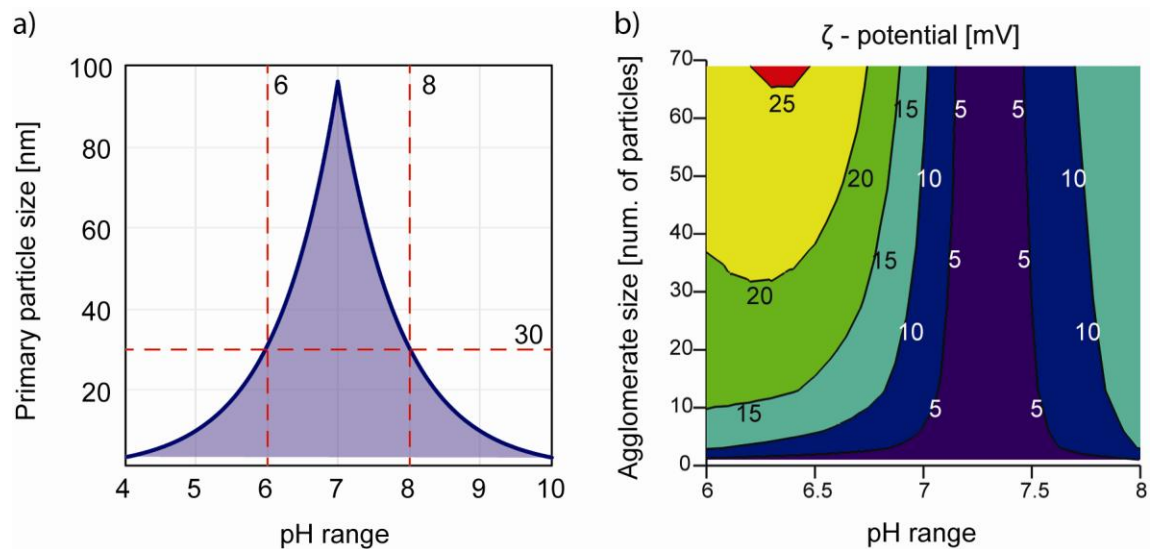


Figure 2. Limits of applicability for the presented model. a) – primary particle diameter and pH limitations; filled area represents the limits of applicability of the model based on the diffuse ion layer thickness. b) – contour plot of the agglomerate's zeta potential as a function pH and number of constituent primary particles; the suggested model is applicable when the agglomerate zeta potential is less than 10 mV at room temperature.

Figure 3 illustrates the effective nano-agglomerate charge as a function of the number of its constituent primary particles for the case of compact (a) and linear (b) agglomerates. The figure shows that the increase of the agglomerate size results in a much faster effective charge growth for the linear agglomerates rather than for the compact ones. This is due to the fact that particles in compact

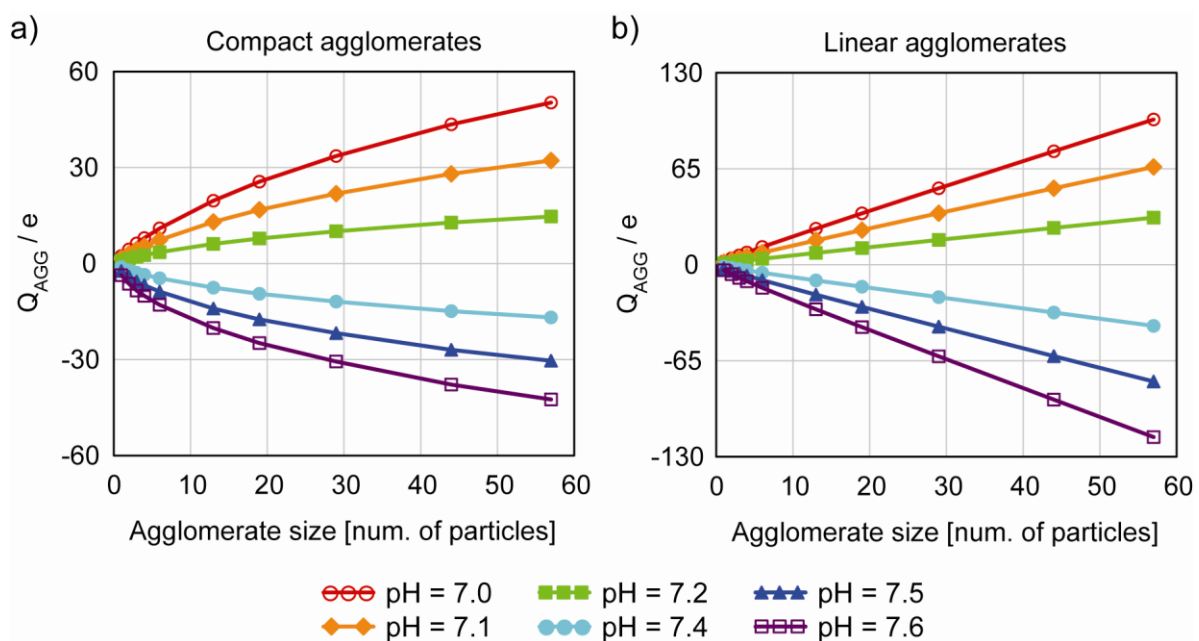


Figure 3. Effective agglomerate charge as a function of the number of its constituent primary particles for a) compact agglomerates and b) linear agglomerates at different pH values. The effective agglomerate charges are normalized to the elementary charge.

agglomerates have more neighbours than in linear agglomerates. As all particles have a charge of the same sign, particles in compact agglomerates tend to decrease their charges though the charge regulation process more, than in linear agglomerates.

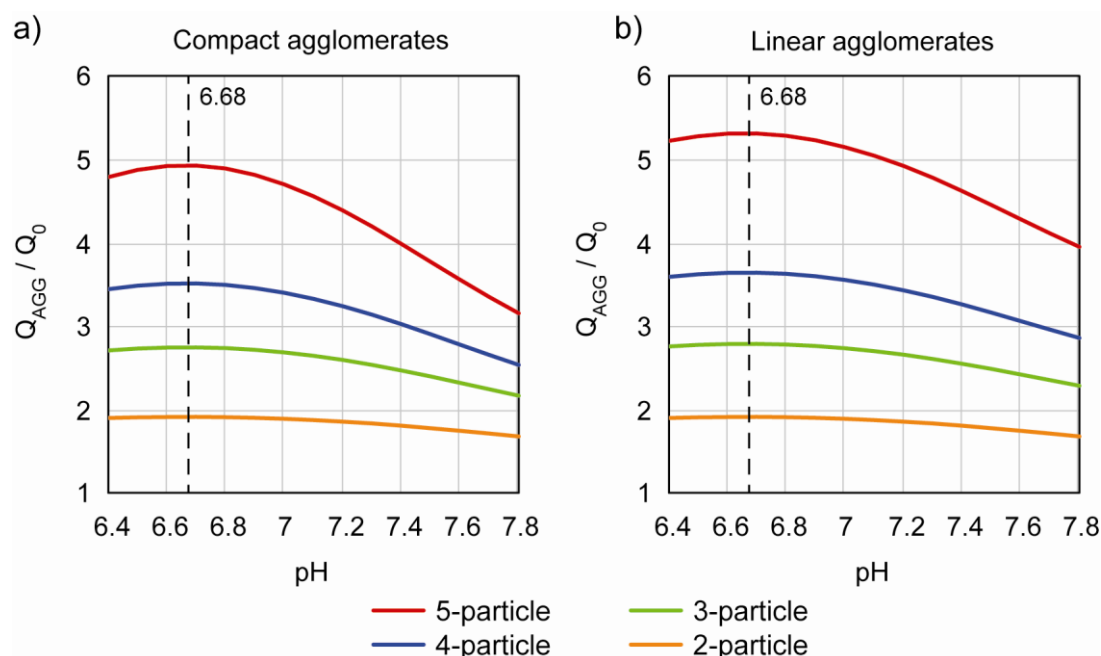


Figure 4. Relative effective agglomerate charge as a function of pH for a) compact agglomerates and b) linear agglomerates with different number of constituent particles. The effective agglomerate charges are normalized to the effective charge of the isolated primary particle at given pH.

Figure 4 depicts the effective agglomerate charge normalized the charge of an isolated primary particle as a function of pH. This dependency demonstrates a maximum at $\text{pH} = 6.68$. According to figure 1, said value corresponds to equal amounts of H^+ and OH^- ions adsorbed on the surface. But, more importantly, at this pH value the nanoparticle's surface has the least amount of adsorbed ions that are actively involved in chemical reactions. This means that the charge regulation process is least active at $\text{pH} = 6.68$, hence the maximum in relative charge. It should also be noted that the point of zero charge $\text{pH} = 7.3$ (see figure 1a) does not significantly impact the relative curves shown in figure 4, while causing the minimum for the pH dependency of the absolute charge values (see figure 3).

Finally, figure 5 shows the dependency of nano-agglomerate surface charge density on the number of its constituent primary particles. The agglomerate surface charge densities are normalized to those of the individual isolated primary particles. Presented are the charge densities for compact and linear agglomerates at 4 different pH values. The size-dependent surface charge density of a compact agglomerate is generally demonstrates a maximum. The location of this maximum depends on pH and shifts into bigger agglomerate sizes when moving further away from the $\text{pH} = 6.68$ value. Similarly to the curves on figure 4, the point of zero charge $\text{pH} = 7.3$ does not impact the pH-dependent surface charge maximum location for compact agglomerates.

Figure 5 also shows that the mean surface charge density is generally higher for compact agglomerates than for linear ones. However, the surface charge of linear agglomerates varies significantly based on the location in the agglomerate and reaches its maximum value on the tip of the particle chain. This is explained by the least amount of neighbours for the particles sitting on the tips of the linear or dendritic agglomerates. As shown in figure 5d, the maximum surface charge density of a linear agglomerate can overtake the mean surface charge of a compact agglomerate given the significantly high pH or constituent particle count.

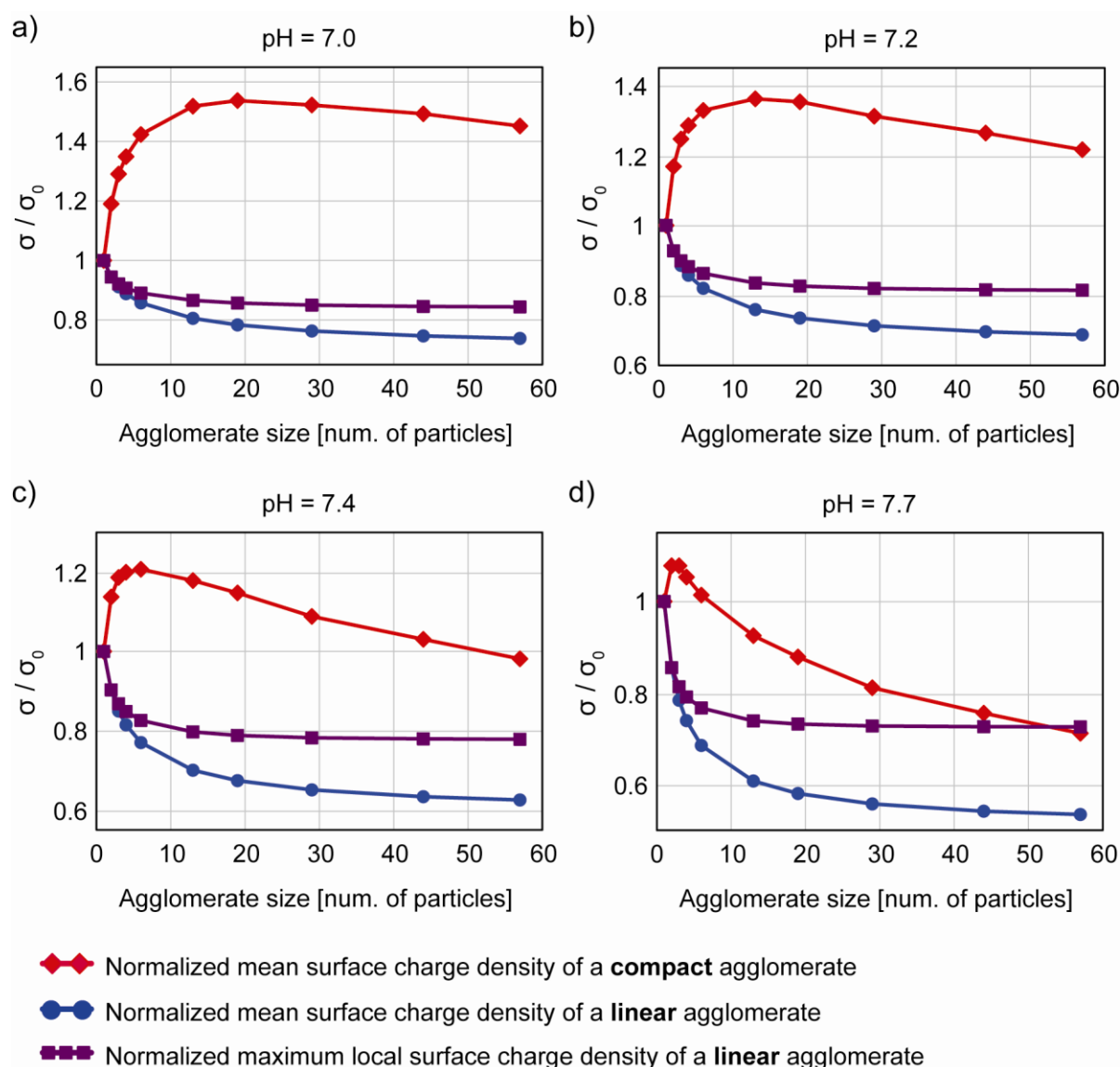


Figure 5. Normalized effective agglomerate surface charge density as a function of the number of its constituent primary particles for a) pH = 7.0; b) pH = 7.2; c) pH = 7.4; d) pH = 7.7. The effective agglomerate surface charge density is normalized to the effective surface charge density of the isolated primary particle at given pH.

Acknowledgments

This work was financially supported by the Government of Russian Federation, Grant 074-U01.

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