

Continuous agglomerate model for identifying the solute-indifferent part of colloid nanoparticle's surface charge

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Abstract. This work proposes an explicit analytical model for the surface potential of a colloidal nano-agglomerate. The model predicts that when an agglomerate reaches a certain critical size, its surface potential becomes independent of the agglomerate radius. The model also provides a method for identifying and quantifying the solute-indifferent charge in nanocolloids, that allows to assess the stability of toxicologically significant parameters of the system.

1. Introduction

Biocompatibility of inorganic colloidal nanoparticles (NPs) depends greatly on their surface charge. This charge governs the state of agglomeration in nanocolloids, which, in turn, affects internalization, distribution, metabolism, and excretion of NPs in biological systems [1-6]. It was recently reported that the surface charge itself also has an impact on the toxicity of NPs [1,7-9].

Synthesized metal oxide NPs in aqueous solutions can acquire surface charge through a number of mechanisms: adsorption and desorption of protons on surface hydroxyl groups; physical adsorption of ions; reversible and irreversible chemical adsorption of ions; isomorphic substitution [10,11]. Most of these processes are dependent on the pH of the solution. Therefore, the effect of the medium on the surface charge is usually studied by measuring the surface potential of agglomerated NPs in a relevant pH range.

However, the part of the surface charge arising due to irreversible chemical adsorption and/or isomorphic substitution can be indifferent to the solution used for titration. When NPs are released into a solution of unknown chemistry, the species responsible for this constant charge may react with the medium, leading to neutralisation of their charge. As a result, the surface potential can significantly deviate from the expected values, presenting a considerable toxicological threat.

During experimental studies of colloidal systems, one often observes agglomerates rather than individual particles. We assume that, while for solid particles charging occurs only on the surface, agglomerates, like porous particles, can exhibit volumetric charging. Consequently, it is important to focus theoretical studies of the colloidal charging phenomena not just on individual NPs, but on their agglomerates as well.

In the present work, we propose an analytical model of a colloidal nano-agglomerate that allows to identify the presence of the constant solute-indifferent charge (SIC) and study its effect on the surface potential.



2. Methods

We consider a spherical agglomerate of metal oxide NPs. The agglomerate is immersed in a solution of a strong inert monovalent electrolyte in deionized water. The solution is isolated from atmospheric CO_2 . The pH of this colloidal solution can be varied using acid-base titration at constant ionic strength $I = \text{const}$.

The agglomerate is assumed to be a porous particle. The volume fraction of void space in the agglomerate (porosity Ω) depends on the ordering of constituent NPs and their hydration.

Nanoparticles inside the agglomerate acquire surface charge by protonation and deprotonation of surface hydroxyl groups. They can also carry a SIC originating from isomorphic substitution and/or irreversible chemisorption. Due to the porosity of the agglomerate we assume that the adsorption and desorption of protons on NP surface occurs in the entire volume of the agglomerate.

It is now generally agreed that the adsorption and desorption of protons happens on two types of surface hydroxyl groups, basic and acidic in nature respectively [12-16]:



where $\text{M}-\text{OH}_b$, $\text{M}-\text{OH}_a$ - basic and acidic surface OH groups; K_b , K_a - equilibrium constants for protonation (1) and deprotonation (2) reactions. We consider the reactive surface hydroxyls to be evenly split between acidic and basic type [13,14].

Surface density of hydroxyl groups for NPs usually lies in the range of $\gamma_s = 1-20 \text{ nm}^{-2}$ [10,12-14,17]. It should be noted that the average density of reactive sites on NPs comprising the agglomerate could be lower than the values for individual NPs.

When NPs do not possess the constant charge (SIC), the pH at which the particle's surface charge is zero (*point of zero charge*) can be found as:

$$\text{PZC}_0 = \frac{\text{p}K_b + \text{p}K_a}{2} , \quad (3)$$

where PZC_0 - point of zero charge in absence of SIC; $\text{p}K_b = -\log_{10}(K_b)$ and $\text{p}K_a = -\log_{10}(K_a)$. Parameters $\text{p}K_b$ and $\text{p}K_a$ have the physical meaning of pH values at which half of the basic (acidic) sites are protonated (deprotonated). We can now express:

$$\text{p}K_b = \text{PZC}_0 - \Delta\text{p}K \quad \text{and} \quad \text{p}K_a = \text{PZC}_0 + \Delta\text{p}K , \quad (4)$$

where $\Delta\text{p}K = \text{p}K_a - \text{p}K_b$. Values of $\Delta\text{p}K$ for metal oxide NPs can span over a wide range of $\Delta\text{p}K = 1-14$ [18].

Electrostatic potential φ in the described system is governed by the Poisson-Boltzmann equation [10]. A number of assumptions were made to derive an analytical solution to the Poisson-Boltzmann problem for the potential inside and outside of the agglomerate. First, the Debye-Huckel approximation for low potentials in the system is used. According to this approximation, the maximum potential in the system should satisfy the condition: $\max(\varphi) < kT/e$ (k - Boltzmann constant; T - temperature; e - elementary charge). Second, we consider only the non-saturated regime of protonation/deprotonation: $\text{p}K_b < \text{pH} < \text{p}K_a$. Finally, the internal space of the agglomerate is approximated with continuous distributions of effective volume charge density ρ and dielectric permittivity ε_A :

$$\rho(\mathbf{r}) = e \frac{1-\Omega}{V_{\text{NP}}} \left(Z_c + \frac{P}{2} \left[10^{-\Delta\text{pH}} \left\{ 1 - \frac{e\varphi(\mathbf{r})}{kT} \right\} - 10^{\Delta\text{pH}} \left\{ 1 + \frac{e\varphi(\mathbf{r})}{kT} \right\} \right] \right) + \varepsilon_A \varepsilon_0 \cdot \Omega \kappa^2 \cdot \varphi(\mathbf{r}) , \quad (5)$$

$$\varepsilon_A = \varepsilon_{\text{NP}}(1-\Omega) + \varepsilon_M \Omega , \quad (6)$$

where Z_C - average charge number of SIC per NP, $P = S_{NP} \cdot \gamma_s \cdot 10^{-\frac{1}{2}\Delta pH}$ - charge regulation parameter; V_{NP} , S_{NP} - volume and surface area of primary NPs; $\kappa^2 = 2I \cdot e^2 / \epsilon_M \epsilon_0 kT$ - Debye-Huckel screening parameter of the solution; ϵ_{NP} , ϵ_M - dielectric permittivities of NPs and the medium (solution); ϵ_0 - dielectric constant; \mathbf{r} - position vector.

By solving the resulting Debye-Huckel problem we obtained the following expression for the surface potential of the agglomerate φ_s :

$$\varphi_s = \frac{e}{\epsilon_A \epsilon_0} \cdot \frac{1-\Omega}{V_{NP}} \cdot \frac{Z_C + P \cdot \sinh[-\ln(10) \cdot \Delta pH]}{\alpha^2 \cdot \left(1 + \frac{\epsilon_M}{\epsilon_A} \cdot \frac{\kappa R + 1}{\alpha R \cdot \coth(\alpha R) - 1}\right)}, \quad (7)$$

where R - agglomerate radius; α - effective Debye-Huckel screening parameter of the agglomerate's interior that is given by:

$$\alpha^2 = \left(\frac{e^2}{\epsilon_A \epsilon_0 kT} \cdot \frac{1-\Omega}{V_{NP}} \cdot P \cdot \cosh[-\ln(10) \cdot \Delta pH] \right) + (\Omega \kappa^2). \quad (8)$$

As follows from (8), the parameter α consists of contributions from the surface charge of constituent NPs (first term) and from ions penetrating the void spaces between the NPs (second term).

3. Results and discussion

3.1. Surface potential as a function of agglomerate size

From expressions (7) and (8) it follows that when $\kappa R \gg 1$, the surface potential becomes independent of agglomerate radius. This behavior is illustrated in figure 1A. The saturated size-independent surface potential of the agglomerate is given by:

$$\varphi_s^{\text{Sat}} = \frac{e}{\epsilon_A \epsilon_0} \cdot \frac{1-\Omega}{V_{NP}} \cdot \frac{Z_C + P \cdot \sinh[-\ln(10) \cdot \Delta pH]}{\alpha^2 \cdot \left(1 + \frac{\epsilon_M}{\epsilon_A} \cdot \frac{\kappa}{\alpha}\right)} \quad (9)$$

The critical radius above which the agglomerate's surface potential becomes size-independent is defined only by the ionic strength of the solution. This relation is shown in figure 1B.

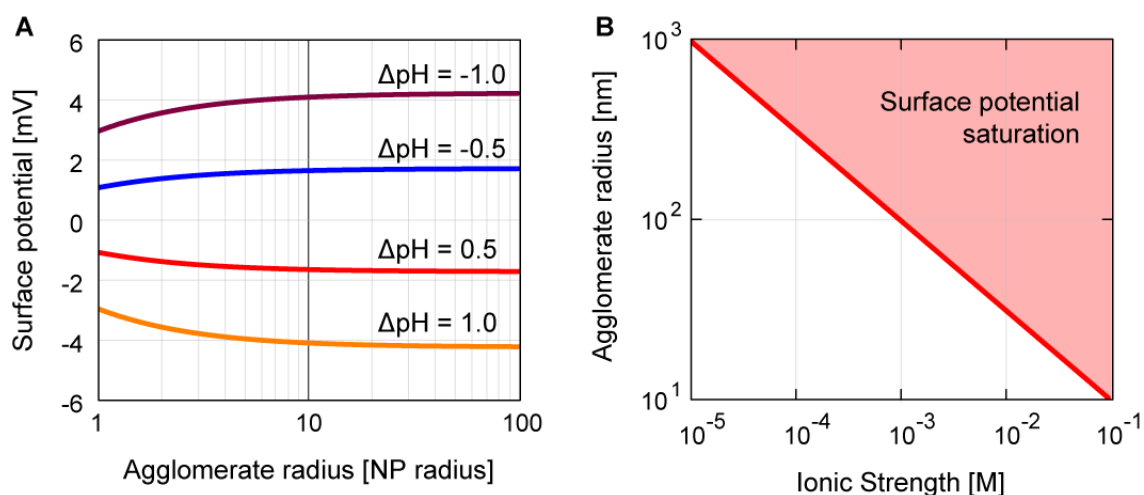


Figure 1. A – surface potential as a function of agglomerate radius (normalized to the primary NP radius) at different values of ΔpH ; B – dependency of critical agglomerate radius on ionic strength of the solution; filled area corresponds to agglomerate radii above the critical value for which surface potential becomes independent of agglomerate size.

3.2. Effect of solute-indifferent charge on the agglomerate's point of zero charge

The model of the agglomerate's surface potential was developed under the Debye-Huckel approximation. Therefore, it is quantitatively valid only at low potentials. This condition is generally not satisfied throughout entire experimental surface potential curves. However, expression (7) is always applicable around the point of zero charge of the agglomerate. Consequently, we can use it to find the condition for zero agglomerate charge in case of non-zero SIC:

$$\frac{Z_c}{P} = \sinh[\ln(10) \cdot \Delta PZC], \quad (10)$$

where $\Delta PZC = PZC - PZC_0$ - shift of point of zero charge in relation to its value in absence of SIC.

Equation (10) shows that the presence of SIC shifts the agglomerate's PZC in relation to PZC_0 (point of zero charge when SIC is zero):

$$\Delta PZC = \log_{10} \left(\frac{Z_c}{P} + \left[\left\{ \frac{Z_c}{P} \right\}^2 + 1 \right]^{\frac{1}{2}} \right); \quad (11)$$

this dependency is illustrated in figure 2A. As a result, it is possible to identify the presence of SIC by detecting such PZC shift.

As shown by (3), PZC_0 lies exactly in the middle between pK_b and pK_a , which signify the onset of protonation and deprotonation saturation correspondingly. We use a numerical non-linear Poisson-Boltzmann model of charged flat surface to demonstrate that non-zero SIC does not alter pH values at which protonation and deprotonation saturate (figure 2B). It is thus possible to assess the position of PZC_0 as a mid-point between the points of saturation onset.

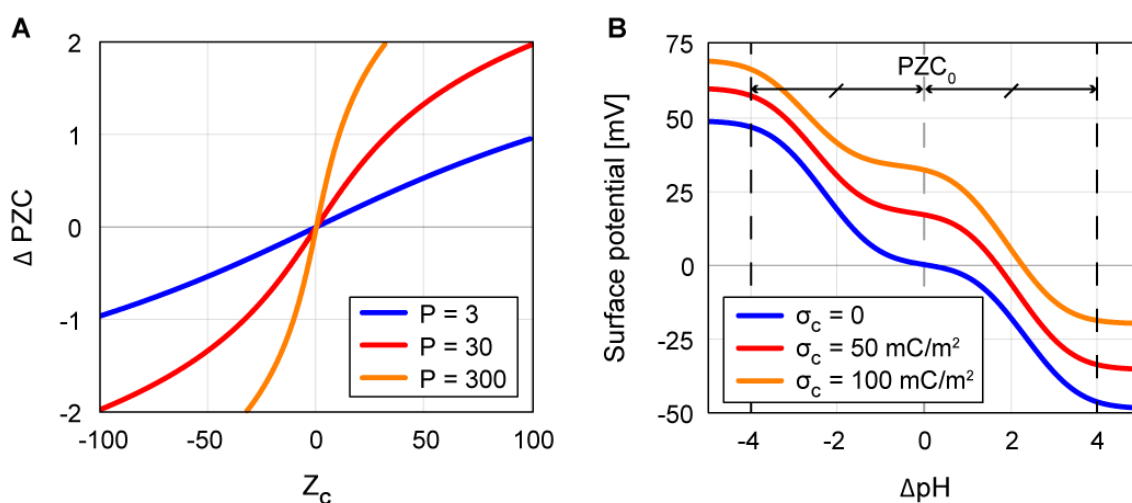


Figure 2. A – point of zero charge shift (ΔPZC) as a function of average charge number of SIC per NP (Z_c) at different values of charge regulation parameter P ; B – surface potential as a function of ΔpH predicted by the numerical model of flat surface at different values of surface charge density of SIC.

3.3. Limiting cases of continuous agglomerate model

We now consider the interior Debye-Huckel screening parameter α . According to (8), this parameter consists of contributions from NPs' surface charge and ions in the inter-particle cavities. In a limiting case when one of these contributions significantly outweighs the other, expression (9) allows for further simplification.

The interior Debye-Huckel parameter α reduces to just the NP surface charge contribution when the following condition is met:

$$\frac{e^2}{\epsilon_0 kT} \cdot \frac{S_{NP}}{V_{NP}} \cdot \gamma_s \cdot 10^{\frac{1}{2}\Delta pK} \cdot \left(\epsilon_{NP} + \epsilon_M \frac{\Omega}{1-\Omega} \right)^{-1} \gg \Omega \kappa^2. \quad (12)$$

We denote this limit as *Case A*. For closed-packed agglomerates of NPs with site density $\gamma_s = 1 \text{ nm}^{-2}$ immersed in electrolyte solution with ionic strength $I = 0.001 \text{ M}$, condition (12) is met when primary NPs radius is less or equal to 25 nm and $\Delta pK \leq 4$.

The simplified agglomerate's surface potential expression for *Case A* is given by:

$$\varphi_s^{\text{Case A}} = \frac{kT}{e} \cdot \frac{Z_C + P \cdot \sinh[-\ln(10) \cdot \Delta pH]}{P \cdot \cosh[-\ln(10) \cdot \Delta pH] \cdot \left(1 + \frac{\epsilon_M}{\epsilon_A} \cdot \frac{\kappa}{\alpha} \right)}. \quad (13)$$

For highly porous agglomerates/particles with large ΔpK in solutions with high ionic strength, the opposite limiting case can be relevant:

$$\frac{e^2}{\epsilon_0 kT} \cdot \frac{S_{NP}}{V_{NP}} \cdot \gamma_s \cdot 10^{\frac{1}{2}\Delta pK} \cdot \left(\epsilon_{NP} + \epsilon_M \frac{\Omega}{1-\Omega} \right)^{-1} \ll \Omega \kappa^2. \quad (14)$$

The interior Debye-Huckel parameter α then reduces to just the contribution from ions in agglomerate's cavities. We denote this limit as *Case B*. For agglomerates with porosity $\Omega \geq 0.5$ composed from NPs with site density $\gamma_s = 1 \text{ nm}^{-2}$ this condition is met in solutions with ionic strength $I \geq 0.001 \text{ M}$ when primary NP radius is greater or equal to 25 nm and $\Delta pK \geq 6$.

The simplified agglomerate's surface potential expression for *Case B* is given by:

$$\varphi_s^{\text{Case B}} = \frac{e \cdot (1-\Omega)}{\epsilon_0 \kappa^2 V_{NP}} \cdot \frac{Z_C + P \cdot \sinh[-\ln(10) \cdot \Delta pH]}{\epsilon_{NP} \Omega (1-\Omega) + \epsilon_M (\Omega^2 + \sqrt{\Omega})}. \quad (15)$$

Expressions (13) and (15) explicitly show the dependency of agglomerate's surface potential on the ionic strength of the solution. In both cases the effect of SIC on the potential increases at lower ionic strengths. Moreover, this dependency is suggested to be stronger for the case of highly porous agglomerates/particles (15).

3.4. Solute-indifferent charge assessment

Simplified expressions (13) and (15) are always valid near to the agglomerate's point of zero charge for the same reason as the original formula (7). Therefore, we can use these expressions to find the relation between the model parameters (Z_C and P) and the first derivative of the surface potential dependency on pH at the point of zero charge.

The derivative of the surface potential curve at PZC can be determined experimentally. Then, by differentiating expression (13) or (15) and using the relation (10), we can find the estimate for the SIC charge number per NP Z_C and the charge regulation parameter P :

$$Z_C = \tanh[\ln(10) \cdot \Delta PZC] \cdot Y, \quad (16)$$

$$P = \text{sech}[\ln(10) \cdot \Delta PZC] \cdot Y, \quad (17)$$

where the Y function is specific to the employed limiting case. For the *Case A* we have:

$$Y_{\text{Case A}} = \left(\frac{\varphi_s' \Big|_{\Delta PZC} \cdot \epsilon_M \cdot \kappa}{\ln(10) \cdot \frac{kT}{e} + \varphi_s' \Big|_{\Delta PZC}} \right)^2 \cdot \left(e^2 \frac{\epsilon_{NP} [1-\Omega]^2 + \epsilon_M \Omega [1-\Omega]}{V_{NP} \epsilon_0 kT} \right)^{-1}, \quad (18)$$

and for the *Case B*:

$$Y_{\text{Case B}} = \left| \frac{\varphi'_s|_{\Delta\text{PZC}}}{\ln(10)} \right| \cdot \frac{\varepsilon_0 \kappa^2 V_{\text{NP}}}{e} \cdot \left(\varepsilon_{\text{NP}} \Omega + \varepsilon_{\text{M}} \frac{\Omega^2 + \sqrt{\Omega}}{1 - \Omega} \right) \quad (19)$$

where $\varphi'_s|_{\Delta\text{PZC}}$ – experimentally determined first derivative of the surface potential dependency on pH at the agglomerate's point of zero charge. Note that this assessment requires the additional knowledge of estimates for the agglomerates porosity Ω and primary NP's volume V_{NP} and dielectric permittivity ε_{NP} .

4. Conclusions

We developed an explicit analytical model for the surface potential of a colloidal nano-agglomerate. Analysis of this model suggests that

- 1) after an agglomerate reaches a certain critical size, its surface potential becomes independent of the agglomerate radius. The value of this critical size is defined solely by the ionic strength of the solution.
- 2) Presence of solute-indifferent charge (SIC) in the agglomerate causes the point of zero charge to shift in relation to its value in absence of SIC. The sign of this shift coincides with the sign of SIC.
- 3) The effect of SIC on the surface potential increases at lower ionic strength. This correlation is stronger for highly porous agglomerates/particles.
- 4) It is possible to identify the presence of SIC by comparing the point of zero charge and the mid-point between the pH values corresponding to protonation and deprotonation saturation onsets. The developed agglomerate model provides a method for quantitative assessment of the average amount of SIC per primary nanoparticle.

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