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Original Scientific Paper

Effect of Charge Distribution on the Stability of Nano-dispersions*

Nikola Kallay, ** **Tajana Preočanin, and Davor Kovačević**

Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

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Abstract. In the course of aggregation of very small colloid particles, *i.e.* nano-particles, the overlap of the diffuse layers is almost complete, so that one cannot apply the common DLVO theory. Since nano-particles are small compared to the extent of the diffuse layer, the process is considered in the same way as for two interacting ions. Therefore, the Brønsted concept based on the Transition State Theory was applied. In this work the effect of charge distribution among nano-particles was examined. Results of numerical simulation show that wider charge distribution causes substantial decrease in the stability of nano-dispersions.

Keywords: nano-dispersions, colloid stability, charge distribution

INTRODUCTION

It is known that nano-dispersions are less stable with respect to the ordinary colloid dispersions. The main reason is relatively low electrical charge of nano-particles.[1] The effect of particle size[2] and polydispersity[3] on aggregation of nano particles, as well as aggregation between different particles[4–6] (heteroaggregation) were examined. Modelling of aggregation on molecular level[7] and Monte Carlo simulations[8] of electrostatic surface interactions were also performed. In the course of the collision of ordinary colloid particles the overlap of diffuse part of the interfacial layers is partial, while it is almost complete in the case of nanoparticles (Figure 1). Therefore the classical DLVO theory is no more applicable for studying the kinetics of aggregation of nano-particles.[9,10]

Two colliding nano-particles form a common ionic cloud in a similar way as two interacting ions. For that reason the Brønsted theory,[11,12] which was developed for the primary salt effect on the kinetics of ionic reactions, was applied.[13]

However, the additional feature characterizing the nano-dispersions is the charge distribution among the particles. It is clear that even in dispersions of particles being identical in their size and shape the charge of the particles cannot be the same for all of the particles.[14,15] This phenomenon is more pronounced in nano-dispersions. For example, if the average charge number of nano-particles is $z = 5$, then one may expect high population of particles $z = 5$, but also a significant portions of particles bearing the charge $z = 4$, and $z = 6$. In addition some of them may exhibit the charge more apart from the mean value of 5. Since the electrostatic repulsion is responsible for the stability of dispersions containing hydrophobic particles in the absence of surfactants, the charge distribution may significantly affect the stability of the nano-dispersions. In this article we shall analyse the effect of charge distribution on the stability of nano-dispersions, or on the rate of aggregation of nano-particles. For that purpose the numerical simulation of the stability of a model system will be performed.

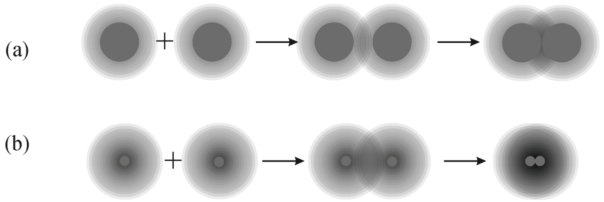

Figure 1. Overlap of electrical interfacial layers in the course of the collision for two ordinary colloid particles (a) and for two nano-particles (b).

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* Dedicated to Professor Emeritus Drago Grdenić, Fellow of the Croatian Academy of Sciences and Arts, on the occasion of his 90th birthday.

** Author to whom correspondence should be addressed. (E-mail: nkallay@chem.pmf.hr)

THEORETICAL

Aggregation of two charged nanoparticles $\mathrm{A}^{z_\mathrm{A}}$ and $\mathrm{B}^{z_\mathrm{B}}$ could be represented by

$$\mathrm{A}^{z_\mathrm{A}} + \mathrm{B}^{z_\mathrm{B}} \rightarrow \mathrm{AB}^{z_\mathrm{AB}} \tag{1}$$

where z denotes the charge number. The rate of aggregation v is proportional to the product of concentrations of interacting particles $[\mathrm{A}^{z_\mathrm{A}}][\mathrm{B}^{z_\mathrm{B}}]$

$$v = k \cdot \left[\mathrm{A}^{z_\mathrm{A}}\right] \cdot \left[\mathrm{B}^{z_\mathrm{B}}\right] \tag{2}$$

where k is the rate constant (coefficient) of aggregation.

Application of the Brønsted concept results in the following relationship applicable to dispersed nanoparticles

$$\log k = \log k_\mathrm{diff} - \frac{z_\mathrm{A} z_\mathrm{B} F^2 \ln 10}{4\pi\varepsilon LRT(r_\mathrm{A} + r_\mathrm{B})} + \frac{2 z_\mathrm{A} z_\mathrm{B} A_\mathrm{DH}\, I_c^{1/2}}{1 + abI_c^{1/2}} \tag{3}$$

where L is the Avogadro constant, R, T and F have their usual meaning and the ionic strength I_c for 1:1 electrolytes is equal to their concentration. The Debye-Hückel constant A_DH depends on the temperature and the electric permittivity of the medium ε ($= \varepsilon_0\ \varepsilon_\mathrm{r}$) as

$$A_\mathrm{DH} = \frac{2^{1/2}}{8\pi L \ln 10} \cdot \left(\frac{F^2}{\varepsilon RT}\right)^{3/2} \tag{4}$$

For aqueous solutions at 25 °C: $A_\mathrm{DH} = 0.509\ \mathrm{mol}^{-1/2}\ \mathrm{dm}^{3/2}$. Coefficient b in Eq. (3) is equal to

$$b = \left(\frac{2F^2}{\varepsilon RT}\right)^{1/2} \tag{5}$$

and a denotes the minimum separation of interacting charged species which could be approximated by the radius (r) of the nano-particles. The rate coefficient of rapid diffusional aggregation for aggregation of particles A and B in absence of repulsion, k_diff, could be obtained from the Smoluchowski theory[16]

$$k_\mathrm{diff} = \frac{k_\mathrm{B} T}{3\eta}\left(\frac{1}{r_\mathrm{A}} + \frac{1}{r_\mathrm{B}}\right) \cdot (r_\mathrm{A} + r_\mathrm{B}) \tag{6}$$

In another form Eq. (3) reads

$$\log k = \log k_\mathrm{diff} - z_\mathrm{A} z_\mathrm{B} \cdot \left(\frac{\beta}{r_\mathrm{A} + r_\mathrm{B}} - 2A_\mathrm{DH}\frac{I_c^{1/2}}{1 + abI_c^{1/2}}\right) \tag{7}$$

where

$$\beta = \frac{F^2 \ln 10}{4\pi\varepsilon LRT} \tag{8}$$

The stability coefficient W is given by

$$\log W = \log(k_\mathrm{diff} / k) = z_\mathrm{A} z_\mathrm{B} \cdot \left(\frac{\beta}{r_\mathrm{A} + r_\mathrm{B}} - 2A_\mathrm{DH}\frac{I_c^{1/2}}{1 + abI_c^{1/2}}\right) \tag{9}$$

Note that for monodisperse systems ($r = r_\mathrm{A} = r_\mathrm{B}$) the above equations have a more simple form.

CHARGE DISTRIBUTION

The numerical simulation will be performed on the basis of the Eq. (9). Nano-dispersion of identical spherical particles with a certain charge distribution will be assumed.

The charge distribution will be defined as follows: the number concentration of particles bearing average charge number z is C_z, The concentration of particles bearing charge number $z-1$ and $z+1$ are

$$C_{z+1} = C_{z-1} = f \cdot C_z \tag{10}$$

The concentrations of particles bearing charge even more apart from the average value are

$$C_{z+2} = C_{z-2} = f \cdot C_{z+1} = f^2 \cdot C_z \tag{11}$$

$$C_{z+3} = C_{z-3} = f \cdot C_{z+2} = f^3 \cdot C_z \tag{12}$$

Accordingly, the absence of the charge distribution will be characterized by $f = 0$, while the wider charge distributions will be characterized by the higher f values being always below 1. The concentration of particles of average charge number z is related to the total particle concentration C_tot by

$$C_z = \frac{C_\mathrm{tot}}{1 + 2f + 2f^2 + 2f^3} \tag{13}$$

By using Eqs. (10)–(13) and assuming certain f value, one calculates the concentrations of different kinds of particles. The different distributions are presented in Figure 2.

According to Eqs. (1) and (9), the overall rate of aggregation of nano-particles B exhibiting the charge distribution is a sum of individual rates of differently charged particles

$$v = \sum k_{i,j} \left[\mathrm{B}^{z_i}\right] \cdot \left[\mathrm{B}^{z_j}\right] = k_\mathrm{dif} \cdot \sum W_{i,j}^{-1} \cdot \left[\mathrm{B}^{z_i}\right] \cdot \left[\mathrm{B}^{z_j}\right] \tag{14}$$

The diffusional rate of uncharged particles is given by

$$v_\mathrm{diff} = k_\mathrm{dif} \cdot [\mathrm{B}]^2 \tag{15}$$

where [B] denotes total concentration of nano-particles.

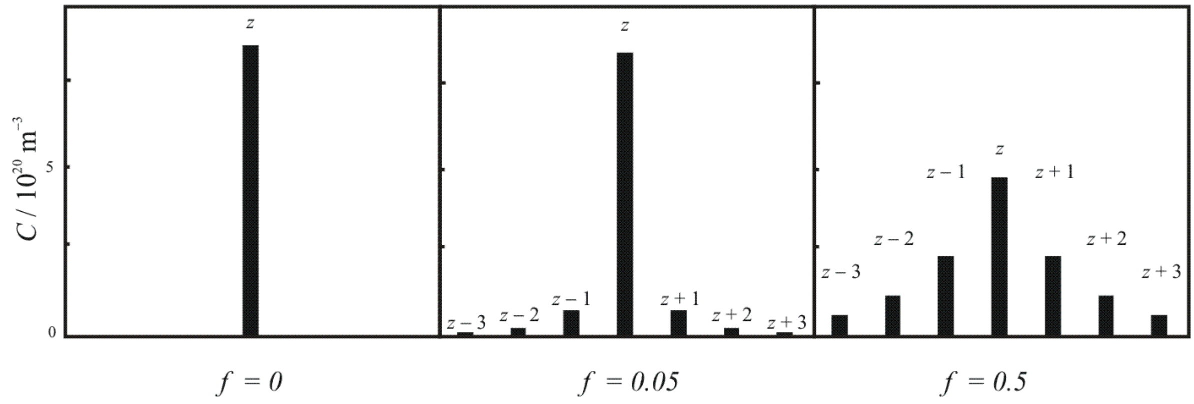

Figure 2. Different distributions of particles in nano-dispersions for different *f* values.

Accordingly, the effective stability coefficient for nano-systems exhibiting charge distribution is

$$W_{\mathrm{eff}} = \frac{v_{\mathrm{diff}}}{v} = \frac{[\mathrm{B}]^2}{\sum W_{i,j}^{-1} \cdot \left[\mathrm{B}^{z_i}\right] \cdot \left[\mathrm{B}^{z_j}\right]} \tag{16}$$

RESULTS AND DISCUSSION

The effect of pH and ionic strength will be examined for a model metal oxide nano-particles of radus 1 nm. The average charge numbers of these model particles will be estimated by using the electrokinetic data for chromium hydroxide.[17]

The potential at the onset of diffuse layer Ψ_{d} will be approximated by the electrokinetic potential ζ. The effective surface charge density, σ_{s}, will be calculated by using the Gouy-Chapman theory for spherical geometry by

$$\sigma_{\mathrm{s}} = \frac{\psi_{\mathrm{d}} \varepsilon (1 + r\kappa_{\mathrm{DH}})}{r} \tag{17}$$

The reciprocal Debye-Hückel distance κ_{DH} can be calculated from

$$\kappa_{\mathrm{DH}} = \left(\frac{2F^2 I_c}{\varepsilon RT} \right)^{1/2} \tag{18}$$

The average charge number of nano-particles of radius *r* is equal to

$$z = \frac{4r^2 \pi \sigma_{\mathrm{s}}}{F} \tag{19}$$

The isoelectric point was taken to be at $\mathrm{pH} = 8.5$. For nano-particles of *r* = 1 nm at the ionic strength of $10^{-3}\,\mathrm{mol\,dm^{-3}}$ the average charge number decreases from approximately 4 at pH = 3 to zero at $\mathrm{pH} = 8.5$, being negative in the basic region almost up to –4 at $\mathrm{pH} = 11$. For same nano-particles at $\mathrm{pH} = 3$ the average charge number decreases with ionic strength from 4, at the ionic strength of $10^{-3}\,\mathrm{mol\,dm^{-3}}$, to almost zero at 1 mol dm^{-3}.

Figure 3 displays the calculation of the effective stability coefficients at low ionic strength of 10^{-3} mol dm^{-3} as a function of pH. The calculations were performed for different charge distributions. In absence of charge distribution $(f = 0)$ the system is stable in the pH-region apart from the isoelectric point, *i.e.* at $7 > \mathrm{pH} > 10$.

At the isoelectric point the particles are uncharged and the system is unstable for any *f* value. The stability of the system significantly decreases as the charge distribution becomes wider. This effect is noticeable up to $f = 0.5$. The further increase of *f* above 0.5 does not

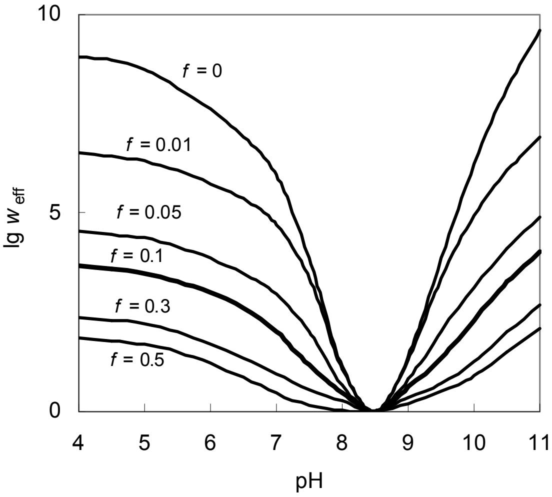

Figure 3. Effect of pH on the stability of a model metal oxide aqueous nano-dispersion (*r* = 1 nm) at *T* = 298 K and the ionic strength of $10^{-3}\,\mathrm{mol\,dm^{-3}}$. Calculations were performed for the absence of the charge distribution $(f = 0)$, as well as for wider distributions $(f > 0)$. Above $f = 0.5$ no significant effect on the stability was observed.

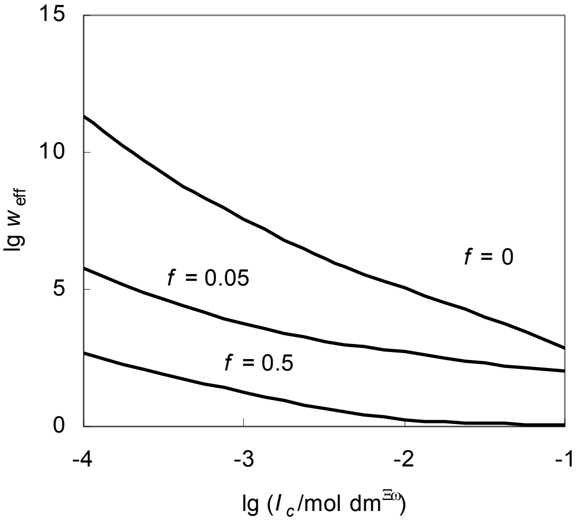

Figure 4. Effect of the ionic strenght on the stability of a model metal oxide aqueous nano-dispersion (r = 1 nm) at T = 298 K and pH = 3. Calculations were performed for the absence of the charge distribution $(f = 0)$, as well as for wider distributions $(f > 0)$. Above $f = 0.5$ no significant effect on the stability was observed.

significantly affect the stability. The reason for such an effect lies in the fact that aggregation of particles of low charge approaches the fast regime of rapid aggregation and cannot be further accelerated. It is clear that the charge distribution markedly reduces the stability of nano-dispersions.

The effect of the ionic strength on the stability of nano-dispersion is examined for the same system at $\mathrm{pH} = 3$. In absence of charge distribution $(f = 0)$ the system is stable at the low ionic strength, *i.e.* below $10^{-3}\,\mathrm{mol\,dm^{-3}}$ (Figure 4.)

The stability decreases with the ionic strength and almost disappears at ionic strengths above 10^{-3} mol dm^{-3}. At high ionic strength the electrostatic repulsion diminishes so that the system becomes completely unstable. In the region of the low ionic strength the stability of the system again decreases as the charge distribution becomes wider which is noticeable up to f = 5. The same behaviour was observed for larger nanoparticles. The only difference was that these systems were more stable.

The analysis performed in this study clearly shows that the charge distribution among the nano-particles markedly reduces the stability of nano-dispersions. However, there is an additional reason why nano-dispersions do not exhibit high stability. For mono-disperse systems of uniform particles bearing the same charge, the integration of Eq. (14) and introduction of the mass concentration γ of dispersed phase of density ρ result in the following expression for the time necessary to reduce concentration of primary particles to the half of the initial value (half-time of aggregation) $t_{1/2}$

$$t_{1/2} = \frac{1}{C_0 k} = \frac{W}{C_0 k_{\mathrm{diff}}} = \frac{4\pi\rho}{3\gamma} \cdot \frac{W}{k_{\mathrm{diff}}} \cdot r^3 \qquad (20)$$

It is clear that for a given stability coefficient W, the time needed to reduce particle concentration to one half of the initial concentration C_0 is markedly lower for smaller particles. Also, the particle number concentration in nano-dispersion might be so high that second order kinetic regime does not hold.

According to the analysis performed in this study one is able to conclude that nano-dispersions are less stable with respect to the ordinary colloid dispersions due to higher particle number concentration but also due to distribution of charges among dispersed nano-particles.

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SAŽETAK

Utjecaj distribucije naboja na stabilnost nanodisperzija

Nikola Kallay, Tajana Preočanin i Davor Kovačević

Zavod za fizikalnu kemiju, Kemijski odsjek, Prirodoslovno-matematički fakultet,
Sveučilište u Zagrebu, Horvatovac 102a, 10000 Zagreb, Hrvatska

Tijekom agregacije vrlo malih koloidnih čestica, tzv. nanočestica, dolazi do gotovo potpunog prekrivanja difuznih slojeva pa u takvom slučaju nije moguće primijeniti uobičajenu DLVO teoriju. Budući da su nanočestice male u usporedbi s difuznim slojem, navedeni proces se može promatrati kao u slučaju interakcija između dva iona. Iz tog je razloga moguće primijeniti Brønstedov koncept zasnovan na teoriji prijelaznog stanja. U ovom je radu ispitan utjecaj distribucije naboja između nanočestica. Rezultati numeričkih simulacija pokazuju da šira distribucija naboja uzrokuje značajan pad stabilnosti nanodisperzija.