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Authors' Review

Introduction of the Surface Complexation Model into the Theory of Colloid Stability*

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This article shows that the introduction of the Surface Complexation model into the »family« of theories that comprise the Theory of Colloid Stability makes that theory »absolute«. This means that one characterizes the electrical interfacial layer, *e.g.* by adsorption measurements, and calculates the equilibrium parameters, such as the equilibrium constants of protonation and deprotonation of amphoteric surface OH groups, equilibrium constants of the association of counterions, capacitances of inner and outer interfacial layers and the total concentration of surface sites. From these equilibrium parameters one evaluates the potential at the onset of the diffuse layer (ϕ_d) and calculates the electrostatic interaction energy yielding the rate constant of aggregation and the stability coefficient. It is shown that counterion association plays an important role in the aggregation phenomena by reducing the value of potential ϕ_d.

Key words: particle aggregation, electrical interfacial layer, surface potentials, interfacial equilibrium, counterion association, surface complexation model, theory of colloid stability, stability coefficient.

INTRODUCTION

Aggregation of colloid particles, often called coagulation, is probably the best example of collision governed kinetics. It is a second order process characterized by the rate constant that may range within as many as six orders

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

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of magnitudes. Depending on the medium composition, the same system may aggregate so rapidly that the process can be hardly followed by classical techniques, but also the aggregation process can be so slow that the system is practically stable. The latter case is associated with the often used term colloid stability.

There are several phenomena that can be interpreted by »absolute theories«, *i.e.* by theories that can quantitatively predict a certain property of the system from its fundamental parameters without using »adjustable parameters«. For example, the Transition State Theory used in chemical kinetics relies on adjustable parameters (enthalpy of transition state formation, transmission factor). The Collision Theory in molecular kinetics includes steric parameters, the values of which are adjustable. The aim of this article is to show that the introduction of the Surface Complexation (SC) model into the present Theory of Colloid Stability makes that theory »absolute« so that the aggregation rate constant can be calculated for the uniform spherical colloid particles of a known size at a certain temperature and composition of the liquid medium from the parameters characterizing the interfacial equilibrium.

PARTICLE AGGREGATION

Particle aggregation can be described, like any other process, by the reaction equation as

$$2\ \mathrm{Pa}_1 \rightarrow \mathrm{Pa}_2\ ; \qquad k_{1,1} \tag{1}$$

where Pa_1 and Pa_2 denote a primary colloid particle (singlet) and an aggregate of two primary colloid particles (doublet), respectively, and $k_{1,1}$ is the rate constant (coefficient) of aggregation of two singlets. The higher ordered processes are represented by

$$\mathrm{Pa}_1 + \mathrm{Pa}_2 \rightarrow \mathrm{Pa}_3\ ; \qquad k_{1,2} \tag{2}$$

$$\mathrm{Pa}_2 + \mathrm{Pa}_2 \rightarrow \mathrm{Pa}_4\ ; \qquad k_{2,2} \tag{3}$$

etc. The rate of aggregation of singlets $v_{1,1}$ is

$$v_{1,1} = k_{1,1}\ [\mathrm{Pa}_1]^2 \tag{4}$$

where $[\mathrm{Pa}_1]$ is the particle number concentration of singlets. For higher order processes, the rate is expressed by

$$v_{1,2} = k_{1,2}\,[\mathrm{Pa}_1]\,[\mathrm{Pa}_2] \tag{5}$$

$$v_{2,2} = k_{2,2}\,[\mathrm{Pa}_2]^2 \tag{6}$$

etc. Due to the geometry, the simplest case for theoretical treatment is the aggregation of singlets (Eqs. 1, 4), the rate of which can be measured by several techniques. Some techniques, *e.g*., the simple light scattering method, measure the average rate v, which can be expressed by

$$v = -\frac{\mathrm{d}[\mathrm{Pa}]}{\mathrm{d}t} = k\,[\mathrm{Pa}]^2 \tag{7}$$

where [Pa] denotes the total concentration of colloid particles ($[\mathrm{Pa}] = [\mathrm{Pa}_1] + [\mathrm{Pa}_2] + ...$) and k is the average rate constant corresponding to the rate constant of singlet aggregation in the early stage of the process (at $t = 0$; $k = k_{1,1}$). Integration of the above equation yields the common rate law for the second order kinetic process

$$\frac{1}{[\mathrm{Pa}]_t} = \frac{1}{[\mathrm{Pa}]_0} + kt \tag{8}$$

where $[\mathrm{Pa}]_t$ and $[\mathrm{Pa}]_0$ are total particle number concentrations at time t and at the onset of the process, respectively.

Theoretical treatment of the aggregation of spherical particles on the basis of the collision concept has two lines, *i.e.* calculation of the collision frequency and of the collision efficiency.

Collision Frequency

Colloid particles ranging from 10 to 100 nm in size can be prepared in the spherical form and uniform in size. The diffusion coefficient of these particles D can be calculated from their radius r and medium viscosity η

$$D = \frac{k_\mathrm{B}T}{6\pi r\eta} \tag{9}$$

where k_B is the Boltzmann constant and T is the thermodynamic temperature. The above equation is exact since colloid particles are large with respect to the water molecules, so aqueous medium can be treated as a homogeneous space in which colloid particles are exposed to the Brownian thermal motion. Also, the hydration layer at the particle surface can be neglected due to the relatively large size of particles, which can be easily determined by electron microscopy or by the light scattering technique. The latter method is especially convenient because dynamic light scattering directly yields the diffusion coefficient of colloid particles.

Diffusion and Brownian motion were solved independently[1] by A. Einstein and by M. von Smoluchowski. Their work enabled Perrin and Svedberg to determine the value of the Avogadro constant. Einstein turned his attention to other phenomena while Smoluchowski continued work in the field of colloid chemistry, solving the problem of collision frequency corresponding to the rate constant of aggregation controlled by diffusion (k_{diff}) when each collision results in aggregation. According to Smoluchowski,[2] the aggregation rate constant of two spherical particles of radii r_1 and r_2 is equal to

$$k_{\mathrm{diff}} = 4\pi\ (D_1 + D_2)\ (r_1 + r_2) \tag{10}$$

where D_1 and D_2 are the corresponding diffusion coefficients. For spherical particles, Eqs. (9) and (10) yield

$$k_{\mathrm{diff}} = \frac{2k_{\mathrm{B}}T}{3\eta}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)(r_1 + r_2) \tag{11}$$

The above equation has been tested experimentally since the diffusion condition for aggregation can be simply achieved. The particles should be uncharged so that no electrostatic repulsion takes place. This condition is present either at the isoelectric point or at a high electrolyte concentration. The exciting feature of colloid systems is that small particles exhibit behaviors of molecules but are still visible. They may be well defined, so their diffusion coefficient is exactly related to their size and shape. Accordingly, the above equation can be rigorously tested because it does not contain »adjustable« parameters. Here, we shall mention three types of experiments that prove the validity of the Smoluchowski equation.

Experimental values of the rate constants of aggregation controlled by diffusion were found to be somehow lower (up to 50%) than the theoretical value.[3] The deviation can be explained by considering the flow of the liquid medium from the space between two approaching particles during the collision. This effect is not included in the original Smoluchowski treatment. It is worth mentioning here that for attachment of colloidal particles to a large sphere, the experimental rate constant was found to be only 5% lower than the theoretical value.[4] However, the Levich theory of conventional diffusion should be applied for such systems.

Another test of the Smoluchowski theory is based on the polydispersity effect. For monodispersed colloids ($r_1 = r_2$), Eq. (11) is reduced to

$$k_{\mathrm{diff}} = \frac{8k_{\mathrm{B}}T}{3\eta} \tag{12}$$

indicating that the rate of aggregation of monodispersed colloid systems does not depend on the particle size. This prediction was experimentally verified by Miller.[5] Function (11) has the minimum at $r_1 = r_2$, so that higher rate constants for polydispersed systems ($r_1 \neq r_2$) should be expected. Semi-quantitatively, this effect could be explained by the fact that larger particles move more slowly but have larger collision diameters. Again, this prediction was verified by Miller.[5]

Temperature dependency of the rate constant was also used to test the Smoluchowski theory.[6,7] The first term in equation (11) depends on the temperature in two manners. It is proportional to the thermodynamic temperature and depends on the medium viscosity, which is a function of the temperature

$$\eta = B \exp(E_\mathrm{v} / RT) \tag{13}$$

where B is the »pre-exponential factor« and E_v is the »viscosity activation energy«. Combination of Eqs. (12) and (13) yields

$$\ln(k_\mathrm{diff} / T) = \ln\left(\frac{8k_\mathrm{B}}{3}\right) - \ln B - \frac{E_\mathrm{v}}{RT} \tag{14}$$

Figure 1. presents the temperature dependency of the aggregation rate constant of silver iodide colloid particles in aqueous medium at an electro-

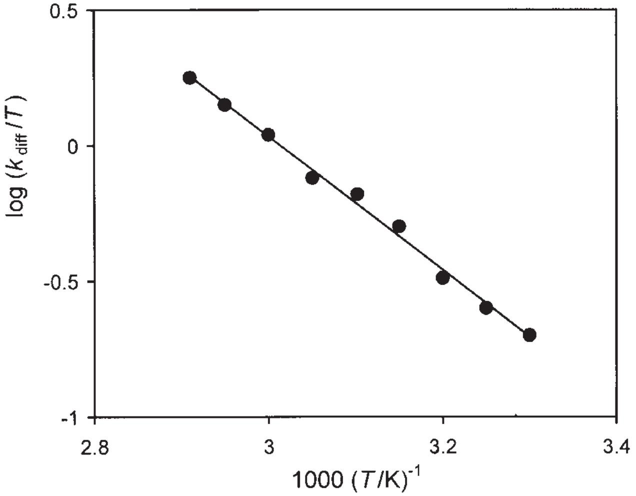

Figure 1. Temperature dependency of the diffusional aggregation rate constant of silver iodide colloid particles, charged negatively ([I$^-$] = 10^{-3} mol dm^{-3}), in aqueous medium[6,7] at counterion concentration higher than c.c.c. ([Mg^{2+}] = 10^{-3} mol dm^{-3}).

lyte concentration higher than the critical coagulation concentration.[6,7] Results are presented according to equation (14) and the slope yields E_v = 18.6 kJ mol^{-1}. This value is, within the experimental error, equal to the value obtained from viscosity measurements (E_v = 17.8 kJ mol^{-1}).

Collision Efficiency

Collision efficiency for colloid particle aggregation α is a reciprocal value of the commonly defined stability coefficient W. It is related to the rate constant of aggregation k by

$$k = \alpha \, k_{\mathrm{diff}} = \frac{k_{\mathrm{diff}}}{W} \tag{15}$$

The general equation was derived by N. Fuchs[8] and is based on the total interaction energy (E_{tot}) between two approaching particles

$$W = 2r \int_{\infty}^{2r} \exp(E_{\mathrm{tot}} / RT) \frac{\mathrm{d}z}{z^2} \tag{16}$$

where z is the interparticle center-to-center distance. In a simple case, the total interaction energy is taken as the sum of short range repulsion (E_r), dispersion van der Waals attraction (E_{vdW}) and the electrostatic repulsion between two particles of the same charge (E_{el})

$$E_{\mathrm{tot}} = E_r + E_{\mathrm{vdW}} + E_{\mathrm{el}} \tag{17}$$

Short range repulsion can be approximated by a »hard wall concept«

$$E_r = 0 \text{ at } x < x_{\mathrm{min}} \text{ and } E_r = \infty \text{ at } x > x_{\mathrm{min}} \tag{18}$$

where x denotes surface-to-surface distance. The dispersion van der Waals attraction is due to the interaction between dipoles (Debye), dipole and induced dipole (Keesom) and two instantaneously induced dipoles (London). Fortunately, all these functions decrease with the distance in the same way, enabling simple summation of interaction energies between all molecules of one particle and all molecules of the other particle. Such a summation was performed independently by Breadly,[9] de Boer[10] and Hamaker.[11] It was found that attraction between particles does not decay with the interparticle distance as sharply as in the case of molecules and that dispersion forces are responsible for aggregation. The interaction energy between two spherical particles of radii r_1 and r_2 (E_H) is given by the Hamaker equation

$$E_H = -A_H \frac{r_1 r_2}{6(r_1 + r_2)x} \tag{19}$$

where x is the distance between the surfaces of two interacting particles. The Hamaker constant A_H depends on the composition of the particles and the medium and can be, in principle, obtained on the basis of the Lifshitz theory.[12]

The above theories were already known before World War II but calculation of the collision efficiency was still not possible, because the electrostatic interaction energy function was missing. During the war, Derjaguin and Landau[13] and Vervey and Overbeek[14] solved the problem independently and, according to them, the theory enabling calculation of the electrostatic interactions is called the DLVO theory. This acronym is often used for the whole system of theories that enable prediction of the aggregation rate, *i.e.* that can quantitatively explain the colloid stability phenomena. Several attempts were made in order to refine the original DLVO approach, *e.g.* by Hogg, Healy and Fuerstenau,[15] Barouch and Matijević,[16] Ohshima,[16] Bhattacharjee, Elimelech and Borkovec,[18] Hsu and Liu,[19] *etc*. In numerous cases, a simple equation derived by Hogg, Healy and Fuerstenau was found to be a suitable approximation for calculation of the interaction energy between two charged particles with surface potentials ϕ_1 and ϕ_2

$$E_\mathrm{el} = \frac{\varepsilon \pi r_1 r_2}{r_1 + r_2} \left\{ 2\phi_1\phi_2 \ln\left(\frac{1+\exp(-\kappa x)}{1-\exp(-\kappa x)}\right) \pm (\phi_1{}^2 + \phi_2{}^2) \ln\left[1-\exp(-2\kappa x)\right] \right\} \qquad (20)$$

The reciprocal Debye-Hückel length (κ) is defined by

$$\kappa = \sqrt{2I_c F^2 / \varepsilon RT} \qquad (21)$$

where I_c is the ionic strength and ε ($= \varepsilon_0 \varepsilon_\mathrm{r}$) is the medium permittivity. Minus sign in the last term of Eq. (20) corresponds to a constant charge condition, when charge densities of interacting surfaces remain constant in the

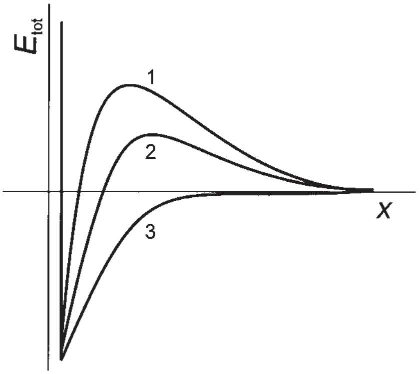

Figure 2. Schematic presentation of the total interaction energy as a function of the distance between particles. The ionic strength increases in the order 1, 2, 3.

course of collision, while the plus sign corresponds to the constant potential case being approximately related to the relaxed electrical interfacial layers. It was shown that the latter case represents better the real situation.[20–22] According to above equations, the total interaction energy between charged particles depends on the ionic strength determined by the electrolyte concentration and on the surface potentials, *i.e.* electrostatic potentials at the onset of the diffuse layer.

Figure 2 is a schematic presentation of the total interaction energy as a function of the distance between the particles. At the closest approach distance the repulsion is infinite, while at short separations the attractive van der Waals attraction prevails over electrostatic repulsion. The electrostatic repulsion dominates at larger separations causing an energy barrier. The barrier is less pronounced at higher ionic strengths, so the collision efficiency, and consequently the rate of aggregation, increases by electrolyte addition, reaching its maximum at the so-called critical coagulation concentration (c.c.c.). This maximum rate corresponds to the process controlled by diffusion, when electrostatic repulsion is compensated by dispersion attraction. A typical experiment with silver iodide colloid particles[23] is presented in Figure 3.

Theoretical interpretation of slow aggregation in the presence of the energy barrier is not exact, so the theory cannot be simply examined and verified. The problem lies in the Hamaker constant (Eq. 19), which is commonly accepted as an adjustable parameter, and also in the unknown values of the surface potentials determining the electrostatic repulsion.

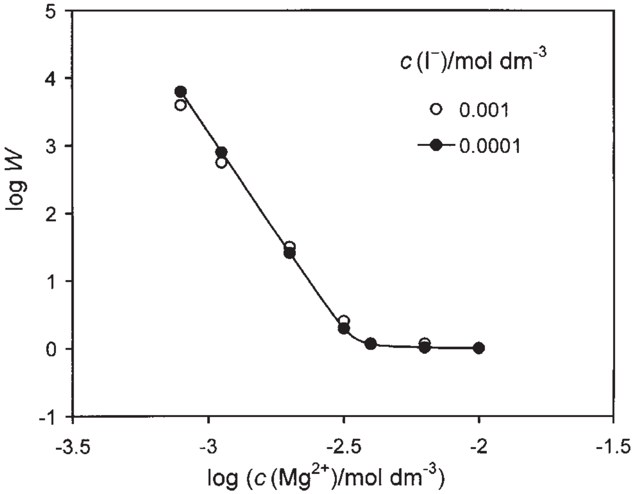

Figure 3. Effect of counterion concentration (Mg^{2+}) on the stability of negatively charged silver iodide colloid particles[6,7] at two different concentrations of potential determining ions (I^-). Temperature of aqueous suspension: 25 °C.

INTERFACIAL EQUILIBRIUM

In general, the term surface potential is used for electrostatic potentials at a certain plane in the electrical interfacial layer, which is in practice more or less clearly defined.

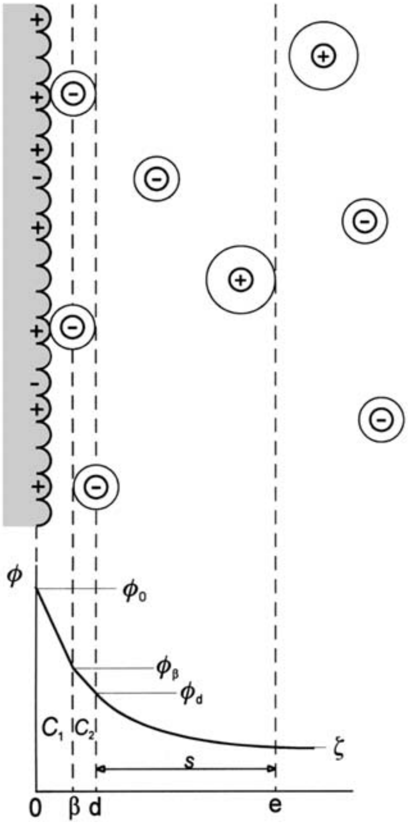

Figure 4. General scheme of the EIL structure.[25]

As used in Eq. (20) for evaluation of the electrostatic interaction energy, it is equal to the electrostatic potential at the onset of the diffuse part of the electrical interfacial layer, ϕ_d, and is not measurable. In the first attempt, it was approximated by the so-called Nernstian potential, ϕ_N, which is for silver iodide equal to

$$\phi_\mathrm{N} = \frac{RT}{F} \log \frac{a(\mathrm{Ag}^+)}{a_\mathrm{pzc}(\mathrm{Ag}^+)} = -\frac{RT}{F} \log \frac{a(\mathrm{I}^-)}{a_\mathrm{pzc}(\mathrm{I}^-)} \tag{22}$$

while for the metal oxides it is

$$\phi_{\mathrm{N}} = \frac{RT}{F}\log\frac{a(\mathrm{H}^+)}{a_{\mathrm{pzc}}(\mathrm{H}^+)} = -\frac{RT}{F}\log\frac{a(\mathrm{OH}^-)}{a_{\mathrm{pzc}}(\mathrm{OH}^-)} \tag{23}$$

However, this hypothetical potential is a linear function of the logarithm of the activity of the potential determining ions (Ag^+ and I^- for silver iodide and H^+ and OH^- for metal oxides) which contradicts the finding that the aggregation rate, *e.g.* of silver iodide particles, does not significantly depend

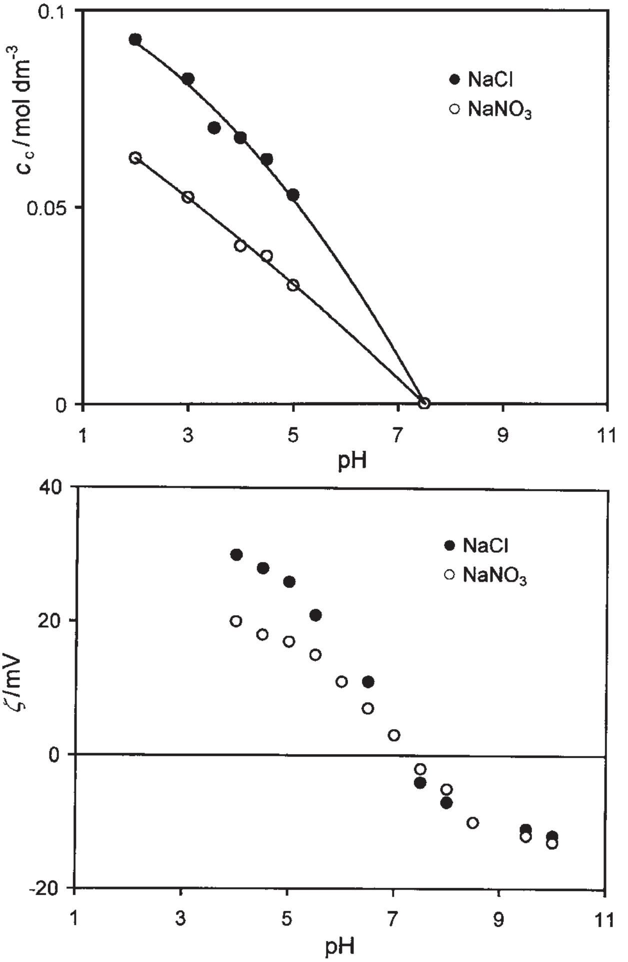

Figure 5. Critical coagulation concentration (c_c) and ζ-potential of hematite particles as a function of pH at 25 °C in the presence of NaCl (open symbols) and $NaNO_3$ (full symbols).[27] Temperature of aqueous suspension: 25 °C.

on the concentration of the potential determining ions (see Figure 3). Use of the ϕ_0 potential instead of ϕ_N (Figure 4) would not change such a situation,[24] since the absolute value of ϕ_0 is close to ϕ_N (80–90%). The second, more appropriate, attempt was to use the electrokinetic ζ-potential as an approximation for ϕ_d. Electrokinetic potential is assumed to correspond to the hypothetical slipping (or shear) plane dividing the immobile part of the liquid that moves together with the colloid particle from the bulk of the liquid medium. The approximation is correct if one assumes that the slipping plane is close to the onset of the diffuse layer. The use of ζ-potential in the interpretation of aggregation kinetics is supported by the results presented in Figure 5, since both the critical coagulation concentration and ζ-potential increase in magnitude going from the isoelectric point, reaching its maximum and an approximately constant value.

However, a more refined approach would be to introduce the concept of the slipping plane separation and to calculate ϕ_d from ζ-potential on the basis of the Gouy-Chapman theory

$$\ln \tanh (F\zeta / 4RT) = \tanh (F\phi_d / 4RT) - \kappa s \tag{24}$$

where s is the electrokinetic slipping plane separation, found[25] to be between 1 and 2 nm. The second approach to the evaluation of the surface potential ϕ_d, being responsible for aggregation kinetics, is based on the Surface Complexation (SC) model. This theoretical concept considers the equilibrium in the interfacial layer on the basis of surface reactions and will be described here on the example of metal oxide/aqueous interface. According to the SC model (2-pK concept), amphotheric surface ≡MOH groups, developed by hydration of the metal oxide surface, can bind (protonation) or release (deprotonation) the proton

$$\equiv\text{MOH} + \text{H}^+ \rightarrow \equiv\text{MOH}_2^+ ; \qquad K_p = \exp(F\phi_0 / RT)\, \frac{\Gamma(\text{MOH}_2^{\,+})}{a(\text{H}^+)\, \Gamma(\text{MOH})} \tag{25}$$

$$\equiv\text{MOH} \rightarrow \equiv\text{MO}^- + \text{H}^+ ; \qquad K_d = \exp(-F\phi_0 / RT)\, \frac{\Gamma(\text{MO}^-)a(\text{H}^+)}{\Gamma(\text{MOH})} \tag{26}$$

where K_p and K_d are equilibrium constants of protonation and deprotonation, respectively, ϕ_0 is the potential affecting the state of charged surface groups MOH_2^+ and MO^-, Γ is surface concentration (amount per surface area) and a is activity in the bulk of the solution.

Charged surface groups can also bind counterions (anions A^- and cations C^+) from the bulk of the solution

$$\equiv MOH_2^+ + A^- \rightarrow \equiv MOH_2^+ \cdot A^- ; \quad K_a = \exp(F\phi_\beta / RT) \frac{\Gamma(MOH_2^+ \cdot A^-)}{a(A^-)\Gamma(MOH_2^+)} \tag{27}$$

$$\equiv MO^- + C^+ \rightarrow \equiv MO^- \cdot C^+ ; \quad K_c = \exp(-F\phi_\beta / RT) \frac{\Gamma(MO^- \cdot C^+)}{a(C^+)\Gamma(MO^-)} \tag{28}$$

In order to interpret the interfacial equilibrium, one needs to introduce a model for the electrical interfacial layer (EIL). Most of the models for the EIL structure described in the literature may be represented by a general scheme[25] (Figure 4). Surface charges MOH_2^+ and MO^- are located in the 0-plane and are exposed to potential ϕ_0. Associated counterions are in the β-plane separated from the »solid surface« by the distance depending on their size. The corresponding potential is ϕ_β. From the d-plane (onset of diffuse layer, potential ϕ_d), ions are distributed according to the Gouy-Chapman theory. The electrokinetic ζ-potential would apply to an imaginary slipping or shear plane (e-plane), located somewhere within the diffuse layer. The general scheme, as shown in Figure 4, could be simplified[26] assuming that β- and d-planes are identical so that $\phi_\beta = \phi_d$. The second choice would be to introduce the potential drop between β- and d-planes, which is then assumed to be identical to the electrokinetic slipping plane.[26] Surface charge densities in 0- and β-planes are

$$\sigma_0 = F\,(\Gamma(MOH_2^+) + \Gamma(MOH_2^+ \cdot A^-) - \Gamma(MO^-) - \Gamma(MO^- \cdot C^+)) \tag{29}$$

$$\sigma_\beta = F\,(\Gamma(MO^- \cdot C^+) - \Gamma(MOH_2^+ \cdot A^-)) \tag{30}$$

The net surface charge density σ_s, corresponding to the charge fixed to the surface, is opposite in sign to that in the diffuse layer σ_d.

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F\,(\Gamma(MOH_2^+) - \Gamma(MO^-)) \tag{31}$$

The total concentration of surface sites Γ_{tot} is equal to

$$\Gamma_{tot} = \Gamma(MOH) + \Gamma(MOH_2^+) + \Gamma(MO^-) + \Gamma(MO^- \cdot C^+) + \Gamma(MOH_2^+ \cdot A^-) \tag{32}$$

The relations between potentials, within the fixed part of EIL, are based on the constant capacitance concept

$$C_1 = \sigma_0 / (\phi_0 - \phi_\beta) \tag{33}$$

$$C_2 = \sigma_s / (\phi_\beta - \phi_d) \tag{34}$$

If the β-plane is assumed to be identical to the d-plane, than $C_2 \rightarrow \infty$ and $\phi_d \rightarrow \phi_\beta$. The diffuse layer is characterized by its thickness, represented by the reciprocal value of the Debye-Hückel parameter κ (Eq. 21). The Gouy-Chapman theory provides the relationship between the surface charge density σ_s and the potential at the onset of the diffuse layer ϕ_d, as

$$\sigma_s = -\sigma_d = -\sqrt{8RT\varepsilon I_c}\ \sinh(-F\phi_d / 2RT) = -\frac{4FI_c}{\kappa} \sinh(-F\phi_d / 2RT) \quad (35)$$

Equilibrium at the metal oxide/liquid interface is characterized by several parameters. They are: total surface concentration of surface sites (Γ_{tot}), four equilibrium constants (K_p, K_d, K_a, K_c), and one or two capacitances (C_1, C_2). The values of these parameters can be obtained by interpretation of adsorption measurements. Higher accuracy can be achieved if adsorption data are simultaneously interpreted along with electrokinetic data.[25] Once the equilibrium parameters are known, it is easy to calculate the potential at the onset of diffuse layer ϕ_d determining the electrostatic interaction energy function (Eq. 20). Another possibility is to use Eq. (24) and calculate the ϕ_d potential from the measured ζ-potential.

EFFECT OF SURFACE POTENTIAL

Dependency of the ϕ_d potential on pH for a typical metal oxide in aqueous electrolyte solution, calculated for a chosen set of equilibrium parameters, is presented in Figure 6. This figure corresponds to hematite dispersed in potassium nitrate and chloride solutions.[27]

It is clear that the ϕ_0(pH) function is almost linear but with the slope (47 mV) lower than the Nernstian one (59 mV). The ϕ_d(pH) function shows leveling below pH_{pzc}, which is more pronounced at higher ionic strengths.

In the above case, the anion association equilibrium constant is taken to be significantly higher than that for cation, so a shift of i.e.p. ($\zeta = \phi_d = 0$) with respect to p.z.c. ($\sigma_0 = 0$) was observed. If the equilibrium constants of cation and anion associations are close (or low), then the isoelectric point will coincide with the point of zero charge ($\sigma_0 = \sigma_s = 0$ and $\phi_0 = \phi_\beta = \phi_d = \zeta = 0$). This condition is related to protonation and deprotonation equilibrium constants by

$$pH_{pzc} = pH_{iep} = 0.5 \log (K_p / K_d) \quad (36)$$

The finding presented in Figure 6, showing that the ϕ_d potential does not change significantly beyond pH_{pzc} ± 2 pH units apart from p.z.c., explains the fact that coagulation kinetics does not depend significantly on the

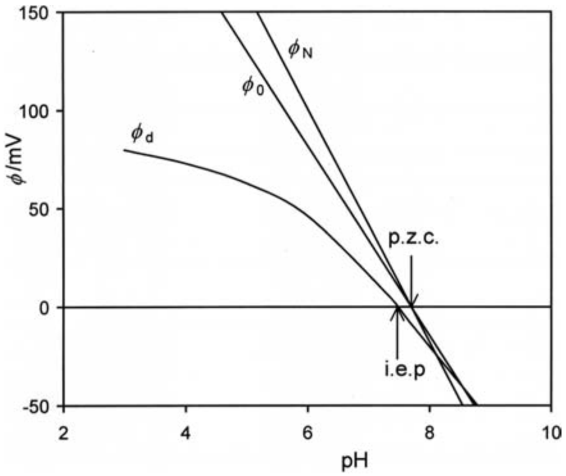

Figure 6. Dependency of ϕ_0 and ϕ_d potentials and the Nernstian potential ϕ_N on pH for hematite/aqueous electrolyte interface at 25 °C; C_1 = 1.81 F m^{-1}; $C_2 = \infty$; Γ_{tot} = 1.5×10^{-5} mol m^{-2}; $K_p = 5 \times 10^4$; $K_d = 5 \times 10^{-11}$; $K_{NO_3^-}$ = 1410 at KNO_3 concentration of 10^{-2} mol dm^{-3}. Values of equilibrium parameters were taken from Ref. 27.

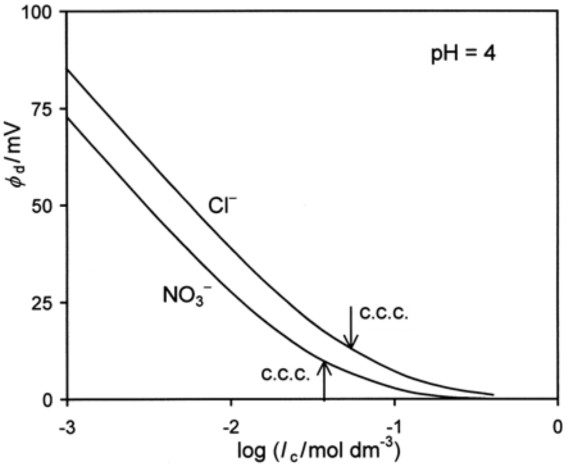

Figure 7. Dependency of the ϕ_d potential on the concentration of KCl and KNO_3 at pH = 4; C_1 = 1.81 F m^{-1}; $C_2 = \infty$; Γ_{tot} = 1.5×10^{-5} mol m^{-2}; $K_p = 5 \times 10^4$; $K_d = 5 \times 10^{-11}$; K_{Cl^-} = 525; $K_{NO_3^-}$ = 1410. Values of equilibrium parameters were taken from Ref. 27.

activity of the potential determining ions, as observed for silver iodide particles (see Figure 3).

Figure 7. shows that potential ϕ_d significantly decreases in magnitude with increasing electrolyte concentration. This decrease is more pronounced

for NO_3^- counterions characterized by a higher association equilibrium constant. The relationship between the ϕ_d potential and the electrolyte coagulation effect is also clear. Critical coagulation concentration of anions corresponds to the ϕ_d value of 7 mV for nitrates, and to 10 mV for chlorides.[27] This finding indicates that electrolyte addition affects the coagulation both by »compression« of the diffuse layer and by a decrease of the ϕ_d potential. In the case of chloride ions, fast coagulation takes place at somehow higher ϕ_d values (with respect to nitrates), but the corresponding ionic strength is higher and so the diffuse layer is more »compressed«. For homocoagulation, *i.e.* for aggregation of the particles of the same size ($r_1 = r_2 = r$) and with the same surface potentials ($\phi_1 = \phi_2 = \phi_d$), the HHF equation (20) for electrostatic interaction is reduced to

$$E_{el} = 2\pi\varepsilon r\phi_d^2 \ln\,[1 + \exp(-\kappa x)] \qquad (37)$$

According to Eq. (37), electrostatic interaction is proportional to the product of two terms. The first is ϕ_d^2 and the second is a function of κ. By increasing the electrolyte concentration, both terms decrease and reduce the electrostatic repulsion. These effects are displayed on a relative scale in Figure 8. Ionic strength of 10^{-3} mol dm^{-3} was taken as a reference. Accordingly, the effect of electrolytes on the energy barrier due to the change in surface

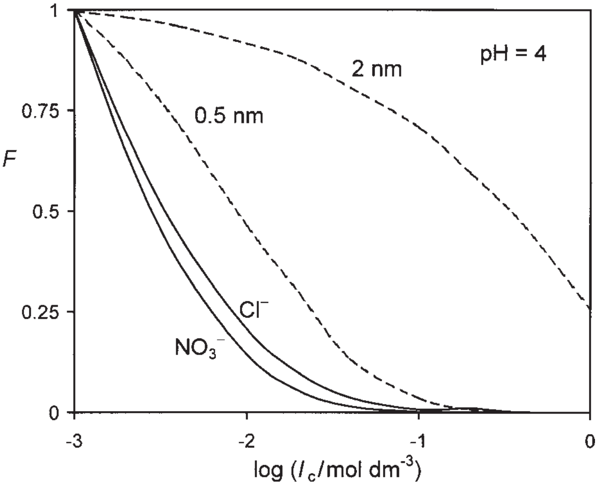

Figure 8. Relative contributions (F) of ϕ_d^2 and ln (1 + exp($-\kappa$s)) terms, according to Eq. (37). Full lines show the decrease of electrostatic repulsion due to a decrease of ϕ_d. Dashed lines show the effect of »diffuse layer compression« due to the increase of the ionic strength for two limiting separation distances (0.5 and 2 nm). Reference system: $I_c = 10^{-3}$ mol dm^{-3}.

potential was calculated as the ratio $\phi_d^2 / \phi_{d,ref}^2$. Analogously, the electrolyte effect on the energy barrier due to the »compression« of the diffuse layer is $\ln [1 + \exp(-\kappa x)] / \ln [1 + \exp(-\kappa_{ref} x)]$, where $\phi_{d,ref}$ and κ_{ref} correspond to the reference ionic strength of 10^{-3} mol dm^{-3}. Full lines in the figure show the decrease of electrostatic repulsion due to a decrease of ϕ_d. As expected, this decrease is more pronounced for nitrate ions characterized by a higher association equilibrium constant and thus exhibiting a lower critical coagulation concentration. Dashed lines show the effect of »diffuse layer compression« due to the decrease of the ionic strength for two limiting separation distances (0.5 and 2 nm) since within these limits one may expect appearance of the energy barrier. It is obvious that electrostatic repulsion between particles is reduced by electrolyte addition due to the lowering of the ϕ_d potential, which is specific and determined by the counterion association constant, and also due to »compression« of the diffuse layer which is not specific, but depending just on the ionic strength.

The foregoing discussion shows that counterions characterized by a higher equilibrium constant of surface association will reduce the surface potential more effectively and, thus, they will affect the aggregation rate more efficiently.[28] Within the SC model these counterions will be also characterized by higher values of the inner layer capacitance (C_1) and are assumed to be effectively smaller.[27] This simplified concept is based on the assumption that effectively small counterions may approach the surface ionic groups more closely, resulting in a more pronounced electrostatic attraction and, consequently, in a higher value of the association equilibrium constant. Also, close separations will cause higher capacitance. The question that remains unsolved is the physical meaning of the effective size. If we consider a series of cations as Li^+, Na^+, K^+ and Cs^+ and their hydration, the effective size will decrease in the mentioned order, which will be also reflected in their molar conductivities. Consequently, the coagulation efficiency will increase in the same order. If counterions lose their hydration shell at the interface, the order will be reversed. According to the above discussion, introduction of the SC model into the Theory of Colloid Stability explains the effect of lyotropic series in coagulation kinetics. Figure 9 is a schematic presentation of different contributions to the theory of colloid stability, enabling calculation of the rate constant and the rate of aggregation.

Within the SC model, the effective equilibrium constant is a product of the thermodynamic equilibrium constant and the exponential term taking into account the effect of the overall electric field at the surface. Another approach to counterion association at the interface is based on the Bjerrum concept. This approach was originally suggested by Težak[29] but the problem was not solved quantitatively. Težak assumed that associated counterions

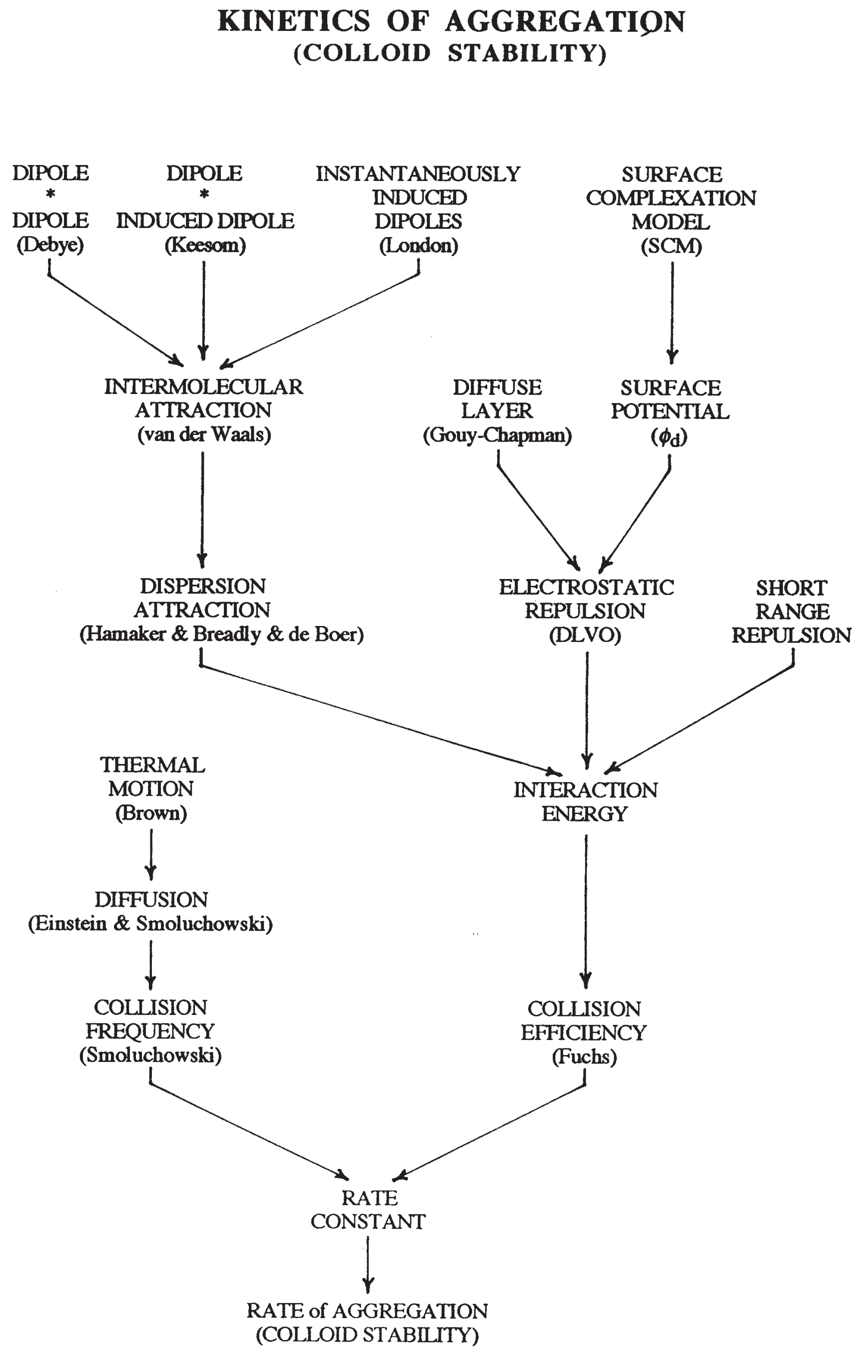

Figure 9. Different theoretical contributions to the Theory of Colloid Stability. Abbreviation DLVO stands for Deryaguin, Landau, Vervey and Overbeek.

are located at the Bjerrum critical distance (d_{crit}), which contradicts the Bjerrum concept, according to which the associated counterion is distributed in the space between the minimum distance d_{min} and d_{crit}. Associated counterion is not fixed at d_{crit} where the statistical probability of finding the counterion has its minimum value. The problem of introducing the Bjerrum concept into the association of counterions at the surface was later solved by Kallay and Tomić;[30,31] the value of d_{crit} was found to depend on the electric charge at the surface so that the association space becomes larger at higher surface potentials. Also, the association space is larger for effectively smaller counterions characterized by lower d_{min} values. The interesting result of this Association Space (AS) concept is that a certain critical surface potential is required for counterion association. At this critical potential the value of d_{crit} becomes higher than d_{min} enabling appearance of the association space. For effectively smaller counterions, the critical potential is lower. The theory has shown that association equilibrium constants of counterions of higher charge numbers are higher due to an increase in d_{crit} and, consequently, expanded association space. The association equilibrium constant increases with the surface potential and is higher for effectively smaller counterions.

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SAŽETAK

Uvođenje modela površinskog kompleksiranja u teoriju koloidne stabilnosti

Nikola Kallay i Suzana Žalac

Ovaj članak pokazuje da teorija koloidne stabilnosti postaje tzv. »apsolutna teorija« uvođenjem modela površinskog kompleksiranja. To znači da je potrebno karakterizirati električki međusloj između čestica i otopine (npr. adsorpcijskim mjerenjima) i izračunati ravnotežne parametre kao što su ravnotežne konstante protoniranja i deprotoniranja amfoternih površinskih OH skupina, ravnotežne konstante za asocijaciju protuiona, električki kapaciteti unutrašnjeg i vanjskog dijela međupovršinskog sloja i ukupna koncentracija aktivnih površinskih skupina. Ti ravnotežni parametri omogućuju računanje elektrostatskog potencijala na početku difuznog sloja (ϕ_d), potrebnog za izračunavanje elektrostatske interakcijske energije dviju čestica, što daje konstantu brzine agregacije, odnosno koeficijent stabilnosti. Pokazano je da asocijacija protuiona igra važnu ulogu u agregacijskom procesu uslijed smanjenja vrijednosti potencijala ϕ_d.