

Stability of Nanodispersions: A Model for Kinetics of Aggregation of Nanoparticles

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In the course of aggregation of very small colloid particles (nanoparticles) the overlap of the diffuse layers is practically complete, so that one cannot apply the common DLVO theory. Since nanoparticles 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. The charge of interacting nanoparticles was calculated by means of the Surface Complexation Model and decrease of effective charge of particles was also taken into account. Numerical simulations were performed using the parameters for hematite and rutile colloid systems. The effect of pH and electrolyte concentration on the stability coefficient of nanosystems was found to be more pronounced but similar to that for regular colloidal systems. The effect markedly depends on the nature of the solid which is characterized by equilibrium constants of surface reactions responsible for surface charge, i.e., by the point of zero charge, while the specificity of counterions is described by their association affinity, i.e., by surface association equilibrium constants. The most pronounced is the particle size effect. It was shown that extremely small particles cannot be stabilized by an electrostatic repulsion barrier. Additionally, at the same mass concentration, nanoparticles aggregate more rapidly than ordinary colloidal particles due to their higher number concentration. © 2002 Elsevier Science (USA)

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INTRODUCTION

It is commonly accepted that the stability of colloidal systems is, in most cases, the result of an extremely slow aggregation process. The main reason for such a slow aggregation process is a high electrostatic energy barrier, and in some cases a protective layer of adsorbed chains. The theory of Colloid Stability considers collision frequency and efficiency (1, 2). Collision frequency was theoretically solved by Smoluchowski (3), while the basis for evaluation of the collision efficiency was given by Fuchs (4). In order to use the Fuchs theory one should know the interaction energy as a function of the distance between interacting parti-

cles. The effect of dispersion forces was solved by Hamaker (5), Bradly (6), and de Boer (7), while electrostatic repulsion could be evaluated on the basis of the Derjaguin, Landau, Vervey, Overbeek (DLVO) theory (1, 8). Recently, more sophisticated models were elaborated (9–14). In most of the cases the theory of Colloid Stability explains the experimental data, especially if the correct values of the electrostatic surface potentials, as obtained from the Surface Complexation model (15–19), are used (20–22). However, small particles, with sizes below 10 nm (called nanoparticles), generally do not show electrostatic stabilization. According to de Gennes (23), the reason for the instability of nanocolloidal systems might be in their low charge (surface charge density times surface area). In some cases stable systems of nanoparticles could be prepared (24, 25) but no kinetic measurements were published.

In this paper we analyze the theoretical aspect of the kinetics of aggregation of nanoparticles based on the Brønsted theory (26, 27), which was developed for the salt effect on the kinetics of ionic reactions (primary salt effect). The reason for such a choice lies in the fact that the classical DLVO approach cannot be used for nanoparticles: nanoparticles are small with respect to the thickness of the electrical diffuse layer, so that in the course of the collision of two nanoparticles a complete overlap of two diffuse layers takes place. Let us consider extension of the diffuse layer. According to the Gouy-Chapman theory, depending on the ionic strength and surface potential, the latter is reduced to 10% of its original value at a distance of 2 to 2.5 reciprocal κ values. This means that at the ionic strength of 10^{-2} mol dm⁻³ the diffuse layer is extended up to 6 nm from the surface. As shown on Fig. 1, in such a case overlap of diffuse layers of two nanoparticles is practically complete. In the case of ordinary colloid particles the overlap is partial so that the DLVO theory is applicable.

A nanoparticle surrounded by a diffuse layer is similar to an ion situated in the center of an ionic cloud. In the course of collision two nanoparticles in contact have a common diffuse layer or “ionic cloud.” Therefore, interaction of nanoparticles could be considered in a manner similar to that for two interacting ions, and consequently described by the Brønsted theory. This theory considers the “transition state” or “activated complex” which is a pair of two interacting ions with a common ionic cloud. The

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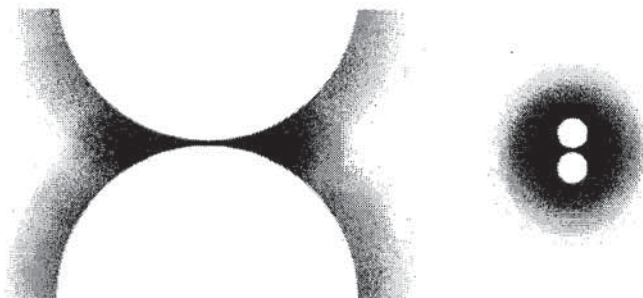


FIG. 1. Overlap of electrical interfacial layers for two ordinary colloid particles ($r = 30$ nm) and for two nanoparticles ($r = 3$ nm).

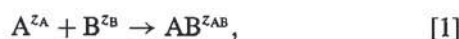
equilibration of the transition state is fast, while the transformation of the transition state into product(s) is slow, and thus the rate determining step.

THEORY

Introduction of the Brønsted Concept to Kinetics of Aggregation of Nanoparticles

The quantitative interpretation of kinetics of aggregation of nanoparticles will follow the Brønsted concept (26, 27). It will be based on the Transition State theory using the activity coefficients as given by the Debye-Hückel limiting law.

Aggregation of two charged nanoparticles A^{z_A} and B^{z_B} could be represented by

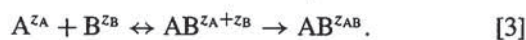


where z denotes the charge number. The rate of aggregation v is proportional to the product of concentrations of interacting particles $[A^{z_A}][B^{z_B}]$

$$v = k[A^{z_A}][B^{z_B}], \quad [2]$$

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

According to the Brønsted concept, in the course of aggregation two charged nanoparticles undergo reversible formation of the transition state with charge number being equal to the sum of the charges of interacting species. The transition state $AB^{z_A+z_B}$ undergoes the next step (binding) which is slow and is therefore the rate determining step



Note that equilibration of the interface may result in a change of the total charge of the doublet. In such a case $z_A + z_B \neq z_{AB}$. Since the equilibration of the first step is fast, and the second process is slow, the overall rate of reaction (v) is proportional to

the concentration of the transition state

$$v = k'[AB^{z_A+z_B}], \quad [4]$$

where k' is the rate constant (coefficient) of the second process. Equilibration of the first step is fast so that one calculates the concentration of the transition state $[AB^{z_A+z_B}]$ from the relevant equilibrium constant K^\ddagger taking into account the activity coefficients γ of reactants and of the transition state

$$K^\ddagger = \frac{\gamma(AB^{z_A+z_B})}{\gamma(A^{z_A})\gamma(B^{z_B})} \frac{[AB^{z_A+z_B}]}{[A^{z_A}][B^{z_B}]}. \quad [5]$$

The equilibrium constant K^\ddagger is defined in terms of activities, and consequently its value does not depend on the ionic strength; i.e., it corresponds to infinite dilution. Equations [4] and [5] result in

$$v = k'K^\ddagger \frac{\gamma(A^{z_A})\gamma(B^{z_B})}{\gamma(AB^{z_A+z_B})} [A^{z_A}][B^{z_B}]. \quad [6]$$

According to the above equation, the overall rate constant, as defined by Eq. [2], is given by

$$k = k'K^\ddagger \frac{\gamma(A^{z_A})\gamma(B^{z_B})}{\gamma(AB^{z_A+z_B})}. \quad [7]$$

It is clear that the overall rate constant k depends on the ionic strength of the medium through activity coefficients. Activity coefficients could be obtained from the Debye-Hückel equation derived for ionic solutions. The same equation is assumed to be applicable for extremely small particles i of charge number z_i

$$\log \gamma_i = -\frac{z_i^2 A_{DH} I_c^{1/2}}{1 + a b I_c^{1/2}}. \quad [8]$$

The ionic strength I_c for 1 : 1 electrolytes is equal to their concentration. The Debye-Hückel constant A_{DH} depends on the electric permittivity of the medium $\epsilon (= \epsilon_0 \epsilon_r)$

$$A_{DH} = \frac{2^{1/2}}{8\pi L \ln 10} \left(\frac{F^2}{\epsilon RT} \right)^{3/2}, \quad [9]$$

where L is the Avogadro constant and R , T , and F have their usual meaning. (For aqueous solutions at 25°C: $A_{DH} = 0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2}$.) Coefficient b in Eq. [8] is equal to

$$b = \left(\frac{2F^2}{\epsilon RT} \right)^{1/2}, \quad [10]$$

while parameter a is the distance of closest approach of the interacting charges, which is in the case of nanoparticles related

to their radius. By introducing Eq. [8] into Eq. [7] one obtains

$$\log k = \log k' + \log K^\ddagger + \frac{2z_A z_B A_{DH} I_c^{1/2}}{1 + ab I_c^{1/2}}. \quad [11]$$

Equation [11] suggests that the plot of the experimental $\log k$ value as the function of $I_c^{1/2}/(1 + ab I_c^{1/2})$ should be linear with the slope of $2z_A z_B A_{DH}$ which is true if charges of interacting species do not depend on the ionic strength. However, as it will be shown later, the charge of a colloidal particle decreases with ionic strength due to association of counterions with surface charged groups.

Estimation of the Equilibrium Constant of the Transition State Formation

To analyze the effect of repulsion between two charged particles on the equilibrium constant K^\ddagger we shall split the Gibbs energy of the transition state formation $\Delta^\ddagger G^\circ$ into electrostatic term, $\Delta^\ddagger G_{el}^\circ$, and the rest, which we shall call the chemical term, $\Delta^\ddagger G_{ch}^\circ$. The latter includes van der Waals dispersion attraction

$$\begin{aligned} -RT \ln K^\ddagger &= -RT \ln(K_{ch}^\ddagger K_{el}^\ddagger) = \Delta^\ddagger G^\circ \\ &= \Delta^\ddagger G_{ch}^\circ + \Delta^\ddagger G_{el}^\circ, \end{aligned} \quad [12]$$

where $\Delta^\ddagger G_{ch}^\circ = -RT \ln K_{ch}^\ddagger$ and $\Delta^\ddagger G_{el}^\circ = -RT \ln K_{el}^\ddagger$.

As noted before, the equilibrium constant K^\ddagger is based on the activities of the interacting species and its definition (Eq. [5]) considers the corrections for the nonideality. It corresponds to the zero-ionic strength so that the value of K_{el}^\ddagger could be obtained considering simple Coulombic interactions between two nanoparticles. Accordingly, the (molar) electrostatic energy between particles A^{z_A} and B^{z_B} of radii r_A and r_B in the medium of the permittivity ϵ is

$$\Delta^\ddagger G_{el}^\circ = \frac{z_A z_B F^2}{4\pi \epsilon L (r_A + r_B)}, \quad [13]$$

where $r_A + r_B$ is the center to center distance between interacting particles in close contact. In the case of two identical particles ($r_A = r_B = r$ and $z_A = z_B = z$)

$$\Delta^\ddagger G_{el}^\circ = \frac{z^2 F^2}{8\pi \epsilon L r}. \quad [14]$$

This approach, based on the Coulomb law, could be tested by the Hogg-Healy-Fuerstenau (HHF) theory (9). For two equal spheres of the same surface potential φ , separated by surface to surface distance x , the electrostatic interaction energy, expressed on the molar scale, is equal to

$$\Delta^\ddagger G_{HHF}^\circ = 2\pi \epsilon L r \varphi^2 \ln[1 + \exp(-\kappa x)], \quad [15]$$

where κ is the Debye-Hückel reciprocal thickness of the

electrical interfacial layer

$$\kappa = \left(\frac{2I_c F^2}{\epsilon RT} \right)^{1/2}. \quad [16]$$

At the zero-ionic strength ($I_c \rightarrow 0$) the surface potential φ of a sphere of radius r and the charge number z is

$$\varphi = \frac{z e}{4\pi \epsilon r}. \quad [17]$$

(Note that φ potential is in fact the electrostatic potential at the onset of diffuse layer.) Under such a condition the diffuse layer extends to infinity ($\kappa \rightarrow 0$), so that for zero separation ($x \rightarrow 0$) Eq. [15] reads

$$\Delta^\ddagger G_{HHF}^\circ = \frac{z^2 F^2}{8\pi \epsilon L r} \ln 2. \quad [18]$$

The comparison of Eq. [18] with Eq. [14] shows that HHF theory results in $\sim 30\%$ lower value of energy than the Coulomb law. This discrepancy is not essential for the purpose of this study, so that in further analysis we shall use the Coulomb expression.

By introducing Eqs. [12] and [13] into Eq. [11] for the rate constant of aggregation of nanoparticles A^{z_A} and B^{z_B} , one obtains

$$\log k = \log k' + \log K_{ch}^\ddagger - \frac{z_A z_B F^2}{4\pi \epsilon L (r_A + r_B)} + \frac{2z_A z_B A_{DH} I_c^{1/2}}{1 + ab I_c^{1/2}} \quad [19]$$

or in another form

$$\log k = \log k_0 - z_A z_B \left(\frac{B}{r_A + r_B} - 2A_{DH} \frac{I_c^{1/2}}{1 + ab I_c^{1/2}} \right), \quad [20]$$

where

$$B = \frac{F^2 \ln 10}{4\pi \epsilon L R T} \quad [21]$$

and

$$k_0 = k' K_{ch}^\ddagger. \quad [22]$$

At high ionic strength the counterion association is so pronounced that the effective charge number of nanoparticles approaches to zero. In such a case the electrostatic repulsion diminishes and the aggregation is controlled by the diffusion ($k = k_{diff}$), as described by the Smoluchowski theory. Accordingly,

$$k = k_{diff} \quad [23]$$

The stability coefficient (reciprocal of the collision efficiency), commonly defined as $W = k_{\text{diff}}/k$, is then equal to

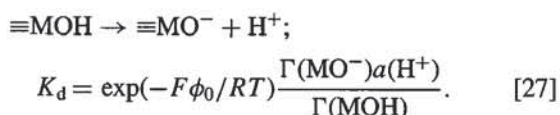
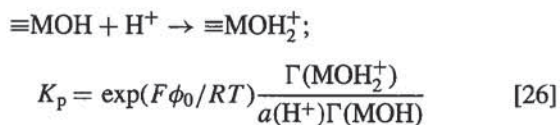
$$\log W = \log \frac{k_0}{k} = z_A z_B \left(\frac{B}{r_A + r_B} - 2A_{\text{DH}} \frac{I_c^{1/2}}{1 + abI_c^{1/2}} \right). \quad [24]$$

In the case of aggregation of identical nanoparticles the above equation is reduced to

$$\log W = \log \frac{k_0}{k} = 2z^2 \left(\frac{B}{r} - A_{\text{DH}} \frac{I_c^{1/2}}{1 + abI_c^{1/2}} \right). \quad [25]$$

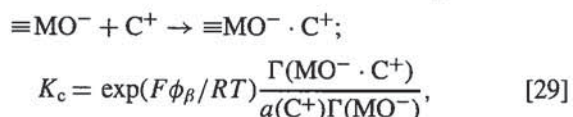
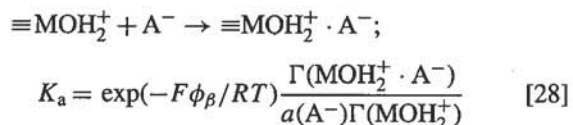
Evaluation of the Charge Number

For a given electrolyte concentration, the stability coefficient of the nanodispersion could be obtained by Eq. [24] (or by Eq. [25], in the case of uniform particles), once the charge number of particles is known. The surface potential (as used in the theory of Colloid Stability) and charge number are determined by the ionic equilibrium at the solid/liquid interface which will be considered here for metal oxide particles dispersed in aqueous electrolyte solutions. The Surface Complexation model (2-pK concept) considers (15–22) amphoteric surface $\equiv\text{MOH}$ groups, developed by the hydration of metal oxide surfaces, that could be protonated (p) or deprotonated (d)



K_p and K_d are equilibrium constants of protonation and deprotonation, respectively, ϕ_0 is the potential of the 0-plane affecting the state of charged surface groups MOH_2^+ and MO^- , Γ is the surface concentration (amount per surface area), and a is activity in the bulk of solution.

Charged surface groups bind counterions, anions A^- (surface equilibrium constant K_a), and cations C^+ (surface equilibrium constant K_c)



where ϕ_β is the potential of β -plane affecting the state of associated counterions

From the d-plane (onset of diffuse layer, potential ϕ_d), ions are distributed according to the Gouy-Chapman theory.

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

$$\begin{aligned} \Gamma_{\text{tot}} &= \Gamma(\text{MOH}) + \Gamma(\text{MOH}_2^+) + \Gamma(\text{MO}^-) \\ &\quad + \Gamma(\text{MO}^- \cdot \text{C}^+) + \Gamma(\text{MOH}_2^+ \cdot \text{A}^-). \end{aligned} \quad [30]$$

Surface charge densities in the 0- and β -planes are

$$\begin{aligned} \sigma_0 &= F(\Gamma(\text{MOH}_2^+) + \Gamma(\text{MOH}_2^+ \cdot \text{A}^-) \\ &\quad - \Gamma(\text{MO}^-) - \Gamma(\text{MO}^- \cdot \text{C}^+)) \end{aligned} \quad [31]$$

$$\sigma_\beta = F(\Gamma(\text{MO}^- \cdot \text{C}^+) - \Gamma(\text{MOH}_2^+ \cdot \text{A}^-)). \quad [32]$$

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

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F(\Gamma(\text{MOH}_2^+) - \Gamma(\text{MO}^-)). \quad [33]$$

The relations between surface potentials, within the fixed part of electrical interfacial layer (EIL), are based on the constant capacitance concept

$$C_1 = \frac{\sigma_0}{\phi_0 - \phi_\beta}; \quad C_2 = \frac{\sigma_s}{\phi_\beta - \phi_d}, \quad [34]$$

where C_1 and C_2 are capacities of the so-called inner and outer layer, respectively. The general model of EIL could be simplified (19) by introducing $\phi_\beta = \phi_d$, which corresponds to $C_2 \rightarrow \infty$. The equilibrium in the diffuse layer is described by the Gouy-Chapman theory.

For planar surfaces (relatively large particles)

$$\sigma_s = -\sigma_d = -\frac{2RT\varepsilon\kappa}{F} \sinh(-F\phi_d/2RT) \quad [35]$$

and for small spherical particles (nanoparticles)

$$\sigma_s = \frac{\varepsilon\phi_d}{r} \left(1 - \frac{r}{r + \kappa^{-1}} \right)^{-1}. \quad [36]$$

Once the system is characterized, the Surface Complexation model enables calculation of the colloid particle charge number under given conditions. This means that one should know equilibrium constants of surface reactions, capacitances of inner and outer layers, and total density of surface sites. By an iteration procedure one obtains the net surface charge density σ_s (defined by Eq. [33]) from which the particle charge number is

$$z = 4r^2\pi\sigma_s/\rho \quad [37]$$

Numerical Simulation and Discussion

The above theory, developed for kinetics of aggregation of nanoparticles (nanocoagulation), will be demonstrated on a few examples. Two systems (hematite and rutile) under different conditions will be examined. The values of equilibrium parameters, used in calculation of the particle charge number, were obtained by interpretation of adsorption and electrokinetic data for ordinary colloid particles (21, 22). It was assumed that these parameters approximately describe the properties of corresponding nanosystems. In the evaluation the Gouy-Chapman equation for spherical interfacial layer, Eq. [36], was used. Once the charge number was obtained, the stability coefficient was calculated via Eq. [25].

Figure 2 demonstrates the effect of electrolyte concentration on the stability of hematite nanodispersions containing particles of $r = 3$ nm. It is obvious that the stability of the system decreases rapidly with electrolyte addition. At pH 4, particles are positively charged so that association of anions with the surface charged groups takes place. Nitrate ions were found to aggregate the system more effectively with respect to the chloride ions, which is due to lower values of the surface association equilibrium constant of the latter counterions. The effect of electrolyte concentration is explicitly included in Eq. [25] through ionic strength. However, particle charge number also depends on the electrolyte concentration due to counterion association so that both effects result in a decrease of stability at

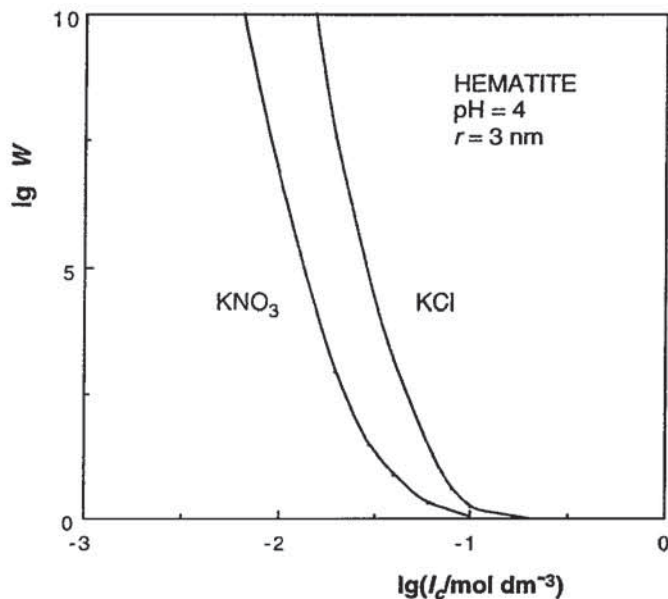


FIG. 2. Effect of electrolytes on the stability of hematite aqueous nanodispersion ($r = 3$ nm) at $T = 298$ K and pH 4, as obtained by Eq. [25]. The charge number was calculated by the Surface Complexation model (Eqs. [26]–[39]) using parameters obtained (21) with hematite colloid dispersion ($r = 60$ nm): $\Gamma_{\text{tot}} = 1.5 \times 10^{-5}$ mol m^{-2} ; $K_p = 5 \times 10^4$; $K_d = 1.5 \times 10^{-11}$; $\text{pH}_{\text{pzc}} = 7.6$; $K(\text{NO}_3^-) = 1410$; $K(\text{Cl}^-) = 525$; $C_s(\text{NO}_3^-) = 1.88 \text{ Eq m}^{-2}$; $C_s(\text{Cl}^-) = 1.81 \text{ Eq m}^{-2}$; $C_s(\text{OH}^-) = 78.54$

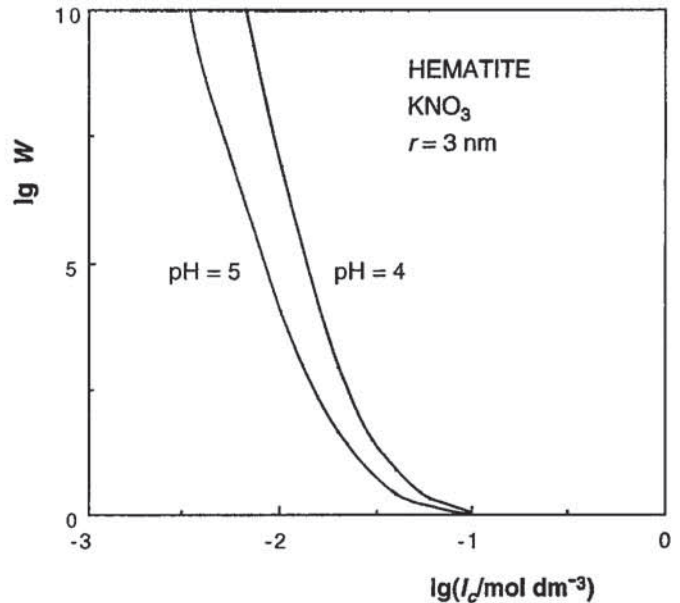


FIG. 3. Effect of pH on the stability of hematite aqueous nanodispersion ($r = 3$ nm) in the presence of potassium nitrate at $T = 298$ K. The parameters used in calculations are the same as in Fig. 2.

higher electrolyte concentrations. Figure 3 demonstrates the effect of the activity of potential determining H^+ ions. At lower pH values particles are more positively charged, the system is more stable, and higher electrolyte concentration is necessary for aggregation. The effect of particle size on the stability of the system is dramatic. As shown in Fig. 4, systems with smaller

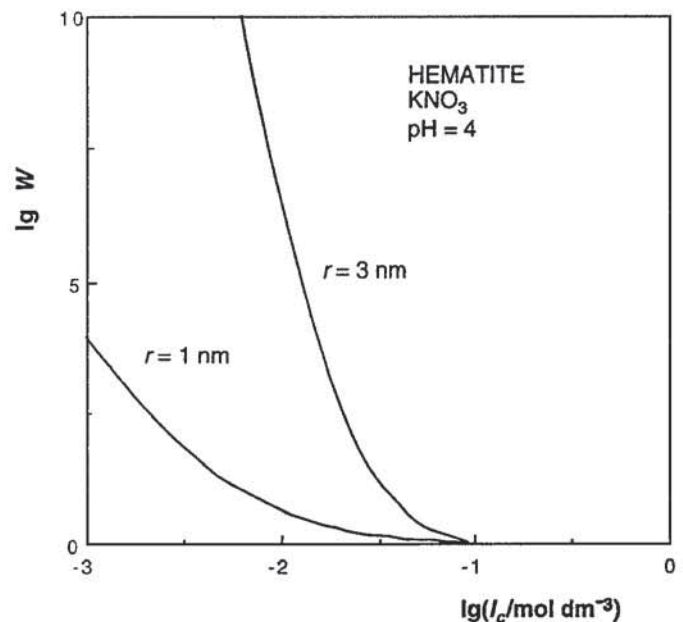


FIG. 4. Effect particle size on the stability of hematite aqueous nanodispersions in the presence of potassium nitrate at pH 4 and $T = 298$ K. The parameters used in calculations are the same as in Fig. 2.

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