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Kinetics of Diffusional Detachment of Colloidal Particles From Surfaces*[†]

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Experimental and theoretical problems related to the detachment of spherical particles from plane surfaces are reviewed. The diffusional kinetics is considered only by taking electrostatic, van der Waals, and short range repulsion energies into account. The rate of the detachment was treated in terms of the first order kinetic process, using a single or a multipopulation model.

INTRODUCTION

Phenomena of particle detachment from surfaces have been a subject of interest because they relate to many practical applications, such as in detergency, corrosion, adhesion, filtration, chromatographic separations of colloidal species, etc. The relevant problems have been treated extensively both experimentally¹⁻¹¹ and theoretically.¹²⁻¹⁶ The impetus for the experimental studies resulted from the availability of well defined systems and convenient techniques, which provided the necessary information for the interpretation of data.

In the absence of chemical bonds between particles and the substrate, the detachment may be affected by diffusion alone, which is controlled by the total interaction energy of the system. Alternately, particle removal may be caused by the application of forces (e. g., shear, centrifugal, gravitational). This article deals only with the former case; i. e., the particle separation takes place when their inherent kinetic energy exceeds the energy barrier.

It is noteworthy that detachment studies can provide useful information on the double layer properties and short range interactions between unlike surfaces.^{17,18}

An extended review of the particle detachment processes is offered elsewhere.¹⁹ Here is given a summary of the essential aspects of the problems including some new theoretical developments.

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TYPICAL EXPERIMENTAL DATA

Detachment of particles has been measured as a function of time either using a through-flow packed column technique or a batch procedure. In both cases the particles are first deposited on a substrate and then the removal affected by changing the conditions. At low ionic strength the deposition of particles dispersed in a liquid is carried out most efficiently when the charge on both surfaces is opposite in sign. In many instances the surface charge can be controlled by pH, such as with metal oxides, metals, glass, silica, latexes, red blood cells, etc. The detachment may take place if the pH is properly adjusted to produce the same sign of potential on both surfaces.

Figure 1. illustrates the described phenomena on the system steel/colloidal spherical hematite particles. The uppermost diagram shows the corresponding electrophoretic mobilities, while the middle plot gives the pH range of particle deposition. By lowering or raising pH particle removal is achieved, as

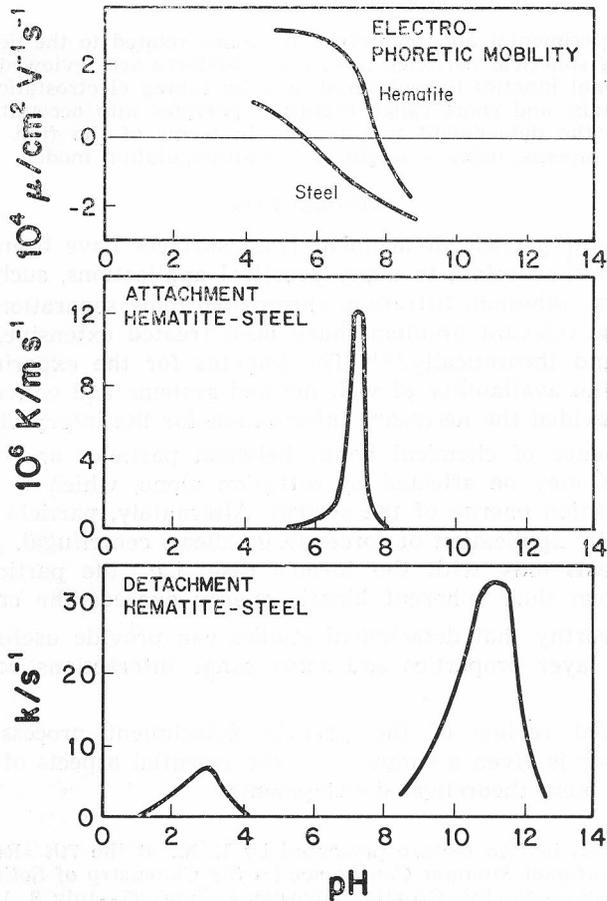


Figure 1. Adhesion effects on the model system steel beads/colloidal hematite particles. Top: electrophoretic mobilities, middle: rate constant of deposition; bottom: rate constant of detachment, all as a function of pH^{3,6-11}.

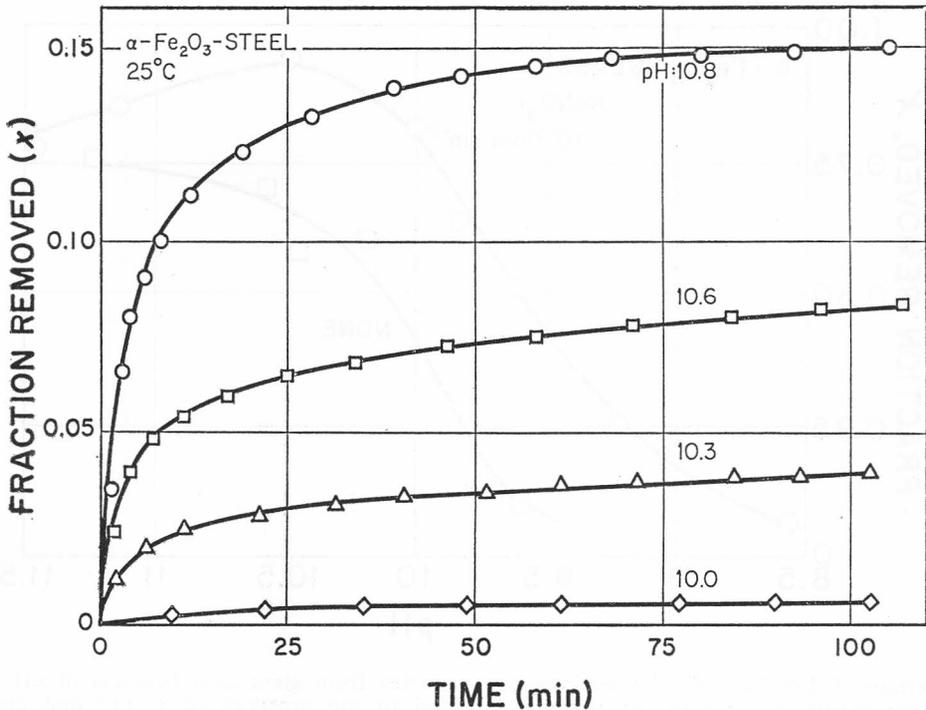


Figure 2. Fraction of hematite particles, x , removed from steel by rinsing the bed with NaOH solutions of different pH as a function of time at 25 °C. pH values: 10.8, ○; 10.6, □; 10.3, △; 10.0, ◇. The initial number of particles adhered: $2.6 \cdot 10^9$ per gram of steel; aging time before rinsing 250 hr.⁹

indicated by the pronounced maxima in acidic and basic regions (bottom part). It is obvious that detachment takes place when both surfaces acquire sufficiently high potential of the same sign. However, at rather high and low pH values ionic strength increases sufficiently to cause particle redeposition.

Figure 2. shows that, for the same steel/hematite system, the fraction of removed particles changes with time, with the rate depending on the pH. Such data lend themselves for the kinetic analysis of the detachment process. It should be emphasized that the rate of particle separation and the final amount of released solids is exceedingly sensitive to the pretreatment of the system and it also depends on the topography of the substrate.⁹ For example, the removal of adhered particles can be substantially diminished by rinsing the column with a solution that does not by itself affect adhesion. This effect is due to lateral mobility of deposited solids, which relocate onto sites of lower energy.

Since the properties of the double layer have a dominant effect on adhesion phenomena, it is expected that the addition of neutral electrolytes would greatly influence the detachment process. Intuitively one would expect that an increase in ionic strength would retard the particle escape. In reality, this may or may not be the case. Indeed, it was demonstrated¹⁸ with the

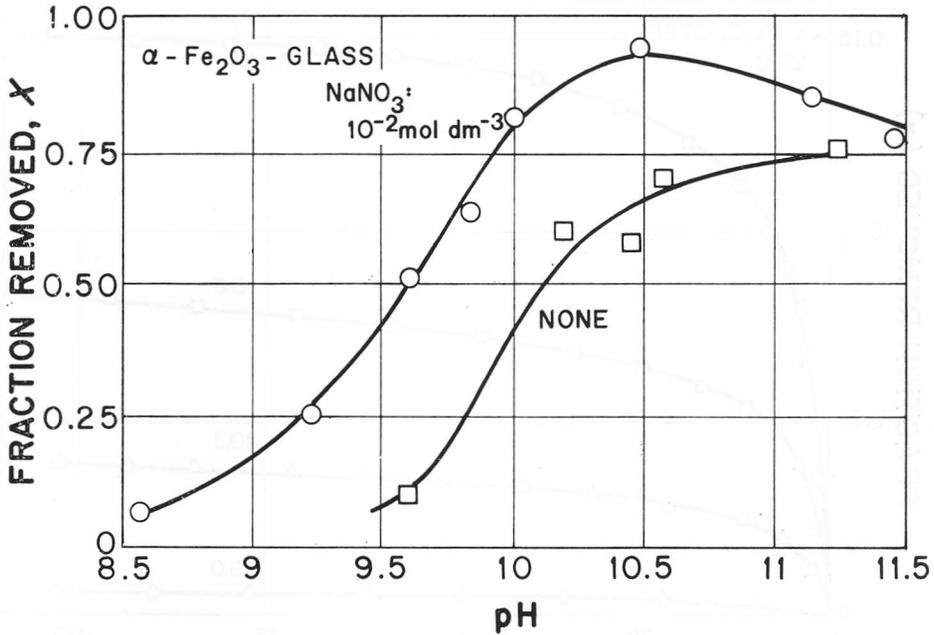


Figure 3. Fraction of released hematite particles from glass as a function of pH of the rinsing solution in the absence (□) and in the presence of $1 \cdot 10^{-2} \text{ mol dm}^{-3}$ NaNO_3 (○). Rising time 70 min; temperature 25°C .

system glass/hematite that the fraction removed increased with the addition of NaNO_3 at a given pH (Figure 3.). This effect is to be expected if, in considering the total interaction energy, short range repulsion is taken into account. As a result, the increase in the ionic strength reduces the depth of the first minimum and the height of the repulsion barrier, resulting in a lesser activation energy of both the detachment and deposition processes. The finding, as illustrated in Figure 3, is only possible when redeposition is avoided, such as by using a short packed column.

Once equilibration is permitted, which is the case with batch experiments,³ the redeposition dominates, resulting in fewer finally separated particles as the electrolyte content increases (Figure 4.).

Since the structure of the double layer is primarily determined by the surface potential and the concentration and charge of the counterions, the latter should exercise a pronounced effect on the rate of particle detachment, as actually observed. Figures 5. and 6. compare the removal of colloidal chromium hydroxide from glass rinsed with solutions of various concentrations of Ca^{2+} and $\text{Co}(\text{dipy})_3^{3+}$ ions, respectively. Both counterions reduce the particle release, but one order of magnitude higher concentration of Ca^{2+} is required to achieve the same effect. In these experiments redeposition took place.

ANALYSIS OF DATA

The simplest approach to the problem of detachment kinetics assumes that the particles located at the surface gain sufficient kinetic energy to

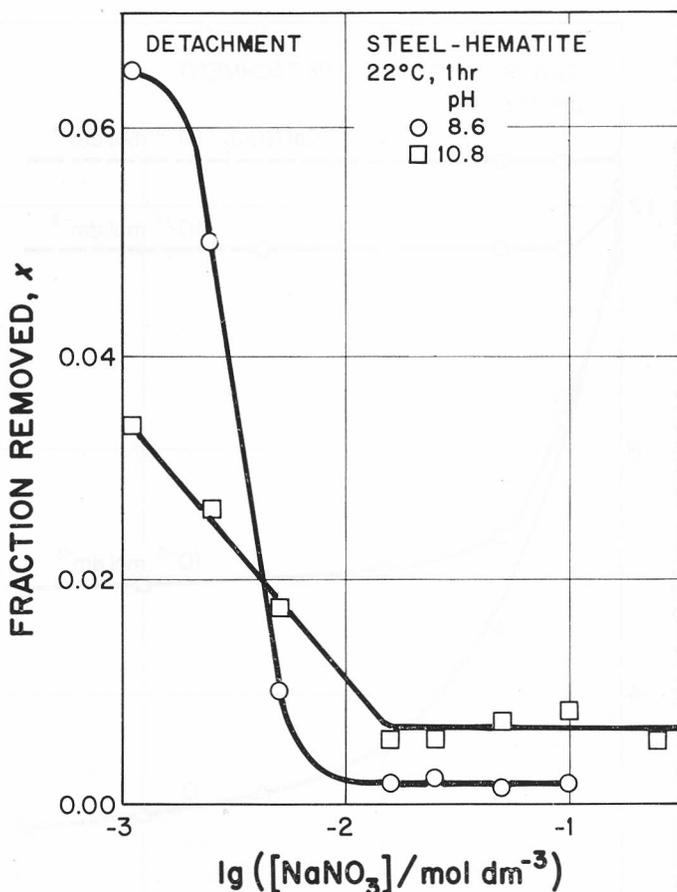


Figure 4. Fraction of hematite particles removed from steel beads as a function of the concentration of NaNO_3 in suspension after 1 hour of rotation in Teflon tubes at 1 r.p.m. at 22°C. pH: 8.6 (○) and 10.8 (□).

overcome the repulsion barrier. The rate of escape should also be proportional to the surface concentration of adhered solids. In view of chemical and physical inhomogeneities of interacting surfaces, one may expect different particles to require varying amounts of energy in order to separate.

In an ideal case (approximated, for example, by the system consisting of glass in contact with spherical colloidal chromium hydroxide) the rate of detachment of all adhered particles is controlled by the same rate constant.⁴ In other systems distribution of rate constants was established experimentally.

For the single population model the detachment is given by

$$-dN^s/dt = dN/dt = kN^s \quad (1)$$

where N^s is the number of adhered particles, N is the number of released particles (into the bulk of solution), and k is the rate constant of detachment. The integration of equation (1) gives

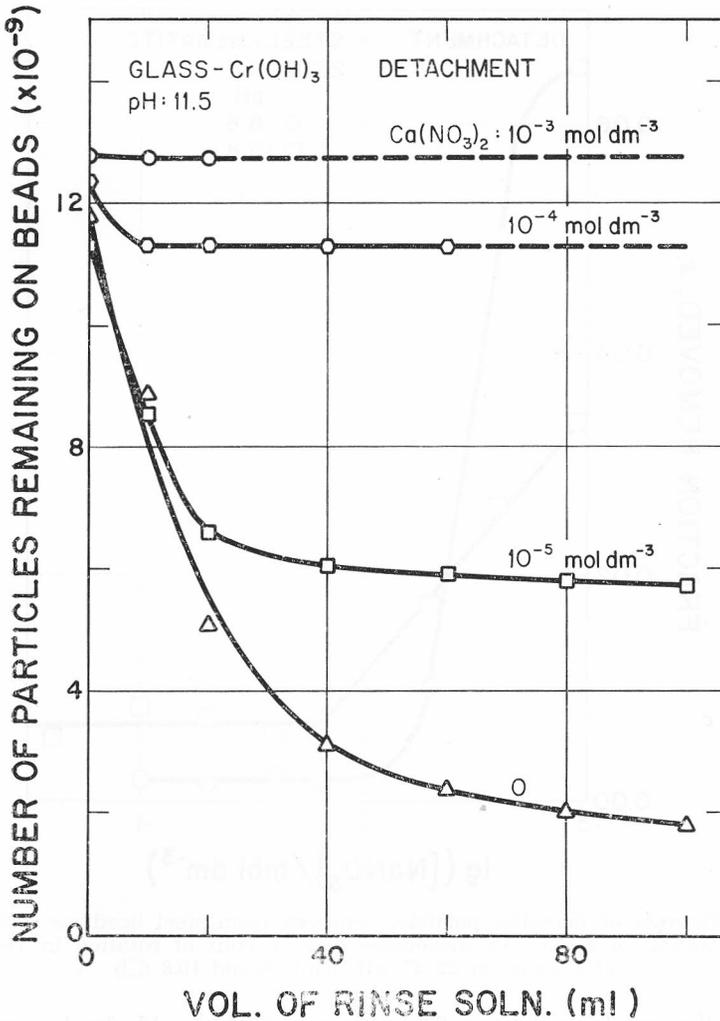


Figure 5. Effect of different concentrations of $\text{Ca}(\text{NO}_3)_2$ on detachment of chromium hydroxide particles from glass at pH 11.5. $\text{Ca}(\text{NO}_3)_2$: none (Δ); $1 \cdot 10^{-5}$ (\square); $1 \cdot 10^{-4}$ (\diamond); $1 \cdot 10^{-3}$ mol dm^{-3} (\circ).⁴

$$\ln(N_\infty - N) = \ln N_\infty - kt \quad (2)$$

This equation is frequently written in terms of the fraction of particles released ($x = N/N_0^s$):

$$\ln[(x_\infty - x)/x_\infty] = -kt \quad (3)$$

The model is applicable if, after a sufficient period of time, all adhered particles are released; i.e., $N_\infty = N_0^s$, or $x_\infty = 1$.

The same equation can be employed for a system in which a fraction of particles remains irreversibly bound to the surface. In this case x_∞ is an adjustable parameter having values < 1 .

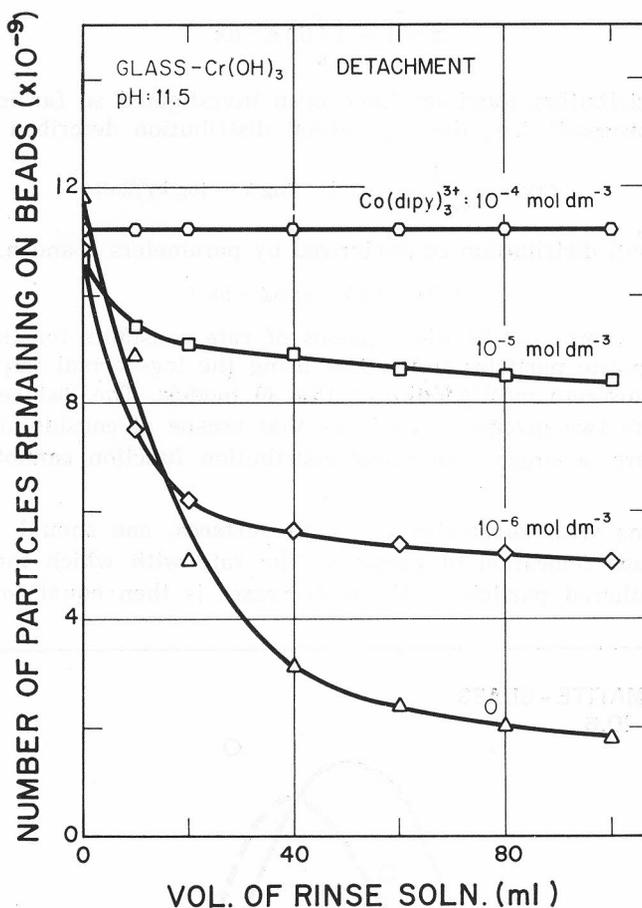


Figure 6. The plots as in Figure 5 for the same system in the presence of Co(dipy)₃(ClO₄)₃: none (○); 1 · 10⁻⁶ (◇); 1 · 10⁻⁵ (□); 1 · 10⁻⁴ mol dm⁻³ (◊).

If the rate of particle release can be interpreted in terms of two different rate constants the following equation applies:

$$x = x_r + x_s = x_\infty - x_{s,\infty} \exp(-k_s t) - x_{r,\infty} \exp(-k_r t) \tag{4}$$

where

$$x_\infty = x_{s,\infty} + x_{r,\infty} \tag{5}$$

Subscripts *s* and *r* denote »slow« and »rapid« release. Usually one finds $x < 1$, indicating that there are particles which cannot be detached. The above analysis was applied to a number of investigated systems.⁷⁻⁹

Generally, a distribution of discrete rate constants is assumed according to

$$x = \sum x_i = \sum x_{i,\infty} (1 - e^{-k_i t}) \tag{6}$$

The sum in Eq. (6) may be approximated by an integral over continuous distribution of *k*, *f*(*k*). Since the sum of all fractions is *f*(*k*), one may write:

$$x = 1 - \int_0^{\infty} f(k) e^{-kt} dk \quad (7)$$

Two such distribution functions have been investigated so far in relation to detachment process²⁰, i. e., the log normal distribution described by:

$$f(k) = \frac{1}{k\sigma\sqrt{2\pi}} \exp[-(\log k - \overline{\log k})^2/2\sigma^2] \quad (8)$$

and the Weibull distribution characterized by parameters b and n .

$$f(k) = bnk^{n-1} \exp(-bk^n) \quad (9)$$

Figure 7. compares the distributions of rate constants for the release of spherical hematite particles from glass using the log-normal (Eq. 8), Weibull (Eq. 9), and discrete multipopulation (Eq. 6) models. The last result (circles) would indicate two groups of particles that escape at considerably different rates; therefore, a single continuous distribution function cannot be applied in this case.

In systems with substrates of rough surfaces, one should consider the possible surface relocation of particles. The rate with which the number of detachable adhered particles, dN_d^s/dt decreases is then equal to the sum of

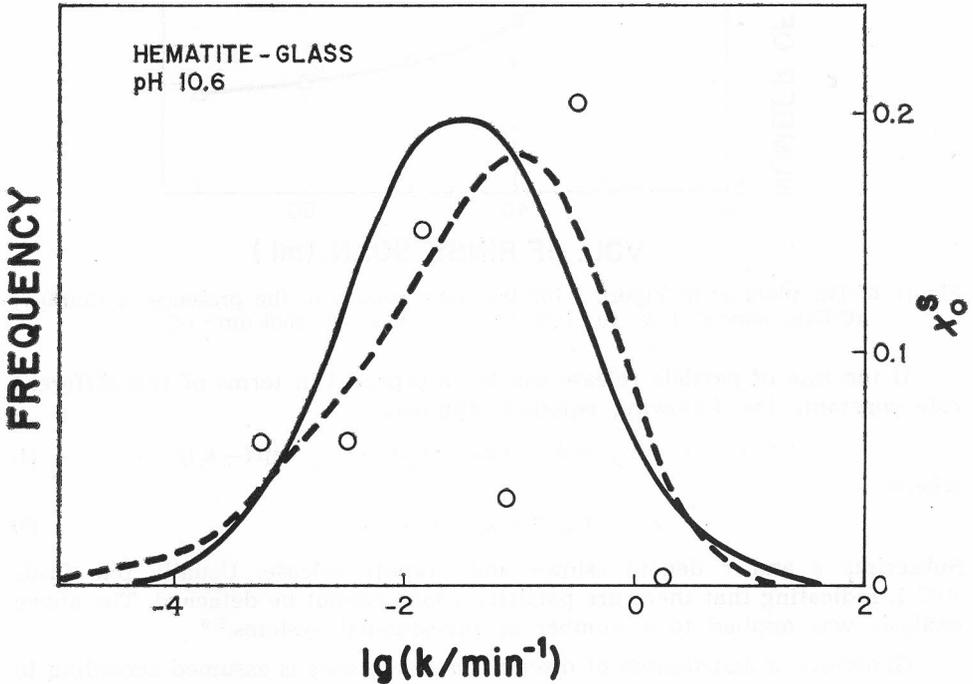


Figure 7. Distribution of rate constants for detachment of colloidal hematite particles from glass at pH 10.6. Full line: log-normal distribution (Eqs. 7 and 8); dashed line: Weibull distribution (Eqs. 7 and 9). Circles are fitted values of x_s^s (Eq. 6), assuming six kinds of particles.²⁰

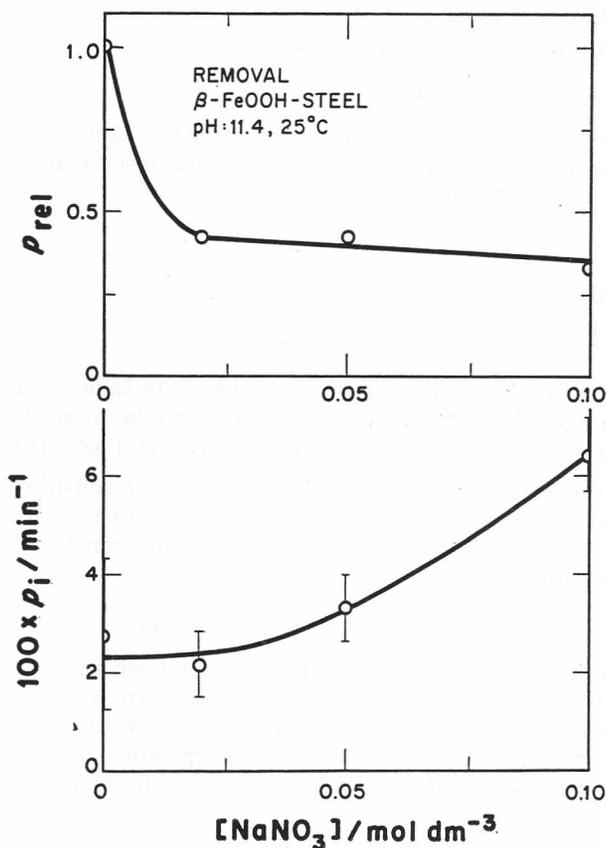


Figure 8. Upper: Relative values of rate constants for detachment of rod-like β -FeOOH particles from steel as a function of the sodium nitrate concentration. Lower: Rate constants of irreversible attachment for the same system.¹⁰

the rates of escape into the solution bulk and of relocation of particles on the surface into a permanently bound state:

$$-dN_d^s/dt = dN/dt + dN_b^s/dt = (p_d + p_b) N_d^s \quad (10)$$

where p designates rate constants of the detachment and relocation processes designated by subscripts d and b , respectively. Integration of this expression and introduction of fractions with respect to the initial (total) number of adhered particles yield^{9,11,21}

$$\ln(x_\infty - x) = \ln x_\infty - (p_d + p_b) t \quad (11)$$

where the fraction of released particles at infinite time, x_∞ , is given by

$$x_\infty = p_d x_{d,0}^s / (p_d + p_b) \quad (12)$$

A plot according to Eq. 11 gives the apparent rate constant of removal

$$k' = p_d + p_b \quad (13)$$

While the absolute values of p_d and p_b cannot be ascertained, it is possible to obtain a relative value of $p_{d,rel}$, as follows:

$$p_{d,rel} = p_d x_{d,o}^s = x_{\infty} k' \quad (14)$$

If a series of experiments is carried out with the same sample, subdivided into several portions, the evaluated constants are interrelated. It is possible to estimate the range of $x_{d,o}^s$ from

$$x_{\infty} \leq x_{d,o}^s \leq 1 \quad (15)$$

and the combination with Eq. 14 gives

$$p_{d,rel} \leq p_d \leq k' \quad (16)$$

To best estimate $x_{d,o}^s$ for a given system one needs to take x_{∞} from the fastest detachment process (Eq. 15). This value can then be used to calculate the corresponding rate constants (p_d and p_b) using Eq. (14) and (13).

Figure 8. illustrates the analysis of the release of rod-like β -FeOOH particles from steel. The upper part shows the relative rate constants of detachment, whereas the lower part represents the rate constant of irreversible adhesion of the same particles.

THEORETICAL CONSIDERATION

The interaction energy of particle detachment from surfaces is short range in nature, resulting in the necessity to consider a Born wall repulsion together with the more common electrostatic and van der Waals energies. The total interaction energy E_{tot} may be given by a superposition of the Born repulsion energy E_B , the van der Waals attraction E_{vdW} and the electrostatic energy E_{el} , namely

$$E_{tot} = E_B + E_{vdW} + E_{el} \quad (17)$$

The interaction energy E_{tot} is essentially obtained from two potentials: molecular and electrostatic. The former is taken as the classical Lenard-Jones 6—12 potential, which gives both the van der Waals and the Born repulsion terms in E_{tot} .^{15,16} The electrostatic potential, obtained from the Poisson-Boltzmann equation, yields the energy obtained as surface integrals.

The ranges and the relative magnitude of various components of E_{tot} differ considerably. At very short separations the dominant term is E_B . It represents a very powerful repulsion, whose effect is only felt when the particles almost touch each other; it is hardly felt beyond 20 Å. The van der Waals attraction is a long range effect and its influence is felt over all separations of interest. The electrostatic interaction energy has a very complicated structure, whose properties have been discussed in detail elsewhere.²¹⁻²⁴ At large separations the electrostatic force is always repulsive for a system with the same sign potentials. When the potentials are marginal in magnitude, partial attraction develops at intermediate distances which turns into a net attraction at a "collapse" separation. There, the electrostatic attraction is added to the van der Waals energy, and the two terms complement each other until repulsion of the wall E_B takes over. This fact increases the magnitude of the acti-

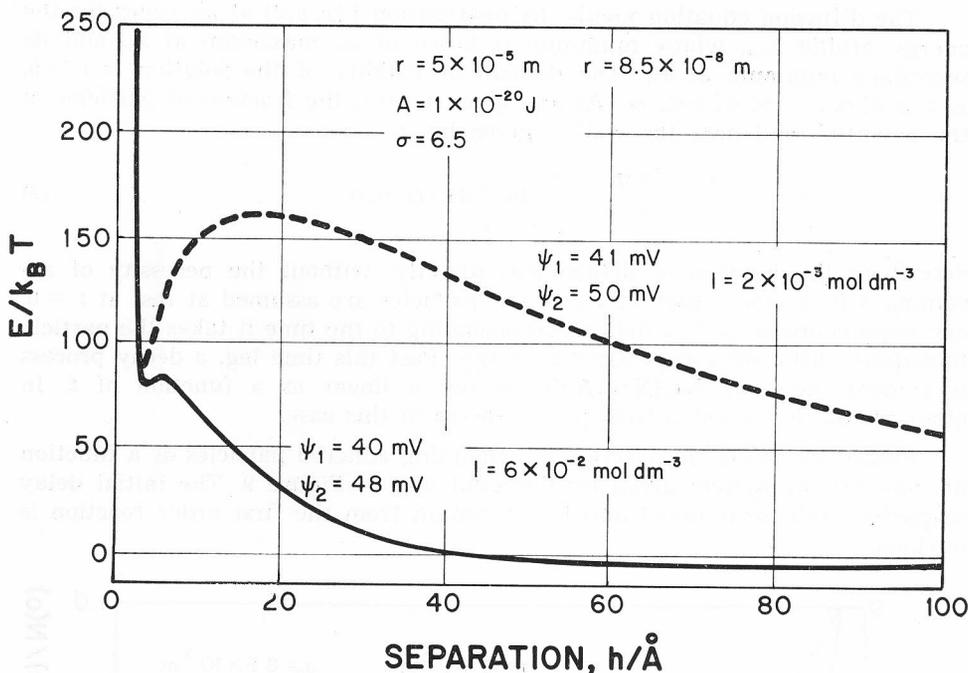


Figure 9. Total interaction energy as a function of distance for two spheres of radii $r_1 = 5 \cdot 10^{-5}$ m and $r_2 = 8.5 \cdot 10^{-8}$ m; $A = 1 \cdot 10^{-20}$ J, $\sigma = 6.5$. Dashed line: $\psi_1 = 41$ mV, $\psi_2 = 50$ mV, $I = 2 \cdot 10^{-3}$ mol dm $^{-3}$. Solid line: $\psi_1 = 40$ mV, $\psi_2 = 48$ mV, $I = 6 \cdot 10^{-2}$ mol dm $^{-3}$.

vation energy, causing the particle escape to be a more energy consuming process.

Figure 9. illustrates two different total interaction energy functions for greatly different particle sizes, approximating the plate/sphere configuration. The parameters correspond to systems studied experimentally.⁶ The cases were chosen to show a big difference in the activation energies. The system represented by the solid line should allow a rapid release of adhered particles.

Detachment is described analytically as a diffusion process. In the absence of external forces, the diffusing particles are assumed to be initially largely at rest at the bottom of the potential well. At time $t = 0$ a forced diffusion starts to take place. The particle distribution function satisfies a modified Navier-Stokes equation,^{16,27,28} i. e., the Kramers equation, given explicitly by

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} + \frac{1}{m} \left(- \frac{\partial E_{\text{tot}}}{\partial x} \right) \frac{\partial f}{\partial u} = \frac{\eta}{m} \frac{\partial}{\partial u} \left(u f + \frac{k_B T}{m} \frac{\partial f}{\partial u} \right) \quad (18)$$

where x, u represent the location and velocity of the particle of mass m , η is the constant friction coefficient, T the absolute temperature and k_B Boltzmann's constant.

The diffusion equation yields the distribution $f(x, u, t)$ at all times for the energy profile E_{tot} , whose minimum is taken at x_0 , maximum at x_1 , and its secondary minimum at x_{12} . The domain of validity of the solution is $t > 0$, $x_0 \leq x < \infty$, $-\infty < u < \infty$. At any given time t , the fraction of particles in the potential well near the wall is given by

$$\frac{N(t)}{N(0)} = \int_{-\infty}^{\infty} du \int_{x_0}^{x_1} dx f(x, u, t) \quad (19)$$

describing the kinetics of detachment directly, without the necessity of assuming a first order reaction. Since the particles are assumed at rest at $t = 0$, one expects and obtains a delay, corresponding to the time it takes the particle to acquire sufficient escape kinetic energy. Past this time lag, a decay process is evident; however $\log[N(t)/N(0)]$ is not a linear as a function of t . In other words this is not a first order process in this case.

Figure 10. shows the fraction of remaining adhered particles as a function of time for the system given by the solid line in Figure 9. The initial delay in particle release is noted and the deviation from the first order reaction is obvious.

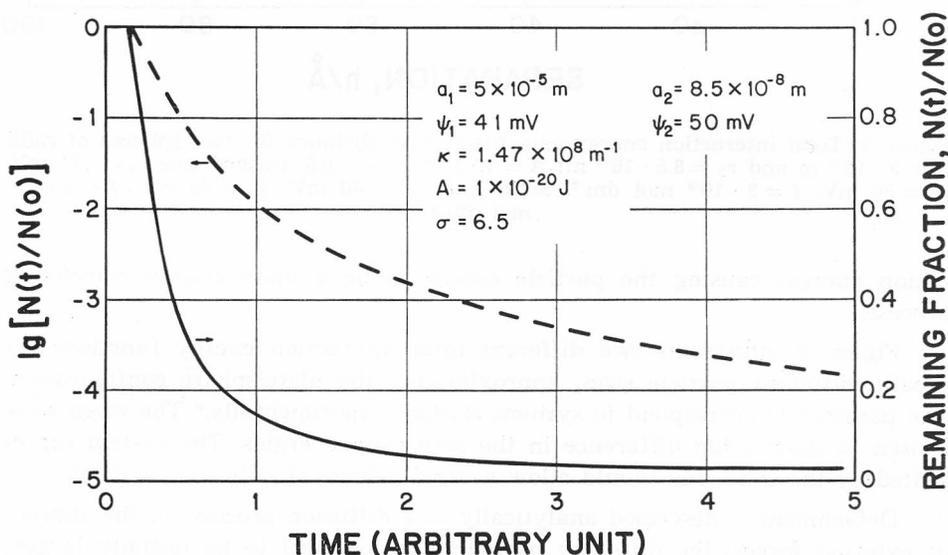


Figure 10. Fraction of particles remaining adhered as a function of time for a system with parameters as given in the figure.

DISCUSSION

In the studies of detachment processes from solid surfaces, the experimentally determined quantity is the number of released particles as a function of time. This information must then be used in the evaluation of data. The theoretical model is based on the plate/sphere configuration. When the real system approaches the model, the interpretation of the detachment results

is relatively straightforward; i. e., the experimental rate constant corresponds to the theoretical one. However, such a case is relatively rare and only a fraction of the adhered particles is located on a plane surface of the substrate. In order to take the surface inhomogeneity into consideration, distribution of rate constant was interpreted in different ways (continuous or multipopulation type). In most cases data could be sufficiently well described by assuming a bimodal distribution of rate constants, recognizing that a fraction of particles is permanently bound ($x_\infty < 1$). The faster detachment should correspond, then, to the theoretical model, assuming that no surface relocation of particles into crevices takes place. The testing of this condition if possible by examining the effect of the pretreatment of the packed column on the detachment efficiency.⁹

The kinetics of particle escape is determined by the total interaction energy profile as a function of distance. It is essential to take into consideration the short range repulsion, in addition to electrostatic and London-van der Waals contributions. In treating the short range effect, one can either assume the existence of a hard wall^{6,29} or operate with a Born-type function.^{21,22} In view of the steepness of the Born repulsion term, the two models give

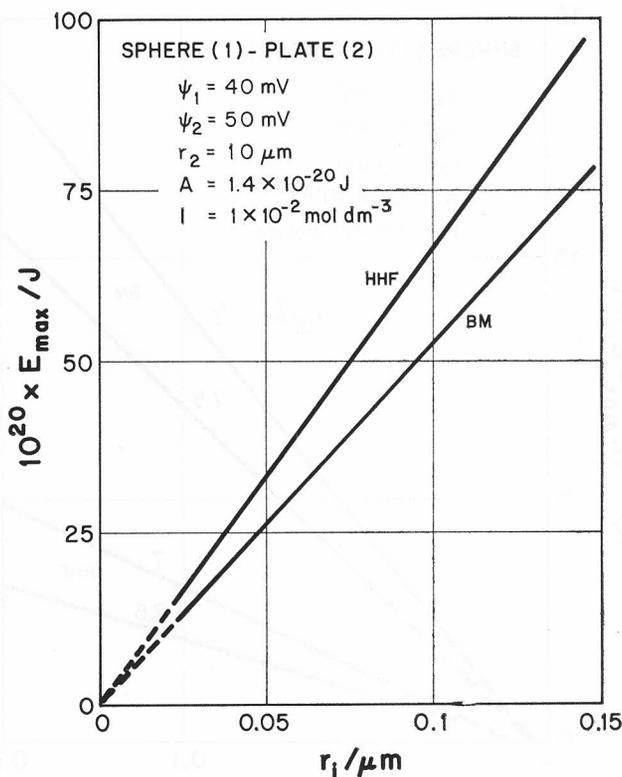


Figure 11. Computed dependence of the total interaction energy on the size of one particle while the size of the other particle is kept constant at $10 \mu\text{m}$ in radius. $\psi_1 = 40 \text{ mV}$, $\psi_2 = 50 \text{ mV}$, $I = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$, $A = 1.4 \cdot 10^{-20} \text{ J}$. The electrostatic energy contribution was calculated using the Hogg, Healy and Fuerstenau (HHF)³⁰ and Barouch and Matijević (BM)²² expressions, respectively.

essentially the same answer; e.g., the position of the first minimum of the interaction energy curve was found in both cases to be at $\sim 7 \text{ \AA}$.

Inclusion of the short range repulsion determines the depth of the first minimum. Since both the minimum and the maximum are sensitive to all parameters (particle size, surface potential, and the ionic strength), the activation energy of the detachment process, which is the difference between the depth of the first minimum and the height of the repulsion maximum, varies considerably. It is this energy that controls the rate of release.

The change in the magnitude of the activation energy as a function of the ionic strength can be utilized to test the constant potential against constant charge assumptions. Indeed, it was possible to show from the kinetics of particle detachment that the constant potential case in agreement with the experimental finding¹⁸. Consequently, the electric double layer relaxation seems to take place.

The effect of various parameters on the interaction energy has been examined and some of the results are offered here. Figure 11. displays the values of the total interaction energy at its maximum as a function of the

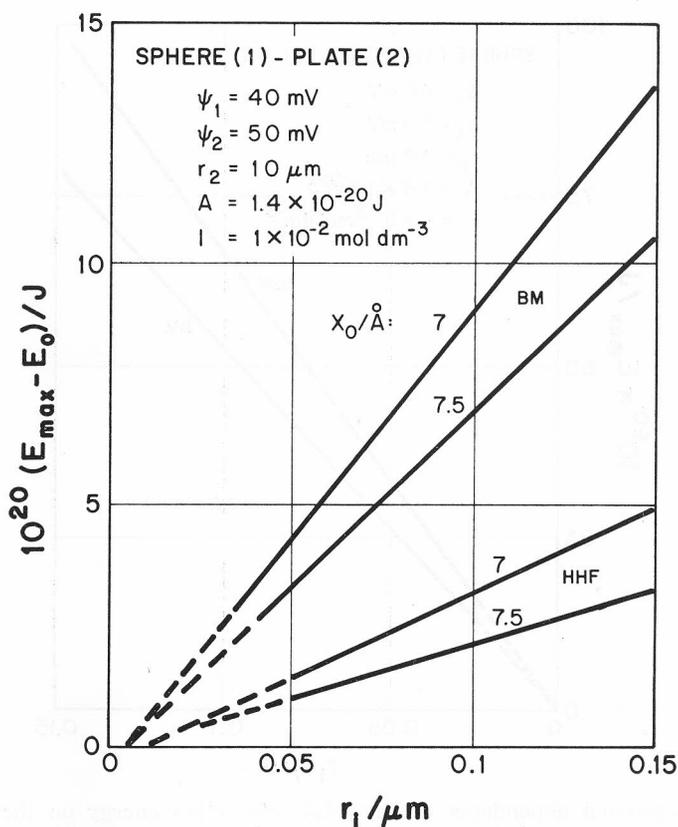


Figure 12. Computed dependence of the activation energy for the same system as in Figure 11 at two different values of the closest separation, $x_0 = 7$ and 7.5 \AA , respectively.

radius of one particle while that of the other particle is kept constant. The size of the latter was chosen large enough for systems to represent a sphere/plate configuration. In calculating the electrostatic contribution both Hogg, Healy and Fuerstenau (HHF)³⁰ and Barouch and Matijević (BM)²² models were taken.²² A linear decrease in energy with reduced particle size is found; the extrapolated value at point size particle is zero. Although this result may appear surprising, an inspection of the relevant equations indicates approximately the linear relationship for the sphere/plate configurations. The calculations using the HHF expression consistently give higher energies.

The changes in magnitude of the activation energy for the same system at two different values of the closest separation (x_0) are shown in Figure 12.

The influence of the ionic strength on the rate constant of particle detachment (k), for the same parameters as shown in Figure 10 for three different sizes of spherical particles, is illustrated in Figure 13. The total interaction

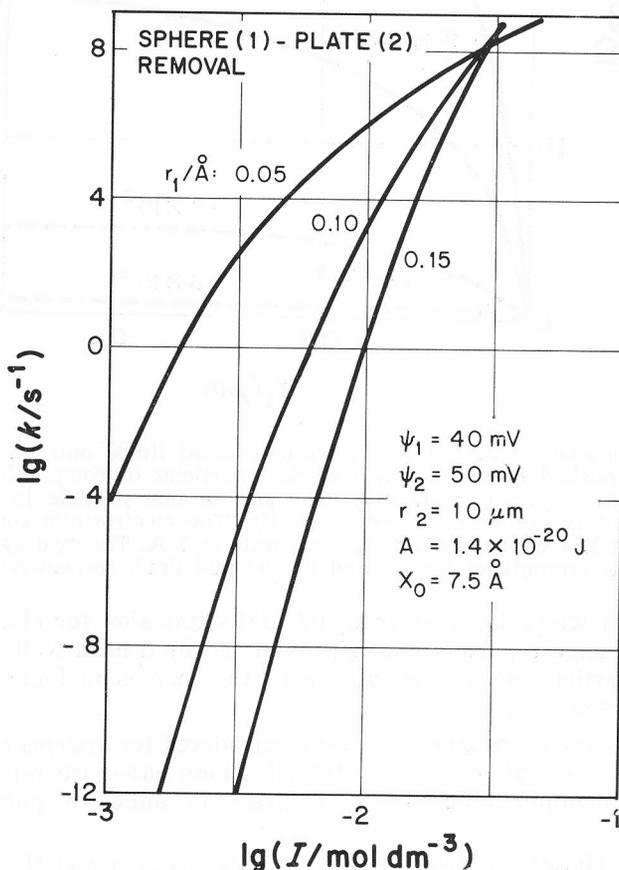


Figure 13. Computed dependence of the rate constant for particle detachment as a function of the ionic strength for spheres of three different sizes. The electrostatic contribution was calculated using the BM expression and a hard wall at $x_0 = 7.5 \text{ Å}$ was assumed. All other parameters were the same as in Figure 11.

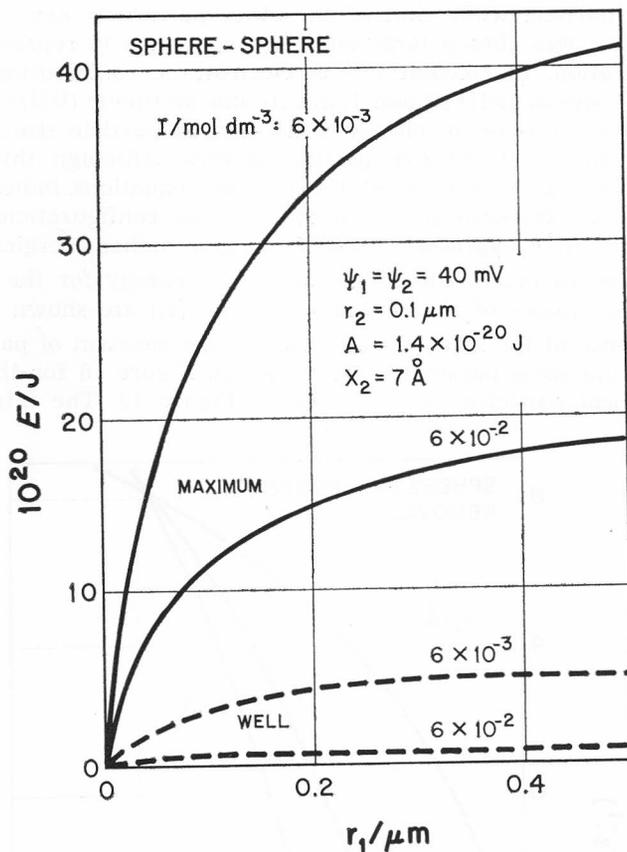


Figure 14. Computed energy at the maximum (solid lines) and the depth of the potential well (dashed lines) for two spherical particles of comparable size and of the same potential ($\psi_1 = \psi_2 = 40 \text{ mV}$). The size of one particle is kept constant, while the size of the other is varied gradually. The electrostatic contribution was calculated using BM expression and a hard wall at 7 \AA . The two systems refer to ionic strength of $6 \cdot 10^{-3}$ and $6 \cdot 10^{-2} \text{ mol dm}^{-3}$, respectively.

energy function was calculated using the BM expression for electrostatic part and the short range repulsion was approximated by a hard wall at $x_0 = 7.5 \text{ \AA}$. The rate of particle escape increases with the increasing ionic strength and decreasing particle size.

The corresponding relationships were considered for systems of two spheres of comparable size and the same potential. These cases are representative of coagulation/peptization processes in contrast to adhesion phenomena illustrated above.

Figure 14. shows the height of the energy maxima and the depth of the well, as a function of the size of one particle, while the radius of the other particle was kept constant. Two sets of data refer to different ionic strengths. With increasing particle size both energy values rise, but they eventually level off in contrast to the sphere/plate system. At the lower ionic strength

the height of the maximum, as well as the depth of the minimum, is larger than at the higher ionic strength. Consequently, both the coagulation and peptization processes are enhanced by the addition of electrolyte; however, the agglomeration of the dispersion will prevail.

The effect of ionic strength was further examined in more detail for three different cases of identical or similar spheres. Figure 15. shows that the same trends are observed; i. e., in all cases with increasing electrolyte content, there is a decrease of the energy barrier, both for coagulation and peptization processes.

This review has shown that considerable progress has been made in the understanding of the interactions of unlike particles. When their sizes differ considerably, one deals with adhesion phenomena, whereas in systems of comparable sizes, one deals with colloid stability. Some of the results of the theo-

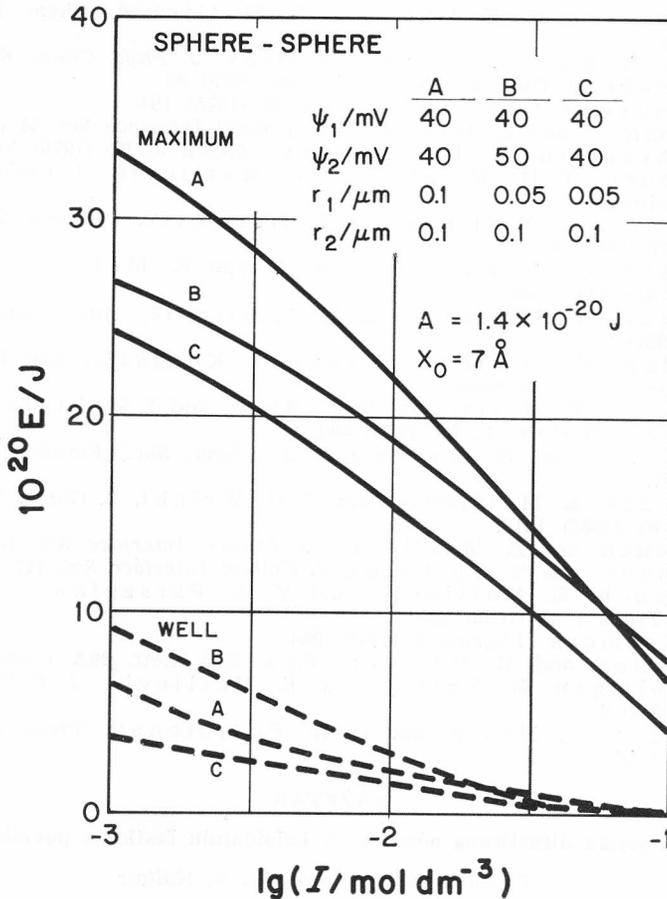


Figure 15. Computed dependence of the energy at the maximum (solid lines) and the depth of the potential well (dashed lines) on the ionic strength for systems of identical or similar spheres. The calculations were carried out in the same manner as for Figure 14. The actual parameters are given in the figure.

retical analysis appear counterintuitive, but the conclusions are born out by experimental evidence. It is also shown that the particle detachment process can yield valuable information with respect to the properties of the electrical double layer.

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SAŽETAK

Kinetika difuzijskog odpuštanja koloidalnih čestica s površina

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Opisani su eksperimentalni i teorijski problemi koji se javljaju pri proučavanju odvajanja sfernih čestica od ravne površine. U razmatranju difuzijske kinetike uzete su u obzir elektrostatičke i van der Waals-ove interakcije te odbijanje na malim razmacima. Brzina odvajanja prikazana je kao kinetički proces prvog reda, upotrebljavajući jedno- ili višepopulacijski model.