A Fundamental Investigation of Coagulation in Water Works (1)

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Introduction

There are very few water supplies in which the water does not require some kind of treatment before distribution to consumers. The necessity of water treatment is ever increasing in proportion to the growth of raw water pollution caused by the rapid and never ending growth of modern industries and human communities. The objectionable substances in water for domestic, industrial and other uses are contained in raw waters in a suspended or dissolved form. For the treatment of polluted waters, either natural or man made, a number of unit operations such as plain sedimentation, sedimentation with chemical coagulation, sand filtration, vacuum filtration, ion exchange, disinfection, softening, evaporation, aeration etc. have been developed to meet the necessities of the modern community.

The sizes of substances which are suspended in water, range from the order of 10^{-8} cm to 10^{-1} cm. According to the size of the suspended matter the water is sometimes called a suspension and sometimes a solution.

The order of the sizes of these particular matters are listed in Figure 1 with the applicable unit operations for their removal.

Among these the process of sedimentation is one of the most important unit operations for the removal of suspended matters from water and has been used from ancient times as a powerful means for water clarification. Solids heavier than water are held in suspension while the water is moving. When the water becomes still or approximately so, suspended matter will settle, the downward rate depending upon the specific gravity and viscosity of the liquid and the size, shape, specific gravity and concentration of the suspended particles.

The size of the suspended solids in raw waters range between colloidal matters and coarse sand grains, depending on whether the water comes from a lake, swamp, impounding reservoir, underground aquifer, rapid stream or gentle flow. According to the A. S. T. M. (or U. S. Bureau of Soil, Public Road Administration) the solids are classified according to the diameter of the particles as follows; colloids $<$ 0.001 mm $<$ clay $<$ 0.005 mm $<$ silt $<$ 0.05 mm $<$ fine

sand < 0.25 mm < coarse sand.

The rate of settling in still water at 10°C is known as the hydraulic settling value of a particle and is expressed in millimeters per second or centimeters per second. The hydraulic settling values of particles with a specific gravity of 2.65, among which may be considered such inorganic suspended matters in the raw water as sand, are 2.9 mm/sec for a fine sand particle (diameter: 0.05 mm); 0.0385 mm/sec for a silt particle (d: 0.005 mm); 0.00154 mm/sec for a clay particle (d: 0.001 mm); and less than 0.00154 mm/sec for a colloidal particle (d < 0.001 mm). The hydraulic settling values of particles with a specific gravity of 1.20, which corresponds to organic suspended matters are 0.000084 mm/sec for 0.001 mm particles, and 0.0021 mm/sec for 0.005 mm particles.

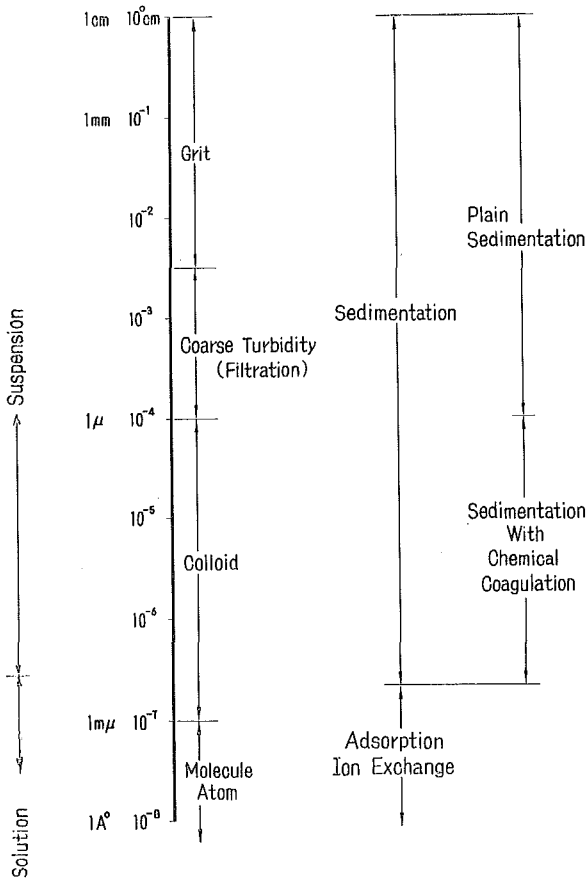


Fig. 1.

Coarser components of suspended solids, such as sand and coarse clay, can be removed from the water when the suspensions are drawn into quiescent intermittent draw and fill settling basins or continuous-flow tranquil basins. This unit operation is called plain sedimentation.

The settling velocity of finely divided and colloidal suspended matters is so small that removing them from the water in a settling basin having ordinary dimensions is impossible from a viewpoint of engineering. Therefore, it is necessary to devise means to agglomerate the very small particles into larger ones which would have a higher settling velocity and which could be settled in a tank of reasonable size. The agglomeration of the finely divided particles can be performed by an addition of some chemicals to the suspension. Heavy gelatinous or flocculent precipitates are formed which entangle the suspended particles in them. This process is called coagulation and flocculation. After this process, the water is allowed to stand quietly in, or to flow slowly through, a sedimentation basin in which the coagulated and flocculated small particles settle to the bottom of the tank. These operations are customarily considered to comprise two distinct phases: mixing, wherein the dissolved coagulant is rapidly dispersed throughout the water to be treated, usually by a violent agitation; and flocculation, involving agitation of the water at lower velocity for a much longer period, during which the very small particles grow, coalesce, and agglomerate into wellgrown floc particles of a sufficient size to settle readily.

As is seen in Figure 1, processing by coagulation and flocculation is applicable for a wide range of suspended particle sizes. Therefore, this procedure is adopted as one of the most important treatment methods in water works, followed by sand filtration. The combination of sedimentation with chemical coagulation and rapid sand filtration has been one of the most powerful standard treatment methods since the beginning of this century. Now, a great number of purification plants of this kind are designed and operated all over the world.

Historically, the idea of rapid sand filtration system was developed from slow sand filtration. Thus, it was long believed that the sand filter was the main part of the process. Accordingly, the coagulation, flocculation, and sedimentation was considered as a preliminary, or pre-treatment, for the sand filtration. However, the importance of the pre-treatment, i.e., the coagulation and flocculation, has gradually been recognized as being much more important than the so-called main treatment, i.e., the sand filter, itself. As a result of this idea, the sand filter is beginning to be considered only as a finishing or post-treatment in the whole rapid sand filtration system. Accordingly, the so-called rapid sand filtration should be understood as a combination of sedimen-

tation with chemical coagulation and flocculation, and finishing sand filtration. Therefore, the largest portion of the investigations of the rapid sand filtration system has naturally been concerned with the coagulation and flocculation followed by the sedimentation. Based upon these research works and practical experiences, it is possible to make a reasonable reliable design. However, deep basic theories have not been established and accepted as yet. Thus, it is quite inconvenient or sometimes impossible to organize individual research and experience for a practical design and operation, and for future development. Thus, rule of thumb methods are still in used for designs and operation. Hence, only a person who has wide and deep experience can make good designs for the successful operation of this process.

It has been the intention of the author to perform basic investigations in the basic part of the treatment process in order to give a framework for the rationalization of the design process and operation. The author has studies the process of the sedimentation with chemical coagulation and flocculation for eight years. In this paper the very basic part of the coagulation theory is presented among his results.

A Theoretical Consideration

Historically, two theories have been advanced in the field of colloid science to explain under what conditions small particles remain in water as a stable suspended phase or settle from water as coagulated particles under gravitational force. One is a chemical theory, the other is a physical theory. The former and older theory assumes that aggregation of colloids are defined chemical structures of the colloids themselves. That is to say, the primary charge of colloidal particles arises from the ionization of complex inorganic groups present on the surface of the dispersed particles, and the destabilization, or coagulation, of colloids is due to chemical interaction. The newer theory assumes the existence of an electric double layer; defines the zeta potential; and explains phenomena from the viewpoint of the electro-kinetics of a colloidal surface. This physical or double-layer theory has been developed in great detail and has been widely accepted as the most effective and reliable theory for understanding and controlling stability and instability of colloidal suspensions.

The stability and coagulation phenomena of suspended minute particles in water works, sewage works, and industrial waste treatment systems are too complex to discuss by the double layer theory alone. It is correct, however, to say that electrokinetic phenomena on the surface of colloid particles are the most essential items to be considered at first in the investigation of coagulation. In addition to this it is important to consider the chemical factors

in order to have a complete understanding of the phenomena.

In the coagulation of natural water, the following types of colloids should be considered: (1) suspended turbidity in the water composed mainly of clay minerals, and organic color colloids contained in the water, both negative and (2) the particles formed by added metal coagulants whose charge will depend upon the pH of the water but which is usually positive, and (3) colloidal coagulant aids, when used.

There are two types of factors simultaneously affecting every colloid: (1) instability factors which tend to bring about coagulation of the colloid, and (2) stability factors which tend to disperse the colloid.

a) Stability and Instability Factors

The most important instability factors are the Brownian movement of colloidal particles or the turbulent fluctuation movement in coarser particles and the London–Van der Waals force of attraction. The Brownian movement is a rapid and random movement of the colloids suspended in the water caused by the collision of water molecules (under thermal agitation) with the colloidal particles. The Brownian movement has two important aspects as an instability factor: (1) it brings particles very near to each other and prepares opportunities for collisions, (2) it gives to the colloidal particles the kinetic energy necessary to overcome the repulsive electric potential on the surface of colloids. The kinetic energy E_K of a particle under the Brownian movement is shown as[1] follows:

$$E_K = \frac{1}{2} m\overline{v'^2} = \frac{1}{12}\rho\pi d^3\overline{v'^2} = \frac{3}{2}KT \qquad (1)$$

where m = the mass of the particle
$\overline{v'^2}$ = the mean square velocity of the particle
ρ = the density of the particle
d = the diameter of the particle
K = the Boltzmann constant
= 1.381×10^{-16} erg/°C
T = the absolute temperature

This kinetic energy is constant for a given temperature regardless of the particle size. The magnitude of the energy E_K at 25°C is:

$$E_K(25°\mathrm{C}) = 3/2 \times 1.381 \times 10^{-16} \times 298$$
$$= 6.175 \times 10^{-14} \text{ erg or g·cm}^2/\text{sec}^2 .$$

If the density ρ of a particle is taken as 2.65 (i.e. ordinary clay particles)

the root mean square fluctuation velocity is calculated for different particle sizes as shown in Table 1.

TABLE 1.

d	10^{-7} cm (1 mμ)	10^{-6} cm (10 mμ)	10^{-5} cm (100 mμ)	10^{-4} cm (1 μ)	10^{-3} cm* (10 μ)
$\sqrt{v'^2}$	9430 cm/sec	296 cm/sec	9.43 cm/sec	0.296 cm/sec	0.00943 cm/sec

* Out of colloidal range.

As in Table 1, larger particles are not effectively displaced by the Brownian movement. After some size limit is reached, it is necesaary to consider the other driving force which brings the particle in close proximity to each other and provides opportunities for collisions and imparts the kinetic energy to overcome the repulsive electric forces between particles. This driving force results from the turbulent fluctuation of small water masses under forced agitation conditions. According to Kolmogolov's[2,3] idea of local isotropic turbulence, the turbulent velocity of an eddy in the region of the viscous subrange where the turbulent fluctuation is effective for the collision of micro-floc particles is given as $\beta\sqrt{\varepsilon_0/\mu}\cdot d$, in which ε_0 denotes the energy dissipation occuring in the flow per unit volume per unit time, μ is the viscosity, and β is a proportionality constant. Thus, if the value of the Brownian fluctuaction velocity decreases to the order of $\beta\sqrt{\varepsilon_0/\mu}\cdot d$ with an increasing particle diameter the main driving force of the coagulation phenomenon will change to turbulent fluctuation. Therefore, there exists a certain transition diameter condition for coagulation from the viewpoint of the driving factor of the phenomenon.

The London–Van der Waals' force[4,5] may be described as a molecular cohesive force. Although it is based upon electric action, it does not involve two net charges; it is always attractive; and it decreases very rapidly with distance. This force is due to the interaction of dipoles which may be either permanent dipoles of poler particles or induced dipoles of nonpolar but polarized materials. The force resulting from an ion dipole interaction decreases, roughly, with the cube of the distance. According to Fritz London the electric field induced by a dipole in a nonpolar particle decreases with the seventh power of distance, and is indeed a short distance force.

The force which acts both as an instability and as a stability factor and hence is considered to be the controlling factor in coagulation is the coulombic force. The coulombic force is created by the electric charge attracted to the surface of the colloid particles or initially born on the surface of colloidal particles. As discussed in the following paragraphs, these electrical charges in

the particle change sharply when the condition of the surrounding medium is changed by an addition of coagulants and pH controlling agents. Hence, water treatment engineers utilize the adjustment of these variables as a principal method of coagulation control. The effects of this force on the coagulation phenomenon can best be understood, if first the diffused electric double layer and the electric potential in the double layer are defined.

The factor which generally acts only as a stability factor is hydration of colloidal particles. Hydration is a phenomenon in which large numbers of water molecules are attracted to the surface of a particle. Thus contact between particles is hindered and we have an aqueous molecular "sandwich".

b) Electric Dobule Layer and the Zeta Potential[7,8,9]

For the sake of simplicity of explanation, the layer in which surface electrokinetic actions occur is assumed to be thin relative to the diameter of the particle, and hence is considered to an equivalent infinite plane. See Figure 2.

Because the experimentally measured parameter is a potential instead of a force, it is most convenient to describe the surface phenomenon in terms of potential.

Consider a particle which is uniformly and negatively charged on the surface and is suspended in water where positive and negative ions are distributed homogeneously. If thermal motion were absent, an equivalent amount of counter ions would be attracted by the wall of the particle and would cover it, precisely neutralizing its charge. The wall and these neutralizing counter ions would form a "double layer". The electric potential would drop to zero within the double layer.

In an actual suspension wherein the counter ions are attracted to and the similiions are repelled from the surface of the particle, contemporneous thermal agitation of the suspension moves both the particles and the ions in a manner which tends to cause a uniform distribution of all such particles and of all such ions of both signs. As a result of these combined movements, there exists a distribution of counter-ions which has its highest concentration on the surface of the particle, the decreases with the distance, and must have the same concentration as the bulk of the solution far distant from the particle. Likewise the distribution of similiions must have a zero concentration on the surface of the particle and increase with the distance until the concentration of similiions in the bulk of solution is reached. Though the counter-ion concentration can be increased many-fold in the bulk of the solution, the concentration of the similiions can at best only reach zero, so that the effect of the

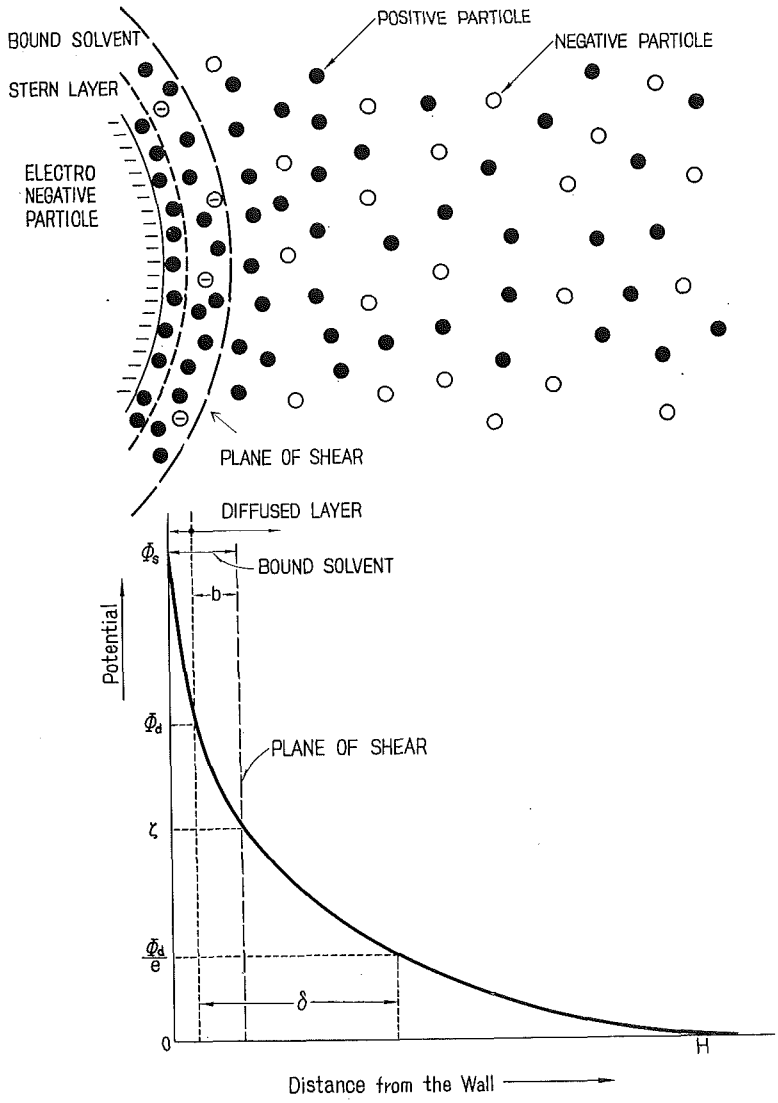


Fig. 2.

counterions on the potential distribution at the surface of the particle ordinarily predominates. The layer so created is called the "diffused" double layer or the Gouy double layer.

Very near to the surface of the particle where the electrostatic forces are very strong, and are even reinforced by the London–Van der Waals' force, no thermal motion can disperse the counter ions. Therefore, a compact fixed

layer of counterions of oppositely charged minute particles is created on the surface of the particle. This layer is called the Stern layer. This Stern layer is in dynamic equilibrium with the Gouy layer. These two layer comprise the outer atmosphere of colloidal particles and are called the Gouy–Stern double layer.

This Gouy–Stern double layer is defined by three special potentials and the thickness of the double layer. The first potential is the surface potential, Φ_s, of the particle; the second is the potential Φ_d of the boundary between the Stern layer and Gouy layer; and the last is the zeta potential, ζ, which is defined as follows. When a particle moves with respect to a suspending medium, some of the liquid moves with it. Between the attached liquid and the bulk of the liquid there exists a surface of shear. The potential of the Gouy layer at the plane of shear is defined as the zeta potential of the double layer, or simply the zeta potential. Of these three potentials, only the zeta potential can be measured easily, and therefore, it is used as the main index of the nature of the double layer. The thickness of the double layer is considered to be the distance over which the potential drops $1/e$ of its initial value. It is impossible to measure this thickness directly.

The electric potential distribution in the double layer of a particle is changed by an addition of an electrolyte of minute particles having an opposite charge in the manner shown in Figure 3. Originally the electric potential distribution of the double layer on a particle is assumed to be the curve 0. The counterions cause the concentration of these ions in the diffused double layer to increase. Then both the potential and the thickness of the layer become small. At the same time by static attraction or adsorption the concentration of counterions in the Stern layer also increases and the Stern and Gouy boundary layer potential, Φ_{d1}, at the end of the reaction becomes very small compared with the initial potential, Φ_{d0}, of the layer at the beginning. But the surface potential, Φ_s, of the particle is considered to remain constant. If this is so, the potential gradient in the Stern layer must become relatively greater. The phenomenon is especially prominent when the counterions have a high valency. If much more electrolytes of oppositely charged minute particles are added, Φ_d approaches zero, so that the zeta potential also becomes the isoelectric point, i.e., zero zeta potential. If the number of counterions of oppositely charged particles adsorbed in the Stern layer increases greatly, the boundary potential, Φ_d, is reversed to positive, and therefore the zeta potential is also reversed as shown in Figure 3. Further addition increases the reversed Φ_d only to some limit where the Stern layer is saturated by the counterions or oppositely charged minute particles. Thus, the zeta potential also reaches

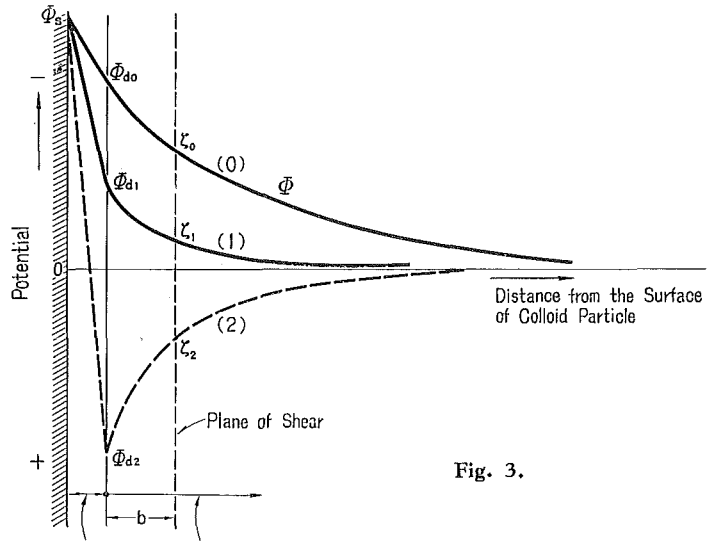


Fig. 3.

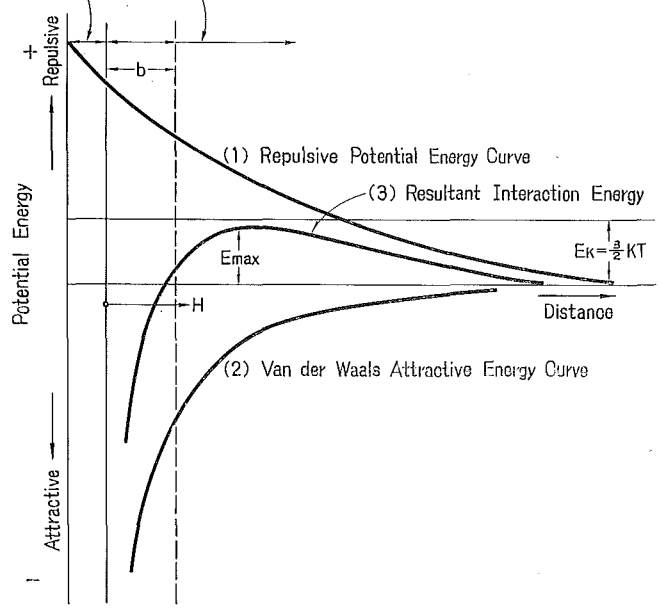


Fig. 4.

a limiting value. This value of the zeta potential is called the saturation zeta-potential. However, the mechanism of charge reversal is still not well understood and no acceptable explanation can be seen.

c) Fundamental Equation of Coagulation

As stated before, the coagulation phenomena are affected by factors such as the potentials in the double layer, the Brownian movement or turbulent fluctuation of minute particles, the London–Van der Waals' force, and the hydration of the particle surface. The last factor, which is difficult to treat and affects only hydrophilic colloids, is omitted from consideration in this paper.

The problem of interaction, or coagulation, between two similar particles can be studied by considering the energy of interaction as shown in Figure 4. Analysis of the energy balance of the coagulation phenomena is desirable because it allows a comparision of the energy of Brownian or turbulent fluctuation of particles with the energy of electrical interaction.

The repulsive electric potential energy curve (1) in Figure 4 can be calculated by multiplying the effective charge with the potential distribution of Figure 3. This function is given by Derjagun[10] as Equation 2 for the case of small surface potentials and relatively large particle diameter.

$$E_r = \frac{ad\Phi_d^2}{2} \ln\left\{1+\exp(-\kappa H)\right\} \qquad \kappa a \gg 1 \qquad (2)$$

where E_r = the repulsive energy of two spheres (erg)

a = the radius of the particle (cm)

D = the dielectric constant (non dimension)

Φ_d = the potential between the Stern and Gouy layers (e.s.u.)
(c.f. The effective potential to contribute to the repulsion is not considered the surface potential Φ_s but Φ_d). This means that the adsorbed oppositely charged minute particles in the Stern layer mask the surface potential Φ_s of the particle. Thus the particle behaves like one bearing potential Φ_d.

H = the shortest distance between two particles (cm)
(c.f. exactly speaping this is the distance between the Stern and Gouy boundary layers of the two particles).

$1/\kappa$ = the thickness of the Deby–Hückel ionic atmosphere (cm)

$$= \sqrt{\frac{4\pi e^2 \sum n_i Z_i^2}{DKT}} \qquad (3)$$

where e = the elementary charge, 4.803×10^{-10} e.s.u.

n_i = the number of ions of species i per cubic centimeter in the bulk of solution

Z_i = the valency of an ion of species i

K = Boltzmann's constant

T = the absolute temperature

The attractive potential energy curve (2) in Figure 4 is given by Hamaker's[11] equation modified as follows for the case of two equal spheres of radius a with the shortest distance H.

$$E_a = -\frac{A}{6}\left[\frac{2a^2}{H^2+4aH}+\frac{2a^2}{(H+2a)^2}+\ln\frac{H^2+4aH}{(H+2a)^2}\right] \qquad (4)$$

where E_a = the attractive energy (erg)

A = the London–Van der Waals constant

(c.f. The London–Van der Waals Constant A has never been determined in an independent way, but it is estimated in the order of $A=10^{-12}$ erg).

For small distances between spheres, i.e. for small values of H, the following equation[11] can be used.

$$E_a \doteqdot -\frac{Aa}{12}\cdot\frac{1}{H} \qquad (4\text{–a})$$

The addition of Equations 2 and 4 or 4–a the combined potential energy curve in Figure 4 is calculated as follows.

$$E_i = \frac{aD\Phi_d^2}{2}\ln\{1+\exp(-\kappa H)\} - \frac{A}{6}\left[\frac{2a^2}{H^2+4aH}+\frac{2a^2}{(H+2a)^2}+\ln\frac{H^2+4aH}{(H+2a)^2}\right] \qquad (5)$$

or

$$E_i = \frac{aD\Phi_d^2}{2}\ln\{1+\exp(-\kappa H)\} - \frac{a}{12}\cdot\frac{A}{H} \qquad (5\text{–a})$$

where E_i = the interaction energy (erg).

The resultant interaction potential energy distribution curve (3) which is found by the addition of tne two curves (1) and (2), i.e., the result of Equation 5, ordinarily has a hump very near the particle surface. From the composite curve it can be inferred that to bring a particle from a distant place to the point where the Van der Waals' attraction dominates, i.e. to cause two particles to collide, it is necessary that work equivalent to the maximum potential energy, $E_{\max}$, be exerted by some external force. The source of energy for this work is the kinetic energy of either Brownian movement or turbulent fluctuation or both. Then the following relationship should hold for the occurrence of coagulation.

$$E_{\max} < E_K = 1/2\, m\overline{v'^2}\,. \qquad (6)$$

d) The Worst Diameter Condition for Coagulation

The relative effectiveness of the Brownian movement and turbulent fluctuation as driving factors in coagulation is explained in the following way. According to Smoluchowski[12], for like particles, the total number of contacts per unit volume of suspension per second is

$$N_{br} = 8\pi D_{br} d n_0^2 \tag{7}$$

where N_{br} = the total number of contact per unit volume per unit time
D_{br} = the Brownian diffusion coefficient of dispersed particles
d = the diameter of the particle
n_0 = the number of particles per unit volume at the initial moment.

After Levich[13], in the zone where the turbulent fluctuation exceeds the Brownian fluctuation, the number of collisions per unit time per unit volume is

$$N_{tub} = 12\pi\beta\sqrt{\frac{\varepsilon_0}{\nu\rho}}\, d^3 n_0^2 \tag{8}$$

where N_{tub} = the number of contacts per unit volume per unit time
β = the proportionality coefficient
ε_0 = the energy losses occuring in the flow per unit volume per unit time
ν = the kinematic viscosity
d = the diameter of the particle
n_0 = the number of the particles per unit volume at the initial moment
ρ = the density of the liquid

The magnitude of ε_0 can be determined from quantities characteristic of large scale turbulent motion as Equation 9.

$$\varepsilon \doteqdot \rho(\Delta U)^3/l \tag{9}$$

where ΔU = the change in the average velocity over a distance equal to the scale of eddy l.

By means of Equations 7 and 8, a quantitative comparison of the rates of coagulation resulting from turbulent agitation and Brownian movement is carried out as Equation 10, from the point of diffusivity, i.e., chances of collisions.

$$\frac{N_{tub}}{N_{br}} = \frac{12\pi\beta\sqrt{\frac{\varepsilon_0}{\nu\rho}}\, d^3 n_0^2}{8\pi D_{br} d n_0^2} = \frac{3d^2}{2D_{br}}\beta\sqrt{\frac{\varepsilon_0}{\nu\rho}} \tag{10}$$

According to the Einstein formula

$$D_{br} = \frac{KT}{3\pi\mu d} \tag{11}$$

By the substitution of $T=298°$, $K=1.38\times10^{-16}$ erg/°C, and $\mu=0.0089$ g/sec/cm (at 25°C), the Brownian diffusion coefficient for colloidal particles in water at 25°C is

$$D_{br}(25°\mathrm{C}) = (4.91\times10^{-13})/d \tag{11 b}$$

According to the Kolmogolov's locally isotropic turbulence theory, turbulent fluctuation velocities, v_λ, are calculated as Equation 12.

$$\begin{aligned} v_\lambda &= \alpha(\varepsilon_0\lambda/\rho)^{1/3} && \text{for} \quad \lambda \gg \lambda_0 \\ v_l &= \beta\sqrt{\varepsilon_0/\mu}\cdot\lambda && \text{for} \quad \lambda \ll \lambda_0 \end{aligned} \tag{12}$$

where α = the proportionality coefficient in the inertia subrange
β = the proportionality coefficient in the viscous subrange
λ = the scale of turbulent eddy
$\lambda_0=(\nu^3\rho/\varepsilon_0)^{1/4}$ = the inner-scale or micro-scale of turbulence.

The coefficient α is roughly estimated to be in the order of unity. Thus the following relationship can be used for the rough estimation of the value of β at $\lambda=\lambda_0$

$$(\varepsilon_0\lambda_0/\rho)^{1/3} \fallingdotseq \beta\sqrt{\varepsilon_0/\mu}\cdot\lambda_0 \tag{13}$$

From this equation β may also be considered to be in the order of unity. Therefore, Equation 2–10 at 25°C is

$$N_{tub}/N_{br} = 3.24\sqrt{\varepsilon_0}\cdot d^3\times10^{13} \tag{10 b}$$

Thus the transition diameter of particles from the region where Brownian movement is predominent to where turbulent fluctuation is predominent, from the viewpoint of diffusivity, is given,

$$d = (3.09\times10^{-14}\times\varepsilon_0^{-1/2})^{1/3}\,. \tag{14}$$

Under the usual condition of agitation in water works, including jar tests, the value of ε_0 in the rapid mixing stage is about the order of 10^3 erg/cm·sec. Substituting this value into Equation 14, a transition diameter condition, d_t, from the Brownian diffusion region of coagulation to the turbulent diffusion region is given.

$$d_t = (3.09\times10^{-14}\times10^{-1.5})^{1/3} = 2.13\times10^{-5}\ \mathrm{cm}\,.$$

In addition to this, it is necessary to discuss the relative magnitude of the driving energy condition by the Brownian and turbulent movement from the viewpoint of interaction energy equilibrium.

The kinetic energy, driving energy, of a particle being generated by the Brownian movement at 25°C is,

$$E_{K,br} = 3/2 \cdot KT = 6.175 \times 10^{-14} \text{ erg} . \tag{1 a}$$

The kinetic energy of a particle generated by turbulent fluctuation is given by Equation 15.

$$E_{K,tub} = 8/3 \cdot \gamma_s \cdot \pi \cdot (\varepsilon_0/\nu) \cdot a^5 \text{ erg} \tag{15}$$

where a = the radius fo the particle
γ_s = the specific gravity of the particle.

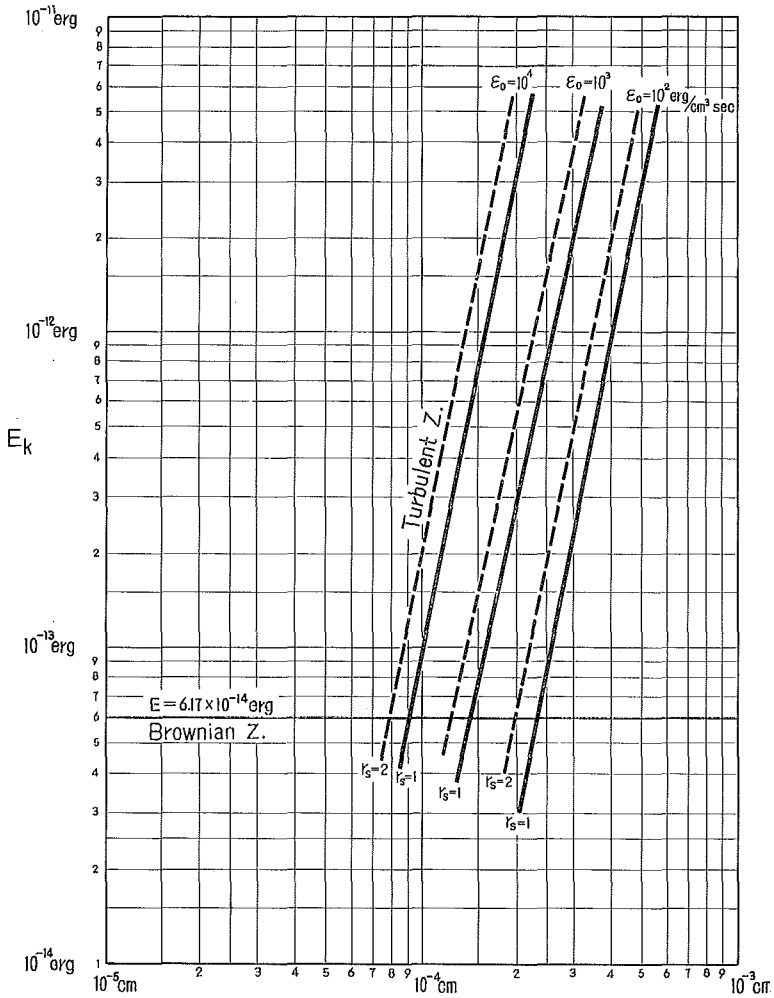
Substituting the value of $\varepsilon_0 = 10^3$ erg/cm^3·sec, $\gamma_s \doteqdot 1.00$, $\nu = 0.009$ cm^2/sec at 25°C into Equation 15 gives,

$$E_{K,tub} = 9.30 \times 10^5 \times a^5 \text{ erg} \tag{15 a}$$

By equating Equations 1a and 15a the critical radius, a, at which the dominant kinetic energy or driving energy of a particle changes from that of the Brownian movement to the turbulent is calculated as follows:

$$a = (6.175/9.30 \times 10^{-19})^{1/5} = 1.46 \times 10^{-4} \text{ cm} .$$

Therefore, in the region where particle size is smaller than the diameter which is given as a transition point of the kinetic energy curve of the Brownian movement and the turbulent movement with respect to variable particle sizes, (c.f. Figure 5 being drawn for several value of ε_0), the Brownian movement is considered to be the main driving factor of coagulation phenomena from a viewpoint of energy equilibrium. For particles of larger diameter than this critical size, however, the turbulent movement becomes predominant. According to Equation 5, the energy of interaction increases linearly with respect to the increase of the particle diameter. Therefore, in the zone where kinetic energy is mainly exerted by the Brownian movement and is considered constant regardless of the particle diameter, the larger particle is more difficult to coagulate from the viewpoint of energy equilibrium. However, in the zone where the turbulent movement of small water masses is the main source of the kinetic energy of the particles, the kinetic energy, E_K, of a particle increases in proportion to the fifth power of the particle diameter under the condition of constant agitation intensity; and the interaction energy, on the other hand, increases only linearly with respect to increasing diameter. Thus, in this zone, smaller particles are more difficult to coagulate from the point of view of energy equilibrium. Therefore, the most difficult coagulation condition with respect to diameter appears at the point where the kinetic energy lines of the Brownian movement and turbulent fluctuation of a particle intersect, as shown



a

Fig. 5.

in Figure 5. In practice, this most difficult diameter is considered to be around a few microns. If the initial particles are larger than the worst diameter condition for coagulation, the initial condition is the worst diameter condition of coagulation for the suspension.

e) Critical Zeta potential for Coagulation

When the isoelectric point is reached, coagulation can occur from the standpoint of interaction energy. However, usually a little before or after the

isoelectric point is reached, coagulation can occur in the relatively low zeta potential zone. This permissible potential deviation from the isoelectric point is called the critical zeta potential, sometimes it is said to be 5 mv and sometimes 10 mv or 20 mv[14]. However, these so-called critical zeta potential values are dependent solely upon the experience of operators and no theoretical presentation of dependable value has ever been given. Thus in this paper the author proposes to present a theoretical means to estimate the critical zeta potential of coagulation.

The critical zeta potential is without doubt not only a definite value but is dependent upon the conditions of the suspension. There exist two factors to control the critical zeta potential; (1) the kinetic energy of a suspended particle, E_K and (2) the maximum interaction energy E_{max}.

As stated before, the kinetic energy of a particle is dependent on the Brownian movement when the particle sizes are smaller than the worst diameter condition, and on the turbulent movement when larger. The maximum interaction energy, E_{max} is affected by a particle diameter, the surface potential, of the particle, and the ionic concentration in the bulk of the solution. Among these factors, when the worst diameter condition is assumed as stated before, E_K is calculated by Equation 1 under a temperature condition. The effect of temperature change on the value of E_K is not large in practical operation conditions of water works, so that it can be considered almost constant. Therefore, the remaining main factors affecting the critical zeta potential are surface potential Φ_d of the particle and the thickness of the Deby–Hückel ionic atmosphere, $1/\kappa$.

An average worst diameter for coagulation is considered from Figure 5 to be around 3×10^{-4} cm.

TABLE 2.

	Seattle	Chicago	Washington, D. C.	New Orleans
Ca^{++}	6.3 ppm	32 ppm	25 ppm	47 ppm
Mg^{++}	0.6	10	5.2	14
Na^{+}	0.4	3.5	6.1	21
K^{+}	—	1.0	—	
HCO_3^-	22	138	71	161
SO_4^{--}	2.1	77	32	51
Cl^-	0.6	6.5	3.8	24
pH	7.3	8.2	7.7	7.5
κ (cm^{-1})	7.85×10^5 ($10^{5.90}$)	2.16×10^6 ($10^{6.37}$)	1.83×10^6 ($10^{6.26}$)	2.59×10^6 ($10^{6.41}$)

The range of values for κ in practical case is estimated from water quality data[15] of several cities in the United States.

These κ values are those of raw water, so that after coagulation these values should be a little higher by the added coagulant ions. Therefore, the possible variable range of κ for ordinary water processed in a water purification plant is estimated to be in the zone between $\kappa=10^{5.5}$ and $10^{6.5}\,\mathrm{cm}^{-1}$.

The practical distribution range of the Φ_d cannot be estimated, so that the wider range from 0 to some higher value should be considered. In this study, values from 0 to 50 mv of Φ_d-values are condidered. According to this consideration, substituting the combination of the value listed in Table 3 into

TABLE 3. Value Used for the Calculation

a :	1.5×10^{-4} cm
D :	78.54 (at 25°C of water temperature)
A :	10^{-12} erg
Φ_d :	0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 (1 mv $=3.336\times10^{-6}$ e.s.u.)
κ :	$10^{5.5}$, $10^{5.6}$, $10^{5.7}$, $10^{5.8}$, $10^{5.9}$, $10^{6.0}$, $10^{6.1}$, $10^{6.2}$, $10^{6.3}$, $10^{6.4}$, $10^{6.5}$, $10^{6.6}$, $10^{6.7}$, $10^{6.8}$, $10^{6.9}$ (1/cm)
H :	4, 8, 12, ……, 100×10^{-7} cm

Equation 5, the interaction energy curves are calculated by I.B.M. computer 7070. Figure 6 to 15 are the plots of the results of these calculations, i.e., interaction energy curves with respect to the distances between spheres under a constant Stern–Gouy boundary potential and several different thicknesses of the Deby–Hückel ionic atmosphere.

Under the worst diameter condition, the kinetic energy, E_K, necessary to bring about particle collision is 6.175×10^{-14} erg. As stated above, when the peak potential energy of interaction $E_{\max}$ is less than the value of E_K, coagulation is possible from the point of view of energy balance. Therefore, a curve which has a point of tangency at its maximum value, $E_{\max}$, to the straight line $E=E_K$ gives the critical thickness of the Deby–Hückel ionic atmosphere for coagulation.

The inverse of critical thickness κ of the Deby–Hückel ionic atmosphere are plotted with respect to the Stern–Gouy boundary layer potential, Φ_d, as shown in Figure 16. According to this curve critical Φ_d increases rapidly with respect to the decreasing thickness of the double layer. However, it is impossible to know the values of Φ_d directly so that this critical relationship curve between Φ_d and κ should be rewritten as the curve between κ and the zeta potential, which is the only directly measureable potential in the double layer.

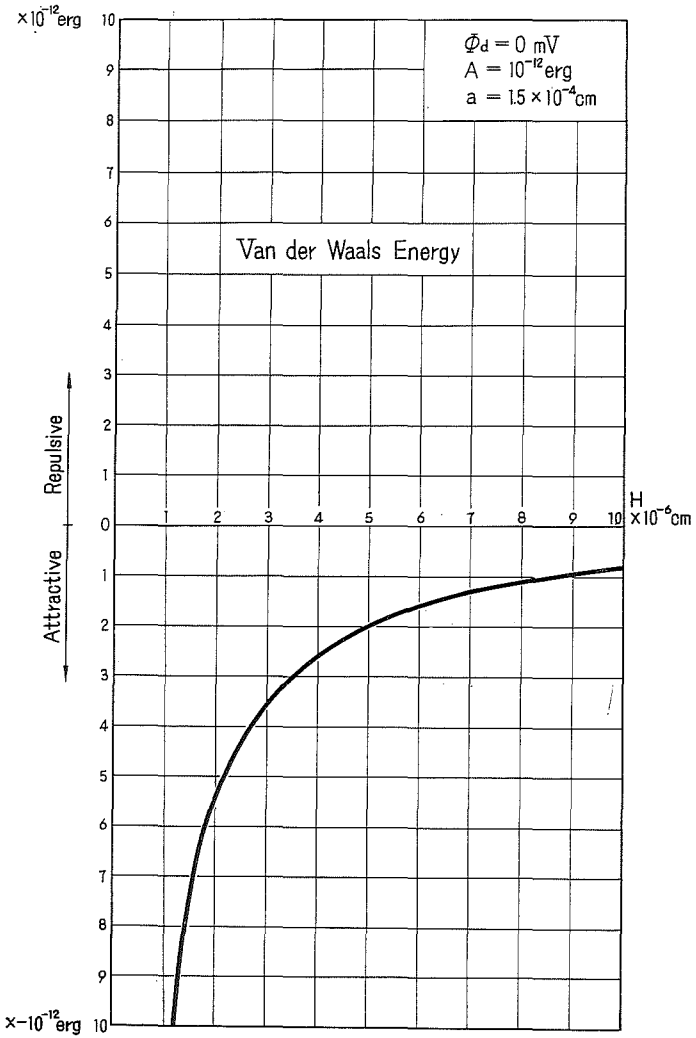

×10⁻¹²erg
Φd = 0 mV
A = 10⁻¹²erg
a = 1.5 × 10⁻⁴cm
Van der Waals Energy
Repulsive
Attractive
H
×10⁻⁶cm
×−10⁻¹²erg

Fig. 6.

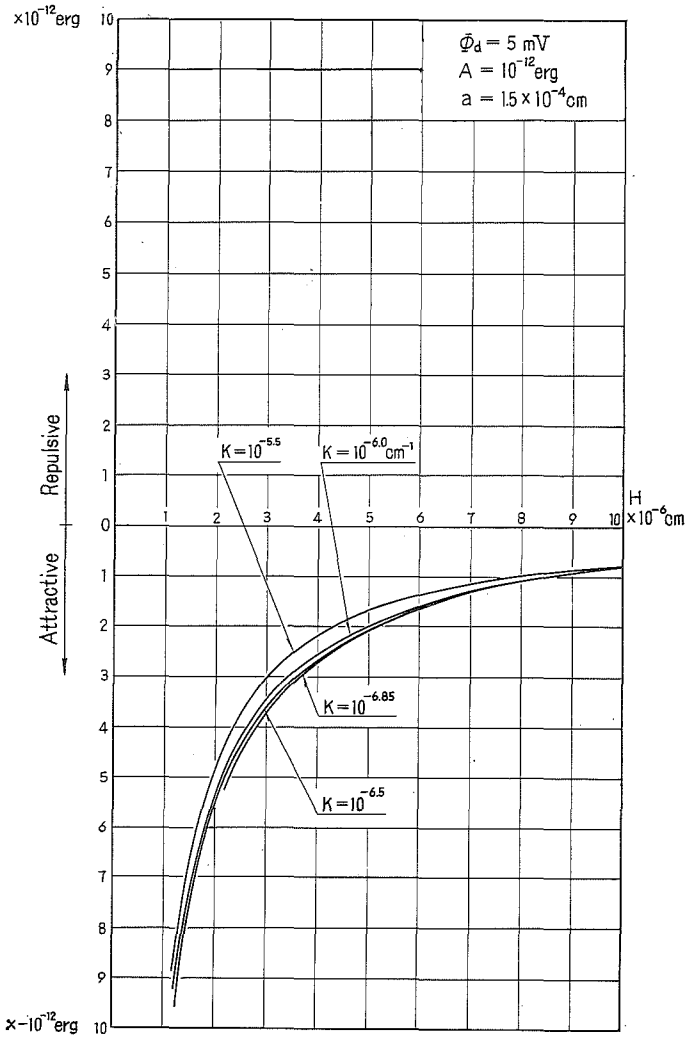

×10⁻¹²erg
Φd = 5 mV
A = 10⁻¹²erg
a = 1.5 × 10⁻⁴cm
K=10⁻⁵·⁵
K=10⁻⁶·⁰cm⁻¹
K=10⁻⁶·⁸⁵
K=10⁻⁶·⁵
Repulsive
Attractive
H
×10⁻⁶cm
×−10⁻¹²erg

Fig. 7.

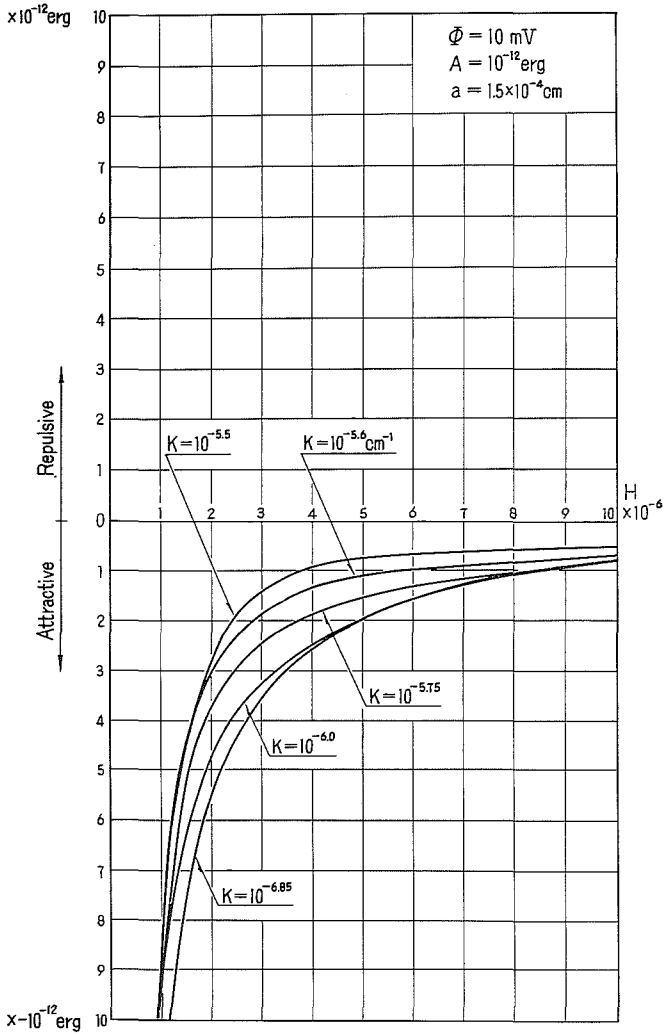

×10⁻¹²erg
Φ = 10 mV
A = 10⁻¹²erg
a = 1.5×10⁻⁴cm
Repulsive
Attractive
K=10⁻⁵·⁵
K=10⁻⁵·⁶cm⁻¹
K=10⁻⁵·⁷⁵
K=10⁻⁶·⁰
K=10⁻⁶·⁸⁵
H
×10⁻⁶
×-10⁻¹²erg

Fig. 8.

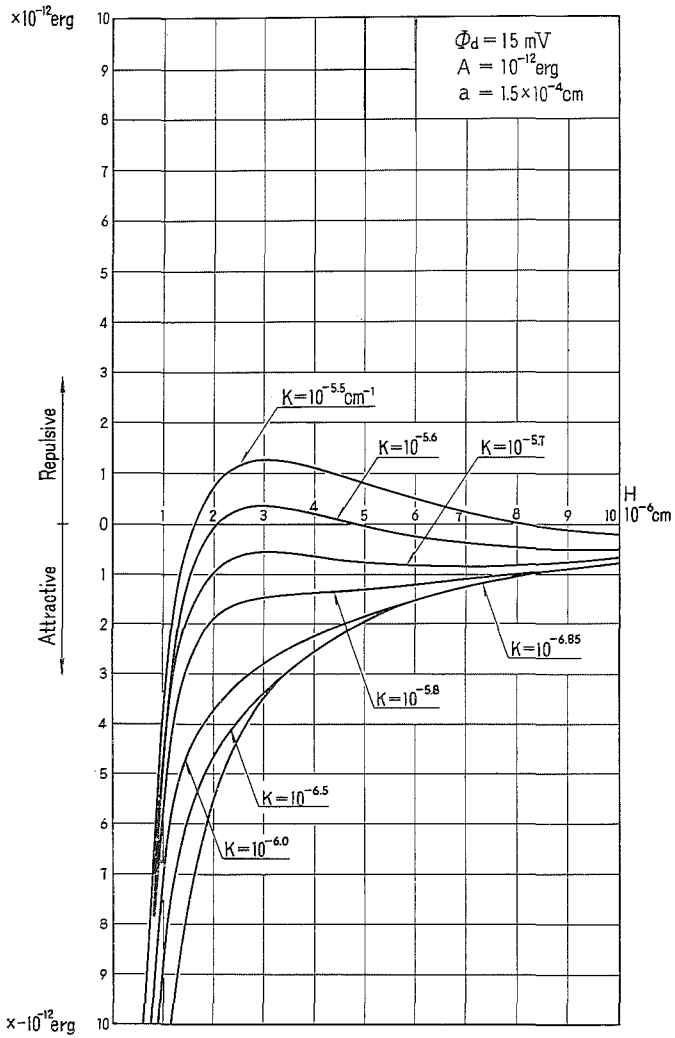

×10⁻¹²erg
Φd = 15 mV
A = 10⁻¹²erg
a = 1.5×10⁻⁴cm
Repulsive
Attractive
K=10⁻⁵·⁵cm⁻¹
K=10⁻⁵·⁶
K=10⁻⁵·⁷
K=10⁻⁶·⁸⁵
K=10⁻⁵·⁸
K=10⁻⁶·⁵
K=10⁻⁶·⁰
H
10⁻⁶cm
×-10⁻¹²erg

Fig. 9.

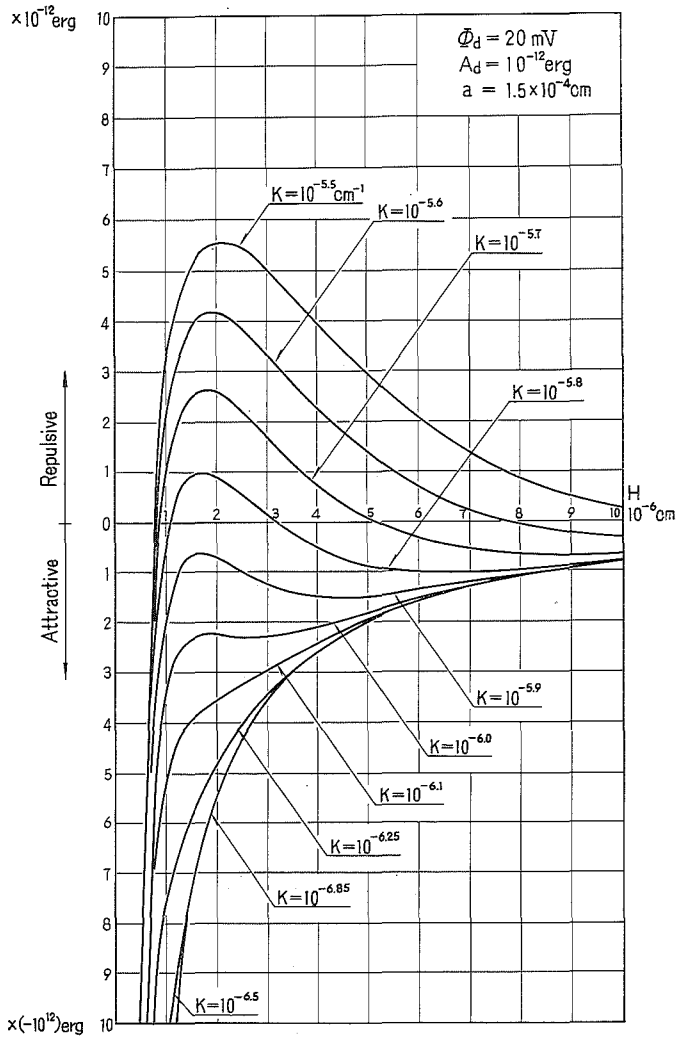

×10⁻¹²erg
Φd = 20 mV
Ad = 10⁻¹²erg
a = 1.5×10⁻⁴cm
K=10⁻⁵·⁵cm⁻¹
K=10⁻⁵·⁶
K=10⁻⁵·⁷
K=10⁻⁵·⁸
K=10⁻⁵·⁹
K=10⁻⁶·⁰
K=10⁻⁶·¹
K=10⁻⁶·²⁵
K=10⁻⁶·⁸⁵
K=10⁻⁶·⁵
Repulsive
Attractive
H
10⁻⁶cm
×(-10¹²)erg

Fig. 10.

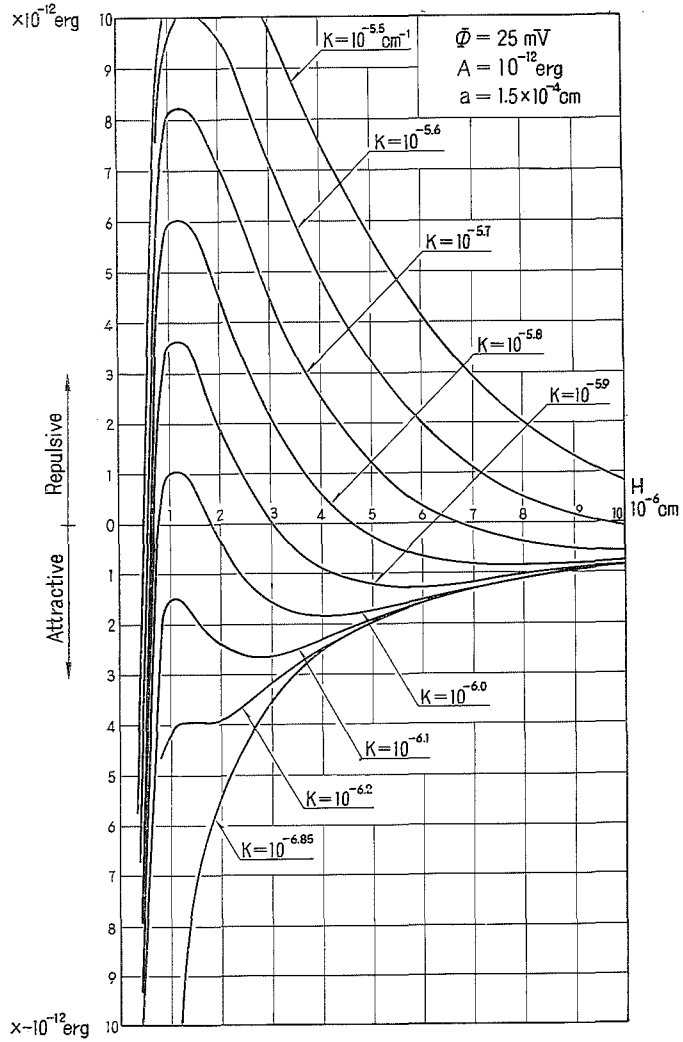

×10⁻¹²erg
Φ = 25 mV
A = 10⁻¹²erg
a = 1.5×10⁻⁴cm
K=10⁻⁵·⁵cm⁻¹
K=10⁻⁵·⁶
K=10⁻⁵·⁷
K=10⁻⁵·⁸
K=10⁻⁵·⁹
K=10⁻⁶·⁰
K=10⁻⁶·¹
K=10⁻⁶·²
K=10⁻⁶·⁸⁵
Repulsive
Attractive
H
10⁻⁶cm
×-10⁻¹²erg

Fig. 11.

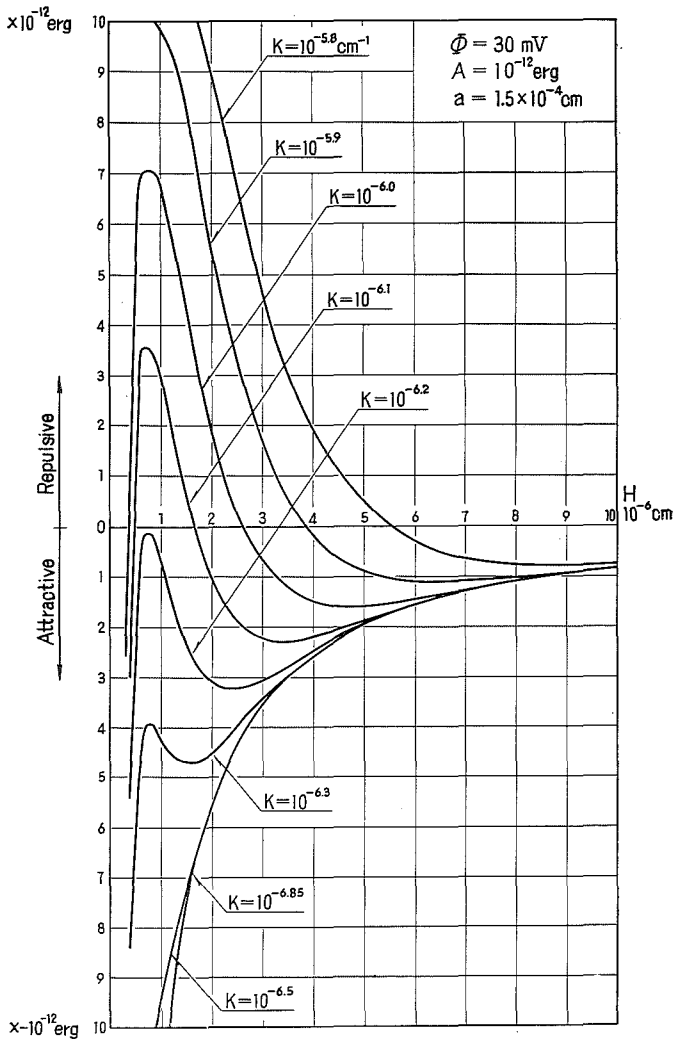

×10⁻¹² erg
Φ = 30 mV
A = 10⁻¹² erg
a = 1.5×10⁻⁴ cm
K=10⁻⁵·⁸ cm⁻¹
K=10⁻⁵·⁹
K=10⁻⁶·⁰
K=10⁻⁶·¹
K=10⁻⁶·²
K=10⁻⁶·³
K=10⁻⁶·⁸⁵
K=10⁻⁶·⁵
Repulsive
Attractive
H
10⁻⁶ cm
×-10⁻¹² erg

Fig. 12.

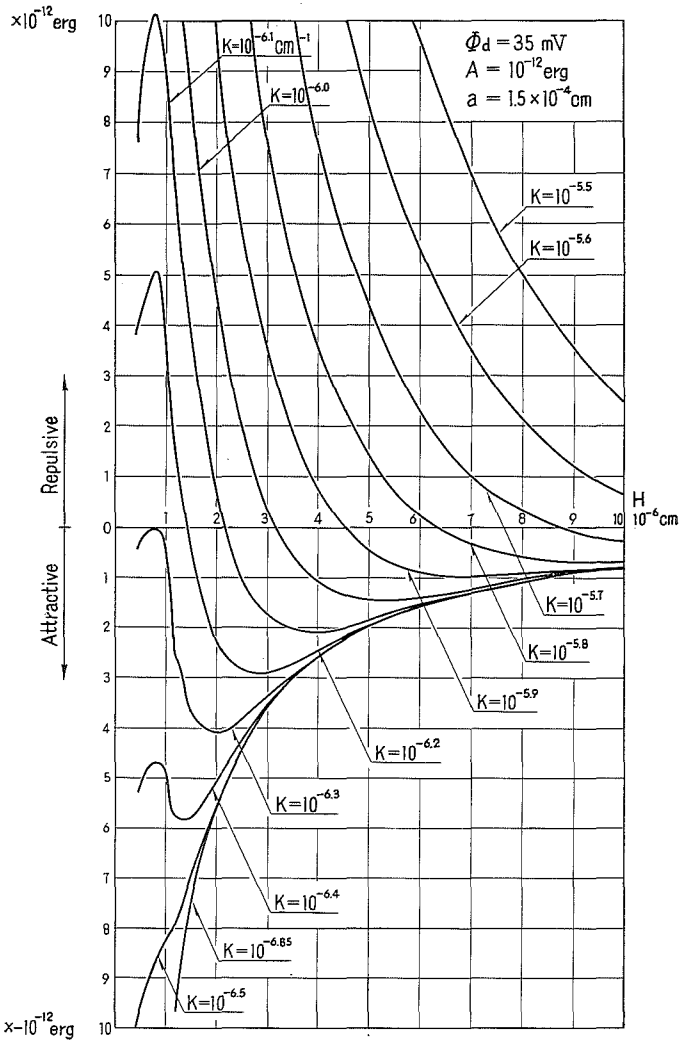

×10⁻¹² erg
Φd = 35 mV
A = 10⁻¹² erg
a = 1.5×10⁻⁴ cm
K=10⁻⁶·¹ cm⁻¹
K=10⁻⁶·⁰
K=10⁻⁵·⁵
K=10⁻⁵·⁶
K=10⁻⁵·⁷
K=10⁻⁵·⁸
K=10⁻⁵·⁹
K=10⁻⁶·²
K=10⁻⁶·³
K=10⁻⁶·⁴
K=10⁻⁶·⁸⁵
K=10⁻⁶·⁵
Repulsive
Attractive
H
10⁻⁶ cm
×-10⁻¹² erg

Fig. 13.

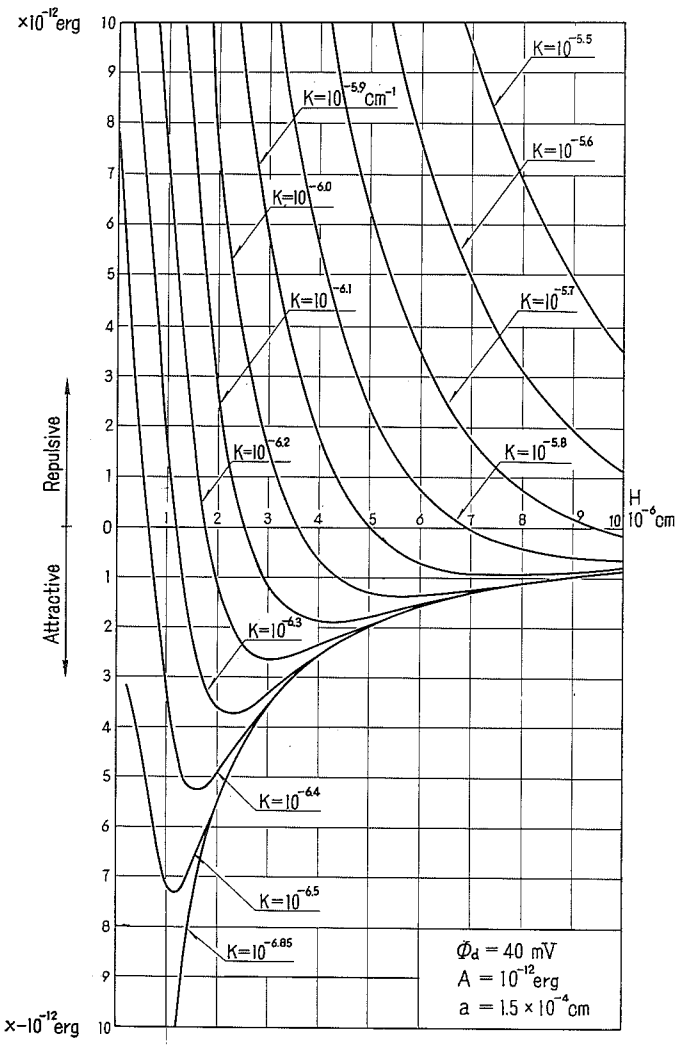

×10⁻¹²erg
Repulsive
Attractive
x-10⁻¹²erg
H
10⁻⁶cm
K=10⁻⁵·⁵
K=10⁻⁵·⁹cm⁻¹
K=10⁻⁵·⁶
K=10⁻⁶·⁰
K=10⁻⁶·¹
K=10⁻⁵·⁷
K=10⁻⁶·²
K=10⁻⁵·⁸
K=10⁻⁶·³
K=10⁻⁶·⁴
K=10⁻⁶·⁵
K=10⁻⁶·⁸⁵
Φd = 40 mV
A = 10⁻¹²erg
a = 1.5 × 10⁻⁴cm

Fig. 14.

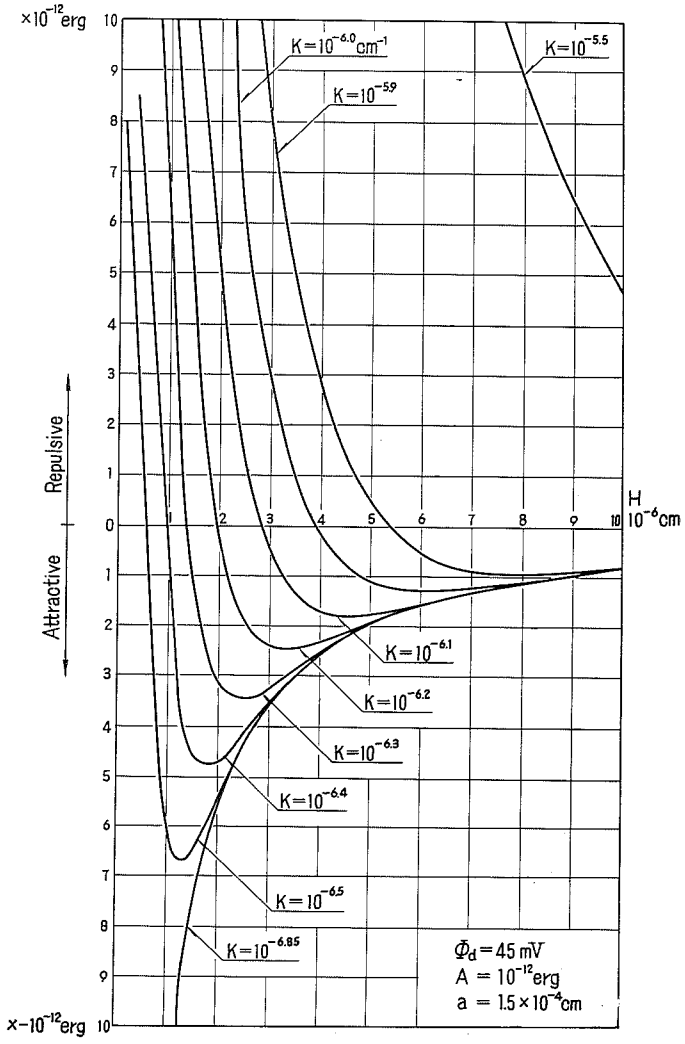

×10⁻¹²erg
Repulsive
Attractive
x-10⁻¹²erg
H
10⁻⁶cm
K=10⁻⁶·⁰cm⁻¹
K=10⁻⁵·⁵
K=10⁻⁵·⁹
K=10⁻⁶·¹
K=10⁻⁶·²
K=10⁻⁶·³
K=10⁻⁶·⁴
K=10⁻⁶·⁵
K=10⁻⁶·⁸⁵
Φd = 45 mV
A = 10⁻¹²erg
a = 1.5 × 10⁻⁴cm

Fig. 15.

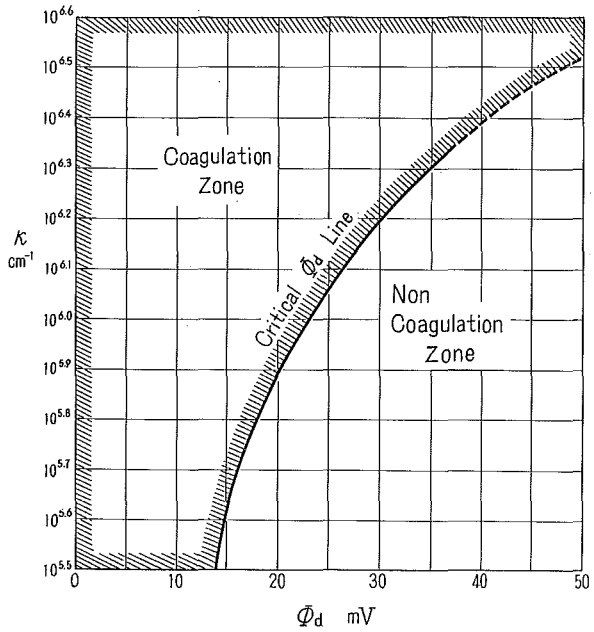


Fig. 16.

As an equation which gives potential distribution in the diffused layer around the sphere, we have the Deby–Hückel[16] equation as follows:

$$\zeta = \Phi_d a \frac{e^{-\kappa b}}{a+b} \doteqdot \Phi_d e^{-\kappa b} \qquad a \gg b\,. \tag{16}$$

Where b = the distance between the Stern–Gouy boundary plane and the Shear plane.

In many cases the values of b are accepted as constant. However, the value of b is not given exactly and is considered to be in the range of 8–100 Å[17]. In these calculations, 65 Å is chosen as the value of b.

According to the experimental work which is presented in the latter part of this paper the value of b is calculated from experiments as 63–68 Å.

Then, substituting the corresponding critical values of κ and Φ_d obtained from Figure 16 into Equation 16, a critical zeta potential with respect to the κ is calculated. This calculation yields the critical zeta potential curve in Figure 17. When the condition of a suspension is on the left side of the critical curve, coagulation is possible from the point of view of interaction energy.

It is interesting to note that the critical zeta potential is almost constant

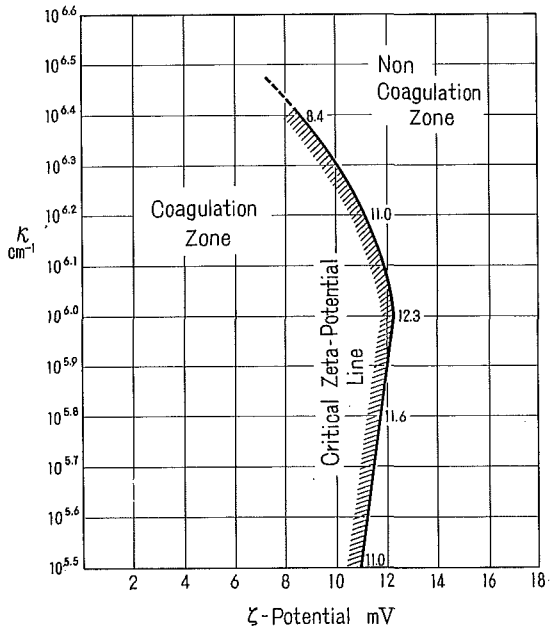


Fig. 17.

under conditions prevailing during the coagulation of ordinary water, that is to say a little higher than 10 mv. However, when the ionic concentration becomes very high, i.e. $\kappa > 10^{6.5}$, the critical zeta potential decreases rapidly, so that for the coagulation of highly mineralized industrial waste or domestic sewage it is necessary to bring the zeta potential to a very low value, i.e. almost zero.

Attention is called to the fact that this discussion can be applied only to particles whose diameters are smaller than the so-called worst diameter conditions. Therefore, if the particle sizes of a suspension are coarser than 3 μ, coagulation can occur at much higher zeta potential values.

Thus the control of coagulation by zeta potential measurement could be performed by using 10 mv as a threshold value of coagulation. It must be remembered, however, that while the bringing about of potential balance under the critical value is necessary for coagulation, other factors are frequently involved.

f) Summary

The deep basic mechanism of chemical coagulation in water purification plants are discussed from the viewpoint of energy equilibrium.

a) As the driving energy sources, the Brownian movement and turbulent fluctuation are considered. As a result the transition radius at which the dominant kinetic energy or driving energy of a particle charges from that of the Brownian movement to the turbulent is calculated at about 1.5×10^{-4} cm under ordinary agitation conditions.

b) From a viewpoint of diffusivity, the transition diameter from the region where the Brownian movement is predominant to where the turbulent fluctuation is about 2×10^{-5} cm under ordinary conditions.

c) From the combined equation of Dejagun and Hamaker (i.e., Equation 5), and the magnitude of the driving energy, the transition diameter condition, defined from a point of view of driving energy, is considered also the worst diameter condition for coagulation. That is 1.5×10^{-4} cm under ordinary agitation intensity of the rapid mixer.

d) Applying Derjagn and Hamaker's equation under conditions of the worst diameter, the critical Gouy–Stern boundary layer potential for coagulation with respect to varying ionic strength in the bulk of the solutions is calculated.

e) From the critical Gouy–Stern boundary layer potential, Φ_d, and several experimental results of jar tests, the average distance from the Gouy–Stern boundary layer to the shear plane, where zeta-potential is defined, is calculated at about 65 Å.

f) Substituting the critical Gouy–Stern boundary plane and shear plane into Deby–Hückel's equation (i.e., Equation 16), the critical zeta-potentials for coagulation with respect to the thickness of Deby–Hückel ionic atmosphere (i.e., the ionic strength of the bulk of the solution) are calculated.

g) These calculated critical zeta-potentials have a fairly constant value of about 11 mv to 12 mv for the usual waters in water supply systems. Thus, from the viewpoint of practice, it is possible to say that there exists a critical zeta-potential of coagulation (i.e., about 12 mv).

h) Based on the findings of the existence of a critical zeta-potential, the usefulness of the measurement of the zeta-potential, i.e., electrophoretic studies of coagulation, is demonstrated as one of the most important tools to discuss ane control the phenomenon of coagulaton.

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