

# Recent Developments in the Understanding of Colloid Stability

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The stability of suspensions and emulsions against coagulation is governed by the forces between the particles. The main forces are: van der Waals attraction, electrostatic repulsion, and the repulsion due to the interaction of adsorbed large molecules. It is stressed that coagulation and redispersion are rate phenomena. Smoluchowski's classical theory on coagulation as modified by Fuchs to include interaction forces between particles has been the basis of theories of colloid stability. Corrections to these theories are needed to account for the hampering of Brownian motion when the particles are close together. Furthermore it is pointed out that the duration of a Brownian collision is long enough to allow redistribution of the double layer and of the conformation of adsorbed macromolecules, but too short for adaptation of the surface charge or of the adsorption of macromolecules. Repeptization requires the existence of a distance of closest approach between particles which is of the order of one or two solvent molecules.

## I. INTRODUCTION

In suspensions and emulsions, in general in dispersions of fine particles in a liquid, frequent encounters between particles occur due to Brownian movement, to gravity (creaming, sedimentation), and to convections. Whether such encounters result in permanent contact or whether the particles rebound and remain free is determined by the forces between them. A dispersion is *stable in the colloid-chemical sense* when its particles remain permanently free. In dilute dispersions it is sufficient to consider only interactions between pairs of particles. In very concentrated systems it may be necessary to take also multiparticle interactions into account.

On the basis of pair interaction and considering only electrostatic repulsion and van der Waals attraction a satisfactory understanding of the stability of hydrophobic suspensions (also called *electrostatic* systems) was reached in the Forties (1, 2). In particular, a theoretical explanation of the extremely large effect of the valence of the counterions on the

stability (rule of Schulze (3) and Hardy (4)) could be given.

An important extension was reached when protective action and sensitization of dispersions were interpreted as due to the adsorption of long molecules: originally, proteins, gums, and other polysaccharides; later, nonionic detergents, synthetic polymers, and polyelectrolytes. After a rudimentary, but essentially correct, theory by Mackor and van der Waals (5) a fairly large number of authors have worked out the theory in much greater detail (6-11). Since this subject is treated in the paper of D. H. Napper on "Steric Stabilization" we shall limit our discussion here to a few brief remarks.

Another feature of the stability of colloidal dispersions is the role of chemical reactions, in particular chemical complexing studied extensively by Matijević (12).

Then we should mention briefly new tools that have been introduced into the study of colloid stability. The availability of isodisperse latices (13) of different particle sizes and

chemical nature has made it easier to obtain quantitative comparisons between theory and experiments. Many new spectroscopic techniques such as NMR, ellipsometry, and laser-beat methods have been applied successfully to colloid and surface chemistry.

Although obviously coagulation is a rate process, nevertheless colloid theory has shown a tendency to concentrate its attention more on the thermodynamics (surface thermodynamics) behind the rate processes (adsorption equilibria, electrochemical equilibria) than on the rate processes themselves.

In this paper I want to discuss *coagulation as a rate process* and in particular I want to show that it is really a combination of several processes each occurring at its own rate and that these rates may vastly differ in some cases. I shall also spend some time discussing the inverse process, *redispersion or reepitization* and the rates involved in it.

II. FORCES BETWEEN TWO PARTICLES

As mentioned in the Introduction, encounters between particles are frequent and the result of such an encounter is determined by the forces between the particles. We distinguish three types of forces.

*a. Van der Waals forces.* Van der Waals forces are always attractive between particles of the same nature. Hamaker (14) derived equations for these forces on the basis of additivity of van der Waals energies between pairs of atoms or molecules, and assuming these energies to be proportional to the inverse sixth power of the distance. Casimir and Polder (15) introduced the influence of retardation, which changes the power law to an inverse seventh power at large separations. For the special case of metals they also could abandon the assumption of additivity by using continuum considerations. Lifshitz (16) generalized the continuum treatment to dielectrics. In his treatment the interaction energy between macroscopic bodies is the result of charge fluctuations in these bodies.

The law describing the change of the force (or energy) with the distance is accurately

known, except for the precise value of the proportionality constant (Hamaker constant,  $A$ , retarded constant,  $B$ ) and the characteristic length connected with the transition from nonretarded forces (small distances) to retarded forces (large distances). In most practical examples of colloid stability only the nonretarded van der Waals forces are important.

In the special case of the attraction between two spherical particles of radius,  $a$ , at a distance,  $H$ , (distance between the centers =  $2a + H = R$ ) Hamaker, considering only nonretarded forces, found for the energy of attraction,  $V_{\text{attr}}$ ,

$$V_{\text{attr}} = -\frac{A}{6} \left( \frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln \frac{R^2 - 4a^2}{R^2} \right), \quad [1]$$

where  $A$  depends on the properties of the particles and of the dispersion medium.

This somewhat awkward equation can be approximated by using expansions in powers of  $H/a$  (small distances) or  $a/R$  (large distances) but these expansions converge rather slowly. Expansions which converge more rapidly are obtained by introducing for small distances

$$L = a + (3H/4) \quad [2]$$

and for large distances

$$Q^4 = R^2(R^2 - 4a^2). \quad [3]$$

In these new variables Eq. [1] can be approximated quite accurately by

$$V_{\text{attr}} (H/a < 1) = -\frac{AL}{12H} \left\{ 1 + \frac{2H}{L} \ln \frac{H}{L} - \frac{15}{16} \left( \frac{H}{L} \right)^2 - \frac{3}{32} \left( \frac{H}{L} \right)^3 \right\} \quad [4]$$

and

$$V_{\text{attr}} (a/R < 1) = -\frac{16Aa^6}{9Q^6} \left\{ 1 - \frac{6}{5} \left( \frac{a}{Q} \right)^4 + \frac{18}{7} \left( \frac{a}{Q} \right)^8 \right\}. \quad [5]$$

At  $H < 0.4a$  ( $R < 2.4a$ ), Eq. [4] is accurate to better than 0.1% and at  $H > 0.4a$ , Eq. [5] is accurate to better than 0.5%. At  $H < 0.1a$  the first two terms of Eq. [4] are already accurate to better than 1.5% and at  $H > 1.6a$  ( $R > 3.6a$ ) the first term of Eq. [5] alone is accurate to 1% or better.

The existence of the logarithmic term in Eq. [4] causes  $V_{\text{attr}} = -AL/12H$  or  $V_{\text{attr}} = -Aa/12H$  to be rather poor approximations unless  $H/a$  is very small.

*b. Electrostatic forces.* Electrostatic forces, due to the interaction of the electrical double layers surrounding the particles, always lead to a repulsion between particles if they are of the same chemical nature and have surface charges and surface potentials of the same sign and magnitude.

This repulsion is due to the interaction of the ions adsorbed at the surfaces, mitigated by the space charges in the double layers. It also contains an entropic contribution, since the ionic concentrations in the double layers vary during interaction. Furthermore, insofar as the adsorption of ions at the surfaces changes, this contributes a chemical term to the interaction energy.

When the surface charge is generated by the adsorption of *potential determining ions*, the surface potential,  $\phi_0$ , is determined by the activity of these ions and remains constant during interaction at least if complete adsorption equilibrium is maintained. In that case interaction occurs at *constant surface potential*. Lack of adsorption equilibrium, or other mechanisms to generate the surface charge or simply a shortage of potential determining ions (very low concentrations) may cause the interaction to take place at *constant surface charge* or at some situation intermediate between constant charge and constant potential.

Whereas Van der Waals forces fall off as an inverse power of the separation between the particles and have a range comparable to the particle size, the electrostatic repulsion falls off as an exponential function of the distance and has a range of the order of the thickness of the electrical double layer (equal to the

Debye-Hückel length,  $1/\kappa$ )

$$1/\kappa = (\epsilon\epsilon_0RT/F^2 \sum c_i z_i^2)^{-1/2}, \quad [6]$$

where  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon$  is the relative permittivity (=dielectric constant) of the dispersion medium,  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant,  $c_i$  and  $z_i$  are the concentration and the charge number of the ions of type  $i$  in the dispersion medium.

No simple expression can be given for the energy of repulsion but the following expressions are reasonable approximations (17).

For small surface potentials ( $\phi_0$ ) and small  $\kappa a$  (extension of double layer larger than particle radius),

$$V_{\text{rep}} = 2\pi\epsilon\epsilon_0a\phi_0^2 \frac{\exp(-\kappa H)}{1 + H/2a}. \quad [7]$$

For large  $\kappa a$ , symmetrical electrolytes (only one electrolyte with ions of charge number  $+z$  and  $-z$ ), and relatively large distances ( $\kappa H$  large),

$$V_{\text{rep}} = 32\pi\epsilon\epsilon_0a(RT\gamma/zF)^2 \times \ln [1 + \exp(-\kappa H)], \quad [8]$$

with

$$\gamma = \tanh(zF\phi_0/4RT). \quad [9]$$

For small values of  $\phi_0$  and small values of  $\exp(-\kappa H)$  this expression simplifies to

$$V_{\text{rep}} = 2\pi\epsilon\epsilon_0a\phi_0^2 \exp(-\kappa H). \quad [10]$$

In the above expressions it is assumed that during the approach of two particles the surface potentials  $\phi_0$  remain constant. It is also possible to calculate the repulsion when instead of the surface potential  $\phi_0$  the surface charge,  $Q$ , remains constant. For large separations (small interaction) the interaction energy is independent of the choice,  $Q$  constant or  $\phi_0$  constant, but at small distances the repulsion is stronger at constant charge than at constant potential. Frens (18) has described a method of deriving the interaction energy at constant charge, when that at constant potential is given.

Just as in the case of the van der Waals forces, the dependence of the electrostatic re-

pulsion on the distance is well known, but there is uncertainty about the absolute value, since the value of  $\phi_0$  in Eqs. [7]–[10] is often not known. In the first place, the equations as given above do not take account of the finite size of the ions and the potential to be used in calculating the repulsion is the potential,  $\phi_\delta$ , in the *Stern plane* (plane of closest approach of the ions to the surface) rather than the surface potential  $\phi_0$ . In cases, such as AgI-aqueous solution, where the surface potential is governed by an equilibrium of potential determining ions,  $\phi_0$  may be rather accurately known. Even then  $\phi_\delta$  can only be estimated from  $\phi_0$ , when the double-layer structure has been analyzed e.g., by capacity determinations. In some other cases the surface charge density,  $\sigma$ , may be well known and assuming a simple diffuse double-layer structure, without incomplete dissociation or specific adsorption of ions,  $\phi_\delta$  may be calculated. In most cases, however, the nearest practical approximation to  $\phi_\delta$  is the  $\zeta$ -potential and this presupposes that the Stern plane and the slipping plane are (nearly) identical.

*c. Forces connected with adsorbed macromolecules.* The third group of forces between particles, which is relatively well understood now, is due to the interaction of long-chain molecules adsorbed on the particles. When two particles, each carrying an adsorbed layer of dangling chains (or loops), approach one another closely, two effects lead to repulsion. In the first place each chain—if its extended length is larger than the distance between the surfaces—loses some of its otherwise available conformations, and thus its contribution to the free energy of the system is increased, resulting in a repulsive force (“volume restriction” effect). Moreover, when the chains belonging to the two particles start to overlap, this amounts to a local increase of the concentration and again to an increase in the free energy (“osmotic” effect). As a rule the quantitative influence of the osmotic effect is the more important of the two. Many authors have contributed to the quantitative calculation of these effects (5–11). The repulsion increases

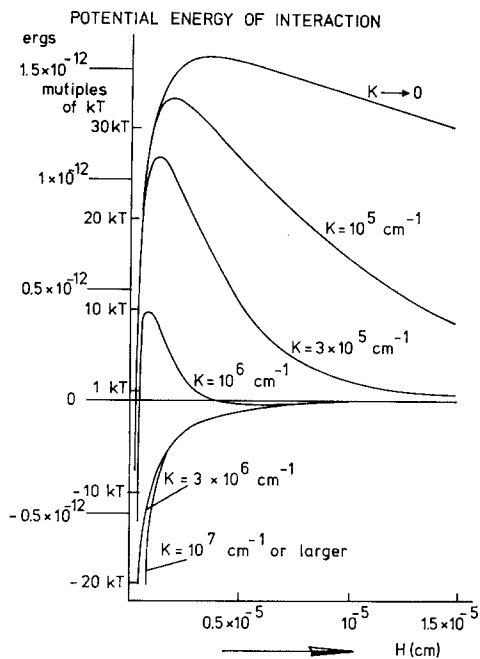
with the chain length, with the quality of the solvent for the chains (distance from the  $\theta$ -temperature), and with the number of chains per unit area. The repulsion as a rule is quite steep, also compared with the slope of the van der Waals force.

A difficulty in the application of this effect to practical cases is that the protective chains must be well soluble in the solvent, but the molecules as a whole must contain parts that are adsorbed to the particles (anchor groups) and since adsorption from solution is always a competition between adsorbate and solvent it is often difficult to predict how strong the adsorption will be, quite apart from the technical difficulty of preparing molecules with two parts having partially conflicting properties.

From the above it will be clear that the same type of adsorbed molecules *may lead to attraction* rather than to repulsion either if they contain two or more anchor groups adsorbed on different particles or if the solvent is changed, so as to be below the  $\theta$ -temperature.

*d. Combination of forces.* The combination of van der Waals attraction and electrostatic repulsion leads in general to interaction curves with a maximum and a minimum if the energy is plotted versus the distance. Both at small and at large distances the van der Waals energy, proportional to  $H^{-x}$  (where  $x$  varies from 1 to 7) surpasses the repulsion, which is proportional to  $\exp(-\kappa H)$ . But at intermediate distances the repulsion energy may be the larger of the two. Electrolyte concentrations and valence act via  $\kappa (\sim \sum c_i z_i^2)^{1/2}$  on the interaction curves. Figure 1 gives an example how the total interaction depends on the electrolyte concentration. If we assume that an energy barrier of  $10 kT$  is enough to prevent two particles from colliding, we see that under the conditions of Fig. 1  $c$  must be smaller than  $0.001 M$  ( $\kappa < 10^6 \text{ cm}^{-1}$ ) for stability.

The combination of van der Waals forces with “steric” repulsion (interaction of adsorbed chains) again leads to a minimum in the energy at large separations since the van der Waals energy decays more slowly than the steric energy. But, as a rule, if the repulsion



$$\alpha = 10^{-5} \text{ cm}; A = 10^{-12} \text{ ergs}; \Psi_0 = \frac{RT}{F} \approx 25.6 \text{ mV}.$$

FIG. 1. Energy of interaction of two spherical particles as a function of the distance,  $H$ , between the surfaces. For monovalent ions  $c$  (in moles liter $^{-1}$ ) =  $10^{-15} \kappa^2$  (in  $\text{cm}^{-1}$ ).

is strong enough to overcome the van der Waals attraction at some intermediate distance repulsion is found at all shorter distances.

Figure 2 taken from Evans and Napper's work (10) shows how sensitive the repulsion is to the quality of the solvent.

We shall not go into the effects of the simultaneous presence of all three types of forces.

### III. RATE OF COAGULATION

#### III. 1. Classical Theory

Suspensions and emulsions are never stable in the thermodynamic sense. Their large interfacial area will always lead to coarsening by recrystallization or droplet growth, possibly slowly, but inexorably. Whether coarsening by coagulation occurs rapidly, slowly, or hardly at all will depend on the interaction forces discussed in the previous section. The fre-

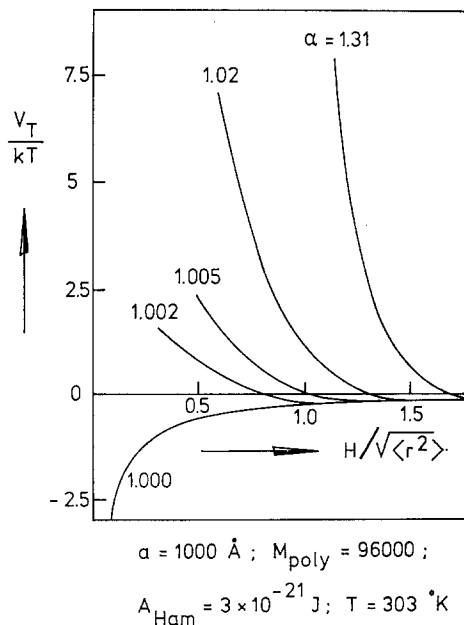
quency of Brownian encounters determines the maximum rate of coagulation in the absence of forces. The maximum energy of repulsion acts as an activation energy decreasing the rate of coagulation.

Rate effects are therefore clearly important as a sensitive test of our understanding of the interaction of colloidal particles. They are also important in practical applications. A suspension coarsening with a half-life of 5 years is stable for most practical purposes. If its half-life is 1 week, it is stable enough for many laboratory uses, and if its half-life is 10 minutes it is a good object for investigating rates of coagulation.

Already in 1916 Smoluchowski (20) developed an admirable theory of the rate of coagulation. He described coagulation as a bimolecular reaction, obeying the equation

$$-dn/dt = k_r n^2, \quad [11]$$

where  $n$  is the number of particles per unit volume,  $t$  the time, and  $k_r$  the rate constant.



$$\alpha = 1000 \text{ \AA}; M_{\text{poly}} = 96000;$$

$$A_{\text{Ham}} = 3 \times 10^{-21} \text{ J}; T = 303 \text{ }^\circ\text{K}$$

FIG. 2. Energy of interaction between two spheres.  $\alpha$  is the parameter introduced by Flory (19), giving the expansion factor of a coiled chain and intimately connected with the quality of the solvent.

He calculated the rate constant for *rapid coagulation* from the frequency of Brownian collisions assuming no interaction between the particles except a short-range force leading to permanent contact on the first encounter. An additional assumption that the particle dimension is large compared to the mean free path of the fluid molecules is always true in hydro-sols but is not necessarily so in aerosols.

The collision frequency was derived by considering the mutual rate of diffusion of two spherical particles of equal size toward one another. The collision frequency appears to be independent of the size since the slower Brownian motion of the larger particles is exactly compensated by their larger collision cross section. Furthermore, when the particles are of different, but not too widely different, size the collision frequency is only slightly modified. Even the collision frequency between small molecules, as determined from the rates of diffusion-controlled reactions, is of the same order of magnitude as that between colloidal particles (21).

Smoluchowski expressed his results in terms of the half-life of the suspension, i.e., the time  $T_{\frac{1}{2}}$ , in which the number of particles was reduced to one-half the original value,  $n_0$ . He found

$$T_{\frac{1}{2}} = 1/k_r n_0 = 1/8\pi D a n_0, \quad [12]$$

where  $D$  is the diffusion coefficient of the particles and  $a$  their radius. Using the expression

$$D = k_B T / 6\pi\eta a, \quad [13]$$

where  $k_B$  is the Boltzmann constant and  $\eta$  the viscosity of the medium we further have

$$T_{\frac{1}{2}} = \frac{3\eta}{4k_B T n_0} \approx \frac{2 \times 10^{11}}{n_0} \text{ cm}^{-3} \text{ sec}, \quad [14]$$

where the last equality holds for water (or any other liquid with the same viscosity) and ambient temperature.

For coagulation, slowed down by the presence of an energy barrier, Smoluchowski wrote simply

$$T_{\frac{1}{2}} (\text{slow}) = T_{\frac{1}{2}} (\text{rapid})/\alpha, \quad [15]$$

where  $\alpha$  is the fraction of the number of collisions leading to permanent contact.

In 1934 Fuchs (22) showed how  $\alpha$  could be related to the energy of interaction by considering the encounter of two particles as a diffusion in a field of force. He found

$$T_{\frac{1}{2}} (\text{slow}) = \frac{1}{8\pi D a n_0} \cdot 2a \int_{2a}^{\infty} \exp(V/k_B T) \frac{dr}{r^2}, \quad [16]$$

where  $V$  is the energy of interaction at a distance  $r$  between the centers of the two particles.

Since rates of coagulation can be measured rather accurately, especially if isodisperse latices are used and since a great deal is known or supposed to be known about the interaction energy, Eq. [16] and some of its consequences form a sensitive test of our understanding of interactions in suspensions, the more so since attraction and repulsion must be nearly balanced in order to obtain rates that are neither too slow, nor too fast.

The factor by which coagulation is slowed down is called  $W$ .

$$W = 1/\alpha = 2a \int_{2a}^{\infty} \exp(V/k_B T) dr/r^2. \quad [17]$$

Since  $V$  is approximately proportional to the particle radius,  $a$ , it is expected that, other things being equal (in particular the surface potential  $\phi_0$  or  $\phi_s$  and the electrolyte concentration), the coagulation of large particles is slowed down more strongly than that of small particles (23). This, however, has not been confirmed by experiments (23, 24). The experiments show more nearly that  $W$  is independent of particle size.

This discrepancy between theory and experiment has led to a reexamination of a number of aspects of the theory.

It may not be superfluous to point out here that the usual determination of  $W$  by light scattering or light absorption is based on the

assumption that the optical properties of pairs and higher aggregates are the same in rapid and in slow coagulation. This assumption, although plausible, may not always be correct.

Theoretical calculations of  $W$  only apply to pairs formed from primary particles and therefore the comparison between theory and experiment has to be limited to the initial phase of the coagulation. Similarly, for the absolute value of the collision frequency it is essential to work with initially isodispersed sols, use only the very first part of the coagulation, and have an accurate theory of the optical properties of single particles and of doublets.

### III. 2. Modified Collision Theory

Following a remark made by Deryagin in 1966 (25) a number of authors (Deryagin and Muller (26), Spielman (27), Honig, Roeberson, and Wiersma (28), and independently of these, Deutch and Felderhof (29)) have recalculated the collision frequency, taking into account that the last part of the approach of two particles is slowed down because it is difficult for the liquid to flow away from the narrow gap remaining between the particles. This effect is calculated quantitatively by estimating the mobility or diffusion coefficient along the line interconnecting the centers of the particles as a function of the distance,  $H = R - 2a$ , between the particles. The problem has been solved exactly by Brenner (30) but it leads to a fairly complicated expression. Honig *et al.* (28) give a very useful approximation in the form of a rational function.

$$\frac{D(H)}{D(H \rightarrow \infty)} = \frac{2H}{a} \left( \frac{1 + 3H/2a}{1 + 13H/2a + 3H^2/a^2} \right) \\ = \frac{1 + 2a/3H}{1 + 13a/6H + a^2/3H^2}. \quad [18]$$

Since  $D$  approaches zero as  $2H/a$  when the particles are close together, actual Brownian encounters could never occur, unless there is some attraction at least proportional to  $a/H$ .

Van der Waals attraction satisfies this requirement and therefore collisions do occur,

but their frequency depends on the value of the van der Waals forces.

The simplest check on this extension of the collision theory is the absolute measurement of the rate of rapid coagulation of a suspension of isodisperse spheres. This has been performed by Lichtenbelt (31), who determined the rate of coagulation of a series of isodisperse polystyrene latices, using a stopped-flow technique with extremely rapid mixing of latex and coagulating electrolyte ( $\text{LaCl}_3$ , 0.0058 mole liter<sup>-1</sup>;  $\text{BaCl}_2$  and  $\text{MgCl}_2$ , 0.05 mole liter<sup>-1</sup>;  $\text{NaCl}$ , 0.4 mole liter<sup>-1</sup>) and interpreting the increase in turbidity on the basis of a Rayleigh-Gans-Debye calculation of the light scattering by doublets.

The essence of his results can be expressed in the value of  $k_r$ , as introduced in Eq. [11], and comparing this value with the value  $k_r$  (Smol) it should have according to Smoluchowski's theory.

$$k_r (\text{Smol}) = 4k_B T / 3\eta. \quad [19]$$

Table I gives the comparison. Table I mentions two sets of values of  $k_r$  depending on whether the particle diameter derived by Dow from their electronmicroscopic measurements is accepted as correct, or assuming that the diameters are about 5% smaller as appears to follow from quite a number of remarks in the literature (32-37).

Whatever the correct choice may be, it is obvious that Lichtenbelt found  $k_r$  to be lower than the Smoluchowski value, independent of the particle size, and in agreement with the value based on Eq. [18] if Hamaker constants as mentioned in Table 1 are accepted as correct. The value  $A = 7.0 \times 10^{-21}$  J is in agreement with the Lifshitz theory and of the same order as some other estimates for the van der Waals interaction of polystyrene particles in water.

We may thus consider the hydrodynamic correction to the collision theory as expressed in Eq. [18] to be confirmed by experiment.

Unfortunately this does not help us to solve the original discrepancy about the influence of the particle size on the factor  $W$  (Eq. [17])

TABLE I

Rate Constant,  $k_r$ , at 20°C of Rapid Coagulation Found with Experiments on Latices and Compared to the Smoluchowski Value,  $k_r(\text{Smol}) = 4k_B T/3\eta$

(Dow) diameters of polystyrene spheres	$k_r \times 10^{12} \text{ cm}^{-3} \text{ sec}^{-1}$ Dow diameters assumed to be correct	$\frac{k_r}{k_r(\text{Smol})}$	$k_r \times 10^{12} \text{ cm}^{-3} \text{ sec}^{-1}$ Dow diameters minus 5%	$\frac{k_r}{k_r(\text{Smol})}$
$2a = 91 \text{ nm}$	3.2	0.60	2.6	0.49
$2a = 109 \text{ nm}$	2.95	0.55	2.35	0.44
$2a = 176 \text{ nm}$	3.4	0.63	2.8	0.52
$2a = 234 \text{ nm}$	2.65	0.50	2.25	0.42
$2a = 312 \text{ nm}^a$	1.95 <sup>a</sup>	0.37 <sup>a</sup>	1.65 <sup>a</sup>	0.32 <sup>a</sup>
$2a = 357 \text{ nm}$	2.75	0.51	2.3	0.43
Average value <sup>a</sup>	3.0	0.56	2.45	0.46
<i>Theoretical</i>				
$A_{\text{Ham}} = 7.0 \times 10^{-21} \text{ J}$	3.0	0.56		
$A_{\text{Ham}} = 1.5 \times 10^{-21} \text{ J}$			2.45	0.46
Smoluchowski	5.4	1.00	5.4	1.00

<sup>a</sup> Results of the 312 nm latex are not included in the average.

since, if the hydrodynamic correction is now applied to the case of slow coagulation, it leaves the influence of  $a$  on  $W$  nearly unchanged.

This is dramatically illustrated in Fig. 3, where calculated values of  $\log W$  are plotted

against  $\frac{1}{2} \log c_{\text{el}}$  ( $c_{\text{el}}$  = electrolyte concentration) for a series of values of  $G$  (which is proportional to the particle radius  $a$ ). The theoretical curves depend strongly on  $G$  and thus on  $a$  whereas the measurements by Ottewill

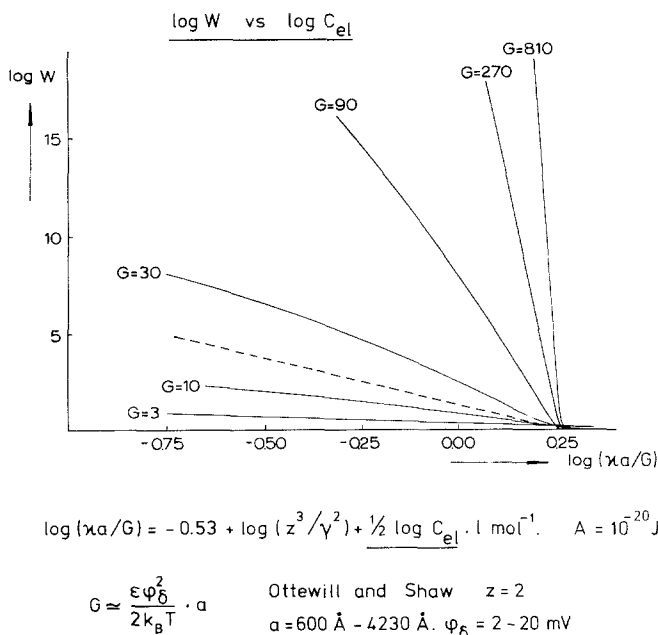


FIG. 3. Double logarithmic plot of the delay factor,  $W$ , against  $\kappa a/G$  for various values of  $G$ .  $G \approx \epsilon \phi_0^2 a / 2k_B T$ ;  $A = 10^{-20} \text{ J}$ . The dotted curve corresponds to the average of the experimental values of Ottewill and Shaw (24).



and Shaw (24) on the average follow one line (dotted in Fig. 3) although they worked with particle diameters ranging from 120 to 846 nm and values of  $G$  (assuming  $\phi_s = \zeta$ ) varying from about 2 to over 100. Further refinements by Roeberson and Wiersema (38) taking the initial non-steady state during coagulation into account did not help to explain the discrepancy.

The whole matter deserves further effort, both from the theoretical and from the experimental side. Experimentally measuring with higher and more varied surface potentials than those used by Ottewill and Shaw, varying the charge number of the coagulating electrolyte, and possibly using sols other than polystyrene latex (e.g., gold-sols) would be worthwhile. Theoretically the influence of variations of the surface potential and/or surface charge with electrolyte concentration, and slow rates of charge adjustment should be reconsidered.

### III. 3. Rate Effects in a Single Collision

In calculating the interaction between colloidal particles it is usually assumed that complete equilibrium exists between the particle surface and the surrounding liquid (dispersion medium) at any separation between the particles. This, however, is not necessarily correct, since the adjustment of equilibrium takes time and this time may be longer than the time involved in a collision or even than the coagulation time.

Let us therefore examine the rates of the separate processes involved in coagulation and start with electrostatic systems.

The time needed for *adding a coagulant* and mixing depends on the technique used and may vary from a millisecond (turbulent mixing in a small chamber as used in the study of fast reactions) to a few seconds or more (conventional mixing techniques).

The time needed for adjusting the structure of the double layer (*relaxation time of the double layer*) is equal to the average time needed for

displacement of ions across the double layer

$$t_{\text{relax}} \sim \frac{(1/\kappa)^2}{2D_i} \simeq \frac{5 \times 10^{-11} \text{ sec}}{c/\text{mole liter}^{-1}} \sim 10^{-8} \text{ sec}, \quad [20]$$

where  $D_i$  is the ionic diffusion coefficient. The numerical values given apply to aqueous solutions at room temperature and a concentration of about 5 mM.

If the double-layer equilibrium involves adsorption of potential determining ions, the surface potential tends to stay constant and after a change in composition of the solution or in a Brownian collision the *surface charge has to be adjusted*.

Surface charge densities,  $\sigma$ , are of the order of  $1 \mu\text{C}/\text{cm}^2$  and the rate of charge adjustment is determined by the exchange current density,  $i_0$ .

For exchange current densities,  $1 \text{ A cm}^{-2}$  is a high value and  $10^{-10} \text{ A cm}^{-2}$  a low one. The time for charge adjustment may therefore vary from

$$t_{\text{charge}} \sim \frac{\sigma}{i_0} = \frac{10^{-6} \text{ C cm}^{-2}}{(10^{-10} - 1) \text{ A cm}^{-2}} = 10^{-6} \text{ to } 10^4 \text{ sec.}$$

Finally the *time of a Brownian collision* is the average time needed for a particle to travel through the thickness of the double layer. This time is given by

$$t_{\text{Brown}} = ((1/\kappa)^2/2D_p) = 3\pi\eta a/\kappa^2 k_B T, \quad [21]$$

where  $D_p$  is the diffusion coefficient of the particles.

For a particle with a radius of  $1000 \text{ \AA}$  and  $1/\kappa$  varying from 1 to 10 nm (i.e., electrolyte concentrations from  $10^{-1}$  to  $10^{-3} \text{ M}$ ) in water at room temperature

$$t_{\text{Brown}} \simeq 10^{-5} - 10^{-7} \text{ sec.}$$

*Coagulation times* may vary widely depending on particle size and concentrations, but in order to be studied in the laboratory they have to be considerably longer than the mixing time, say 0.1 sec and up.

Comparing the different time scales we may conclude that double-layer adjustment is fast even when compared to the short time of the Brownian encounter, but the charge adjustment will often be too slow to follow the single encounter. It may be even too slow to adjust the charge within the coagulation time. Consequently, in calculating the interaction energy of two particles the condition of constant charge is probably a better approximation than that of constant potential and intermediate cases may be met in practice.

For the interaction of particles with *adsorbed long chains* similar considerations apply (11). Relaxation times involved in the adjustment of the conformation of an adsorbed chain or loop can be estimated from oscillatory flow measurements and have been found by Thurston *et al.* (39) to be  $2 \times 10^{-4}$  sec for polystyrene of  $M = 50\,000$  dissolved in a liquid with a viscosity of 2 P. The time of adjustment of the loop size distribution (i.e., of the adsorption) is at least several minutes (40). The time involved in a Brownian encounter may now be considered as the time needed for a particle to travel over a distance equal to the thickness of the adsorbed layer. Taking the layer thickness as 6 nm, the particle radius as 100 nm, and the viscosity again as 2 P, we have

$$t_{\text{Brown}} = \frac{(6 \text{ nm})^2}{2D_p} = \frac{(6 \text{ nm})^2 \cdot 3\pi\eta a}{k_B T} \approx 2 \times 10^{-3} \text{ sec.} \quad [22]$$

We conclude that the conformation adjustment can follow the collision process, but the rates

of adsorption and loop size redistribution are too slow.

#### IV. REPEPTIZATION

##### IV. 1. Facts and Simple Theory

It is obviously both of practical and theoretical importance to know whether a flocculated system can be made to redisperse (repeptize) by changing the composition of the medium and with little or no stirring or grinding.

In the case of stabilization by adsorbed polymers flocculation can be caused by adding a nonsolvent for the polymers or by changing the temperature. Repeptization after return to the original conditions is the expected behavior unless desorption or recrystallization of the particles occur.

With electrostatic sols redispersion after flocculation is not expected. As a matter of fact other names for these sols are “irreversible” or “irresoluble.” From the most simplistic point of view redispersion is impossible since at  $H = 0$  (contact between particles) the van der Waals energy is minus infinity. But even if we realize that the van der Waals minimum is not infinitely deep, Fig. 4 shows a more essential reason for the lack of redispersion. If the potential energy diagram for the approach of two particles shows the usual maximum and two minima, then, after lowering the maximum by the addition of salt, flocculation occurs in the left-hand side, deep, so-called primary minimum. Then after eliminating the flocculating electrolyte the original energy diagram is restored, but for repeptization the particles still have to overcome the energy barrier, which, if high enough to prevent coagulation,

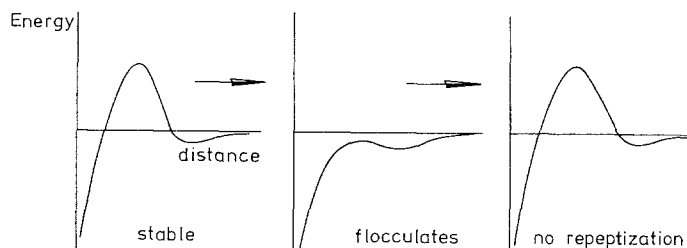


FIG. 4. Potential energy diagrams for a pair of particles at short distances, showing that after flocculation restoration of the original diagram does not lead to redispersion.

is certainly high enough to prevent passage from the other side.

Nevertheless reptization of electrocratic systems is quite frequent and when it occurs it usually requires very little mechanical action, especially if only a short time is allowed to pass between coagulation and reptization. We mention clays; ferric and many other oxides and hydroxides for which reptization is often a step in the normal way of preparing a sol; HgS, which after precipitation and washing finally "runs through the filter." AgI can be reptized and the Carey Lea silver sol is prepared and cleaned by reptization. It looks as if reptization is the rule rather than the exception, at least with monovalent coagulating electrolytes.

Reptization can be demonstrated and measured quantitatively with a simple technique proposed by Frens (41). Coagulation is carried out in the sample cell of a spectrophotometer. After a preselected degree of coagulation (preselected extinction) is reached the sample is diluted, e.g., five times, and the resulting extinction is compared to one-fifth of the extinction of the original sol before and

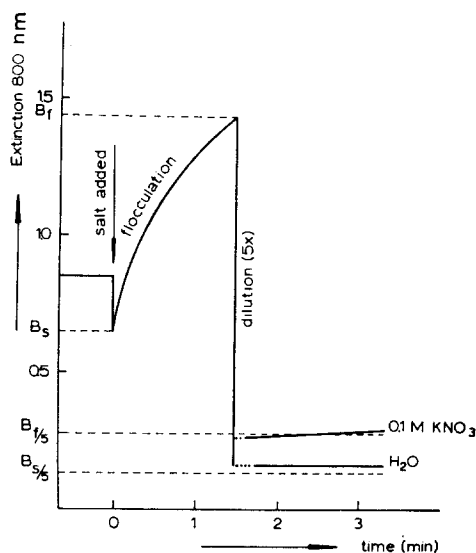


FIG. 5. Extinction,  $B$ , versus time for an aqueous AgI-sol, coagulated with  $\text{KNO}_3$  and diluted with either  $0.1 \text{ M KNO}_3$  (no reptization) or with water (nearly complete reptization).

TABLE II

Coagulation and Repeptization of a Negative AgI-sol with Bivalent Ions<sup>a</sup>

Coagulate with	Dilute with	Result
115 mM $\text{KNO}_3$	0.4 mM $\text{Ba}(\text{NO}_3)_2$	Repeptization
1.67 mM $\text{Ba}(\text{NO}_3)_2$	30 mM $\text{KNO}_3$	No repeptization

<sup>a</sup> Final concentrations in both experiments: 24 mM  $\text{KNO}_3$  and 0.32 mM  $\text{Ba}(\text{NO}_3)_2$ .

after coagulation. If the extinction corresponds to that of the sol before coagulation reptization is complete; if it corresponds to the extinction of the sol after coagulation reptization is absent. Figure 5 illustrates this type of measurement.

It was found that after coagulating a negative AgI-sol with  $\text{KNO}_3$  reptization was nearly complete after dilution with about two-thirds (or less) of the coagulation concentration. Repeptization after coagulation with bivalent cations did not occur, unless the coagulating ions were first exchanged with a large excess of monovalent ones. Table II shows that a sol coagulated with monovalent ions reptizes after dilution with a low concentration of bivalent ions, but if the bivalent ions are used for coagulation, dilution with a low concentration of monovalent ions does not result in reptization, although the final concentrations are the same in the two experiments.

#### IV. 2. Theoretical Considerations

For understanding reptization both thermodynamic and kinetic aspects are important. In the first place spontaneous reptization can only occur if the free energy decreases in the process. Moreover the activation energy should be low or absent. Figure 6 shows this in energy vs distance diagrams. In the middle sketch curves for two situations are given for which reptization does not occur, the lower curve because it would require an increase in free energy, the upper one, although it would lead to an energy decrease, because the activation energy is too high. Then the question presents itself: How is it possible to obtain an energy curve such as that in the r.h.s. diagram

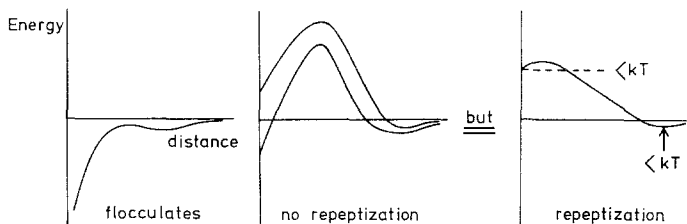


FIG. 6. Energy vs distance diagrams comparable to Fig. 4. Only the r.h.s. diagram corresponds to reptization.

of Fig. 6? On the basis of van der Waals attraction and electrostatic repulsions this is only possible if the particles in the flocculated state remain separated by a finite distance that we will call  $2\delta$ , as if each of the particles is covered with a layer of solvent, that can not be pushed away, at least not in the time between flocculation and redispersion. Moreover, a high surface potential,  $\phi_\delta$ , and a low Hamaker constant,  $A$  favor redispersion. Here kinetic arguments mentioned in the previous section may be invoked. After adding the coagulating electrolyte, the double layer is compressed, the surface potential is lowered (at constant charge), and the surface charge will increase only slowly to restore the original surface potential,  $\phi_0$ . Even after charge adjustment, the potential at the Stern-plane,  $\phi_\delta$ , will still remain below its value in the original solution before the addition of electrolyte.

After dilution of the electrolyte in the coagulated sol, the double layer will expand and the surface potential and the Stern potential will shoot up, reaching values above the final equilibrium values which they will subsequently reach only slowly after a loss of surface charge.

It is therefore a consequence of the whole conception that flocculation occurs at low  $\phi_\delta$  and reptization at high ones. Frens and Overbeek (18) made a number of calculations in this area and found that very modest values of  $\delta$  (e.g., 0.2 or 0.3 nm), when combined with quite reasonable values of  $A$  and of  $\phi_\delta$  are sufficient to explain both coagulation and redispersion at realistic concentrations. Figures 7 and 8 show two energy diagrams, one for

flocculation (depth of minimum about  $80 kT$ ) and one for reptization (energy decrease about  $135 kT$ , energy barrier about 1 or  $2 kT$ ).

The curious influence of the order of addition of monovalent and divalent counterions shown in Table II can be explained in the following way. The situation after flocculation either with  $KNO_3$  or with  $Ba(NO_3)_2$  corresponds to the l.h.s. diagram of Fig. 6. Immediately after diluting the  $KNO_3$  flocculate with  $Ba(NO_3)_2$  only a small fraction of the  $Ba(NO_3)_2$  is close to the double layers and exchanges against  $KNO_3$ , but the double layer is still mainly composed of  $K^+$  ions. The concentration is such that an energy diagram of the type

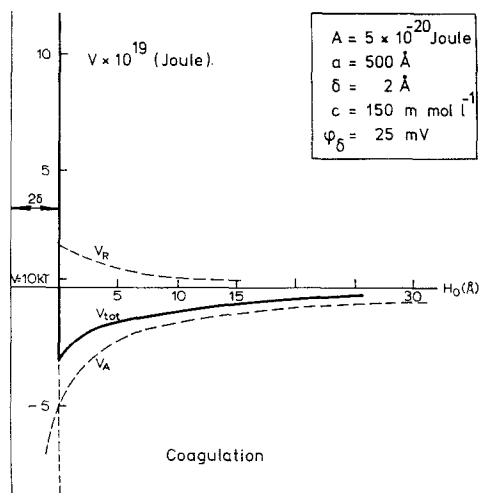


FIG. 7. An energy diagram leading to coagulation.  $V_A$  = Van der Waals attraction, Eq. [1] or [4];  $V_R$  = electrostatic repulsion at constant charge;  $\delta$  is the thickness of the Stern-layer; 1-1 electrolyte;  $V_{tot} = V_A + V_R$ .

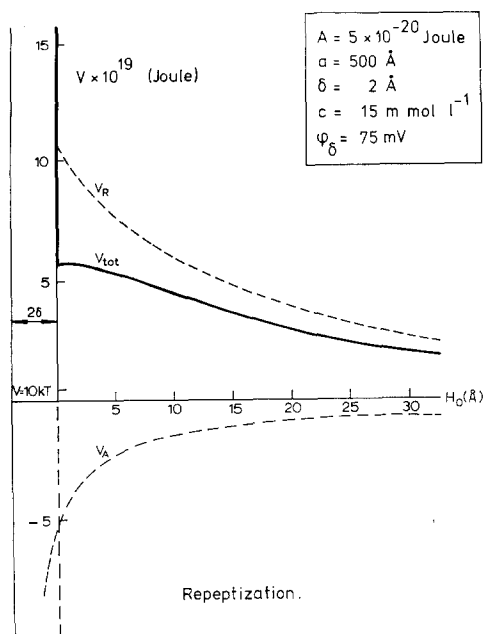


FIG. 8. An energy diagram for reptization. Note the higher potential (75 mV instead of 25 mV) and lower electrolyte concentration (15 mM instead of 150 mM) as compared with Fig. 7.

in the r.h.s. of Fig. 6 results, reptization follows and only after reptization further exchange of  $\text{Ba}^{2+}$  against  $\text{K}^+$  occurs which modifies the energy diagram in the direction of the middle curves of Fig. 6, allowing the sol to remain stable. If, however, the  $\text{Ba}(\text{NO}_3)_2$  flocculate is diluted with  $\text{KNO}_3$ ,  $\text{Ba}^{2+}$  in the double layer is only for a small part exchanged against  $\text{K}^+$  and although the double layer expands and the surface potential goes up, the resulting energy diagram is of the middle type of Fig. 6. So there is no reptization, although ion exchange of  $\text{Ba}^{2+}$  against  $\text{K}^+$  continues and the final double-layer structure is the same for both experiments.

It should be obvious, and further calculations confirm this, that the shape of the energy curves is very sensitive to the values of  $\delta$ ,  $\phi_\delta$ , and  $A$ . It would therefore seem to be profitable to investigate reptization in more detail, especially with the now available isodisperse systems, and determine exactly the conditions where reptization will just take place. This

should be a good approach to obtaining more quantitative information on the distance of closest approach  $2\delta$ , the Stern potential  $\phi_\delta$ , and the Hamaker constant,  $A$ .

## V. EMULSIONS

With emulsions one has to distinguish coagulation, usually followed by rapid creaming, and coalescence. Emulsions that are only coagulated or that have creamed are easily redispersed with a little shear, because the individual droplets are fairly large (except in micro-emulsions). Since the droplets are large the whole energy diagram is on a large scale and the secondary minimum may be deep enough to be the cause of coagulation.

Coalescence, that is, the flowing together of drops to form one large coherent mass, is more difficult to understand, especially since we may have to accept the existence of a tightly adhering layer of the dispersion medium around the droplets, just as such a layer was essential for the understanding of reptization in the case of solid particles.

The process of coalescence is formally similar to the breaking of foam lamellae for which Vrij (42) and Sheludko (43) have developed a theory, based on the spontaneous growth of long wave fluctuations in the surface. Also with foams, however, this mechanism may either lead to the breaking of the lamellae or to the formation of ultrathin black soap films. It is not yet clear whether this same approach will help in the understanding of emulsion coalescence, but it is worth a try. Coalescence is certainly one of the still open problems in colloid science.

## VI. NEW APPLICATIONS OF COLLOID STABILITY AND PROBLEMS WAITING FOR A SOLUTION

The number of applications of colloid stability is constantly growing but on the whole this is more in the direction of extending fields of application already known than in completely new applications. It is true that a few fields, such as pharmaceutical and agricultural applications of suspensions and emulsions to

the distribution and regulation of the rate of uptake of active substances, are growing rapidly. Applications to biological and to environmental problems, e.g., the dispersion of oil spills by emulsification, get more attention.

Nonaqueous dispersion media and micro-emulsions, which, by the way, do not fit well into the present theoretical conceptions, are attracting many investigators.

There are of course still a number of problems that seem to be more or less ready for a solution but have not yet been solved. I want to mention—

- a. understanding the influence or lack of influence of particle size on slow coagulation,
- b. making more use of the rate of coagulation and of the conditions for redispersion to obtain a better quantitative knowledge on van der Waals forces and double-layer structure,
- c. understanding the conditions for coalescence of emulsions,
- d. obtaining better quantitative understanding (and prediction!) of the anchoring of polymers at interfaces,
- e. obtaining better quantitative data on the influence of chainlength and solubility ( $\alpha$ ) of steric stabilizers,
- f. better understanding of the density of flocs and being able to control it, since easy filtration requires open flocs but for transport and storage a high density is preferable.

Summarizing, we may state that the main recent developments in the understanding of colloid stability are the theoretical explanation of protective action and sensitization (steric repulsion by long chains) and a much greater awareness of the rate effects occurring in stable, coagulating, and redispersing colloids.

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