

On Coagulation in the Primary Minimum

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The DLVO theory offers conceptual problems now that it appears to be established that double layer potentials are low at the critical coagulation concentration in colloids which follow the Schulze-Hardy rule, and that the predicted relation between the rate of slow coagulation and the particle size is not found experimentally. In this paper we explore the hypothesis that competition between aggregation and reptitization determines the net rate of slow coagulation, and that aggregates become progressively more irreversible after their formation. A theory of this kind could account for many experimental observations. It predicts that the double layer potential ϕ_δ at c_c increases with the counterion valency and that there is some critical potential ϕ_δ^0 below which coagulation can begin.

From the effects of the concentration and valency of counterions on the rate of coagulation it is evident that the stability of electrostatic colloids depends on the repulsion of electrical double layers.¹⁻³ Fuchs' theory⁴ of diffusion in a field of long range (double layer repulsion and van der Waals attraction) forces enables calculations to be made of the retardation of the rate of coagulation relative to the rate of rapid coagulation which was derived by von Smoluchowski.⁵ One obtains a retardation of the coagulation by a factor

$$W = \int_{2a}^{\infty} x^{-2} \exp(V_x/kT) dx \quad (1)$$

since a fraction of the Brownian collisions is prevented from occurring by the repulsive forces. V_x is the potential energy of interaction at an interparticle distance $x = H + 2a$ between two spherical particles of radius a .

The DLVO theory^{2,3} computes V_x , by addition of the contributions V_R of the double layer repulsion and V_A of the van der Waals forces. The largest contributions to the Fuchs-integral [eqn (1)] are from the range of x values where V_x has a positive maximum. In the absence of such a maximum, $W = 1$ approximately. Relating changes in V_x , and especially in its maximum value, to changes in the electrolyte concentration c , Verwey and Overbeek found that a plot of $\log W$ against $\log c$ should consist of two linear parts, intersecting at the critical coagulation concentration c_c . Identifying c_c as the concentration where the positive maximum vanishes, they also gave a derivation which shows that (for large double layer potentials) $c_c \times z^6$ is constant. This is the DLVO expression for the empirical Schulze-Hardy rule: the counterion valency has a very large effect on coagulation rates. These two results, the derivation of a Schulze-Hardy rule and the prediction plus experimental verification⁶ of the shape of ($\log W$, $\log c$) curves have been taken as evidence for the validity of the DLVO approach. As one of the first theories for the absolute rate of a reaction the DLVO theory was remarkably successful.

However, some questions remain; and not only about the application of this

theory to practical colloids. It is difficult to reconcile the observation that colloids with electro-kinetic ζ -potentials as low as 25 mV obey the Schulze-Hardy rule with the assumption that the diffuse layer potential φ_δ is high enough to allow the DLVO derivation of this rule ($\tanh ze\varphi_\delta/4kT \approx 1$, i.e., $ze\varphi_\delta > 200$ mV). Also, now that well defined monodisperse colloids are available, it has been found that $d \log W/d \log c$ is hardly dependent on the particle size.⁷ This result is in conflict with the theory, which predicts that it should be proportional to a .

In this paper we discuss an alternative possibility for the way in which double layer repulsion and van der Waals attraction affect the coagulation process *via* the potential energy diagram. We assume that there is coagulation in the primary minimum at short interparticle distances, but that the net rate of slow coagulation is determined by the probability of spontaneous (Brownian) reptization of the aggregates. The idea that a fraction of the particles may break away from an aggregate is not altogether new,⁸⁻¹⁵ but has been explored before in formal analyses of the kinetic implications of aggregate reversibility, applicable to coagulation in the primary as well as in the secondary minimum of the interaction curve. For small (colloidal) particles the primary minimum is the only relevant potential energy minimum. In this paper we attempt to discuss some of the physical concepts involved and experimental conditions required for the reversibility of aggregates consisting of two particles in this primary minimum.

In von Smoluchowski's calculation of the rate of rapid coagulation, and also in the DLVO theory, it is assumed that every collision results in the formation of a permanent aggregate. These theories count the number of collisions per unit time. Long range forces may prevent a fraction of the collisions [eqn (1)] and thus retard the coagulation. At short interparticle distances they can also account for irreversibility: V_R varies as $\exp(-\kappa H)$ and V_A as H^{-1} so that V_x becomes strongly negative as $H \rightarrow 0$. Taken together these arguments explain why slow coagulation often proceeds at a "retarded Smoluchowski" rate,^{16,17} in which a constant fraction of the collisions remains ineffective. The probability that a collision between two particles is prevented by an energy barrier V_x remains independent of the number of primary particles and of the number and size of the aggregates. With reversible aggregates one would expect an aggregation-reptization equilibrium to be established.¹⁰ The coagulation process would slow down (limited coagulation), as has been observed with polymer stabilized suspensions and in secondary coagulation. Indeed, there are a few observations of limited coagulation with small particles and highly irreversible colloids,¹⁶⁻¹⁹ which seem puzzling. If it is assumed that the rates of slow coagulation are retarded because of spontaneous reptization of aggregates, as in this paper, then it has to be explained why in so many other experiments one observes "retarded Smoluchowski" rather than "limited" coagulation kinetics. Relating these observations to the rates at which double layers are equilibrated after a Brownian collision we obtain an alternative explanation for irreversibility.

Some years ago in studies of the reptization of electrostatic colloids after coagulation in the primary minimum,²⁰⁻²² it was found that the experimental observations can be explained with the traditional type of potential energy diagrams ($V_R + V_A$ as a function of H) if it is assumed that

- (a) the charge σ rather than the potential φ of the double layer remains constant during a Brownian collision;
- (b) that there is, therefore, a distance of closest approach $H = 2\delta$ in an aggregate. δ is the distance between a particle surface and the corresponding Outer Helmholtz Plane;

(c) the potential ϕ_δ in the O.H.P., which varies with the electrolyte concentration c , must be used to compute the potential energy diagrams.

Ageing of the aggregates was given as an explanation for the progressive irreversibility of flocs which could be rezeptized shortly after their formation.

In fig. 1 it is shown that these assumptions have a considerable effect on the shape of the potential energy diagrams. The pronounced maxima which govern the DLVO theory have disappeared, since the introduction of a (small) distance of closest approach has obscured the sharp increase of the attraction for $H \rightarrow 0$. Another feature becomes manifest when the "critical" parameter Z_∞ is introduced.²⁰ $Z_\infty =$

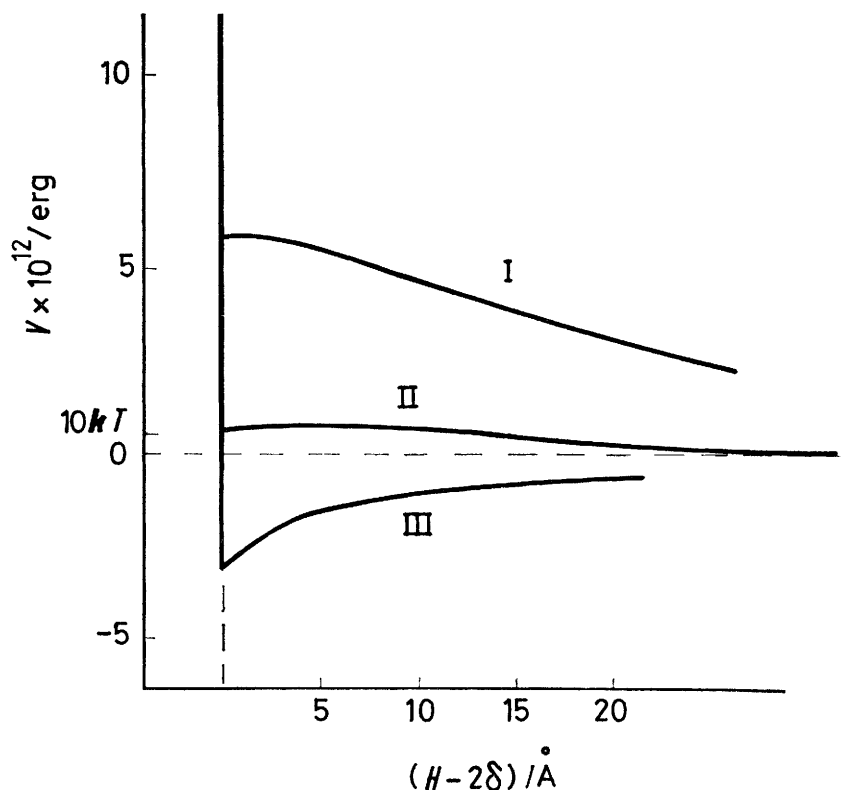


FIG. 1.—Potential energy diagrams. I: $Z_\infty = 3$, $c = 15 \text{ mmol dm}^{-3}$, 1-1 electrolyte. II: $Z_\infty = 2$; $c = 60 \text{ mmol dm}^{-3}$, 1-1 electrolyte. III: $Z_\infty = 1$, $c = 150 \text{ mmol dm}^{-3}$, 1-1 electrolyte. $a = 500 \text{ \AA}$; $A = 5 \times 10^{-13} \text{ erg}$; $\delta = 2 \text{ \AA}$.

$ze\phi_\delta/kT$ for $H = \infty$. It is a measure of the diffuse layer potential ϕ_δ of a single particle, which can be identified tentatively with the electro-kinetic ζ -potential. Z_∞ is the value of Z_∞ for which $V_R + V_A = 0$ at $H = 2\delta$, i.e., in the primary minimum. A condition for coagulation in the primary minimum is that $Z_\infty < Z_\infty^c$; coagula will rezeptize if $Z_\infty > Z_\infty^c$.

From these studies the picture emerges of a primary minimum, which may be deep (compared with kT), shallow or nonexistent depending on the experimental conditions. The probability of two particles remaining aggregated for some length of time after a collision depends on the depth of the primary minimum. By Fuchs' theory the rate of rezeptization is related to the potential energy diagram. The depth

of the primary minimum itself is related to the electrolyte concentration, and c_c is the concentration where the probability of reptitization of aggregates becomes negligible.

The maximum of V_x in the DLVO theory and the depth of the minimum in the theories of secondary coagulation are rather insensitive to double layer potentials. They follow from variations in the range of the repulsion relative to that of the van der Waals attraction. The depth of the primary minimum depends on φ_δ and especially on the changes in Z_∞ relative to Z_∞^c . Thus the coagulation rate is related to the ionic strength *via* the effects of the electrolytes on the structure and the capacity of the electrical double layer²³ rather than *via* its mere thickness.

POTENTIAL ENERGY DIAGRAMS

Fig. 2 shows the repulsive energies V_R^c and V_R^q for constant σ and φ_δ , respectively, for spherical double layers at a number of values Z_∞ ($G = z^2/aV_R$). At $H = 2\delta$ it is found that G is approximately proportional to Z_∞^2 , more so for constant φ_δ than for constant σ . This implies that the potential energy at $H = 2\delta$ is proportional both to a and to φ_δ^2 . For a given Z_∞ it is independent of κ . Since the attraction energy $V_A (= aA/12H$ for small H/a) is also fixed for a given A and δ this means that changes in the depth of the primary minimum, resulting in changes in coagulation rate, can only be brought about by changes in φ_δ . The potential φ_δ depends on the kind and the concentration of the electrolyte.

The dependence of φ_δ on c is discussed in the Stern theory of the double layer²⁴ and in more sophisticated treatments based upon it.²⁵ We shall, in this paper, use a simple formula from this theory, originated by Frumkin,²⁵ and write for $\varphi_\delta \leq 0$,

$$\varphi_\delta = \mp(\text{constant}) \pm \frac{kT}{ze} \ln c. \quad (2)$$

This approximate formula is rather effective in the description of experimental results. It can account not only for electrokinetic data, but also for electrode kinetics and the effects on it of varied concentrations of inert electrolyte.^{25,26}

We have introduced Z_∞^c , which implies that there exists a value of φ_δ and, therefore, some electrolyte concentration c_0 , for which $V_R = -V_A$ at $H = 2\delta$. For $c > c_0$ the potential is lowered, and the depth of the primary minimum is the difference in the values of V_R^q at c and at c_0 . In a discussion of *one* colloid we may define c_0 as the unit of concentration. Then it is seen that the constant in eqn (2) becomes the value φ_δ^0 at $c = c_0$ for this colloid. The depth of the primary minimum is then found to be

$$V_{\min} = aK \left[\left(\frac{kT}{ze} \ln c \right)^2 - \frac{2kT}{ze} \varphi_\delta^0 \ln c \right] \quad (3)$$

assuming $G = KZ_\infty^2$.

It would be interesting if a concentration c_0 and a corresponding potential φ_δ^0 could be determined as a threshold for the coagulation of an electrocratic sol. Below this concentration there would be no coagulation in a primary minimum, although there might remain secondary coagulation and Ostwald ripening to coarsen the suspension. These threshold values would directly be related to the strength (A) of the van der Waals attraction.

Aggregates age; their double layer potentials revert to the (Nernst) equilibrium value during the period after their formation. The repulsion energy diminishes accordingly, from V_R^c to V_R^q at the same Z_∞ , which is a decrease of the order of $10 kT$ in a typical colloid. If two particles remain trapped for some time in (even a

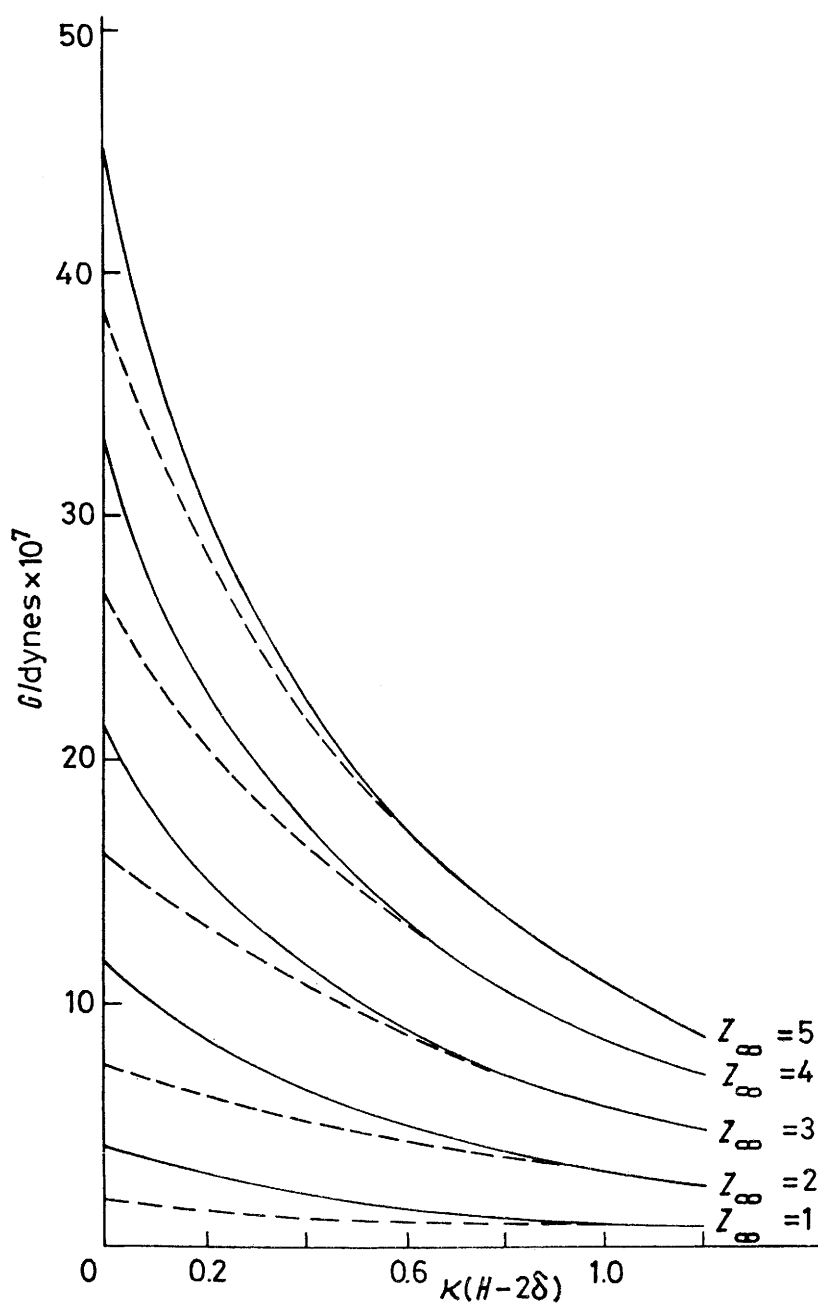


FIG. 2.— $G = z^2/aV_R$ as a function of $\kappa(H - 2\delta)$ for different values of Z_∞ . Full line, constant σ . Broken line, constant ϕ_δ .

shallow) primary minimum, they will sink irreversibly into a rather deep potential well. Such a mechanism is not effective in, *e.g.*, secondary coagulation. There the double layers are virtually unaffected by the interaction and screen the surface charge. But aggregates in a primary minimum must eventually be rendered irreversible by the relaxation to equilibrium of the strongly interacting double layer systems.

COAGULATION KINETICS

Once it is established that there exists a probability of reptization for newly formed aggregates, the treatment of coagulation kinetics becomes analogous with that for secondary coagulation. In a suspension of Brownian particles the number of collisions with one particle per unit time is:

$$J_a^0 = 8\pi DRn_0 \quad (4)$$

where D is the diffusion coefficient of the particles, n_0 their concentration and $R \approx 2a$ is the distance x at which an encounter is counted as a collision. Without interaction these collisions remain without consequence and doublet dissociation (J_r^0) occurs at the same rate as doublet formation. Interaction forces hinder the collisions and also the breaking up of doublets. According to eqn (1)

$$J_a = J_a^0 \left(\int_{2a}^{\infty} x^{-2} \exp(V_x/kT) dx \right)^{-1}; \quad (5)$$

the analogous expression for the reptization of aggregates is

$$J_r = J_r^0 \left(\int_{2a}^{\infty} x^{-2} \exp(V^1/kT) dx \right)^{-1} \quad (6)$$

where V^1 is the potential energy at a point x measured relative to V_{\min} , the depth of the primary minimum. $V^1 = V_x - V_{\min}$, and the integration is in both cases over the whole "reaction coordinate" which contains all interparticle distances. The net number of collisions which result in aggregation at the beginning of the coagulation is a fraction of J_a^0 , given by

$$J_n = J_a - J_r = J_a^0 \left(\frac{1}{\int_{2a}^{\infty} x^{-2} \exp(V_x/kT) dx} - \frac{\exp(V_{\min}/kT)}{\int_{2a}^{\infty} x^{-2} \exp(V_x/kT) dx} \right). \quad (7)$$

The two Fuchs' integrals in this expression are equal, and approximately equal to $W = 1$ if the potential energy diagram has a primary minimum and no pronounced positive maximum. Thus

$$J_n = J_a^0 \cdot \frac{1}{W} [1 - \exp(V_{\min}/kT)] \quad (8)$$

and the effective retardation factor becomes

$$W_{\text{eff}} = W[1 - \exp(V_{\min}/kT)]^{-1}, \quad (9)$$

analogous with expressions for secondary coagulation^{12,13} which have been derived making the, too simple, assumption that there is a Boltzmann distribution of aggregate energies, and that aggregates with energies above $-V_{\min}$ will break up. More rigorous treatments of coagulation kinetics with reversible aggregates follow the Fuchs approach.^{8,14,15} Eqn (9), in combination with an expression for V_{\min} , like

eqn (3), should permit construction of $(\log W, \log c)$ diagrams. Expanding the exponential it is easily seen that $\log W = [\text{some constant}] - \log (\ln c/c_0)$. The constant contains a , which makes the value of the critical coagulation concentration (corresponding to $V_{\min} = kT$) dependent on the particle size, though $d \log W / d \log c$ is independent of a . The descending branch of the $(\log W, \log c)$ curve is not really straight, but it resembles a straight line in the practical range of slow coagulation. Near the intersection at c_c ($W_{\text{eff}} = 1$) the curve becomes rounded, [cf., ref. (12)].

However, reversible aggregation can not be the whole story in slow coagulation kinetics. So far we have used a model which predicts limited coagulation and the establishment of a coagulation-repeptization equilibrium. Limited coagulation of electrocratic colloids has only been observed^{16,18,19} at extremely low initial rates of aggregation. The more common processes ($10 > W_{\text{eff}} > 1$) show retarded Smoluchowski kinetics.^{7,16,17} This implies that near the critical coagulation concentration there may be a constant fraction of the newly formed aggregates which break up, but that the remaining older flocs stick irreversibly together. It has been suggested²⁷ that there is a progressive irreversibility as the aggregates increase in size because primary particles would almost never succeed in breaking more than one contact at a time. This may be an explanation as to why limited coagulation processes do continue after some time and has been given as such; it cannot account for retarded Smoluchowski kinetics during the initial stages of coagulation.

The decrease in the potential energy of an aggregate from V_R^a to V_R^e makes it irreversible during a period after its formation. Two particles will cling together, even if there was only a shallow primary minimum during the collision, unless their aggregate is broken up by their independent Brownian motion before it is too late. Thus the fraction of the doublets which will eventually break up becomes dependent on the relative rates of two processes. The rate of spontaneous repeptization depends on the momentary value of V_{\min} and continues to decrease, until V_{\min} has reached the value at which repeptization stops. The changes in V_{\min} are caused by the adjustment of the double layer potential to the Nernst equilibrium value; the rate of this adjustment is determined by the exchange current density at the interface. The rates of repeptization and of ageing are, therefore, independent of the number and the size of aggregates.

Their ratio remains constant during the coagulation process; this results, again, in retarded Smoluchowski kinetics. A constant fraction of the fresh aggregates can dissolve, but the remaining, older, aggregates no longer participate in spontaneous repeptization.

Double layer relaxation will be most effective in making aggregates irreversible when they stay intact for a comparatively long time. Therefore, it is indeed expected that limited coagulation is observed in very slow coagulations, whereas retarded Smoluchowski rates occur with rather small values of W_{eff} and rather deep primary minima. This effect makes the descending branch of experimental $(\log W, \log c)$ curves steeper than indicated by eqn (9); the change in slope near c_c also becomes more abrupt.

The rate of adaptation for double layers on different materials may differ considerably. This must affect the shapes of $(\log W, \log c)$ curves and also the values of c_c . For one material, a shallow primary minimum will give sufficient stability to most aggregates to make them irreversible before they can break. In another sol the particles would need to be kept together for a long time, in a primary minimum of several kT , to make them stick. In this model the critical coagulation concentration is not only dependent on A and ϕ_δ , but also on the electrode kinetics at the surface of the particle.

CRITICAL COAGULATION CONCENTRATIONS

For a given colloid the depth of the minimum at c_c should not depend on the kind of electrolyte present. This, rather than the condition of a vanishing maximum becomes the criterion for c_c and the basis for a discussion of the Schulze–Hardy rule in terms of the Gouy–Stern double layer.^{3,28} In fig. 2 it is seen that if $\phi_\delta = 25$ mV at c_c for monovalent counterions (*i.e.*, $Z_\infty = 1$) it must become 35 mV with divalent and 40 mV with trivalent ions to give the same value of V_R^g , *i.e.*, of V_{min} . In fig. 3 it is shown how the Stern model permits an estimate of the electrolyte concentrations at which these conditions will obtain for one equilibrium value of the total double layer potential ϕ_o . A Schulze–Hardy type variation of c_c with z is obtained, not very dependent on the potential ϕ_o and at low potentials ϕ_δ of the diffuse layer. The model can, of course, be refined considerably by including for example, ion size, specific adsorption and discreteness of charge in the double layer model. But it is to be expected that a more complete theory will have many of the same features, since experimental, *e.g.*, electrokinetic, diffuse layer potentials have a “Schulze–Hardy-like behaviour”.^{29,30}

Eqn (3) was based on the even cruder approximation that G is proportional to Z_∞^2 . This would give the simple formula $(1/z)\ln c/c_o = \text{constant}$ for the Schulze–Hardy rule, which is an expression for a constant “critical potential” in a given sol and for the ancient “logarithmic” version³¹ of the Schulze–Hardy rule. Something

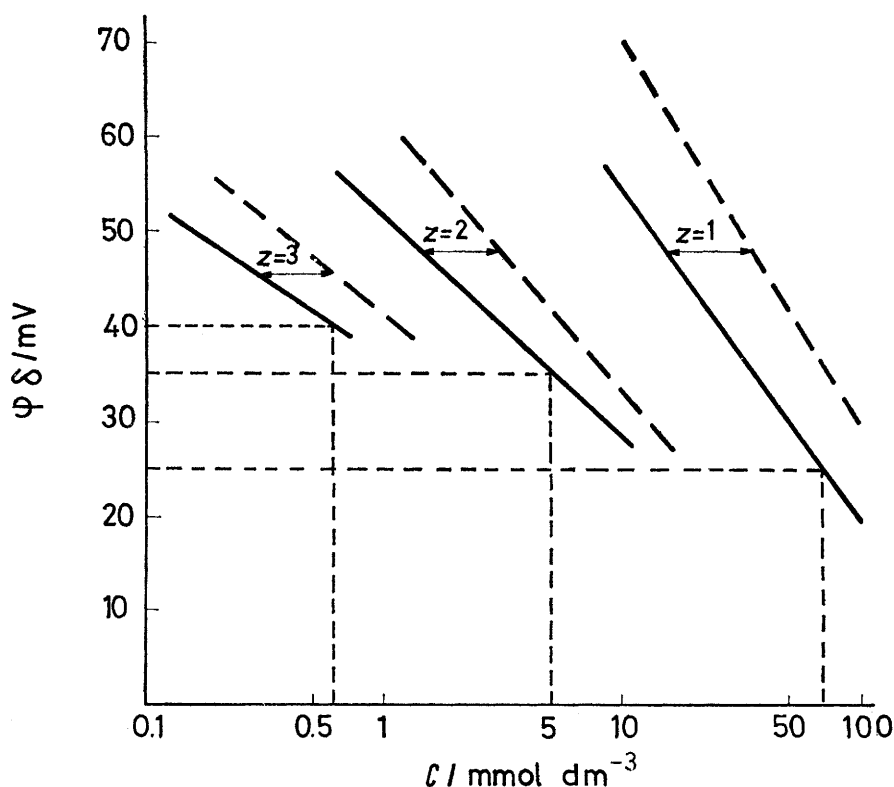


FIG. 3.—The Schulze–Hardy rule. Stern model without specific adsorption³ and different values of ϕ_o (full line $\phi_o = 200$ mV, broken line $\phi_o = 300$ mV).

of this kind had to be expected: a theory which involves V_{\min} is a theory of ϕ_δ at c_c , and has, therefore, a link with the old adsorption theories¹ of colloid stability. However, the approximation in eqn (3) is not very good; the more complete theory using numerical computation of V_R values gives better results. It predicts that the diffuse layer potential at c_c should increase with z .

V_{\min} is constant at c_c for a given sol, and V_{\min} is also proportional to the radius a of particles in an aggregate. This explains the observation of fractionated coagulation. Experiments on fractionated coagulation have been carried out as follows: sets of monodisperse colloids were prepared, all of one material and of the same (electrolyte) composition, but with different particle sizes. In these sets c_c can be determined as a function of a and it has been found that c_c decreases when a increases. Extrapolation of c_c to $a = \infty$ gives a value for the coagulation threshold c_0 since for a large a even the shallowest primary minimum in the potential energy diagram is enough to make an aggregate irreversible. We have repeated such an experiment and found that in sets of citrate containing Au-sols, which presumably had equal $H = 2\delta$ values, c_0 was about 15 mmol dm⁻³ of a 1-1 electrolyte.

In experiments of this kind one might identify a threshold concentration c_0 for different colloids. Comparable experiments,^{6,32-34} and also those in which larger particles are removed from a polydisperse colloid by fractionated coagulation, indicate that c_c decreases as a increases. This decrease implies that the feature of the potential energy diagram which is proportional to a and which constitutes the criterion that c_c has been reached was a minimum rather than a vanishing maximum in all these experiments. In some experiments with large particles, secondary coagulation cannot be ruled out completely as an explanation. But this seems unlikely in the experiments with colloidal gold where a was of the order of 100 Å.

CONCLUSION

In this paper we have discussed in a qualitative way what the implications would be if it is assumed that the rate of slow coagulation of electrocratic colloids is determined by competition between aggregation and spontaneous reeptization from the primary minimum. Such a hypothesis, in combination with the idea that the relaxation of the interacting double layers causes progressive irreversibility in aggregates, seems to give a reasonable account of ($\log W$, $\log c$) diagrams, the Schulze-Hardy rule, limited coagulation, (retarded) Smoluchowski kinetics and fractionated coagulation, under the experimental conditions where these phenomena are observed. In such a theory the potential ϕ_δ across the diffuse part of the double layer becomes, once more, the key factor in colloid stability. It would predict that a critical value ϕ_δ^* can be found which constitutes the threshold value for coagulation. At the critical coagulation concentration (c_c), ϕ_δ should increase with the valency z of the counterions. These predictions can be verified experimentally, especially since it seems possible to do experiments with stable colloids with fine particles under conditions where coarser sols of the same material coagulate.

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