

# Physico-chemical Studies on Surface Active Agents. (I)

## Theory of Coagulation of Hydrophobic Sols

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The theory of coagulation of hydrophobic sols has been extended to include the case of collisions between particles consisting of more than two primary particles. It has been found that under certain conditions the stability factor, defined by the ratio of the rates of rapid and slow coagulations, could be related to the free energy of interaction between particles by the same expression as proposed by Fuchs for the case of homogeneous coagulation. By using this relation, a theory has been developed relating the stability factor of a sol to the surface potential and the ionic strength of the medium. Combining this theory with a proposed equation relating the Stern potential of the particles and the surface active agent concentration, which has been obtained by using the Stern and the Debye-Hückel theories, a final equation has been obtained relating the stability factor to the surface active agent concentration.

### I. GENERAL INTRODUCTION

Many kinds of soap like materials have been found in natural products and used for a long time as surface active agents. For example, the detergent action of *Sapindus* is ascribed to the so called saponins contained in it, which have strong foaming properties, and the action of *Algin* as textile chemicals to the polyuronic acids (alginic acids) in it, the alkali salts of which behave like the usual soaps. In view of the fact that many surface active agents, including the soaps of fatty acids, are being manufactured from the natural sources as well as by organic syntheses and play a major part in many processes of great technical importance, *e. g.* in detergency<sup>1)</sup>, emulsification<sup>2)</sup>, the separation of minerals by froth flotation<sup>3,4)</sup>, *etc.*, the fundamental study of the physico-chemical properties of these substances is one of the most important problems for the practical application of surface active agents. Moreover, this kind of work is of immense biological importance as well, since it provides with much information about the surfaces or interfaces which exist, as the seats of biological reactions, around every kinds of cells in the plant or animal bodies, around the nuclei, fibrils, *etc.*, and on both sides of cell membranes.

Although a large amount of literature has been devoted to the description of experiments on the action of surface active agents<sup>5,6,7)</sup>, fundamental treatments of the reactions occurring at the interface are rare. The present work was undertaken in order to study theoretically and experimentally the manner in which surface

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active agents modify the electrical double layer of charged particles, and thus bring about conditions leading to coagulation, flotation, solubilisation, *etc.* In general, it is found that these agents decrease the charge of the sol particles at low concentrations, leading to coagulation, and reverse it at higher concentrations, leading to stable sol; an important factor is the adsorption of the surface active agent at the interface.

It has been established by Hamaker<sup>7)</sup> that the stability of hydrophobic sols is determined by the free energy of interaction between the particles; this energy of interaction can be divided into two parts, *i. e.* the electrical repulsion and the van der Waals attraction. As the latter can be considered essentially constant for a given system, the major interest lies in the repulsive energy which is intimately connected with the double layer structure and therefore with sol stability. Although a quantitative theory has been given to describe the influence of the double layer thickness at constant surface potential on sol stability, a situation which occurs when indifferent inorganic electrolytes are added to sols<sup>8,9)</sup>, no quantitative theory has, so far, been derived to explain coagulation due to changes of potential caused by adsorption. In Part 1 a theoretical treatment of this problem is given, leading to a relationship between the stability factor of the sol and the concentration of added surface active agent. In Part 2 an experimental verification of the theory is described.

The surface chosen for the experimental studies was silver iodide, a well defined crystalline material, on which a number of fundamental double layer studies have been carried out<sup>9,10)</sup>; this substance also possesses the advantage of forming stable sols. Moreover, the material behaves as a reversible electrode, and hence the surface potential of the particles has a thermodynamic significance.

Although the influence on stability of a number of large organic ions has been studied, most of this work has been purely qualitative, and unsystematic, in nature and does not allow any detailed interpretation to be made in terms of modern theories of colloid stability. Recently, Rastogi<sup>11,12)</sup> has performed a systematic study of the effect of cationic surface active agents on negatively charged silver iodide sols and obtained a series of results which support the basic idea of *sensitised coagulation* and the importance of adsorption in this process.

In the present work the stability and electrokinetic behaviour of positively charged silver iodide sols, at  $pAg$  3, in the presence of anionic surface active agents, have been studied. Owing to the low concentration of surface active agents required to cause coagulation, the ionic strength in the coagulation range remains virtually constant, allowing this variable to be maintained constant in the theoretical treatment. Thus an analytical solution of the equations is possible and a simplification introduced into the problem of verifying the theory experimentally.

In Part 1 an extended theory is also given which covers the general case of changing ionic strength and potential. A good example of this case is found in the coagulation of sols, protected by surface active ions, on addition of inorganic electrolytes; the experimental details are given in Part 3. In this case the counter ions may decrease the surface potential by binding to the head groups, and at the same time with increasing concentration of inorganic electrolyte the ionic strength may increase sufficiently to cause a large decrease in the repulsive potential energy.

These effects may occur separately, or simultaneously, according to the nature of the added counter ion.

It is interesting to observe that many materials existing in biological systems, *e. g.* cell surfaces, contain carboxyl, phosphate or sulphate groupings<sup>13</sup>. As it was found that the surface of silver iodide particles protected by surface active ions had essentially the properties of the head group, we were able to construct various surfaces, which, to some extent, formed interesting model surfaces of biological systems; these allowed the specific effects of counter ions on model surfaces to be investigated at will.

An important theoretical aspect of this system is that such a protected surface can be considered as an extension of the concept of the ideal polarised electrode<sup>14,15</sup>, thus giving a basis for the study of the specific adsorbability of counter ions. This is discussed in detail in Part 4, together with the proposed model of the double layer structure in the presence of surface active agents.

The solubility of the salt consisting of the counter ion and the surface active ion should be a measure of the strength of the interaction between them. Solubility products were derived from measurements of the changes in turbidity which occurred in surface active agent solutions on the addition of various concentrations of inorganic cations (Part 5). This situation, which can lead to sol formation or precipitation, is complicated by the fact that in some regions nucleation, crystal growth and coagulation appear to occur simultaneously. However, an attempt has been made to identify these various processes and to analyse the kinetics of the overall reaction.

Some experiments have also been carried out on the formation of silver iodide sols in the presence of surface active anions. The crystal formation is modified by the fact that the adsorption of surface active agents occurs, leading in certain regions to neutralisation of the charge, and thus to coagulation. At higher concentrations of surface active agents, extensive adsorption occurs leading to reversal of charge and to stable sol formation. As in the above case, detailed analysis of the process is complicated by these factors.

## II. THE THEORY OF STABILITY OF HYDROPHOBIC SOLS IN THE PRESENCE OF SURFACE ACTIVE AGENTS

The stability of hydrophobic sols is mainly governed by the magnitude of the potential energy of interaction between the double layers of approaching particles. If there is no energy barrier, every collision between particles leads to adhesion (rapid coagulation), while, if there is an energy barrier, only a fraction of the collisions are effective in causing adhesion (slow coagulation)<sup>16</sup>.

The first attempt to give a mathematical expression for the relationship between the stability and the potential energy was made by Fuchs<sup>17</sup>, and has been developed by Reerink and Overbeek<sup>9</sup> to give a quantitative theory for the relation between the stability and ionic strength of a sol.

It has been found that the addition of various complex organic ions to a hydrophobic sol also causes coagulation<sup>10</sup>. This process is characterised by the fact that it occurs at very low concentrations, and at higher concentrations stabilisation is

observed. As this phenomenon has been found to be intimately related to the change in particle charge<sup>18)</sup> due to adsorption of these ions on the particle surface, it was essential to extend the theory to cover the case of changing surface potentials of particles.

## 1. General Treatment of the Stability Factor

### (i) The Relation between the Stability Factor and Free Energy of Interaction

According to Smoluchowski<sup>16)</sup>, coagulation is in principle a diffusion controlled process. If there is an interaction between sol particles, the process can be described by an extended partial differential equation of diffusion in which is included a term of the field of force<sup>19)</sup>, *viz.*

$$\partial N/\partial t = \text{div} [\mathcal{D}' \text{grad} N - (\mathbf{K}/\rho') N] \quad (1)$$

where  $N$  is the number of particles per  $\text{cm}^3$ ,  $\mathcal{D}'$  and  $\rho'$  the relative diffusion and friction coefficients, respectively, and  $\mathbf{K}$  the force vector acting between the particles.

Although equation (1) has not yet been solved completely<sup>20)</sup>, the solution for the stationary state, derived by Fuchs<sup>17)</sup> and Debye<sup>21)</sup>, is sufficiently useful to analyse the phenomena taking place.

As the left hand side of equation (1) is independent of time for this case, the term in the bracket on the right hand side must be a time independent vector, *i. e.*

$$\mathcal{D}' \text{grad} N - (\mathbf{K}/\rho') N = \mathbf{j} \quad (2)$$

According to the divergence theorem of Gauß,  $\mathbf{j}$  must satisfy the following relation,

$$\iiint_v \text{div} \mathbf{j} \, d v = - \iint_S \mathbf{j}_n \, d S = \mathbf{J} \quad (3)$$

where  $v$  is a volume surrounded by a closed surface  $S$ ,  $\mathbf{J}$  the total flux entering the volume through  $S$ , and  $\mathbf{j}_n$  the outward normal component of  $\mathbf{j}$ .

As the interaction between particles is due to the electrical repulsion and the van der Waals attraction, see later, both acting along the line of the centres, we can put

$$\mathbf{K} = -\text{grad} V \quad (4)$$

where  $V$  is the potential energy of interaction between two approaching particles. Substituting equation (4) in equation (2) and using the Einstein formula<sup>22)</sup> for diffusion coefficient,

$$\rho' = 3\pi \eta a = kT/\mathcal{D}' \quad (5)$$

we obtain

$$\mathbf{j} = \mathcal{D}' \exp(-V/kT) \text{grad} [N \exp(V/kT)] \quad (6)$$

Here  $a$  is the particle radius,  $\eta$  the viscosity of the medium,  $k$  the Boltzmann constant and  $T$  the absolute temperature.

It is clear that the system has a spherical symmetry with reference to an arbitrarily chosen particle. Let us, therefore, take the origin of the coordinate,  $r$ , at the centre of this particle. By substituting equation (3), we obtain\*

\*  $J$  is the modulus of the vector  $\mathbf{J}$ .

$$J = 4\pi r^2 \mathcal{D}' \exp(-V/kT) (d/dr) [N \exp(V/kT)]$$

or

$$J (1/r^2) \exp(V/kT) = 4\pi \mathcal{D}' (d/dr) [N \exp(V/kT)]$$

In integrating the both sides of this equation, we can take the following boundary conditions:

For  $r \rightarrow 2a$ ,  $V(r) \rightarrow -\infty$  and for  $r \rightarrow \infty$ ,  $V(r) \rightarrow 0$  and  $N \rightarrow N_b$ , where  $N_b$  is the number of particles per  $\text{cm}^3$  in the bulk phase. Hence, we obtain<sup>19,23)</sup>

$$J \int_{2a}^{\infty} (1/r^2) \exp(V/kT) dr = [4\pi \mathcal{D}' N \exp(V/kT)]_{2a}^{\infty} = 4\pi \mathcal{D}' N_b$$

Up to the present the centre particle has been considered to be stationary. The Brownian motion of this particle can be taken into account by assuming the relative diffusion coefficient  $\mathcal{D}'$  as the sum of the ordinary diffusion coefficients of two particles, *i. e.*  $\mathcal{D}' = 2\mathcal{D}$ . By substituting this value, we obtain the following fundamental equation<sup>17)</sup>:

$$J = 8\pi \mathcal{D} N_b \int_{2a}^{\infty} (1/r^2) \exp(V/kT) dr \quad (7)$$

If  $V=0$  for all  $r$  values, the particles undergo free diffusion (rapid coagulation) and the value of  $J$  under this condition,  $J^r$ , is given by

$$J^r = 8\pi \mathcal{D} R N_b \quad (8)$$

where  $R=2a$  is the distance of closest approach of the centres, see later.

According to Fick's law of diffusion applied to the surface of reaction,  $r=R$ , the change in the number of particles with time due to collision with the central particle is proportional to the flux,  $J$ , if other conditions are the same. Therefore, the ratio  $J^r/J$  gives the rate of rapid coagulation relative to slow coagulation, and is termed the stability factor,  $W$ . From equations (7) and (8),  $W$  is calculated as

$$W = R \int_R^{\infty} (1/r^2) \exp(V/kT) dr = 2 \int_0^{\infty} \exp[V(u)/kT] du / (u+2)^2 \quad (9)$$

where  $u=H_0/a$ ,  $H_0$  being the nearest distance between two particle surfaces.

### (ii) Rapid Coagulation

This problem is important in the sense that a complete solution of the diffusion equation can be obtained<sup>16)</sup>, which reads

$$\partial N / \partial t = \text{div} (\mathcal{D}' \text{grad } N) \quad (10)$$

As  $\mathcal{D}'$  can be assumed constant, this equation becomes

$$\partial N / \partial t = \mathcal{D}' \nabla^2 N \quad (10A)$$

The initial and the boundary conditions are given by

$$\begin{aligned} N(r, 0) &= N_b & \text{for } t=0 & \text{ and } r > 0, \\ N(r, t) &= 0 & \text{for } t > 0 & \text{ and } r = 2a \\ \text{and } N(r, t) &= N_b & \text{for } t > 0 & \text{ and } r \rightarrow \infty, \end{aligned}$$

where spherical symmetry is assumed. The solution of equation (10A) satisfying these conditions is<sup>24,25)</sup>

$$N = N_b \{1 - (2a/r) \operatorname{erfc} [(r-2a)/2\sqrt{\mathcal{D}'t}]\} \quad (11)$$

where  $\operatorname{erfc}(\lambda) = 1 - \operatorname{erf}(\lambda) = (2/\sqrt{\pi}) \int_{\lambda}^{\infty} \exp(-z^2) dz$ .

The flux at the reaction surface,  $r=2a$ , is easily calculated from equation (11), as

$$\begin{aligned} J^r &= 4\pi R \mathcal{D}' N_b (1 + 2a/\sqrt{\pi \mathcal{D}'t}) \\ &= 8\pi R \mathcal{D} N_b (1 + 2a/\sqrt{2\pi \mathcal{D}t}). \end{aligned} \quad (12)$$

It is clear that  $J^r$  approaches equation (8) in the case of the stationary state, *i. e.*  $t \gg a^2/\pi \mathcal{D}$ .

The rate of disappearance of particles in the stationary state is obtained by multiplying the flux by  $N_b$ , as

$$-dN/dt = 8\pi R \mathcal{D} N_b^2. \quad (13)$$

This means that rapid coagulation is essentially a bimolecular reaction with a reaction rate constant  $k_0$ , defined by

$$k_0 = 8\pi \mathcal{D} R = 8kT/3\eta \quad (13A)$$

### (iii) Extension to the Case of Collisions between Higher Order Particles

Although Smoluchowski has extended his theory of rapid coagulation to include coagulations of different kinds of particles<sup>16)</sup>, this does not cover the case of the slow coagulation. Hence, it is not clear whether we can use equation (9) for the stability factor of sols containing aggregates of more than two particles. It is the purpose of this section to clarify this problem deriving the formal extension of the theory.

Equation (1) can be extended to include the collision between  $i$ - and  $k$ -fold particles, as

$$\partial N^k / \partial t = \operatorname{div} [\mathcal{D}^{ik} \operatorname{grad} N^k - (\mathbf{K}^{ik} / \rho^{ik}) N^k] \quad (14)$$

where the centre particle is supposed to be  $i$ -fold, and  $\mathcal{D}^{ik}$ ,  $\rho^{ik}$ ,  $N^k$  and  $\mathbf{K}^{ik}$  are the formal extensions of  $\mathcal{D}'$ ,  $\rho'$ ,  $N$  and  $\mathbf{K}$ . In exactly the same way, the flux  $J^{ik}$  is obtained, as

$$J^{ik} = 4\pi \mathcal{D}^{ik} N^k \iint_{R^{ik}} (1/r^2) \exp(V^{ik}/kT) dr, \quad (15)$$

where  $R^{ik}$  and  $V^{ik}$  are the mutual radius of reaction and the potential energy of the two kinds of particles, respectively.

In the case of rapid coagulation ( $V^{ik}=0$ ), the flux  $J^{ik}$  is given by

$$J^{ik} = 4\pi \mathcal{D}^{ik} R^{ik} N^k \quad (16)$$

The increase in  $N^k$  with time is the algebraic sum of the increase by collisions between  $i$ - and  $j$ -fold particles, where  $i+j=k$ , and the decrease by collisions of  $k$ -fold particles with any other particles. The variation of  $N^k$  is, therefore, given by

$$\begin{aligned}
 dN^k/dt &= (1/2) \sum_{i+j=k}^{\infty} N^i J^{ij} - N^k \sum_{j=1}^{\infty} J^{kj} \\
 &= (1/2) \sum_{i+j=k} N^i N^j 4\pi \mathcal{D}^{ij} R^{ij} I^{ij} - N^k \sum_{j=1}^{\infty} 4\pi \mathcal{D}^{kj} R^{kj} N^j I^{kj}
 \end{aligned} \quad (17)$$

where  $I^{ij} = I^j = 1/R^{ij} \int_{R^{ij}}^{\infty} (1/r^2) \exp(V^{ij}/kT) dr$ .

Now let us assume, following Smoluchowski, that

$$\begin{aligned}
 \mathcal{D}^{ij} R^{ij} &= (\mathcal{D}^i + \mathcal{D}^j) (a^i + a^j) \\
 &= \mathcal{D} a [(1/a^i) + (1/a^j)] (a^i + a^j) = 4 \mathcal{D} a = 2 \mathcal{D} R,
 \end{aligned} \quad (18)$$

when  $a^i$  and  $a^j$  are not widely different.<sup>26, 27, 28</sup> Here  $a^i$  and  $a^j$  are radii of the  $i$ - and  $j$ -fold particles, respectively, and  $R$  is the radius of reaction between two primary particles. Equation (17) therefore becomes on substitution for  $\mathcal{D}^{ij} R^{ij}$

$$dN^k/dt = 4\pi \mathcal{D} R \left( \sum_{i+j=k} N^i N^j I^{ij} - 2 N^k \sum_{j=1}^{\infty} N^j I^{kj} \right) \quad (17A)$$

Hence, the rate of change in the total number of particles is obtained, as

$$(d/dt) \left( \sum_{k=1}^{\infty} N^k \right) = -4\pi \mathcal{D} R \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} N^i N^j I^{ij} \quad (19)$$

In equation (18) an assumption has been made, *i. e.*  $a^i \cong a^j$ . We are, therefore, justified in assuming, under the same condition, that

$$I^{ij} = I^j \cong 1/R \int_R^{\infty} (1/r^2) \exp(V/kT) dr = 1/W,$$

when substitution of this value in equation (19) gives

$$(d/dt) \left( \sum_{k=1}^{\infty} N^k \right) = - (4\pi \mathcal{D} R/W) \left( \sum_{k=1}^{\infty} N^k \right)^2.$$

This differential equation is easily solved under the initial condition, *viz.*

$$\sum_{k=1}^{\infty} N^k = N_b \quad \text{for} \quad t=0,$$

the solution being

$$\sum_{k=1}^{\infty} N^k = N_b / [1 + (t/T_{tr})] \quad (20)$$

where

$$T_{tr} = W / (4\pi \mathcal{D} R N_b) \quad (21)$$

Here,  $T_{tr}$  has the dimension of time and can be called the *extended time of coagulation*; this gives the time when the total number of particles is halved.

The stability factor,  $W$ , has the same form as equation (9), because

$$W = \frac{(d/dt) \left( \sum_{k=1}^{\infty} N^k \right)_{V=0}}{(d/dt) \left( \sum_{k=1}^{\infty} N^k \right)} = R \int_R^{\infty} (1/r^3) \exp(V/kT) dr. \quad (9A)$$

We can, therefore, conclude that the stability factor  $W$  in the form of equation (9) can be used also in the case of coagulation between higher order particles under the conditions given by equations (18).

In the case of particles of a high order, the summation in  $i$  and  $j$  in equation (9A) can be replaced by integration, and hence, by using the mean value theorem of integration, we obtain the more rigorous representation for  $W$ , *viz.*

$$W = \frac{\int \int_{i,j=1}^{\infty} N^i N^j di \cdot dj}{\int \int_{i,j=1}^{\infty} I^{ij} N^i N^j di \cdot dj} = 1/I^{\xi\eta}$$

where  $1 < \xi, \eta < \infty$ .

Finally, the number of  $k$ -fold particles at a time  $t$  is obtained from equations (17A) and (20)<sup>10</sup>, as

$$N^k = \frac{N_b (t/T_{tr})^{k-1}}{[1 + (t/T_{tr})]^{k+1}} \quad (22)$$

where  $k-1$  and  $k+1$  are the power indices.

## 2. The Stability Factor as a Function of Electrical Potential

### (i) The Total Potential Energy of Interaction, $V(u)$

To obtain the explicit formula for the stability factor,  $W$ , it is necessary to assume a proper relation between the potential energy of interaction,  $V$ , and the distance between two approaching particles,  $r$ , or  $u$ . As this energy is the sum of the attractive,  $V_A(u)$ , and the repulsive,  $V_R(u)$ , energies, we have

$$V(u) = V_R(u) + V_A(u). \quad (23)$$

It is generally accepted that there exist attractive forces of the van der Waals type between colloid particles<sup>9</sup>, although some authors have objections<sup>29</sup>. We shall assume, following Hamaker<sup>30</sup>, that the potential energy of attraction,  $V_A(u)$ , between two equal spherical particles is expressed by the following equation:

$$V_A(u) = -A/12u, \quad (24)$$

where  $A$  is the van der Waals constant.

The potential energy of repulsion,  $V_R(u)$ , has various forms according to the conditions. For the experimental conditions to be described in Part 2, the radius of the sol particles is 100 Å and the double layer thickness  $1/\kappa = 81.6$  Å, whence  $\tau = \kappa a = 1.23$ . In such cases,  $V_R(u)$  has a simple approximate expression<sup>9</sup>, *viz.*

$$V_R(u) = \frac{\epsilon a \phi^2}{u+2} \exp(-\tau u). \quad (25)$$

where  $\epsilon$  is the dielectric constant of the medium, and  $\phi$  a part of the potential drop in the double layer which is most important from the view-point of stability. In the case of hydrophobic sols, such as silver iodide, this potential will almost certainly be the Stern potential,  $\psi_s$ , rather than the potential of the physical surface,  $\psi_0$ ,



whereas in the case of emulsion particles it may well be the surface potential,  $\psi_0^{31D}$ ; for the sake of generality the potential  $\psi$  is not specified in detail in this section.

The more exact expression for  $V_R(u)$  is obtained by multiplying the right hand side of equation (25) by a factor which is dependent on  $\tau$  and  $u^{89}$ . As this factor is always smaller than unity, the neglect of this factor means a slight overestimation of  $V_R(u)$ . However, since the factor is always close to unity for small values of  $\tau$ , this will not be large enough for the discussions to fail, and hence we have preferred to use the simple equation (25) in order to make analytical treatments of our problem possible.

The total potential energy of interaction,  $V(u)$ , is now obtained by substituting equations (24) and (25) in equation (23), as

$$V(u) = \frac{\varepsilon a \psi^2}{u+2} \exp(-\tau u) - \frac{A}{12u}. \quad (26)$$

The theoretical curves of  $V/kT$  vs.  $u$  in Fig. 1 are obtained for particles of radius  $100 \text{ \AA}$  and  $\tau=1.23$  for various values of  $\psi$ . It is noticed that all the curves have well defined maxima at  $u$  values in the region between 0.1 and 0.2.

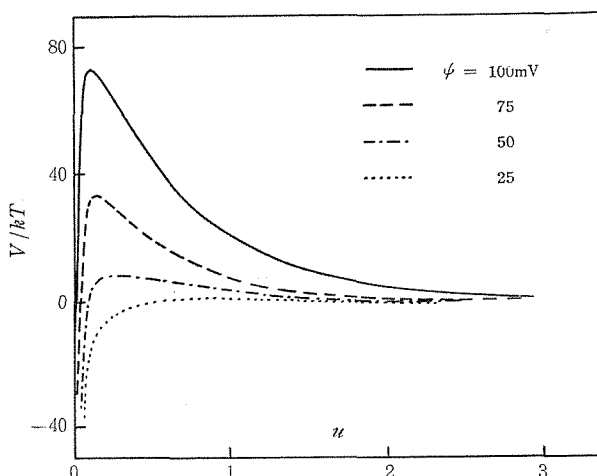


Fig. 1 Theoretical  $V/kT$  vs.  $u$  curves  
 $\tau=1.23, a=10^{-6}\text{cm}$

### (ii) Calculation of the Stability Factor

The stability factor,  $W$ , is obtained by substituting equation (26) into equation (9), viz.

$$W = 2 \int_0^{\infty} \exp \left[ \frac{\varepsilon a \psi^2}{u+2} \cdot \frac{\exp(-\tau u)}{kT} - \frac{A}{12u k T} \right] \frac{du}{(u+2)^2}. \quad (27)$$

In Fig. 2 values of  $W$  obtained by graphical integration for  $a=100 \text{ \AA}$  and  $\tau=1.23$  are plotted against  $\psi$ . However, in order to extend the theoretical treatment of the problem further it is necessary to obtain an analytical expression of  $W$ . This can be done only approximately by using the device of Reerink and Overbeek<sup>9)</sup> by writing equation (9) in a form:-

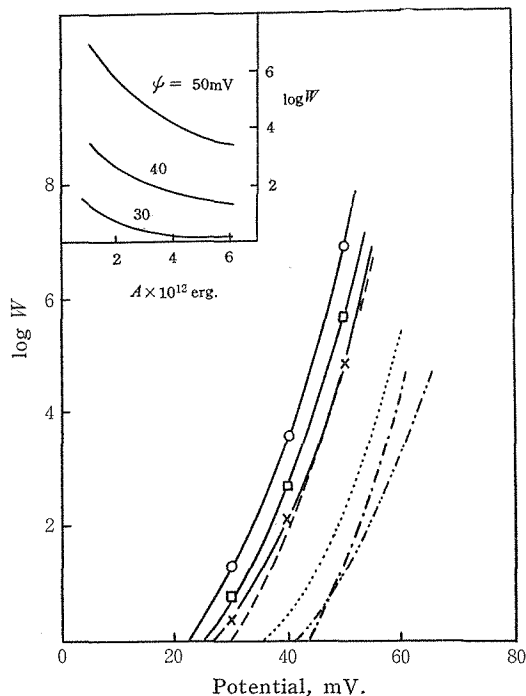


Fig. 2 Theoretical log  $W$  vs.  $\phi$  curves

- $\tau=1.23$   $\tau=3.00$   
 $\bigcirc$   $A=1 \times 10^{-12}$  erg ---  $A=1 \times 10^{-12}$  erg  
 $\square$   $2 \times 10^{-12}$  -.-.-  $3 \times 10^{-12}$   
 $\times$   $3 \times 10^{-12}$   
 ..... Graphical integration  
 -.-.- Corrected for  $\beta$

$$W = \frac{2}{(u_m + 2)^2} \int_0^{\infty} \exp(V/kT) du \tag{28}$$

This implies that the value of  $u$ ,  $u_m$ , giving the maximum  $V$ ,  $V_m$ , does not alter widely for different values of  $\psi$ , and that the value of  $V_m$  is a reasonable estimate of the stability, *vide* Fig. 1. Since  $dV/du=0$  for  $u=u_m$ , the Taylor expansion of  $V(u)$  in the neighbourhood of  $V=V_m$  gives the following series:

$$V = V_m + V_m''(\Delta u)^2/2 + \dots$$

Substitution of this formula in equation (28) with neglect of higher terms gives

$$\begin{aligned} W &= \frac{2 \exp(V_m/kT)}{(u_m + 2)^2} \int_0^{\infty} \exp[V_m''(\Delta u)^2/2 kT] du \\ &= \frac{2 \exp(V_m/kT)}{(u_m + 2)^2} \int_{-u_m}^{\infty} \exp[-p''(\Delta u)^2] d(\Delta u) \end{aligned}$$

where  $p'' = \sqrt{-V_m''/2kT}$ . Replacing the lower limit of integration by  $-\infty$  does not introduce serious errors, so we may write

$$W = [2\sqrt{\pi}/p''(u_m + 2)^2] \exp(V_m/kT) \tag{29}$$

or

$$\ln W = \ln 2\sqrt{\pi} - \ln p'' - 2 \ln (u_m + 2) + V_m/kT. \quad (29A)$$

Now, since it is clear from Fig. 1 that  $u_m$  has normally a numerical value of the order of 0.1 to 0.2, the value of  $\tau u$  is an order of magnitude smaller than 1 under the experimental condition to be given in Part 2, *i. e.*  $\tau = 1.23$ . Hence, we can introduce the following approximation in equation (26):

$$\exp(-\tau u) = 1 - \tau u,$$

and obtain by differentiation an equation, *viz.*

$$\frac{dV}{du} = -\frac{\tau \varepsilon a \phi^2}{u+2} - \frac{(1-\tau u) \varepsilon a \phi^2}{(u+2)^2} + \frac{A}{12 u^2}$$

Since  $V = V_m$  and  $dV/du = 0$  for  $u = u_m$ , we obtain

$$\left(\frac{u_m + 2}{u_m}\right)^3 = C^2 \phi^2 \quad (30)$$

$$\text{where } C^2 = 12 \varepsilon a (1 + 2\tau) / A \quad (30A)$$

and since  $u_m$  must always be positive, it depends on the sign of  $\psi$  which root of equation (30) is taken. Hence we obtain the following expressions for  $u_m$ :

$$\begin{aligned} u_m &= 2/(C\phi - 1) & \text{for } C\phi > 1 \\ \text{or } u_m &= -2/(C\phi + 1) & \text{for } C\phi < -1 \end{aligned} \quad (31)$$

where the positive root of equation (30A) is taken for the value of  $C$ . The conditions of equations (31) are satisfied either by  $\psi > 5$  or by  $\psi < -5$  mV, under the conditions of  $a = 100 \text{ \AA}$ ,  $\tau = 1.23$ ,  $\varepsilon = 80$  and  $A = 10^{-12}$  erg.

The value of  $V$  at the maximum,  $V_m$ , is given by

$$V_m = \frac{\varepsilon a \phi^2 (1 - \tau u_m)}{u_m + 2} - \frac{A}{12 u_m}$$

whence by substitution for  $u_m$  we find

$$V_m = \frac{A}{24} \left( \frac{C^2 \phi^2}{1 + 2\tau} \pm 2C\phi + 1 \right) \quad (32)$$

The second derivative of  $V$  with respect to  $u$  is given by

$$\frac{d^2 V}{du^2} = \frac{A}{6} \left[ \frac{C^2 \phi^2}{(u+2)^3} - \frac{1}{u^3} \right]$$

and its value at the maximum is given by

$$\begin{aligned} V_m'' &= -A (C\phi - 1)^4 / 48 C\phi & \text{for } C\phi > 1 \\ \text{or } &= +A (C\phi + 1)^4 / 48 C\phi & \text{for } C\phi < -1 \end{aligned} \quad (33)$$

We have therefore

$$\begin{aligned} p'' &= \frac{(C\phi - 1)^2}{4} \sqrt{\frac{A}{6 C\phi k T}} & \text{for } C\phi > 1 \\ \text{or } &= \frac{(C\phi + 1)^2}{4} \sqrt{\frac{A}{6 C\phi k T}} & \text{for } C\phi < -1 \end{aligned} \quad (33A)$$

The expression of  $\ln W$  as a function of  $\psi$  is now obtained by substituting equations (31), (32) and (33A) in equation (29A), as

$$\ln W = \frac{A}{24 kT} \left( \frac{C^2 \psi^2}{1+2\tau} - 2C\psi \right) - \frac{3}{2} \ln C\psi + B \quad \text{for } C\psi > 1$$

or

$$= \frac{A}{24 kT} \left( \frac{C^2 \psi^2}{1+2\tau} + 2C\psi \right) - \frac{3}{2} \ln (-C\psi) + B \quad \text{for } C\psi < -1, \quad (34)$$

where

$$B = (1/2) \ln (24 \pi kT) + (A/24 kT) - (1/2) \ln A \quad (35)$$

and  $C = [12 \epsilon a (1+2\tau)/A]^{1/2} \quad (36)$

The two expressions of  $\ln W$  corresponding to the conditions  $C\psi > 1$  and  $C\psi < -1$  are symmetrical with respect to  $\psi$ , and it is the absolute magnitude of  $\psi$  which is effective in coagulation processes; this is already clear from the equation (27) where  $\psi$  comes in a quadratic form. At the same time it is important to point out here that the expression in equation (34) is valid only in the range of  $C\psi$  greater than 1 or smaller than 1, or  $\psi > 5$  or  $\psi < -5$  mV, *cf.* the discussions in Part 3. We shall, therefore, restrict the following discussions only to the case of  $C\psi$  greater than 1.

The quantities which can affect  $W$  as a function of  $\psi$  are particle radius, ionic strength, dielectric constant of the medium, temperature and the value which is taken for the van der Waals constant. In Fig. 2 are given the curves of  $\log W$  *vs.*  $\psi$ , calculated from equation (34) for  $a=100 \text{ \AA}$ , for three values of  $A$  at  $\tau=1.23$  and two values of  $A$  at  $\tau=3.00$ . It can be seen that the curves are almost linear, and at the same time parallel to each others, for high values of  $\psi$ . Comparing these curves with those obtained by graphical integration of equation (27), or with the curve calculated from the exact expression using the tabulated values for interaction at constant potential<sup>9</sup>, it is concluded that, although equation (34) slightly overestimates the stability factor, it reproduces accurately the shape of the  $\log W$  *vs.*  $\psi$  curve.

It can be seen from Fig. 2 that increasing the ionic strength appears to broaden the rapid coagulation range, *i. e.* coagulation commences at a higher value of  $\psi$  for the higher  $\tau$ , and at constant  $\psi$  and  $\tau$  the effect of increasing  $A$  is to decrease stability. The effect of increasing the particle radius is to increase stability at the same  $\psi$ , and the particles of small radius is very unstable even at low  $\tau$ , and require very high values of  $\psi$  for stable sols to be formed, *vide* Verwey and Overbeek<sup>9</sup>. It is also expected that decrease in dielectric constant will decrease stability by reducing the electrostatic repulsion, *vide* equation (27), however, situations will be complicated by the fact that effects other than potential may have to be considered in the case of non-aqueous dispersions<sup>11</sup>, say lyophobic character, *etc.*

### 3. The Stern Potential as a Function of Surface Active Agent Concentration

#### (i) The Charge Distribution in the Double Layer

According to the basic principle of electrostatics, the potential distribution in space surrounding a closed surface is determined only by the surface charge (Gauß' theorem). This means that the potential distribution in the diffuse double layer is defined only by the Stern potential,  $\psi_s$ , and is independent of the difference in charge distribution in layers closer to the surface than this plane, if other conditions, such

as the ionic strength, dielectric constant *etc.*, are the same. We can conclude, therefore, that for sol particles like silver iodide the potential which is important from the point of view of stability is the Stern potential,  $\psi_s$ , rather than the surface potential,  $\psi_0$ , as far as we restrict our discussions to the cases where the mutual perturbation of the double layers of two approaching charged surfaces is negligible, *vide* Part 2.

The electrical double layer at the surface of a sol particle consists of the so called Stern plane, with potential  $\psi_s^*$  and charge density  $\sigma_s^*$ , and the Gouy diffuse double layer, with total charge of the solution column of unit cross section  $\sigma_G^*$ . If the charge density of the particle surface is  $\sigma_0$ , the electroneutrality of the system is expressed by the following equation:

$$-\sigma_0 = \sigma_s^* + \sigma_G^*, \quad (37)$$

where the quantities with asterisks refer to the original sol before addition of surface active agents. On addition of surface active agent molecules to the system, these molecules will be adsorbed in the Stern plane due to their high free energy of adsorption, thus altering the Stern potential to a value  $\psi_s$  and the charge distributions in the double layer to  $\sigma_s$  and  $\sigma_G$ . It will be shown in Part 2 that  $\sigma_0$  is defined by the initial conditions of the sol, *e. g.* for a silver iodide sol by  $p\text{Ag}$ , and does not change on adsorption of surface active ions, within the concentration range of major interest, whence

$$-\sigma_0 = \sigma_s + \sigma_G \quad (38)$$

From equations (37) and (38) we obtain the increase in charge density in the Stern plane,  $\Delta\sigma_s$ , due to adsorption, as

$$\Delta\sigma_s = \sigma_s - \sigma_s^* = \sigma_G^* - \sigma_G \quad (39)$$

On the other hand, this quantity is related to the number of surface active agent molecules adsorbed per  $\text{cm}^2$ ,  $n$ , by an equation:

$$\Delta\sigma_s = z n e \quad (40)$$

where  $z$  is the valency of the surface active ion, including the sign, and  $e$  the fundamental electronic charge.

Now from the Stern equation of adsorption, the following relation holds<sup>32)</sup>:

$$n = \frac{N_1}{1 + (1/x) \exp(\Delta\bar{G}/kT)} \quad (41)$$

where  $\Delta\bar{G}$  is the electrochemical free energy of adsorption,  $N_1$  the number of sites available per  $\text{cm}^2$  and  $x$  the mole fraction of the surface active agent. This equation is valid when the particle radius is large in relation to the size of the adsorbing molecule (approximation of plane surface) and there is no lateral interaction between the adsorbing molecules. Moreover, for high values of surface active agent concentrations second layer adsorption starts to take place and another term must be added to the right hand side of the equation, *vide* Part 2. It will be assumed in the following that  $\Delta\bar{G}$  will remain constant over the whole concentration range; however, this is not valid in rigorous sense, because it can formally be expressed as the sum of the electrical and chemical terms, *i. e.*

$$\Delta \bar{G} = z e \psi_{\delta} + \Delta G \quad (42)$$

where  $\Delta G$  is the chemical free energy of adsorption. However, the above assumption would seem to be fulfilled by the adsorption of materials such as surface active agents where  $\Delta G$  is high, provided that  $\psi_{\delta}^*$  is not too high and hence  $\Delta G \gg z e \psi_{\delta}$ .

Under the experimental conditions of major interest, the surface active agent concentration will be small ( $10^{-3}$  to  $10^{-6}$  M) and that of other ions present will also be small, whence we can take

$$x = c/55.6 \quad (43)$$

where  $c$  is the concentration of the surface active ion in mole per litre. Combining equations (40), (41) and (43) we obtain an equation of the Langmuir type<sup>33</sup>:

$$\Delta \sigma_{\delta} = \frac{z e N_1 k_2 c}{1 + k_2 c} \quad (44)$$

where  $k_2 = \exp(-\Delta \bar{G}/kT)/55.6$  (45)

### (ii) The Change in Stern Potential

For spherical particles at low values of the Stern potential,  $\psi_{\delta}$ , the charge density of the diffuse double layer,  $\sigma_{\delta}$ , is related to  $\psi_{\delta}$  by

$$\sigma_{\delta} = -(\epsilon \psi_{\delta}/4 \pi a)(1 + \tau) \quad (46)$$

whence by using equation (39) we obtain

$$\Delta \sigma_{\delta} = \frac{\epsilon}{4 \pi a (1 + \tau)} (\psi_{\delta} - \psi_{\delta}^*) \quad (47)$$

where the ionic strength and particle radius are assumed to remain constant. From equations (44) and (47) we obtain

$$\psi_{\delta} = \psi_{\delta}^* + \frac{k_1 k_2 c}{1 + k_2 c} \quad (48)$$

where

$$k_1 = \frac{4 \pi a z e N_1}{\epsilon (1 + \tau)} \quad (49)$$

which gives the relation between  $\psi_{\delta}$  and  $c$ . It is clear from the definitions of  $k_1$ , equation (49), and  $k_2$ , equation (45), that the former quantity is proportional to  $N_1$  and  $z$  and the latter gives the measure of the electrochemical free energy of adsorption,  $\Delta \bar{G}$ .

The theoretical curves of  $\sigma_{\delta}$  vs.  $c$  and  $\psi_{\delta}$  vs.  $\log c$  in Fig. 3 and 4 are obtained by using equations (44) and (48). In order that they can be compared with experimental conditions, we have put  $z = -1$ ,  $\psi_{\delta}^* = 140$  mV and  $N_1 = 1.94 \times 10^{13}$  cm<sup>-2</sup>, the value of  $1.94 \times 10^{13}$  being the average value for alkyl sulphates derived from the experiments described in Part 2. The latter curves are extremely interesting since they show that the zero point of  $\psi_{\delta}$  is shifted to lower concentrations of surface active agent with increasing  $k_2$ , that all the curves are parallel to each others and that they have a point of inflexion at the same value of  $\psi_{\delta}$ .

The zero point of  $\psi_{\delta}$ ,  $c = c^0$ , is obtained from equation (48) as

$$\psi_{\delta}^* = -k_1 k_2 c^0 / (1 + k_2 c^0)$$

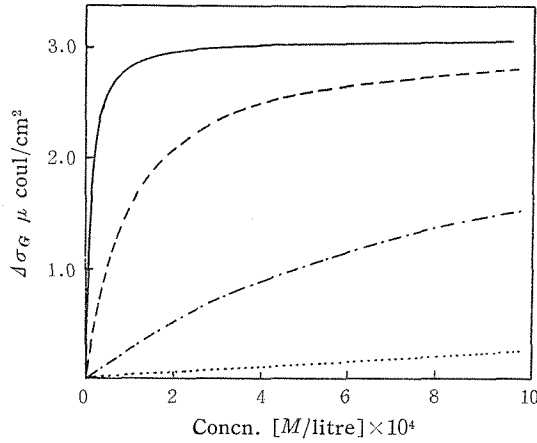


Fig. 3 Theoretical  $\Delta\sigma_G$  vs.  $c$  curves

$\tau=1.23$

$k_2=10^5$  litre/M       $k_2=10^4$  litre/M  
  $10^3$                         $10^2$

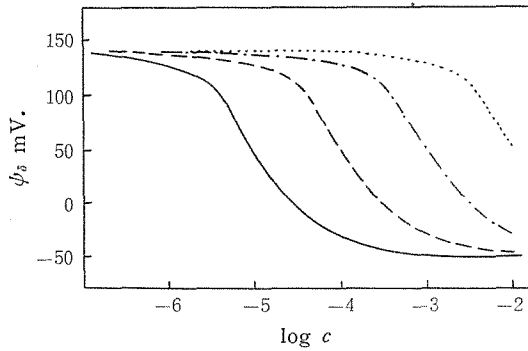


Fig. 4 Theoretical  $\psi_\delta$  vs.  $\log c$  curves

$N_1=1.94 \times 10^{13} \text{cm}^{-2}$ ,  $\tau=1.23$ ,  $a=10^{-6} \text{cm}$ .

$k_2=10^5$  litre/M       $k_2=10^4$  litre/M  
  $10^3$                         $10^2$

and hence

$$\frac{1}{c^0} = -k_2 \left( \frac{k_1}{\psi_\delta^*} + 1 \right) \quad (50)$$

This equation shows that  $c^0$  is smaller for larger value of  $k_2$ , *i.e.* for larger value of the electrochemical free energy of adsorption.

The slope of  $\psi_\delta$  vs.  $\ln c$  curve is obtained by differentiating equation (48), as

$$\frac{d\psi_\delta}{d \ln c} = \frac{k_1 k_2 c}{(1 + k_2 c)^2} \quad (51)$$

whence by combining equations (48) and (51) we obtain

$$\frac{d\psi_\delta}{d \ln c} = (\psi_\delta - \psi_\delta^*) \left[ 1 - \frac{(\psi_\delta - \psi_\delta^*)}{k_1} \right] \quad (52)$$

It is clear from this equation that the slope of the  $\psi_\delta$  vs.  $\ln c$  curve is independent

of  $k_2$ , and hence of the electrochemical free energy of adsorption, and its absolute value is larger for larger  $k_1$ , *i. e.* for larger value of the number of sites available,  $N_1$ . The slope at the zero point of  $\psi_\delta$  is given by

$$\left(\frac{d\psi_\delta}{d\ln c}\right)_{\psi_\delta=0} = -\psi_\delta^* \left(1 + \frac{\psi_\delta^*}{k_1}\right) \quad (53)$$

Equations (50) and (53) will be used in Part 2 for the evaluation of  $N_1$  and  $\Delta\bar{G}$ .

#### 4. The Stability as a Function of Surface Active Agent Concentration

##### (i) The Relation between $\ln W$ and $c$ .

The stability factor,  $W$ , can be expressed as a function of the surface active agent concentration,  $c$ , simply by substituting equation (48) in equation (34) with the assumption,  $\psi = \psi_\delta$ , *viz.*

$$\begin{aligned} \ln W = & \frac{AC^2}{24kT(1+2\tau)} \left(\psi_\delta^* + \frac{k_1 k_2 c}{1+k_2 c}\right)^2 - \frac{AC}{12kT} \left(\psi_\delta^* + \frac{k_1 k_2 c}{1+k_2 c}\right) \\ & - (3/2) \ln \left(\psi_\delta^* + \frac{k_1 k_2 c}{1+k_2 c}\right) + B - (3/2) \ln C \quad \text{for } C\psi_\delta > 1, \end{aligned} \quad (54)$$

or the corresponding equation for  $C\psi_\delta < -1$ . For coagulation of positive sols, *i. e.*  $\psi_\delta^* > 0$ , by the addition of anionic surface active agents, *i. e.*  $z < 0$  or  $k_1 < 0$ , the condition  $C\psi_\delta > 1$  or  $C\psi_\delta < -1$  can be expressed in terms of the concentration,  $c$ , as

$$\begin{aligned} c < & \frac{1 - C\psi_\delta^*}{k_2[k_1 C - (1 - C\psi_\delta^*)]} \\ \text{or} \quad c > & \frac{-(1 + C\psi_\delta^*)}{k_2[k_1 C + (1 + C\psi_\delta^*)]} \end{aligned} \quad (55)$$

In the concentration range between these two limits, the analytical expression in equation (54) breaks down and rapid coagulation occurs, *i. e.*  $\ln W = 0$ . However, within the limitations given by inequalities (55), it can be employed to compute the form of the  $\log W$  *vs.*  $c$ , or the more usual  $\log W$  *vs.*  $\log c$  curves for various values of  $k_2$ ; these are given in Fig. 5 for  $k_2$  values of  $10^5$ ,  $10^4$  and  $10^3$  using the

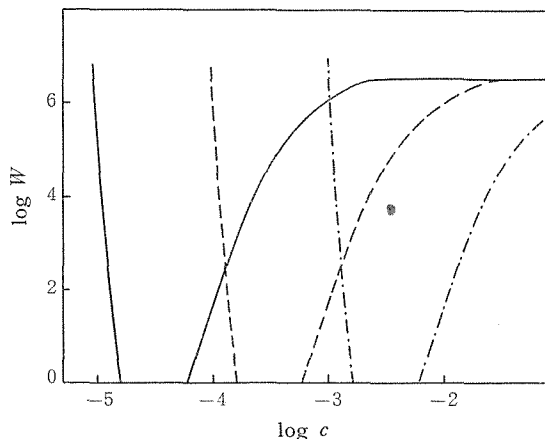


Fig. 5 Theoretical  $\log W$  *vs.*  $\log c$  curves

$\tau = 1.23$ ,  $a = 10^{-6}$  cm.

—————  $k_2 = 10^5$  litre/M    - - - - -  $k_2 = 10^4$  litre/M    - · - · - ·  $k_2 = 10^3$  litre/M



same conditions as for the calculation of Fig. 4. It can be seen that the concentration of surface active agent required to cause coagulation is determined by the values of  $k_2$ ,  $k_1$  and  $\psi_\delta^*$ , but for the same sol with different surface active agents  $k_2$  plays the most important part. The slope of the  $\log W$  vs.  $\log c$  curve is nearly constant over most of the concentration range but, under the conditions used here, the slope of the descending portion is smaller than that of the ascending portion; this is due to the fact that the point of inflexion on the  $\psi_\delta$  vs.  $\log c$  curve occurs for a positive value of  $\psi_\delta$ .

(ii) **The Initial Slope of the  $\log W$  vs.  $\log c$  Curve**

In order to see whether useful information can be obtained from the linearity of the  $\log W$  vs.  $\log c$  curve, it is of interest to work out the theoretical initial slope of this curve. For this purpose, we shall define the following function:

$$\xi = \frac{k_1 k_2 c}{\psi_\delta^* (1 + k_2 c)} \quad (56)$$

Up to the zero point of  $\psi_\delta$  this satisfies the condition  $0 < |\xi| < 1$ , and on transposing equation (54) we obtain:

$$\begin{aligned} \ln W = & \frac{A C^2 \psi_\delta^{*2}}{24 kT (1 + 2\tau)} (1 + \xi)^2 - \frac{A C \psi_\delta^*}{12 kT} (1 + \xi) \\ & - (3/2) \ln (1 + \xi) - (3/2) \ln C \psi_\delta^* + B. \end{aligned}$$

On expanding  $\ln (1 + \xi)$  and collecting terms, we obtain:

$$\ln W = P_0 + P_1 \xi + P_2 \xi^2 + P_3 \xi^3 + \dots \quad (57)$$

where

$$\begin{aligned} P_0 = & \frac{A C^2 \psi_\delta^{*2}}{24 kT (1 + 2\tau)} - \frac{A C \psi_\delta^*}{12 kT} + B - (3/2) \ln C \psi_\delta^* \\ P_1 = & \frac{A C^2 \psi_\delta^{*2}}{12 kT (1 + 2\tau)} - \frac{A C \psi_\delta^*}{12 kT} - \frac{3}{2} \\ P_2 = & \frac{A C \psi_\delta^{*2}}{24 kT (1 + 2\tau)} - \frac{3}{4} \\ P_3 = & -1/2, \quad P_4 = -3/8, \dots \end{aligned} \quad (58)$$

Hence, the slope of the  $\log W$  vs.  $\log c$  curve is given by

$$\begin{aligned} \frac{d \log W}{d \log c} = & \frac{d \ln W}{d \ln c} = \frac{d \ln W}{d \xi} \frac{d \xi}{d \ln c} \\ = & (P_1 + 2 P_2 \xi + 3 P_3 \xi^2 + \dots) \frac{k_1 k_2 c}{(1 + k_2 c)^2 \psi_\delta^*} \\ = & \frac{P_1 k_1 k_2 c}{(1 + k_2 c)^2 \psi_\delta^*} + \frac{2 P_2 k_1^2 k_2^2 c^2}{(\psi_\delta^*)^2 (1 + k_2 c)^3} + \dots \end{aligned} \quad (59)$$

It is clear from equations (57) and (58) that  $\ln W$  is uniquely determined by  $\xi$ . Since  $d \log W / d \log c$  is also a function of  $\xi$  only, it has a value which is independent of  $k_2$  for the same value of  $\xi$ . Hence, in the case of different  $k_2$  values, the slope has the same value for a given  $\log W$ , although the values of  $c$  corresponding to the same value of  $\log W$  or  $d \log W / d \log c$  are dependent on  $k_2$  (parallel transformation on  $\log c$  axis).

For  $\psi_\delta^* = 140$  mV,  $a = 100 \text{ \AA}$ ,  $\tau = 1.23$  and  $A = 10^{-12}$  erg, the values of  $P_1$  and  $P_2$

are 406.5 and 217.2 respectively, and therefore for most of the curve the cube and higher terms in equation (59) can be neglected except near the stability minimum. For the condition of  $k_2=10^5$  we find at concentrations of surface active agent of  $10^{-5}$  and  $1.5 \times 10^{-5}$   $M$  gradients of 38.3 and 17.9, respectively. The comparison with the experimental slopes will be given in Part 2.

### III. GENERALIZED THEORY OF COAGULATION

We have so far restricted our discussions to the case where the change in ionic strength was virtually negligible by the addition of coagulating agents. However, in some cases such as counter ion bindings on protected sol surfaces (Part 3), decrease in surface potential takes place accompanying the increase in ionic strength. The theory of coagulation has, therefore, been extended to include the case of both  $\psi$  and  $\tau$  changings.

#### (i) Fundamental Equation

In the most general case coagulation occurs due to changes of surface potential and ionic strength. Hence, the stability factor,  $W$ , is a function of  $\psi$  and  $\tau$ , *i. e.*

$$W = f(\psi, \tau).$$

However, the variables  $\psi$  and  $\tau$  are not independent, since both are unique functions of the concentration of the coagulating agent,  $c$ , *i. e.*

$$\psi = f_1(c) \quad \text{and} \quad \tau = f_2(c).$$

Therefore, there must be a functional relationship between  $\psi$  and  $\tau$ , *i. e.*

$$\psi = g(\tau)$$

If we take  $\tau$  as an independent variable, the slope of the  $\ln W$  vs.  $\tau$  curve is given by the following equation,

$$\frac{d \ln W}{d \tau} = \left( \frac{\partial \ln W}{\partial \tau} \right)_{\psi} + \left( \frac{\partial \ln W}{\partial \psi} \right)_{\tau} \frac{d \psi}{d \tau} \quad (60)$$

#### (ii) Calculation of $(\partial \ln W / \partial \tau)_{\psi}$ and $(\partial \ln W / \partial \psi)_{\tau}$

It is more precise to calculate these terms using the complete equation for  $W$ , and hence by using equation (26) we obtain:

$$\frac{\partial W}{\partial \tau} = \frac{\partial}{\partial \tau} \left\{ 2 \int_0^{\infty} \exp \left[ \frac{\varepsilon a \psi^2}{u+2} \cdot \frac{\exp(-\tau u)}{kT} - \frac{A}{12 u kT} \right] \frac{d u}{(u+2)^2} \right\} \quad (61)$$

$$= -2 \int_0^{\infty} \left[ \frac{\varepsilon a u \psi^2}{u+2} \cdot \frac{\exp(-\tau u)}{kT} \cdot \exp \left( \frac{\varepsilon a \psi^2}{u+2} \cdot \frac{\exp(-\tau u)}{kT} - \frac{A}{12 u kT} \right) \right] \frac{d u}{(u+2)^2} \quad (62)$$

In this manipulation interchange of integral and differential operators is permissible provided that the limits of integration are constant and the integral in equation (61) converges; this means that we must give the same restrictions on the use of equation (62) as on the use of equation (34). Now, according to the mean value theorem of integration

$$\int_a^b f(x) g(x) dx = f(\xi) \int_a^b g(x) dx$$

where  $a < \xi < b$ . Hence we obtain

$$\frac{\partial W}{\partial \tau} = - \left[ \frac{\varepsilon a u_m \phi^2}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} \right] W$$

or

$$\frac{\partial \ln W}{\partial \tau} = - \frac{\varepsilon a u_m \phi^2}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} \quad (63)$$

Here,  $u_m$  is a certain value of  $u$  which can vary between zero and plus infinity. However, as the integrand of  $W$  has a sharp maximum, see previously,  $u_m$  has the same significance as in equations (28) and (30).

In the same way we can calculate the equation for  $\partial W / \partial \psi$ :

$$\begin{aligned} \frac{\partial W}{\partial \psi} = & 2 \int_0^{\infty} \left[ \frac{2 \varepsilon a \psi}{u + 2} \cdot \frac{\exp(-\tau u)}{kT} \cdot \exp\left(\frac{\varepsilon a \phi^2}{u + 2} \cdot \frac{\exp(-\tau u)}{kT} \right. \right. \\ & \left. \left. - \frac{A}{12 u kT} \right) \right] \frac{d u}{(u + 2)^2} = \left[ \frac{2 \varepsilon a \psi}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} \right] W \end{aligned}$$

or

$$\frac{\partial \ln W}{\partial \psi} = \frac{2 \varepsilon a \psi}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} \quad (64)$$

### (iii) Calculation of $d\psi/d\tau$

The calculation of  $\psi$  for the case of asymmetric electrolytes is a difficult problem. However, for the moment we can use the following formula, *i. e.*

$$\tau = (I \cdot 10^3)^{1/2} \quad (65)$$

for  $a = 100 \text{ \AA}$ , where  $I$  is the ionic strength of the sol. This corresponds to the case of the first order Debye-Hückel approximation. The ionic strength is related to the molar concentration of the added coagulating agent,  $c$ , by the relation

$$I = (1/2) [2 p \cdot 10^{-3} + (n_+ v_+^2 + n_- v_-^2) c] = (p + q c) \cdot 10^{-3} \quad (66)$$

$$\text{where } q = (1/2) (n_+ v_+^2 + n_- v_-^2) \cdot 10^3 \quad (67)$$

Here  $p \cdot 10^{-3}$  is the ionic strength of the original sol and  $n_+$ ,  $v_+$ ,  $n_-$  and  $v_-$  are respectively the numbers and valencies of cations and anions produced by complete dissociation of one molecule of the coagulating agent. Substitution of equation (66) into equation (65) gives,

$$\tau = \sqrt{p + q c}, \quad c = (\tau^2 - p) / q \quad (68)$$

$$\text{and } d\tau / d c = q / 2 \tau \quad (68A)$$

Now, the relation between  $\psi$  and  $c$  is given by equation (48), which can be rewritten by

$$\psi - \psi^* = \frac{\theta N_1 z k_2 (\tau^2 - p)}{\{q + k_2 (\tau^2 - p)\} (1 + \tau)} \quad (69)$$

where

$$\theta = 4 \pi a e / \varepsilon. \quad \text{Hence,}$$

$$\frac{d\psi}{d\tau} = \frac{-N_1 z k_2 [(\tau^2 - p) \{q + k_2(\tau^2 - p)\} - 2\tau q(1 + \tau)]}{(1 + \tau)^2 \{q + k_2(\tau^2 - p)\}^2} \quad (70)$$

(iv) Calculation of  $d \ln W/d\tau$  as a Function of  $\tau$

Substituting equations (63), (64) and (70) into equation (60), we obtain

$$\begin{aligned} -\frac{d \ln W}{d\tau} &= \frac{\varepsilon a u_m \psi^2}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} + \frac{2 \varepsilon a \psi}{u_m + 2} \cdot \frac{\exp(-\tau u_m)}{kT} \\ &\times \frac{z N_1 k_2 \theta [(\tau^2 - p) \{q + k_2(\tau^2 - p)\} - 2\tau q(1 + \tau)]}{(1 + \tau)^2 \{q + k_2(\tau^2 - p)\}^2} \end{aligned} \quad (71)$$

Hence, by using equations (68) and (69) we obtain

$$\begin{aligned} -\frac{d \ln W}{d\tau} &= \frac{\varepsilon a \exp(-\tau u_m)}{kT(u_m + 2)} \left[ \psi^* + \frac{\theta N_1 z k_2(\tau^2 - p)}{(1 + \tau) \{q + k_2(\tau^2 - p)\}} \right] \\ &\times \left[ \left\{ \psi^* + \frac{\theta N_1 z k_2(\tau^2 - q)}{(1 + \tau) \{q + k_2(\tau^2 - p)\}} \right\} u_m \right. \\ &\left. + \frac{2\theta z N_1 k_2 [(\tau^2 - p) \{q + k_2(\tau^2 - p)\} - 2\tau q(1 + \tau)]}{(1 + \tau)^2 \{q + k_2(\tau^2 - p)\}^2} \right] \end{aligned} \quad (72)$$

This is a general relation giving the slope of the  $\ln W$  vs.  $\tau$  curve. This equation applies in principle to the coagulation of a sol whether it is caused by surface active agent adsorption, counter ion binding or compression of the double layer.

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