STRONG AND WEAK POINTS IN THE INTERPRETATION OF COLLOID STABILITY

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CONTENTS

I.   ABSTRACT

Lyophobic dispersions can be stabilized against aggregation by electrostatic repulsion or by "steric" repulsion caused by the presence of large molecules at the interfaces. Theories of colloid stability are briefly reviewed.

Strong and weak points in the present interpretations are pointed out. Two important weak points in the interpretation of electrostatic stabilization are: 1) the assumption that the zeta potential and the Stern potential are about identical, and 2) the apparent lack of influence of the particle size on the rate of slow coagulation.

A list of areas where new experiments and/or further development of theories are expected to be profitable closes the paper. In several of these areas a combination of a fluid mechanical and a colloid chemical approach is called for.

II.   INTRODUCTION

Colloids are defined as dispersed systems of a particle size (a few nm to a few μm) such that sedimentation in normal gravity plays only a minor role. In this paper, I shall limit myself to dispersions in liquids, with aqueous dispersions as the major example.

Colloid dispersions are divided into two groups. The first group, the *lyophilic colloids*, form spontaneously from the ingredients. They are thermodynamically (i.e. indefinitely) stable. Examples are: solutions of macromolecules, soap solutions in which *micelles* are formed and microemulsions. The second group, the *lyophobic colloids*, are formed in a roundabout way -- either by grinding or otherwise subdividing the dispersed material, or by allowing this material to be formed from a low molecular weight solution by controlled particle growth, which is stopped just at the "colloidal size". Examples are: gold sols, silver iodide sols, emulsions, latex, dispersed paints, India ink and photographic film. They all are thermodynamically unstable and coarsen as a consequence of the *Kelvin effect*, which makes small particles more soluble than large ones. This effect is often referred to as *Ostwald ripening*. But even if the solubility is very low and Ostwald ripening is negligible, the particles tend to aggregate, coagulate or flocculate, unless there is a repulsion mechanism sufficiently strong to keep the particles apart. *Colloid stability* is usually understood as stability against this type of aggregation.

The tendency to aggregation is due to the very general *van der Waals attraction* between the particles: it has a fairly long range. The repulsion necessary to counteract this attraction is given either by an electric charge on the particles or rather (on account of electroneutrality) by an *electric double layer* of sufficient strength and extension, *or* by a layer of *adsorbed* or chemically bound *large molecules*.

The electrostatic repulsion between the particles is very sensitive to the electrolyte content of the medium. This phenomenon shows most strikingly in the fact that all electrically stabilized colloids coagulate at a fairly sharp electrolyte concentration -- the critical coagulation concentration (c.c.c.). This c.c.c. is almost completely determined by the charge number of the counterions (ions with a charge opposite in sign to the particle charge). Counterions of high charge number coagulate at a much lower concentration than those of lower charge number. Specific properties of the counterions and the charge number and specificity of the co-ions play only a minor role. The charge of the particles and the specific nature of particles and medium do have an influence on the c.c.c.

The typical influence of the charge number of the ions is known as the rule of Schulze (ref. 1) and Hardy (ref. 2). Tables 1 and 2 give an illustration of these facts.

The stabilization of dispersions by adsorbed (or bound) large molecules was originally known as *protective action*, since it protects against coagulation by electrolyte. The original *protective colloids* were polyelectrolytes such as proteins or gums. The stabilizing effect, however, is much wider. Suitable large molecules can protect nearly any dispersed material in any solvent. Suitability requires that the greater part of the molecule is compatible with (soluble in) the solvent, but at the same time sufficient adsorption or binding to the particles should be present.

TABLE 1

Critical coagulation concentrations in millimol/l.
c_z is the average c.c.c. for counterions with charge number z.

AgI(negat.)			As$_2$S$_3$(negat.) ($= Al_2O_3$(posit.))			Au(negat.)				
z	c_z	c_1/c_z	z	c_z	c_1/c_z	z	c_z	c_1/c_z	z	z^6
1	142	1	1	55	1	1	24	1	1	1
2	2.43	58	2	0.68	80	2	0.38	63	2	64
3	0.068	2090	3	0.09	610	3	0.006	4000	3	729

TABLE 2

Critical coagulation concentration in millimol/l- As$_2$S$_3$-sol; specific effects

c.c.c		c.c.c		c.c.c.		c.c.c.		c.c.c.	
LiCl	58	KNO$_3$	50	MgCl$_2$	0.72	SrCl$_2$	0.635	UO$_2$(NO$_3$)$_2$	0.64
NaCl	51	½ K$_2$SO$_4$	65.5	MgSO$_4$	0.81	BaCl$_2$	0.69		
KCl	49.5	HCl	31	CaCl$_2$	0.65	ZnCl$_2$	0.685		

III. THEORY OF ELECTROSTATIC STABILIZATION

In the 1930's the idea was born that van der Waals forces were the cause of the attraction between colloid particles (ref. 4,5) and the relation between the force (or potential energy) and size, shape and distance of the particles was worked out by Hamaker (ref. 6). The absolute value of the van der Waals-Hamaker attraction was, however, only known as to its order of magnitude. This situation improved after Lifshitz (ref. 7) formulated a continuum theory of dispersion forces based upon the dielectric properties of the bulk material rather than upon the additivity of the forces between pairs of molecules or ions. Parsegian, Ninham (ref. 8) and others (ref. 9, 10) have shown how reliable numerical values for the Lifshitz interaction can be derived from the usually rather limited data on the dielectric permittivity (or the index of refraction) as a function of the frequency.

In the 1940's Derjaguin and Landau (ref. 11) and Verwey and Overbeek (ref. 12) calculated the electrostatic repulsion between particles on the basis of the interaction betweeen two double layers and, combining electrostatic repulsion and van der Waals attraction, formulated a theory of colloid stability.

The essence of this theory is that the attraction falls off as an inverse power of the distance and is nearly independent of the electrolyte content of the medium, whereas the electrostatic repulsion falls off exponentially with a range equal to the Debye and Hückel (ref. 13) thickness ($1/\kappa$) of the ionic atmosphere. The increase of κ with charge number, z, and concentration, c, of the electrolyte is ultimately responsible for the Schulze-Hardy behavior ($\kappa^2 \sim cz^2$). We briefly repeat the equations of what is often called the DLVO theory.

We consider the free energy of interaction between two spheres with radius a at a distance H between their surfaces as shown in Figure 1. Hamaker (ref. 6) gave the exact equation for the van der Waals attraction, V_A, assuming that the London-van der Waals attraction energy between two molecules at a distance, r, is:

$$V_{London} = -\lambda/r^6 \, , \tag{1}$$

writing A for $A = \pi^2 q^2 \lambda$, where q is the number of molecules per unit volume, and assuming strict additivity for all pair interactions.

$$V_A = -\frac{A}{6}\left[\frac{2a^2}{4aH + H^2} + \frac{2a^2}{(2a+H)^2} + \ln\frac{4\,aH + H^2}{(2a+H)^2}\right] \, . \tag{2}$$

For short distances, $H/a < 1$, this expression can be approximated by:

$$V_A = -\frac{Aa}{12H} \text{ or better } V_A = -\frac{A}{12}\left(\frac{L}{H} + 2\,\ln\frac{H}{L}\right) \, , \tag{3}$$

where $L = a + 3H/4$. Typical values for A for particles in water are:

A = 0.3 – 1 x 10^{-20} J for hydrocarbon particles

A = 0.5 – 5 x 10^{-20} J for oxides, halides

A = 5 – 30 x 10^{-20} J for metal particles.

In the above equations, retardation of the dispersion forces is neglected; certainly a good approximation for small particles ($a < 20$ nm), but more questionable for particles above $a = 100$ nm.

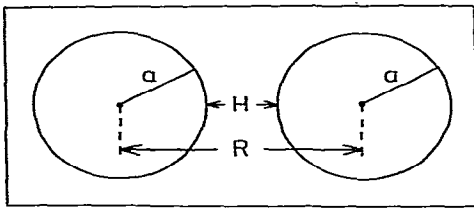Fig. 1. Two spheres with radius a at a distance R between the centers. $H = R - 2a$.

A good approximation for the free energy of electrostatic repulsion, V_R, (there is no exact equation) is:

$$V_R = 2\pi\epsilon_r\epsilon_0 a\left[\frac{4RT}{zF}\gamma\right]^2\ln\left(1 + \exp(-\kappa H)\right) \, , \tag{4}$$

where $\gamma = \tanh\,(zF\phi_{surf}/4RT)$ and ϵ_r is the relative permittivity (dielectric constant) of the medium, ϵ_o the permittivity of the vacuum, z the charge number of the counterions, R,T and F have their usual meaning ($4RT/F = 102.8$ mV at 25°C), ϕ_{surf} is the potential at the surface of the particle and:

$$\kappa^2 = \frac{F^2 \Sigma c_i z_i}{\epsilon_r \epsilon_o RT}\quad ,\tag{5}$$

where z_i and c_i are the charge numbers and concentrations of all ions in the solution. Eq. 4 can be further approximated by replacing $\ln\left[1+\exp(-\kappa H)\right]$ by $\exp(-\kappa H)$. By combining the free energies of attraction and repulsion to the total free energy of interaction, we obtain curves which in the general case show a minimum at large separation (attraction prevails), a maximum (barrier against contact) at intermediate distances and another minimum near contact, where the van der Waals attraction is counteracted by the Born repulsion. The two minima are called secondary and primary minimum, respectively, as shown in Figure 2. Increasing the electrolyte concentration increases κ and decreases the range of the electrostatic repulsion until the barrier disappears and the c.c.c. is reached.
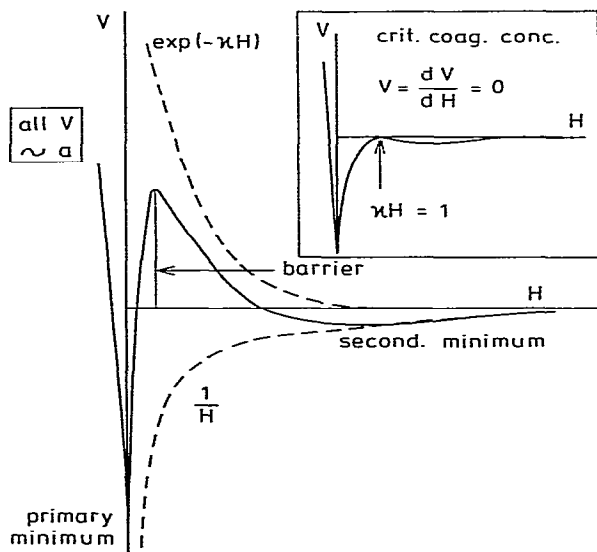

Fig. 2. Total free energy of interaction between two spherical particles. Inset: situation at the c.c.c.

From the conditions:

$$V = V_A + V_R = 0;\qquad dV/dH = 0\tag{6}$$

applied to the combination of the approximated Eqs. 3 and 4, we easily find that $\kappa H = 1$ and thus:

$$V = 0 = -\frac{A\sigma\kappa}{12} + 2\pi\varepsilon_r\varepsilon_0\kappa\left(\frac{4RT}{F}\right)^2\left(\frac{\gamma}{z}\right)^2\exp(-1) \; , \tag{7}$$

or:

$$\kappa z^2 = 24\pi\varepsilon_r\varepsilon_0(4RT/F)^2 \, e^{-1} \, \gamma^2/A \; ; \tag{8}$$

or with Eq. 5 for κ and specializing to a symmetrical $z-z$ electrolyte:

$$c.c.c. = \text{const.} \; \frac{\gamma^4}{A^2 z^6} \; . \tag{9}$$

If the *surface potential*, φ_{surf}, is *high* ($z\varphi_{surf} \gg 100$ mV) $\gamma \approx 1$ and the coagulation concentration appears to be proportional to z^{-6} (in reasonable agreement with the data of Table 1). If, however, the *surface potential* is *low*, the tanh may be replaced by its argument and:

$$c.c.c. = \text{const.} \; \frac{\varphi_{surf}^4}{A^2 z^2} \; . \tag{10}$$

The constants in Eqs. 9 and 10 contain only known quantities. They are proportional to ε_r^3, which explains (at least partly) why the c.c.c.'s in the lower alcohols and acetone and their mixtures with water usually are so much lower than c.c.c.'s in water. Another effect contributing to such low c.c.c.'s is incomplete dissociation in the double layer, leading to low surface potentials (ref. 14).

Eq. 4 has been derived on the assumption that the surface potential is constant during the approach of the particles. Therefore, Eqs. 9 and 10 also include that assumption. In several cases, however, the surface charge density, σ, rather than the surface potential will be constant. This assumption does not affect our conclusion that the c.c.c. is proportional to z^{-6} when φ_{surf} and thus σ are high. But for low surface charge Eq. 10 has to be somewhat modified (ref. 15), leading to a stronger change of the c.c.c. than with z^{-2} (but not very much stronger -- say $z^{-2.5}$ or z^{-3}).

A sensitive test of theories of colloid stability is given by confrontation with experiments on slow coagulation.

Smoluchowski's (ref. 16) theory of rapid coagulation considered as a diffusion controlled bimolecular reaction, and as recently modified by Spielman (ref. 17) and by Honig, Roebersen and Wiersema (ref. 18), has been well confirmed by experiment (ref. 19). If an energy barrier as drawn in Figure 2 is present, the coagulation is slowed down by a factor W given in a first approximation by (cf. ref. 18 for a more accurate equation).

$$\omega = 2a \int_0^\infty \frac{\exp(V/kT)}{(2a+H)^2}\, dH \;.$$ (11)

The value of the integral is mainly determined by the values of V in and around the maximum. Since V is the difference between the attraction term V_A and the repulsion term V_R and V_R is sensitive to the electrolyte concentration, V and thus ω is quite sensitive to the concentration and charge number of the electrolyte.

Approximate equations (confirmed by more accurate numerical work) show that below the c.c.c. log ω increases steeply and nearly linearly with decreasing log c and that -- other parameters being equal -- d log ω/d log c is proportional to the radius of the particles.

Figure 3 (taken from ref. 20) gives the theoretical log ω - log c curves for charge numbers 1 and 2. Figure 4 shows how well the general aspects of the theory are confirmed by early experiments (ref. 21).
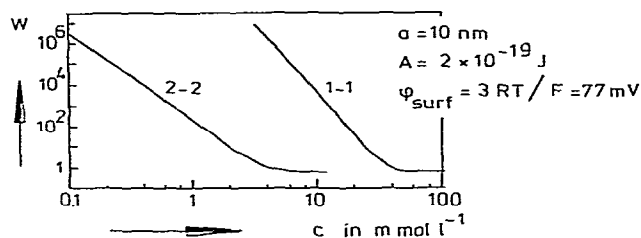

Fig. 3. Slow coagulation factor ω as a function of the electrolyte concentration according to Eq. 11 with $V = V_A$ (Eq. 2) + V_R (Eq. 4).
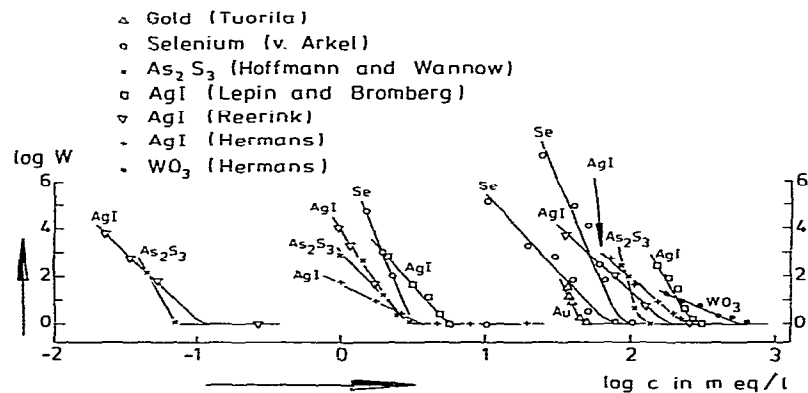

Fig. 4. Rates of slow and of rapid coagulation, plotted as log ω against the logarithm of the electrolyte concentration according to various experiments. The three groups of curves relate to charge numbers 3, 2, 1 of the counterions.

Up to this point we seem to have an attractive theory, in reasonable agreement with the experimental situation. However, when we look more closely, we find a number of points of disagreement between theory and experiment or points where the theory contains intrinsic weaknesses; that, of course, is just the kind of situation in which science may make progress.

IV.   STRONG POINTS IN THE THEORY OF ELECTROSTATIC STABILIZATION

1. The origin of the charge on the particles is well understood. It may be due to adsorption of potential determining ions (lattice ions) or electrons (in the case of redox systems), or to adsorption of specific ions (such as larger organic ions, amphiphilic ions) or to electrolytic dissociation of surface groups. Moreover, quite often the charge can be measured by titration.

2. The Schulze-Hardy behavior follows from compression of the double layer (effect of κ) and strong influence of z in the Boltzmann term $\exp(\pm z F \phi / RT)$.

3. The c.c.c. is rather sharp because a small change in the concentration easily changes the potential barrier by a few times kT.

4. Experimental coagulation concentrations require certain values ϕ_{surf} and A These required values agree roughly with directly measured values and with values found from soap films, Schiller layers and even electrokinetic (ζ) potentials.

5. The slopes d log W/d log c have correct order of magnitude (say 5 - 20).

V.   WEAK POINTS IN THE THEORY OF ELECTROSTATIC STABILIZATION

1. The repulsion equation (Eq. 4) is based on the double layer theory in which the ions are treated as point charges. This treatment is not correct since it allows the ions to reach impossibly high concentrations. This effect manifests itself first at the interface between particles and dispersion medium. Already in 1924 Stern (ref. 22) proposed to consider the part of the double layer immediately adjacent to the interface as a "molecular condenser", with a thickness, d, of a few Ångstrom units and a relative dielectric constant of about 10 in aqueous solutions. The remaining part of the double layer may then be described with ions behaving as point charges (see Figure 5). Although Stern's theory works and allows a good interpretation of $\phi_{surface}$ vs. σ relations (where these are available), the introduction of two adaptable parameters ($\epsilon, \underline{d}$) is a serious drawback. In the stability theory, ϕ_{surf} now has to be replaced by ϕ_d, the potential at the Stern plane (liquid side of the molecular condenser). The repulsion acts across a distance ($H - 2d$) rather than H, making the theory of interaction more complicated and much less *a priori*.

2. A further serious consequence of the Stern-Gouy model is the fact that under coagulation conditions, ϕ_d is neither high nor indepedendent of the concentration and the charge number of the ions; thus the interpretation of the Schulze-Hardy rule by the factor z^6 of Eq. 9 is almost certainly not correct. Remarkably enough,
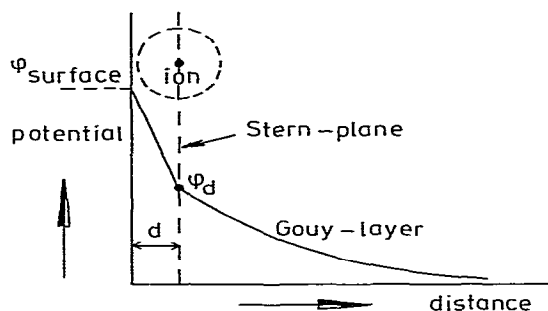
Fig. 5. Stern-Gouy model of the double layer. The Stern layer (thickness d) forms a molecular condenser; the Gouy layer (or Gouy-Chapman [ref. 23, 24] layer) forms the diffuse double layer. The thickness of the Stern layer is determined by the size of the solvated counterions.

if we replace Eq. 9 by its approximation for low surface potentials and if we write φ_d instead of $\varphi_{surface}$, we find for the critical coagulation condition:

$$\frac{\varphi_d^2}{c} = \text{constant} \times A \quad , \tag{12}$$

which very much resembles an equation:

$$\frac{c^2}{c} = \text{constant} \tag{13}$$

proposed already in 1936 by Eilers and Korff (ref. 25) based mainly on dimensional considerations. Unfortunately, although Eq. 13 is confirmed in some experiments (but not in all cases), it gives no clue at which concentration c^2/c reaches its critical value; thus it is not suitable as a theory for the c.c.c.

In order to explain the Schulze-Hardy rule at the low values of φ_d resulting from the Stern-Gouy model for the double layer, it appears to be necessary to assume that counterions are fairly strongly adsorbed in the Stern layer and that the corresponding adsorption potential increases markedly with the charge number z, but is nearly independent of the specific nature of the ions (ref. 26, 27) (somewhat like the formation of Bjerrum's ion pairs, ref. 28).

3. Although the surface charge can often be measured, the surface potential (and especially the Stern potential, φ_d) is not easily accessible because part of the surface charge may be neutralized within the Stern layer. The electro-kinetic zeta potential is good as a first approximation for φ_d, but probably not better than that (cf. Lyklema, ref. 29, for the case of AgI with monovalent counterions).

4. The expected increase of d log W/d log c with the radius a is not confirmed by the few experiments on this relation (ref. 30, 31, 32). It is not clear at

this moment whether this discrepancy is due to the experiments (particles not spherical, ref. 30, particle surface not smooth enough, ref. 31) or whether a serious flaw of the theory shows here.

5. The simple model with the deep primary minimum shown in Figure 2 would make coagulation quite irreversible and would not allow repeptization. However, as shown (among others) by Frens (ref. 15, 33), repeptization is the rule rather than the exception and irreversibility is found only after the particles have been coagulated for some time. Repeptization can only be understood if the coagulated particles remain separated by a few Ångstrom units. Unfortunately, this assumption introduces another *ad hoc* parameter in the theory.

6. Time effects due to various relaxation processes in the double layer (ref. 15, 33, 34) have been considered on an *ad hoc* basis instead of being really incorporated in the theory. These effects are important since the time of an individual collision and even the characteristic coagulation time may be shorter than the relaxation time for charge adjustment at the surface (ref. 35).

7. The recently acquired insight in "structural forces" due to the modification of the liquid structure near interfaces (ref. 36, 37) should be incorporated into the theory of interaction, but the quantitative aspects are still too vague for this purpose.

VI. STERIC STABILIZATION (PROTECTIVE ACTION)

The principles of steric stabilization are well understood. After a first primitive theory by Mackor and van der Waals (ref. 38), many authors (of whom we name only two -- Napper [ref. 39] and Hesselink [ref. 40]) have contributed to the theory. The repulsion between two layers of large molecules adsorbed on or bound to the particle surface is due to two effects, as illustrated in Figure 6.
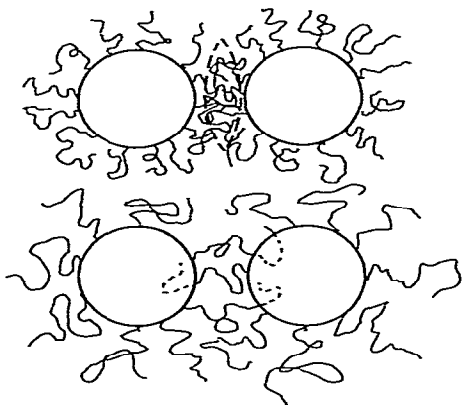

Fig. 6. Schematic pictures of two pairs of particles covered with long chains; upper pair: osmotic effect due to high concentration in region within dotted lines; lower pair: volume restriction effect -- the chains are so long that some of the normal conformations are excluded by the presence of the other particle.

When the two layers come so close together that the outer parts of the molecules start to overlap, this phenomenon is equivalent to a local increase in concentration and, *in a good solvent*, constitutes an increase of the free energy; this effect has been called *osmotic effect*. Even forgetting this overlap, the molecules lose some of their conformational possibilities if the gap between the particles gets too narrow (a second cause for an increase in free energy), which has been called *volume restriction effect*. As a rule, the osmotic effect is the more important one, but near theta conditions, where the osmotic effect is small, the volume restriction effect may predominate.

Quantitative theories have been based on polymer chains sticking out in the form of *loops* or *tails* from the surface. The repulsion appears to be steep and strong so that no primary minimum occurs unless the adsorption is very weak.

Coagulation occurs by lowering the "solubility" of the chains to theta conditions or worse. After restoring the solubility, repeptization occurs.

Polymers with at least two groups (e.g. one at both ends of the chain) that can be adsorbed may lead to *bridging* (especially at low polymer/particle concentration ratio), resulting in so called *sensitized flocculation* (ref. 41). Additional dissolved (but not adsorbed) polymer may cause flocculation since both the volume restriction and the osmotic effect will tend to push the dissolved polymer away from the gap between particles, thus leading to an effective attraction (ref. 42, 43, 44).

VII. STERIC STABILIZATION, STRONG POINTS

1. Coagulation occurs in fact at or near theta conditions for the protecting chains.

2. The same macromolecules may cause protection at high concentration and sensitization at low concentration.

3. The prediction of phase separation or reversible flocculation by dissolved polymers is confirmed in experiments. As expected, the higher the molecular weight of the polymer, the lower the concentration (mass/volume) at which phase separation is seen (ref. 44).

VIII. STERIC STABILIZATION, WEAK POINTS

1. In the present state of the theory, quantitative applicability is limited. How much adsorption is needed? What is the optimum, minimum molecular weight or chain length for effective protection?

2. Adsorption is obviously a key factor in the protection mechanism, but adsorbability is hard to predict.

IX. WHAT TO DO ABOUT THE WEAK POINTS

To begin with, I want to establish that there are so many strong points in our interpretation of colloid stability that we are very likely on the right track. The weak points show where we have to refine and improve our theories.

I will mention now a few areas where more work might generate new insights. I hope that some of these suggestions will be taken up in our discussions.

1. The Stern correction (both ϕ_d and d itself) should be incorporated more routinely in our interpretations; or better still, the influence of the size of the ions and the discreteness of the surface charge should be accounted for in the double layer theory without introducing adjustable parameters.

2. It will be very important to establish the relation between ζ and ϕ_d on a sound experimental and theoretical basis; or (perhaps better) the relation between the electrokinetic mobility and the structure of the outer parts of the double layer that are most involved in the interaction of two double layers. Fluid dynamicists might help the colloid chemists in this area.

3. We need more and better experiments on the influence of the particle size on d log W/d log c, preferably with hard, highly charged particles rather than with latex with a low charge density and possibly a fuzzy surface.

4. In view of the possible interpretation of the Schulze-Hardy rule as partly due to ion pair formation, experiments and theories on ion pairs at an interface are called for.

5. Repeptization is a neglected experimental tool. It can give information on the innermost parts of the double layer and possibly on time effects occurring in seconds and longer times.

6. The various time effects should be incorporated more routinely in the theory.

7. One of the nice aspects of the simple DLVO theory is the fact that stability is governed by the interaction at distances larger than the barrier distance, and that the exact shape of the interaction at shorter distances is relatively unimportant, except with repeptization. Now, where do *structural forces* affect this picture essentially? Only in repeptization? Or is their range comparable to the Debye-Hückel length at coagulation, so that they have a direct influence on some of the c.c.c.'s?

8. New information on concentrated suspensions (and emulsions) is rapidly becoming available. It contains important information on the interaction between particles. I am thinking of light scattering work by Vrij and coworkers (ref. 45) and by others. Phase separation in such suspensions is another source of information (ref. 46). Finally, rheology of concentrated suspensions should be a further field where interactions between particles show up.

9. Flocculation and deflocculation in shear fields and the establishment of a stationary state of particle flocculation is expected to teach us something about interactions.

So far, most of these suggestions refer to electrostatically stabilized systems, but the above numbers 7, 8 and 9 can also be applied to sterically stabilized systems. Moreover, there is a clear need for better experimental data on the influence of the molecular weight of the protecting chains and the amount of adsorption on the stability of sterically stabilized suspensions.

I want to end with an optimistic note. A great deal of exciting new work is going on, both experimentally and in the theoretical field and my weak points may be converted to strong points in the not-too-distant future.

A very last remark -- suspensions and emulsions are widely applied, quite often in highly concentrated form. With the new techniques for investigating concentrated systems, pure science and application get closer to one another, one may hope to the advantage of both.

X.   ACKNOWLEDGEMENT

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