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898
898

HOW COLLOID STABILITY AFFECTS THE BEHAVIOR OF SUSPENSIONS

by

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TABLE OF CONTENTS

Objectives

Prerequisites

Abstract

Introduction

Colloid Stability

- Sedimentation
- Electrodeposition
- Rheology
- Non-aqueous Media

Theory of Colloid Stability

- Van der Waals Attraction
- Electrostatic Repulsion
- Effects of Large Molecules
- Structural Forces

Kinetic Effects in Colloid Stability

Repeptization

Thermodynamic Stability

Conclusions

Acknowledgments

Self-Test

References

10. Skills and Knowledge Taught - Upon completion of this module the student should be able to: describe what is meant by the term colloid stability; discuss the main interactions that determine colloid stability and how they are affected by electrolytes and adsorbable large molecules; and describe how these forces affect mechanical and rheological properties of suspensions and sediments formed from suspensions.

11. Prerequisites - Completion of: general physics and chemistry (sophomore level).

12. Nearest Neighbor Links - The Science of the Interactions of Colloidal Particles and Ceramics Processing, Alan Bleier, JME 7(3); Interfacial Electrochemistry of Disperse Systems, J. Lyklema, JME 7(2):205.

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Objectives

Upon completion of this module, the student should know what is understood by the term colloid stability, and what the main interactions are that determine colloid stability and how they are affected by electrolytes and adsorbable large molecules. Finally, he/she should understand how these forces affect mechanical and rheological properties of suspensions and sediments formed from suspensions.

Prerequisites

Completion of general physics and physical chemistry at sophomore level.

HOW COLLOID STABILITY AFFECTS THE BEHAVIOR OF SUSPENSIONS

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Abstract

The stability of hydrophobic colloids towards added electrolytes, the valence rule of Schulze and Hardy, protective action and sensitization by large molecules are briefly treated. Sedimentation, the nature of the sediments, electrodeposition, and rheology are used to illustrate the difference in behavior between stable and unstable suspensions. The theoretical interpretation of stability is based on Van der Waals attraction, electrostatic repulsion and on the interaction of dissolved and adsorbed long chains ('hairy particles'). The rate of coagulation, repeptization and the possibility of thermodynamic stability are considered.

Introduction

The behavior of suspensions and emulsions during handling or even when left on the shelf is strongly affected by the interaction between the particles. These interactions are fairly well understood. If they are mainly repulsive, and if the suspended particles are small, the system does not change with time and is called colloidally stable. If, however, attraction between the

particles prevails, the particles agglomerate, the suspension flocculates (= coagulates) and macroscopic phase separation results rapidly.

Colloid Stability

These phenomena have been studied extensively with—usually aqueous--colloidal suspensions (called sols) in which the individual particles are so small that they show no sedimentation. Such particles may be formed by mixing two fairly dilute aqueous solutions so that a large number of nuclei are formed and consequently the particles remain small. The formation of a silver iodide sol by mixing $AgNO_3$ and KI solutions is an example.

$$AgNO_3 + KI \longrightarrow AgI + KNO_3 \qquad (1)$$

Contaminating electrolytes, such as KNO_3 in the above example, may be removed by dialysis. The particles are electrically charged by the adsorption of ions, e.g., Ag^+ or I^- and the formation of an electric double layer as discussed by Lyklema (1). Sols coagulate after addition of electrolyte, any electrolyte, to a critical coagulation concentration (c.c.c.), actually a narrow concentration range. The main factor determining the c.c.c. is the charge number of the ions, which are oppositely charged to the particles. This regularity has been known as the Schulze-Hardy rule (2,3). The c.c.c.'s are roughly 100 mM, 1 mM, 0.1 mM for counterions with charge number z = 1, 2, and 3 respectively, as shown in Table 1. Exceptions to the Schulze-Hardy rule occur with ions that are strongly adsorbed or that give rise to chemical reactions or precipitations.

It further appears that coagulation can be prevented by the addition and adsorption of small amounts of large molecules, e.g., gelatin, gums. This is called protective action. A very old example is India ink, which is a suspension of soot in water, stabilized by gum. In many cases protective substances added in amounts too small to give protection sensitize the suspension, i.e., make it more easily flocculable.

TABLE 1
Critical Coagulation Concentrations (4) in m mole/liter

As_2S_3-sol Negatively Charged		AgI-sol Negatively Charged		Fe_2O_3-sol Positively Charged	
LiCl	58	$NaNO_3$	140	NaCl	9.25
NaCl	51	KNO_3	136	$1/2BaCl_2$	9.65
KNO_3	50	$RbNO_3$	126	KNO_3	12
$MgCl_2$	0.72	$Ca(NO_3)_2$	2.40	K_2SO_4	0.205
$MgSO_4$	0.81	$Ba(NO_3)_2$	2.26	$MgSo_4$	0.22
$ZnCl_2$	0.69	$UO_2(NO_3)_2$	3.15	$K_2Cr_2O_7$	0.195
$AlCl_3$	0.093	$Al(NO_3)_3$	0.067		
$1/2(Al)_2(SO_4)_3$	0.096	$La(NO_3)_3$	0.069		
$Ce(NO_3)_3$	0.080	$Ce(NO_3)_3$	0.069		

Sedimentation

If the particles are larger (diameter > 1 μm) than in typical colloids (diameter < 0.1 μm) the difference in rate of sedimentation between stable and flocculating systems is less pronounced but there is a pronounced difference in the behavior of the sediments.

Stable suspensions sediment rather slowly, with a fuzzy boundary between supernatant and sedimenting suspension because the particles sediment individually with speeds varying according to their sizes. The sediment is very compact since the particles can glide along one another until the packing is as dense as possible. Such a sediment makes redispersion difficult and time-consuming. It is a well-known nuisance in a paint which is too well stabilized and has stood too long on the shelf.

If attraction prevails, the suspension coagulates while sedimenting. The sedimentation is faster. The boundary between supernatant and suspension is sharp, since the smaller particles are also caught in the flocs

and sediment together with the larger ones. The final sediment is open. If the particles are not too small they can be easily redispersed by shaking or stirring. A little attraction leading to weak flocculation is good for shelf life. Figure 1, which illustrates this difference, also shows that a soil for agriculture must be flocculated, since it must allow easy passage of water and air.

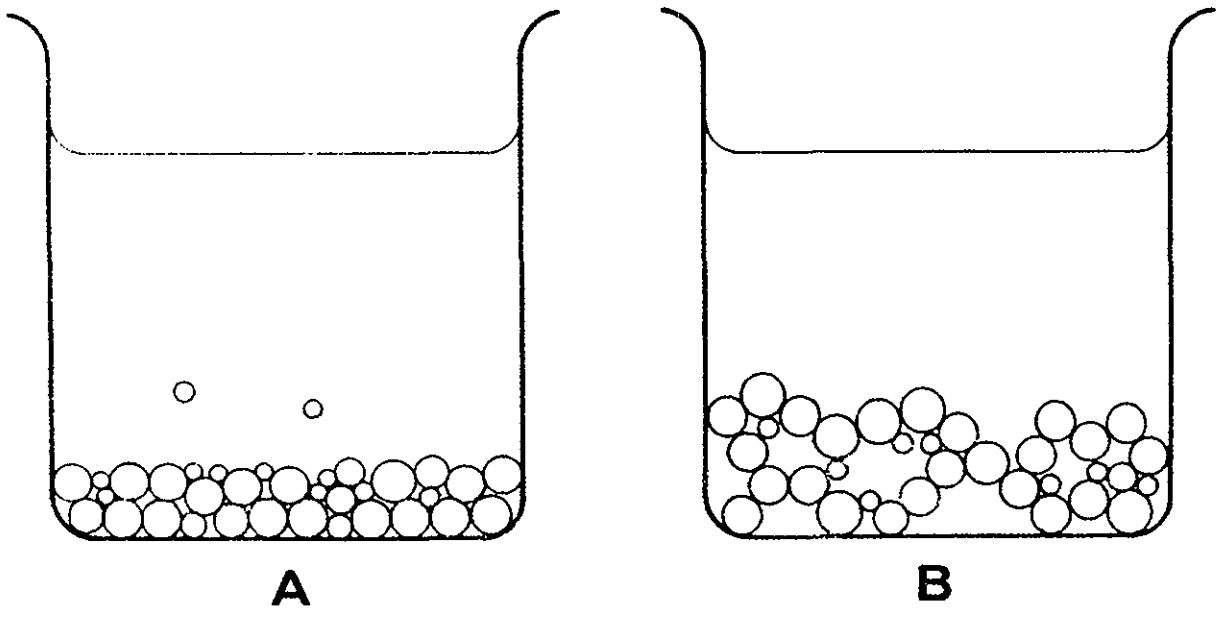

FIG. 1

Structure of sediments. (A) Compact sediment from stable suspension. (B) Loose sediment from flocculated suspension.

Electrodeposition

Since the particles are charged they can be transported towards an electrode by the application of an electric field, just as gravity transports them towards the bottom of the vessel. This process, called electrodeposition, has found important industrial applications, one of them being the painting of car bodies from a suspension. The particles which are in stable

suspension are concentrated in a compact layer (c.f., Fig. 1A) at the electrode, and since the deposited layer has a high electrical resistance, open areas are covered preferentially. The layer becomes quite homogeneous, covers nooks and crevices and even the back side of the electrode. But, building this compact layer is not enough. The particles still repel each other, the layer, although viscous, is still fluid and tends to flow off the electrode. But now the electrode reaction, leading to electrolyte being formed, comes to help. The electrolyte concentration increases just at the electrode and coagulates the concentrated suspension in situ (5). Electrodeposition is a unique way to prepare, in a single step, a layer that is compact and at the same time coagulated.

Rheology

At low rates of shear, dilute stable suspensions show Newtonian behavior, i.e., their viscosity is independent of the shear rate. The viscosity is increased above that of the solvent with a term proportional to the concentration of particles, as shown in Eq. (2);

$$\eta_s = \eta_o(1 + f.\phi_p) \qquad (2)$$

where η_s is the viscosity of the suspension, η_o that of the dispersion medium, ϕ_p the volume fraction of the particles and f a factor, which is 2.5 for spheres [Einstein (6)] and larger for non-spherical particles (7,8). At higher concentrations the viscosity goes up faster than as described by Eq. (2) and becomes extremely high when close packing is approached. Semi-empirical extensions of Eq. (2) often contain a term $(1-\phi_p/\phi_{max})^{-1}$ where ϕ_{max} is the volume fraction at which the viscosity goes to infinity (9,10). An extra complication is shown by suspensions of monodisperse spheres at high concentrations, where they form an ordered quasi crystalline state (9,11,12).

If the particles are charged, an extra increase of the viscosity occurs. There are three of these electroviscous effects. The first one was already

recognized by Smoluchowski (13). The theory, improved by Booth (14) is based upon the dissipation in the double layer in the field of shear. The second one (9,10,15) is due to the electrostatic repulsion between particles, when they pass close to each other in the shear field. The third effect occurs with flexible polyelectrolyte ions and is due to the stretching of these ions caused by the mutual repulsion of their charges.

Exact theoretical expressions for the viscosity of concentrated suspensions, even for monodispersed spherical particles are still lacking because the various interactions, such as the impenetrability of the particles (hard sphere effects), the mutual electrostatic repulsion and the hydrodynamic (16-19) interactions are difficult to evaluate. Moreover, when the particles are small, Brownian motion has to be taken into account, in particular for non-spherical particles and aggregates.

At high rates of shear two completely different effects are observed. At moderate concentrations small but elongated particles show shear thinning when the shear overcomes the randomizing effect of Brownian motion and the particles stay relatively longer in positions, where their contribution to the viscosity is small. At very high concentrations suspensions of more or less spherical particles show shear thickening and ultimately dilatancy (20-22). In high shear the particles, instead of moving smoothly past each other, bump into each other and form a rigid network that blocks the motion.

Flocculated suspensions behave completely differently from stable ones. A concentrated flocculated system may form a continuous network, that stretches from wall to wall and turns the suspension into a gel. One may consider a gel as a suspension in which the sedimentation volume is larger than the total volume. Any influence (such as added salt) that flocculates a dilute suspension turns a concentrated one into a gel. This may also be the result of the addition of a small amount of a second liquid phase that wets the particles preferentially and forms capillary bridges between them (e.g., wet sand). Elongated particles (such as clays, that moreover carry plus and minus charges on each particle) form gels at a lower concentration than spherical or cubic particles.

At low shear stress a gel is elastically deformed, but does not flow. Above the yield stress a sufficient number of bonds are destroyed to allow the system to flow, and at very high shear rates dispersion into primary particles or small flocs is complete (10,23). At intermediate rates of shear flocs break up but are also regenerated, leading to a floc size distribution. Often the regeneration of the flocs is slow which cause the resistance against flow to decrease with time of shearing. The suspension may even lose its yield stress completely, become fluid, and gel only after more or less prolonged standing. This behavior is called thixotropy (24,25) or isothermal sol-gel transformation. In a shear rate against shear stress diagram hysteresis loops are formed as illustrated in Fig. 2.

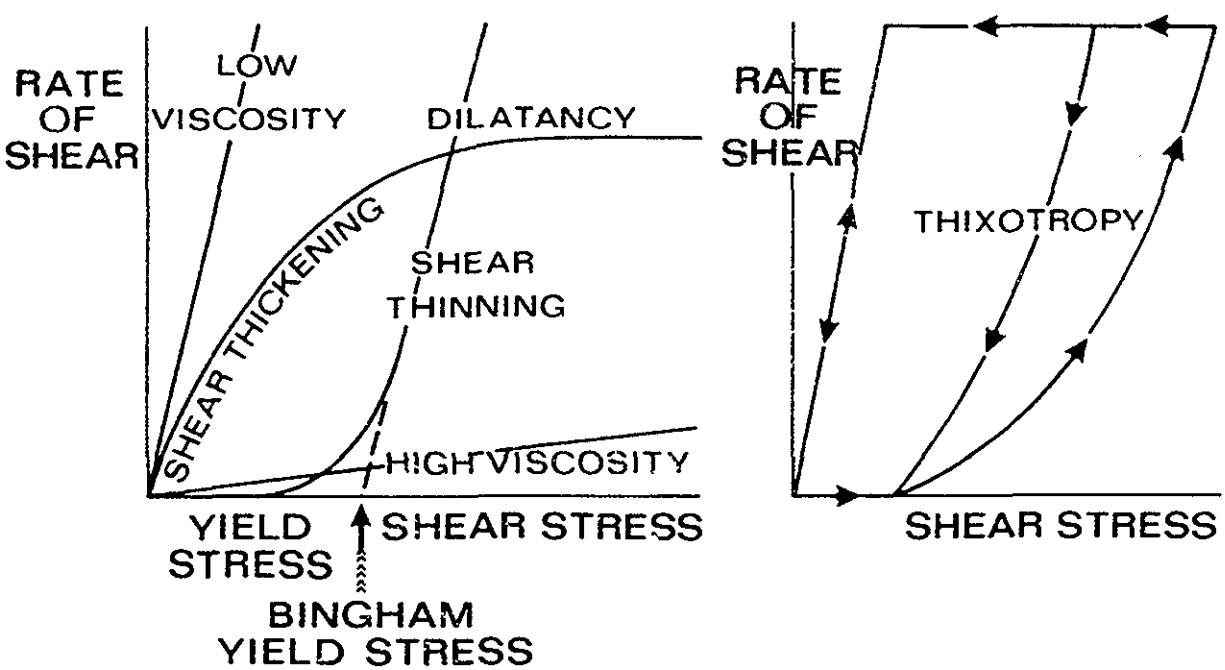

FIG. 2

Various types of rheological behavior. Left: time independent behavior. Right: thixotropy; structure decreases progressively during flow and is restored during rest.

Dispersed paints and drilling muds (26) illustrate the importance of rheological behavior. A dispersed paint should be thixotropic with a fairly short time constant. Then it does not settle in the container, it does not drip off a vertical surface, but during application it flows easily. The drilling mud should be fluid for easy pumping, but on the other hand, it should form a weak gel when the drilling is interrupted, so that the chips and the mud particles do not sediment.

Non-aqueous Media

Without mentioning this explicitly, most of what I said so far was based on the behavior of suspensions in water, not only because water is cheap and omnipresent, and more data are available, but also because it is more difficult to prepare stable non-aqueous suspensions. Suspensions in polar organic solvents, such as the lower alcohols and acetone, behave similarly as aqueous suspensions, but they are much more sensitive to electrolytes (27,28). This is not unexpected because the lower dielectric permittivity, ε, implies stronger electrostatic interactions between the surface charge and the counterions. With non-polar solvents electrostatic repulsion is usually absent, although it can be evoked by the use of large organic ions (29). Protective action based upon the presence of oil soluble long chain molecules is the normal mechanism of stabilization (30-32). Oil based paints are good examples of suspensions in non-polar media. Another example is engine oil, 'doped' in order to keep carbon and other products of incomplete combustion suspended as small particles, that do not cause abrasion.

Theory of Colloid Stability

We mentioned that stable suspensions are obtained when the particles repel each other, and that suspensions flocculate when the interaction between particles is mainly attractive. Then we described a number of differences in behavior between stable and unstable

suspensions. Now we shall analyze the several components of interaction more closely, first in static situations and then briefly also when the rate of changes plays a role.

Van der Waals Attraction

Kallmann and Willstaetter (33) were the first to suggest that Van der Waals forces are the main forces driving suspensions towards coagulation. This idea was worked out by de Boer (34) and Hamaker (35). Since Van der Waals attraction between two atoms or molecules is inversely proportional to the sixth power of the distance and, to a first approximation, all Van der Waals energies are additive, then Van der Waals attraction between particles composed of many molecules has a fairly long range. The attractive energy between the two particles in Fig. 3 may be written;

$$V_{att} = - \int_{v_1} \int_{v_2} \frac{\lambda q_1 q_2}{r^6} \, dv_1 dv_2 \qquad (3)$$

where λ is the London-Van der Waals constant for two molecules, 1 and 2, q_1 and q_2 are the numbers of molecules per unit volume in particles 1 and 2 and v_1 and v_2 are their total volumes. V_{att} is independent of the scale of Fig. 3, since dv_1 and dv_2 are each proportional to the cube of the scale and r^6 is proportional to the sixth power of the scale. The attraction energy between two atoms is of the order of the thermal energy, kT, at a distance of an atomic radius. Thus, the energy between two particles is also of the order of kT at a particle radius distance between their surfaces. The energy of interaction is given as

$$V_{att}(\text{general}) = - f \frac{A}{H^n} \; ; \; V_{att}(2 \text{ spheres}) = - \frac{aA}{12H} \qquad (4)$$

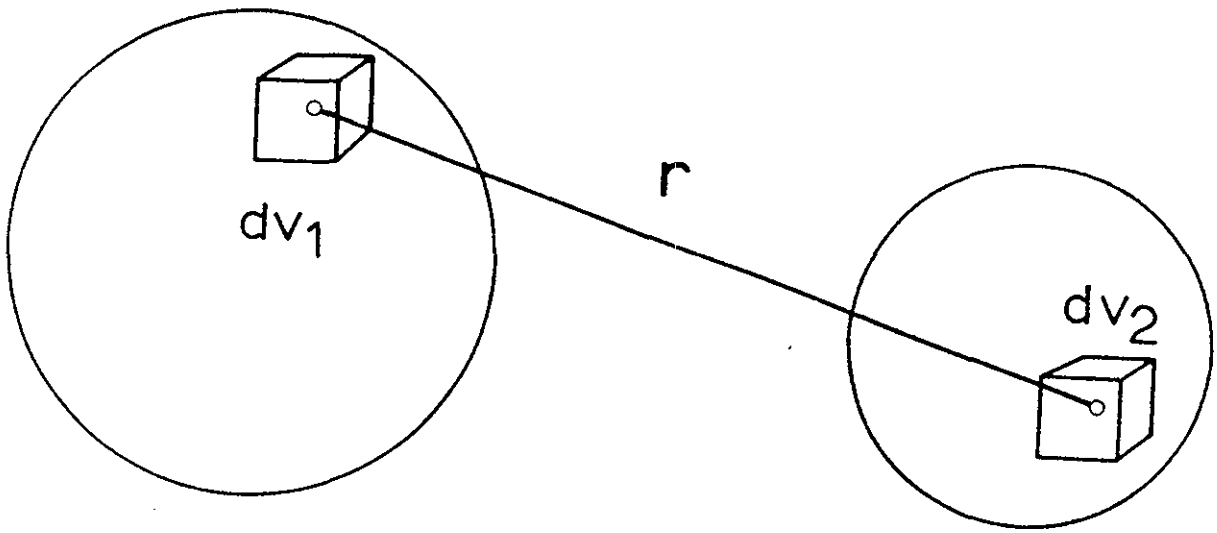

FIG. 3

Van der Waals attraction is built up from the attractions between all pairs of volume elements in the two particles.

where f is the n-th power of a length, $A = \pi^2 q^2 \lambda$ is the Hamaker constant, H is the distance of closest approach between the particles and n varies between 1 (spheres of radius a at small separations) to 6 (for large separations).

For particles suspended in a liquid the net Van der Waals attraction is smaller than in a vacuum, but it remains always an attraction (36). The retardation (37) of the Van der Waals attraction, due to the finite speed of transmission of electromagnetic signals is rarely of practical importance in suspensions, because the attraction is already very small at distances where the retardation becomes significant.

Lifshitz and coworkers (38) have developed a more refined theory of the Van der Waals attraction, not based on the additivity of the interactions between pairs of atoms but on the dielectric properties of the solids and liquids involved. Numerical values of the Hamaker constants obtained in various ways have been compilated by Visser (39). Cf. also Lyklema (28). Typical values for the Hamaker constant A for particles in water are:

$$A(\text{metal-}H_2O\text{-metal}) = 5 - 30 \times 10^{-20}J = 12 - 75kT$$

$$A(\text{oxide-}H_2O\text{-oxide}) = 0.5 - 5 \times 10^{-20}J = 1 - 12kT$$

$$A(\text{hydrocarbon-}H_2O\text{-hydrocarbon}) = 0.3 - 1 \times 10^{-20}J$$

$$= 1 - 2.5\ kT$$

Electrostatic Repulsion

As mentioned before and as discussed more fully by Lyklema (1), particles in suspension are electrically charged and thus repel each other. The repulsion is not simply Coulombic, but complicated due to the overlap of the diffuse parts of the two double layers. Just as the charge and the potential in the double layer fall off exponentially (1), the energy and the force of repulsion decrease as $\exp(-\kappa H)$ both for parallel flat surfaces and for spheres. If the potential at the boundary between the molecular condenser and the diffuse layer is ϕ_d, a good approximation for the energy of repulsion, V_{rep}, between two equal spheres with radius a is given by

$$V_{rep} = 2\pi\varepsilon\varepsilon_0 a \left(\frac{4RT\gamma}{zF}\right)^2 e^{-\kappa H} \simeq 2'\varepsilon\varepsilon_0 a\phi_d^2 e^{-\kappa H} \qquad (5)$$

where $\gamma = \tanh(zF\phi_d/4RT)$, $\kappa = (\Sigma\, z_i^2 c_i F^2/\varepsilon\varepsilon_0 RT)^{1/2}$ = the inverse Debye length, ε is the relative permittivity of the medium (the dielectric constant), ε_0 the permittivity of the vacuum, z_i and c_i the charge number and average concentration of the ions in the solution, z the charge number of the counterions, H is the closest distance between the surfaces of the spheres where the potential is ϕ_d and R, T and F have their usual meaning. The second expression for V_{rep} in Eq. (5) is a good enough approximation when $z\phi_d < 60$ mV.

Addition of electrolyte reduces the repulsion via $\kappa(\sim z\sqrt{c})$, compression of the double layer, and z in γ/z.

The difference in decay with the distance between attraction (exponentially) and repulsion (inverse power of the distance) has the very interesting consequence that at

very large and at very small distances the attraction always prevails and that at intermediate distances the repulsion may prevail. Figure 4 gives a number of combined repulsion and attraction curves, differing only in the steepness (value of κ) of the repulsion curve. If the maximum in V_{tot} is high enough (say 10 or 20kT), the suspension is stable, but if the maximum is low or absent, particle encounters lead to entrapment in the deep, so-called primary, minimum at contact. This minimum is not infinitely deep as might be infered from Fig. 4 because the Born repulsion (= impenetrability of atoms) makes the

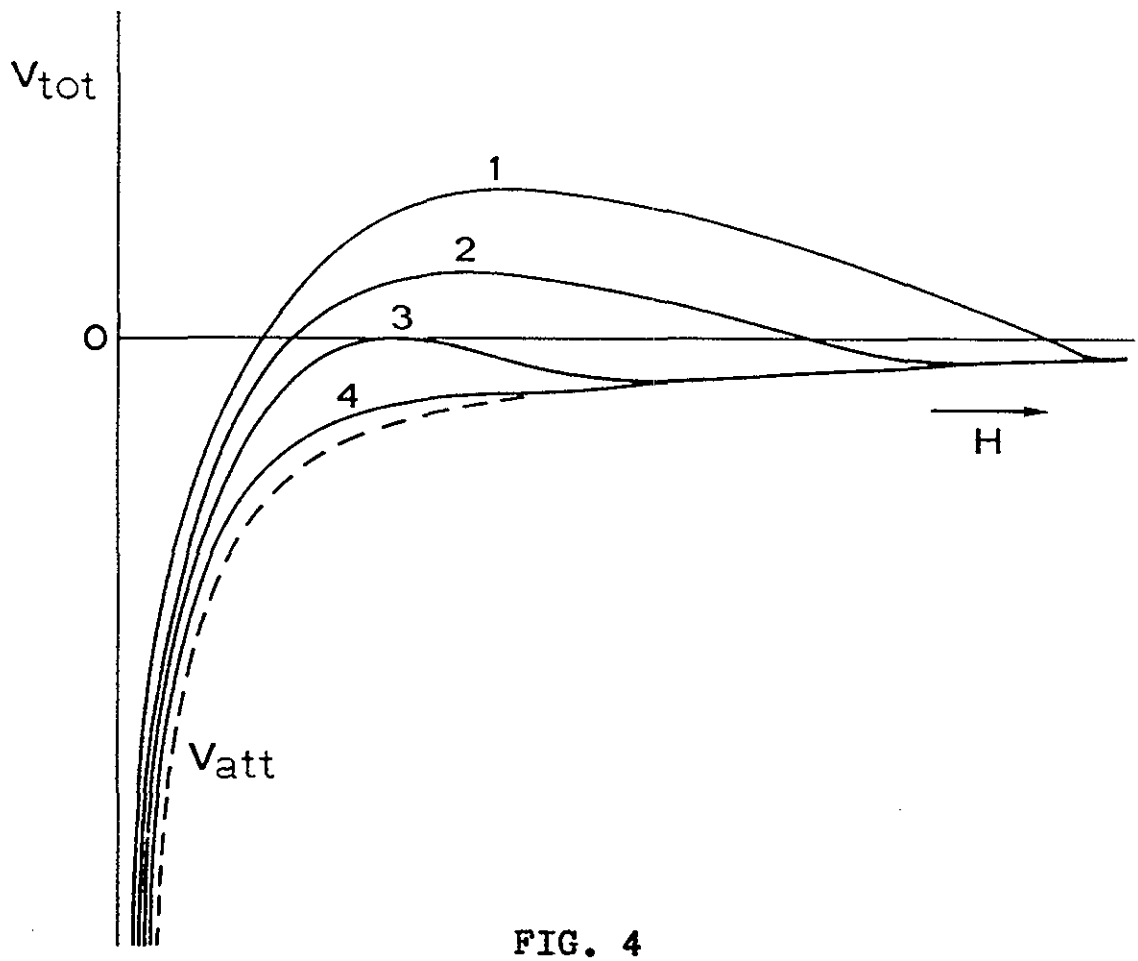

FIG. 4

Total interaction ($V_{tot} = V_{rep} + V_{att}$) between two spherical particles. All cases have the same attraction curve. The repulsion is progressively steeper (higher value of κ) in the direction 1, 2, 3, 4. Case 3 represents the borderline between stability and coagulation; $V_{max} = 0$. Schematic.

curves swing up again near H = 0. Coagulation after the addition of electrolyte is now easily explained as a consequence of the steeper decay of the repulsion. Coagulation in the shallow 'secondary' minimum (at the right in Fig. 4) may occur with large particles.

If the transition between stable and unstable is laid at curve 3 ($V = dV/dH = 0$), and the surface potential is so high ($z\phi_d > 150$ mV) that $\gamma \rightarrow 1$, the c.c.c. is inversely proportional to z^6, in agreement with the Schulze-Hardy rule. However, in most practical cases the ζ-potential ($\simeq \phi_d$) at coagulation is low, and then the coagulation condition already proposed by Eilers and Korff (40) is found.

$$\frac{\phi_d^2}{\kappa} = \frac{\zeta^2}{\kappa} = \text{constant} = \frac{A}{24\pi\varepsilon\varepsilon_0 \exp(-1)} \qquad (6)$$

In order to predict the c.c.c. from this equation a relation between ϕ_d, z and c is required and this again requires an adsorption isotherm for the counterions. The rule of Schulze and Hardy is then found when the charge of the diffuse double layer and the surface potential, ϕ_d, are decreased by adsorption of counterions, especially those with charge numbers above 1 (41).

In the condition $V = dV/dH = 0$ the c.c.c. is independent of the particle radius, a. But all energies involved are proportional to a, and thus large particles are more easily stabilized than small ones because a barrier of a given height (say 20kT) is more easily obtained with large a. When more accurate equations than Eqs. (4) and (5) are used, larger particles may be less stable than smaller ones in exceptional cases (42).

Effects of Large Molecules

A primitive, but essentially correct, explanation of the stabilizing effect of adsorbed large molecules is based upon their solubility in the medium, which prevents them from sticking together, whereas their bulk prevents the Van der Waals forces between the particles from coming into action (43). More refined interpretations start from

the theory of polymer solutions, as given by Flory (44) and Huggins (45). From the many authors who have contributed to this field I mention Hesselink (31), Napper (32) and more recently Fleer and Scheutjens (46). When two surfaces, from which flexible long chains are sticking out into the solution, come close together two effects contribute to the repulsion. In the narrow gap between the surfaces the long chains lose some of their conformations (volume restriction effect). This results in a loss of entropy, in an increase in the free energy and thus in a repulsion. Furthermore the concentration of polymer segments in the gap increases and this so-called osmotic effect results in another contribution to the repulsion. Figure 5 illustrates this schematically.

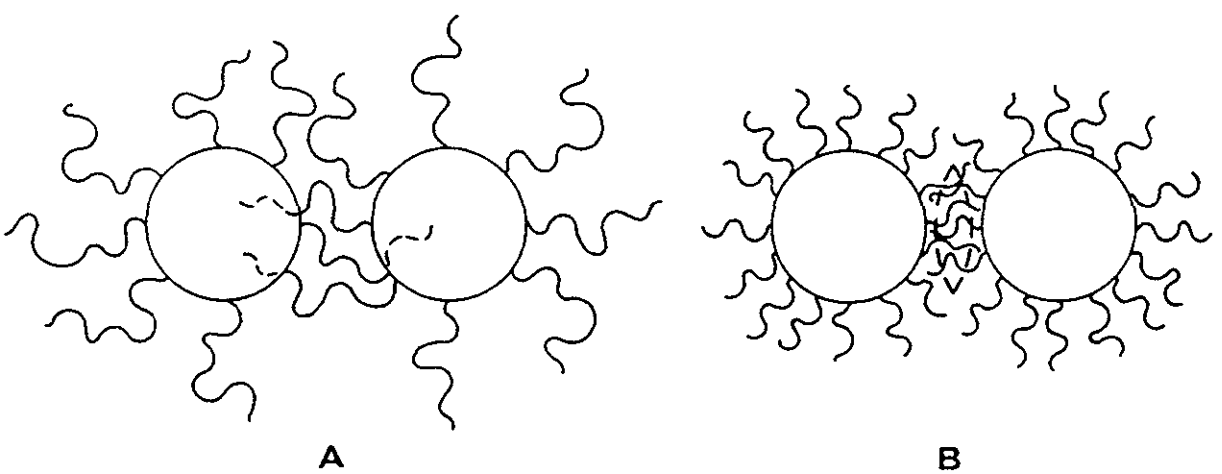

FIG. 5

Schematic illustration of the volume restriction effect (A) and the osmotic effect (B) in stabilization by adsorbed or chemically bound long chains.

From these considerations it follows that stabilization occurs only on the solution side of the θ-point and slightly below it in the case of the volume restriction effect. Changing the solvent to below the θ-point results in flocculation. This flocculation is reversible and after changing the solvent again to above the θ-point the flocs will redisperse.

The adsorption of the long molecules can be due to two different principles.

a. The stabilizing molecule may contain one part that is easily adsorbed (the anchor group) and one part, the chain, that is easily soluble.

b. The molecule is a homopolymer with a relatively weak adsorption per chain element, leading to the attachment of several segments in trains (one or a row of neighboring segments in contact with the surface), but leaving two tails (ends of chains) and many loops (parts of the chain adsorbed at their two ends) sticking out in the solution. For the stabilizing interaction the tails are the most important.

Sensitization (destabilization) occurs when a molecule is attached with two anchors to two different particles. This occurs in particular at low polymer concentration, when the surfaces are incompletely covered with adsorbed molecules.

Free, i.e., not adsorbed, polymers also influence the stability. In a narrow gap between two surfaces polymer coils are forced out of the gap by the volume restriction effect. This leads to a concentration gradient, which pushes solvent out of the gap and thus causes flocculation. In high concentrations of polymer stabilization may result, because too much work is involved in pushing the polymers out of the gap against the now important concentration gradient. These effects have been studied experimentally and theoretically by Scheutjens and Fleer (46), Vincent et al. (47), Vrij (48), Napper (49) and others.

Above a molecular weight of a few thousand the molecular weight of the polymer is not very critical, although at very high molecular weights the solutions may become too viscous and the coil extensions too large compared to particle sizes.

Most but not all water soluble polymers, gums, proteins, carboxymethylcellulose (CMC) are polyelectrolytes. They are good protective agents in which steric effects and electrostatic repulsion are combined. At low concentrations they lead to sensitization. The effects of electrolyte are complex, since they do not only decrease the electrostatic

repulsion but often increase the adsorption of the polyelectrolyte. Polyelectrolyte counterions are of course powerful flocculants.

Structural Forces

The idea that hydration (more generally: solvation) at the surface may keep particles apart has recurred several times in colloid-chemical considerations, but until recently it has never been substantiated. Only in the last five years experimental evidence and model calculations have accumulated to show that the liquid structure near an interface is disturbed over a depth of several, up to ten, layers of molecules and that this disturbance may lead to a steep and strong repulsion. In a series of papers by Ninham, Israelachvili, Parsegian, Derjaguin and others in the proceedings of a recent symposium (50) this 'structural force' is discussed. This effect, on which a great deal of work still has to be done, may be important for colloid stability. On the other hand, so far, no unambiguous evidence about its effect on suspensions of particles has been presented.

Kinetic Effects in Colloid Stability

So far I have treated stability as a static, thermodynamic phenomenon. Kinetics, however, also play an important role. If the barrier is not infinitely high -- and it never is -- one should know at what rate coagulation occurs and even when a barrier is completely absent, coagulation requires a finite time. How much time? This question and related matters have been treated extensively in Dr. Gregory's lecture (59). But one aspect of kinetics has to be treated here (51).

When two particles approach one another, be it in a Brownian encounter or in a systematic motion, as in shear or sedimentation, it is not correct, as we have tacitly assumed, that complete equilibrium reigns at every moment of the approach. Time is required for the rearrangement of the electric double layer, for the rearrangement of the

conformations of macromolecules and for desorption and adsorption processes.

In the case of electrical stabilization we have to compare the time of a Brownian encounter with the relaxation time of the double layer and with the relaxation time involved in adsorption or desorption. The time of a Brownian encounter τ (Brown, double layer) can be defined as the time needed by a particle to diffuse through the thickness of the double layer, $1/\kappa$.

$$\tau(\text{Brown, d.l.}) = \frac{(1/\kappa)^2}{D(\text{particle})} \tag{7}$$

Similarly the relaxation time of the double layer is the time needed by an ion to diffuse through $1/\kappa$.

$$\tau(\text{relax. d.l.}) = \frac{(1/\kappa)^2}{D(\text{ion})} \simeq \frac{5 \times 10^{-11}\ \text{s}}{c/(\text{mol } 1^{-1})} \tag{8}$$

Consequently, with $D_i = kT/6\pi\eta a_i$, where a_i is the radius of the diffusing entity,

$$\frac{\tau(\text{Brown, d.l.})}{\tau(\text{relax. d.l.})} = \frac{a(\text{particle})}{a(\text{ion})} \tag{9}$$

and this is usually 100 or larger. The relaxation time involved in adsorption or desorption is connected with the exchange current density of the electrode process involved and this varies over many orders of magnitude, but is at best of the order of the time of a Brownian encounter and usually a great deal longer (51).

Consequently, in a Brownian encounter the double layer structure rearranges itself so rapidly that equilibrium may be assumed, but as a rule the surface charge does not adjust itself at all and remains constant. Calculations of double layer repulsion should be made for constant charge, not for constant surface potential.

Similar arguments, applied to a layer of adsorbed macromolecules, lead to the conclusion that here also

desorption is too slow to occur during Brownian encounters, but the rearrangement of the conformations of loops and trains occurs easily within the time of the Brownian encounter. The slowness of desorption makes an adsorbed macromolecule a much better protective agent that it would be with complete adaptation.

Repeptization

One of the consequences of the theory of stability as presented so far is the conclusion that coagulation in the primary minimum is irreversible. The minimum is at a negative value of the free energy and spontaneous repeptization is impossible as illustrated in Fig. 6. This agrees with the observation that most coagulated colloids do not return spontaneously to the dispersed

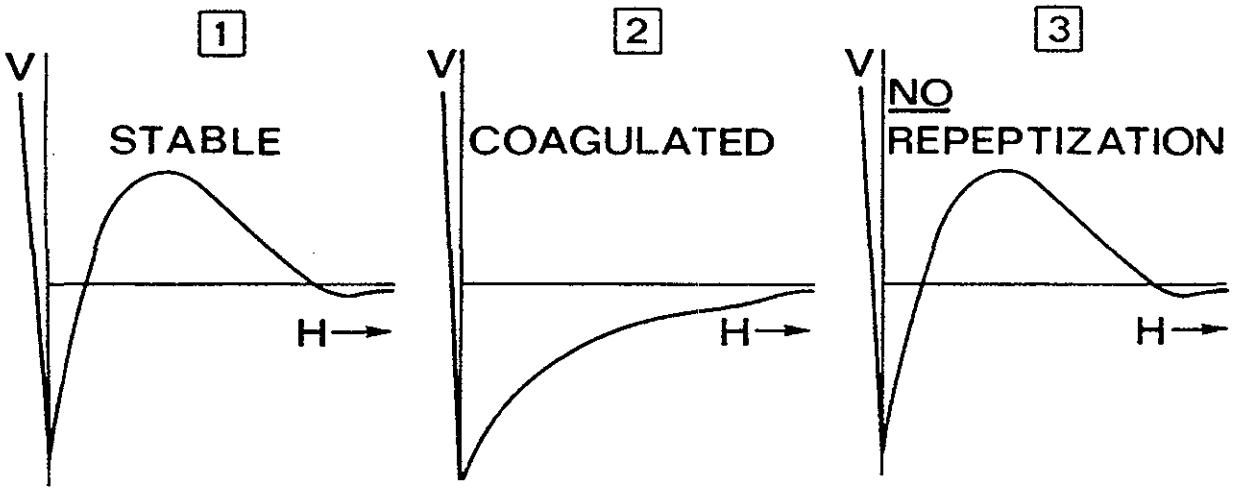

FIG. 6

Schematic energy vs distance diagrams. (1) Stable suspension; (2) electrolyte added, barrier removed, coagulation at H = 0; (3) electrolyte removed, but no repeptization, since this would require an increase in V not only to pass the barrier but also to reach the final dispersed stage (H → large).

state when the coagulating electrolyte is removed. However, a number of cases are known in which repeptization does occur. For some sols (52,53) such as V_2O_5, HgS, Carey Lea's silver, this is even the preferred way of preparation. For many others, e.g., silver halides, $Fe(OH)_3$, other oxides and hydroxides repeptization can be obtained, if the electrolyte is washed out soon after flocculation. Therefore Fig. 6 cannot be correct. Our analysis of this figure shows that two essential elements in repeptization are:

a. The primary minimum must disappear or at least be situated at a positive value of V after removal of the coagulating electrolyte.

b. The energy barrier must be low or absent in the direction of increasing distance.

Both aims can be obtained if a layer of a few Ångstroms, i.e., one or two layers of solvent molecules keep the particles separated. Then instead of Fig. 6, we obtain the situation of Fig. 7.

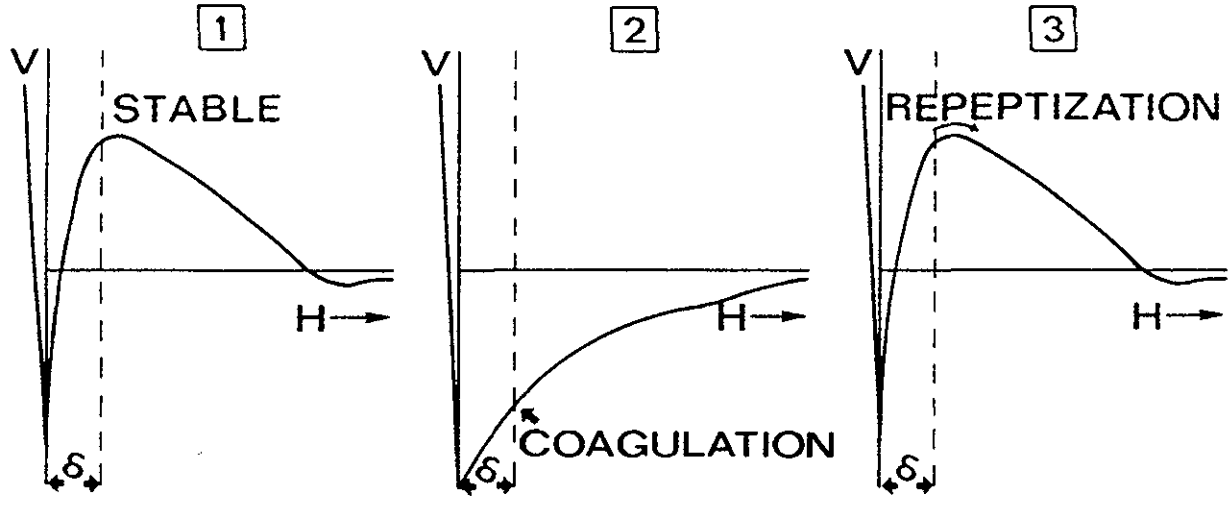

FIG. 7

Schematic diagram with a layer of thickness δ keeping the particles separated. (1) Stable; (2) coagulated, but at distance, δ, between the surfaces; (3) spontaneous repeptization if barrier at H = δ is not more than a few times kT. Numerical examples show that δ need not be more than a few Å (53).

It may well be that the layer δ disappears with time, or that the coagulated material recrystallizes through the layer or that the floccules rearrange themselves so as to have more extended contact. All such processes result in repeptization becoming more difficult and even disappearing on standing.

With coarse primary particles ($a \gg 1\ \mu m$) matters seem to be different, because there aggregates can be redispersed by stirring or shaking, notwithstanding the fact that for the same distance, H or δ, the energies and forces of interaction are proportional to the particle radius, a, as can be read from Eqs. (4) and (5). However, a shear field tends to separate the particles by a force proportional to a^2, because both the velocity difference at the centers of the two particles and their Stokes friction are proportional to a and for large enough particles this can overcome the Van der Waals attraction.

If stabilization is due to protective action, then, as mentioned earlier, repeptization after removing the flocculant is the normal course of affairs.

Repeptization is important for two reasons. It is often used in technical applications and moreover it produces information on details of the interactions at small separations.

Thermodynamic Stability

Suspensions, emulsions and sols are only kinetically, not thermodynamically stable. They cannot be formed by simply mixing the macroscopic phases. The huge interface between particles and medium is a seat of free energy (interfacial tension) and this has to be brought into the system from the outside.

There are exceptions, however, to this too sweeping statement. A group of colloids, known as lyophilic, are thermodynamically stable. They are either solutions of large molecules, e.g., proteins in water, polystyrene in benzene, or solutions in which large but finite aggregates are formed, such as the soap micelles in water.

There are a few other cases in the borderland between lyophilic and lyophobic (= kinetically stable) systems.

Microemulsions (54-56) belong here. Microemulsions are transparent mixtures of oil and water, stabilized by fairly large concentrations of one or two surfactants. Schulman (57) and coworkers, who first described these systems in the early forties, found already that the interfacial tension between the two phases becomes very low ($\ll 1$ mNm^{-1}) after the adsorption of the surfactants. When the interfacial tension is zero (or even, in passing, negative) spontaneous emulsification results, and if enough surfactant is available, the emulsion droplets become very small (~ 10 nm). Microemulsions had disappeared more or less from the scientific scene, but they have recently returned in people's interest, because the low interfacial tensions involved hold promise for applications in enhanced oil recovery.

Extremely low interfacial tensions need not be limited to the oil-water system. An electrical double layer, being formed spontaneously, also causes a lowering of the interfacial tension and there may be cases in which suspensions are thermodynamically stabilized by their double layers. Cases in point are silica in alkaline solutions and aluminumoxide-hydroxide particles at a fairly low pH (58). This is a new field that certainly deserves attention.

Conclusions

Knowledge about colloid stability does not only apply to true colloids, but also to dispersions of larger particles. For large particles gravity and hydrodynamic effects become relatively more important than Brownian motion. Colloid stability has a great influence on the properties of suspensions, especially on their packing and rheology.

Colloid stability is fairly well understood. The Van der Waals attraction is always there and not easily changed. The repulsion is either electrostatic or due to large molecules or possibly to structural forces. It is essential to realize that if one wants to increase or decrease the stability one has to manipulate the electrical double layer or the large molecules and thus

one has to understand the theoretical background of these agents.

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Self-Test

1. A goldsol flocculates at 25 mmol NaCl per liter and at 0.4 mmol $BaCl_2$ per liter. What is the sign of the charge of the particles?

2. Explain why suspended material sediments faster but forms a less dense sediment in sea water than in fresh water.

3. Does the viscosity of suspensions in water change upon addition of electrolyte? If so, in what direction? Compare the expected changes per mole for added NaCl, KCl, $Ba(NO_3)_2$, and Na_2SO_4.

4. Consider a suspension of spherical particles. Use Eq. (4) for the van der Waals attraction and Eq. (5) for the repulsion at high potentials, so that $\gamma=1$. Use the condition $V=dV/dH=0$ for the transition to rapid coagulation and prove that for this case the c.c.c. is proportional to z^{-6}, when z is the charge number of the counter ions.

5. Which of the following polymers are expected to be protective agents in aqueous suspensions? Polyvinylalcohol, polyvinylacetate, polystyrene, sodium polystyrene sulphonate?

6. Calculate the time for a Brownian encounter between two spheres of 1000Å (100 nm) diameter at a monovalent electrolyte concentration of 10^{-3} mol l^{-1}.

(Answer: about 10^{-5} s)

7. Why does prolonged standing in the flocculated condition prevent repeptization after washing away the flocculating electrolyte?

8. Explain why the stability of AgI is hardly affected by the pH of the solution, whereas the pH has a strong influence on the stability of sols of $Al(OH)_3$ or FeO(OH).

9. Does a flocculating suspension of spherical particles show shear thinning or shear thickening at increasing rate of shear? Will it show dilatancy?

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