Colloid Stability

A most important physical property of colloidal dispersions is the tendency of the particles to aggregate. Encounters between particles dispersed in liquid media occur frequently and the stability of dispersion is determined by the interaction between the particles during these encounters.

The principal cause of aggregation is the van der Waals attractive forces between the particles, which are long-range forces. To counteract these and promote stability, equally long-range repulsive forces are required. Solvation tends to be too short-range; however, the molecular ordering associated with solvation can propagate several molecular diameters into the liquid phase and may exert some influence on stability95. The principal stabilizing options are electrostatic (i.e. the overlap of similarly charged electric double layers) and polymeric. Polymeric and/or surfactant additives can influence stability by a variety of mechanisms and the overall situation is often very complicated.

Lyophobic sols

Ideally, lyophobic sols are stabilized entirely by electric double-layer interactions and, as such, present colloid stability at its simplest.

Critical coagulation concentrations*-Schulze-Hardy rule

A most notable property of lyophobic sols is their sensitivity to coagulation by small amounts of added electrolyte. The added electrolyte causes a compression of the diffuse parts of the double layers around the particles and may, in addition, exert a specific effect through ion adsorption into the Stern layer. The sol coagulates when the range of double-layer repulsive interaction is sufficiently reduced to permit particles to approach close enough for van der Waals forces to predominate.

Table 8.1 Critical coagulation concentrations (in mmol per dm^3) for hydrophobic

As$_2$S$_3$ (- ve sol)		AgI (- ve sol)		Al$_2$O$_3$ (+ve sol)	
LiCl	58	LiNO$_3$	165	NaCl	43.5
NaCl	51	NaNO$_3$	140	KCl	46
KCl	49.5	KNO$_3$	136	KNO$_3$	60
KNO$_3$	50	RbNO$_3$	126		
K acetate	110	AgN0$_3$	0.01		
CaCl$_2$	0.65	Ca(N0$_3$)$_2$	2.40	K$_2$SO$_4$	0.30
MgCl2	0.72	Mg(N0$_3$)$_2$	2.60	K$_2$Cr$_2$0$_7$	0.63
MgSO4	0.81	Pb(N0$_3$)$_2$	2.43	K$_2$ oxalate	0.69
AlCl3	0.093	Al(N0$_3$)$_3$	0.067	K$_3$[Fe(CN)$_6$]	0.08
1/2Al$_2$(SO4)$_3$	0.096	La(N0$_3$)$_3$	0.069		
Al(N0$_3$)$_3$	0.095	Ce(N0$_3$)$_3$	0.690		

The critical coagulation concentration of an indifferent (inert) electrolyte (i.e. the concentration of the electrolyte which is just sufficient to coagulate a lyophobic sol to an arbitrarily defined extent in an arbitrarily chosen time) shows considerable dependence upon the charge number of its counter-ions. In contrast, it is practically independent of the specific character of the various ions, the charge number of the co-ions and the concentration of the sol, and only moderately dependent on the nature of the sol. These generalizations are illustrated in Table 8.1, and are known as the Schulze-Hardy rule

The Deryagin-Landau and Verwey-Overbeek theory

Deryagin and Landau and Verwey and Overbeek independently developed a quantitative theory in which the stability of lyophobic sols, especially in relation to added electrolyte, is treated in terms of the energy changes which take place when particles approach one another. The theory involves estimations of the energy due to the overlap of electric double layers (usually repulsion) and the Londonvan der Waals energy (usually attraction) in terms of Interparticle distance, and their summation

to give the total interaction energy in terms of interparticle distance. Colloid stability is then interpreted in terms of the nature of the interaction energy-distance curve. Theoretical calculations have been made for the interactions (a) between two parallel charged plates of infinite area and thickness, and *(b)* between two charged spheres. The calculations for the interaction between flat plates are relevant to the stability of thin soap films, and have been related with a reasonable measure of success to experimental studies in this field. The calculations for the interaction between spheres are relevant to the stability of dispersions and will be outlined. In fact, the conclusions arising from both theoretical treatments are broadly similar.

Double-layer interaction energies

The calculation of the interaction energy, V_R, which results from the overlapping of the diffuse parts of the electric double layers around two spherical particles (as described by Gouy-Chapman theory) is complex. No exact analytical expression can be given and recourse must be had to numerical solutions or to various approximations.

If it is assumed that ion adsorption equilibrium is maintained as two charged particles approach each other and their double layers overlap, two well-defined situations can be recognized. If the surface charge is the result of the adsorption of potential-determining ions, the surface potential remains constant and the surface charge density adjusts accordingly; but if the surface charge is the result of ionization, the surface charge density remains constant and the surface potential adjusts accordingly. At large interparticle separations the difference between constant potential and constant charge interactions will be minimal. Overbeek has considered this problem and concluded that the rate of double-layer overlap in a typical Brownian motion encounter between particles is too fast for adsorption equilibrium to be maintained and that

the true situation will, in general, lie somewhere between constant potential and constant charge.

For the case of two spherical particles of radii a_1 and a_2, Stern potentials, ψ_{d1} and ψ_{d2}, and a shortest distance, H, between their Stern layers, Healy and co-workers have derived the following expressions for constant-potential, V_R^{ψ} and constant-charge, V_R^{σ}, double-layer interactions. The low-potential form of the Poisson- Boltzmann distribution is assumed to hold and κa_1 and κa_2 are assumed to be large compared with unity:

$$V_R^{\psi} = \frac{\pi \varepsilon a_1 a_2 (\psi_{d1}^2 + \psi_{d2}^2)}{(a_1 + a_{2)}} \left\{ \frac{(2\psi_{d1}\psi_{d2})}{(\psi_{d1}^2 + \psi_{d2}^2)} \ln\left[\frac{1+e^{-\kappa H}}{1-e^{-\kappa H}}\right] + \ln(1-e^{-2\kappa H}) \right\} \quad (1)$$

$$V_R^{\sigma} = \frac{\pi \varepsilon a_1 a_2 (\psi_{d1}^2 + \psi_{d2}^2)}{(a_1 + a_{2)}} \left\{ \frac{(2\psi_{d1}\psi_{d2})}{(\psi_{d1}^2 + \psi_{d2}^2)} \ln\left[\frac{1+e^{-\kappa H}}{1-e^{-\kappa H}}\right] - \ln(1-e^{-2\kappa H}) \right\} \quad (2)$$

Where ε is the permittivity of the dispersion medium and κ is interface thickness

Table 8.2 shows the signs of VR that accord with equations (8.1) and (8.2) for different homo-coagulation and hetero-coagulation situations. (N.B. Attraction is negative and repulsion positive.) For equal spheres, with at $a_1 = a_2 = a$ and $\psi_{d1} = \psi_{d2} = \psi_d$, equations (1) and (2) reduce to

$V_R^{\psi} = 2\pi \varepsilon a \psi_d^2 \ln(1+e^{-\kappa H})$ (3) And $V_R^{\sigma} = 2\pi \varepsilon a \psi_d^2 \ln(1+e^{-\kappa H})$ (4)

For small electric double layer overlap, such that $e^{-\kappa H} \ll 1$, these expressions both reduce to

$V_R = 2\pi \varepsilon a \psi_d^2 e^{-\kappa H}$ (5)

Tab2 8.2 Predicted signs of V_R^{*}

Situation	V_R^{ψ}	V_R^{σ}

(a) $\psi_{d1} = \psi_{d2} \neq 0$	+ve	+ve
(b) $\psi_{d1} and \psi_{d2}$ of like sign but unequal magnitude	+ve at large H -ve at small H	+ve
(c) $\psi_{d1} and \psi_{d2}$ of opposite Sign	- ve	-ve at large H +ve at large H
(d) $\psi_{d1} or \psi_{d2} = 0$	- ve	+ve

Another approximate expression for V_R is that given by Reerink and Overbeek. The Debye-Hiickel low-potential approximation is not made, but the interparticle distance is considered to be sufficiently large (i.e. $e^{-\kappa H} << 1$) for the potential at any point between the particles to be given by the sum of the individual potentials at that point for each particle in the absence of the other. For unequal spherical particles,

$$V_R = \frac{64\pi\varepsilon a_1 a_2 k^2 T^2 \gamma_1 \gamma_2}{(a_1 + a_2)e^2 z^2} e^{-\kappa H} \qquad (6)$$ which, for equal spheres,

reduces to

$$V_R = \frac{32\pi\varepsilon a k^2 T^2 \gamma}{e^2 z^2} e^{-\kappa H} \qquad (7)$$ where 2 is the counter-ion charge

number and

$$\gamma = \frac{\exp[ze\psi_d / 2\kappa T] - 1}{\exp[ze\psi_d / 2\kappa T] + 1}$$

If, $ze\psi_d / 2\kappa T < 1$ equation (7) reduces to (5).

[Note that: The symbols V_R and V_A are those traditionally used to represent electric double layer and van der Waals interactions, respectively. The subscripts, R and A, reflect the usual, but not universal, repulsive and attractive nature of these interactions,]

So far, only non-specific ion adsorption in the diffuse part of the electric double layer has been considered. The broad prediction is that VR should

decrease in an approximately exponential fashion with increasing H and that the range of V_R should be decreased by increasing κ (i.e. by increasing electrolyte concentration and/or counter-ion charge number). Specific effects may also influence V_R. Counter-ion adsorption in the Stern layer may cause a reversal of charge so that V_R for a pair of identical particles will be zero at the reversal of charge concentration and positive (repulsion) at both below and above this concentration. In contrast to the effect of electrolyte on the diffuse part of the electric double layer, the amount of added electrolyte required to produce such a specific effect will depend on the total surface area of the particles, The nature of the electric double layer (and of V_R) may also be influenced by ion hydrolysis and/or complexation reactions.

An interesting example of electrostatic attraction of oppositely charged surfaces is that exhibited by kaolinite clay particles. The faces of the plate-like particles tend to be negatively charged and the edges positively charged. This can be demonstrated by introducing negatively charged colloidal gold particles into the clay suspension, then subsequently taking an electron micrograph, which shows the small gold particles adhering to the edges (but not to the faces) of the clay platelets. Edge-to-face attraction between the clay platelets can lead to the formation of a 'card-house' structure with a relatively low particle density.

Van der Waals forces between colloidal particles

The forces of attraction between neutral, chemically saturated molecules, postulated by van der Waals to explain non-ideal gas behavior, also originate from electrical interactions. Three types of such intermolecular attraction are recognized:

1. Two molecules with permanent dipoles mutually orientate each other in such a way that, on average, attraction results.

2. Dipolar molecules induce dipoles in other molecules so that attraction results.

3. Attractive forces are also operative between non-polar molecules, as is evident from the liquefaction of hydrogen, helium, etc. These universal attractive forces (known as *dispersion forces)* were first explained by London (1930) and are due to the polarization of one molecule by fluctuations in the charge distribution in a second molecule, and vice versa.

With the exception of highly polar materials, London dispersion forces account for nearly all of the van der Waals attraction which is operative. The London attractive energy between two molecules is very short-range, varying inversely with the sixth power of the intermolecular distance. For an assembly of molecules, dispersion forces are, to a first approximation, additive and the van der Waals interaction energy between two particles can be computed by summing the attractions between all interparticle molecule pairs.

The results of such summations predict that the London interaction energy between collections of molecules (e.g. between colloidal particles) decays much less rapidly than that between individual molecules.

For the case of two spherical particles of radii a_1 and a_2, separated *in vacuum* by a shortest distance H, Hamaker derived the following expression for the London dispersion interaction energy, V_A:

$$V_A = -\frac{A}{12}\left[\frac{y}{x^2 xy + x} + \frac{y}{x^2 + xy + x + y} + 2\ln\left(\frac{x^2 xy + x}{x^2 + xy + x + y}\right)\right] \quad (8)$$

Where $x = \frac{H}{a_1 + a_2}$ and $y = \frac{a_1}{a_2}$ For equal spheres, with $a_1 = a_2 = a$ (x =H/2a) equation (8) takes the form

$$V_A = -\frac{A}{12}\left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2\ln\left(\frac{x(x+2)}{(x+1)^2}\right)\right] \quad (9)$$

If a small interparticle separation is assumed, such that $H \ll a$ (i.e. $x \ll 1$), this rather awkward equation simplifies to

$$V_A = \frac{A}{12}\frac{1}{2x} = \frac{Aa}{12H} \quad (10)$$

Values of V_A calculated from this equation will be overestimated on account of the above approximation.

Values of VA calculated from any of the above equations will be overestimated at large distances (H > 10 nm) owing to a neglect of the finite time required for propagation of electromagnetic radiation between the particles, the result of which is a weakening of *VA*. In most practical situations relating to colloid stability this *retardation effect* is not likely to be important. The major problem in calculating the van der Waals interaction between colloidal particles is that of evaluating the Hamaker constant, *A*. Two methods are available.

The first of these methods is the London-Hamaker microscopic approach, which has already been mentioned. In it Hamaker constants are evaluated from the individual atomic polarizability and the atomic densities of the materials involved. The total interaction is assumed to be the sum of the interactions between all interparticle atom pairs and is assumed to centre on a single oscillation frequency. These assumptions are essentially incorrect.

The influence of neighboring atoms on the interaction of a given pair of atoms is ignored, van der Waals interaction energies calculated in accord with the microscopic approach are likely to be in error but the error involved is not likely to be so great as to prejudice general conclusions concerning colloid stability.

The other method is the macroscopic approach of Lifshiftz in which the interacting particles and the intervening medium are treated as continuous phases. The calculations are complex, and require the availability of bulk optical/dielectric properties of the interacting materials over a sufficiently wide frequency range.

The values of *A* calculated by microscopic and by macroscopic methods tend to be similar in the non-retarded range. The macroscopic approach predicts a smaller retardation effect (i.e. better applicability of equations 8-10 for relatively large values of *H)* than the microscopic approach.

Hamaker constants for single materials usually vary between about 10^{-20} j and (10^{-19} j some examples are given in Table 8.3. Where a range of values is quoted for a given material, this reflects different methods of calculation within the basic microscopic or macroscopic method.

The presence of a liquid dispersion medium, rather than a vacuum (or air), between the particles (as considered so far) notably lowers the van der Waals interaction energy. The constant *A* in equations (8 -10) must be replaced by an effective Hamaker constant.

Figure 8.1

Consider the interaction between two particles, 1 and 2, in a dispersion medium, 3. When the particles are far apart (Figure 8. la), the interactions are particle-dispersion medium interactions, with Hamaker constants A_{13} and A_{23}. If particle 2 is brought close to particle 1 (Figure 8.1b), dispersion medium must be displaced to the position originally occupied by particle 2 and the above interactions are replaced by particle-particle and dispersion medium-dispersion medium interactions, with Hamaker

constants A_{12} and A_{33}. The effective Hamaker constant is, therefore, given by

$$A_{123} = A_{12} + A_{33} - A_{13} - A_{23} \qquad (11)$$

If the attractions between unlike phases are taken to be the geometric mean of the attractions of each phase to itself

$$A_{12} = (A_{11}xA_{22})^{1/2}, A_{13} = (A_{11}xA_{33})^{1/2}, A_{23} = (A_{22}xA_{33})^{1/2} \quad \text{then equation}$$

(11) becomes $A_{123} = (A_{11}^{1/2} - A_{33}^{1/2})(A_{22}^{1/2} - A_{33}^{1/2})$ \qquad (12)

If the two particles are of the same material, this expression becomes

$$A_{123} = (A_{11}^{1/2} - A_{33}^{1/2})^2 \qquad (13)$$

Giving values of A_{131} for hydrosols of up to about 10^{-19} J

A_{132} will be positive (interparticle attraction) where A_{11} and A_{22} are either both greater than or both less than A_{33}. However, in the unusual situation where A_{33} has a value intermediate between those of A_{11} and A_{22}, then A_{123} is negative - i.e. a repulsive van der Waals interaction between the particles is predicted,

A_{131} for the interaction of particles of the same material is always positive - i.e. the van der Waals interaction energy is always one of attraction. This interaction will be weakest when the particles and the dispersion medium are chemically similar, since A_{11} and A_{33} will be of similar magnitude and the value of A_{131} will therefore, be low.

Table 8.3 Values of Hamaker constants

Material	A_{11} (microscopic) 10^{-20} J	A_{11} (macroscopic) 10^{-20} J
Water	3.3 -6.4	3.0-6.1
Ionic crystals	15.8-41.8	5.8-11.8
Metals	7.6-15.9	22.1
Silica	50	8.6
Quartz	11.0- 18.6	8.0-8.8
Hydrocarbons	4.6-10	6.3
Polystyrene	6.2-16.8	5.6-6.4