

**PARTICLE-PARTICLE INTERACTIONS AND THEIR RELEVANCE TO THE BAYER
PROCESS**

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ABSTRACT

The interaction forces between "particles" present in Bayer liquors have a major influence on the mechanism(s) underlying seeding, precipitation and coagulation. To date these forces have not been explored in the Bayer process. However there is a strong quantitative base for interparticle forces and they have been successfully measured in other systems. The origin of these forces, whether they be electrostatic, van der Waals, or structural, is identified, several mathematical forms quantified and selected measurement techniques are discussed. Examples drawn from the literature, as well as from systems studied in the Ian Wark Research Institute are examined. The significance of the results obtained and their relevance to the Bayer process are highlighted.

KEY WORDS:

Particle interactions; particle interaction theory; particle interaction measurement; Bayer process and particle interactions.

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1.0 INTRODUCTION

Particle-particle interactions are of central importance to the behaviour of dispersions of solids in liquids. In Bayer liquors, interactions between gibbsite "particles" influence the crystallisation and agglomeration processes whilst in red muds, the observed colloidal stability owes its origin to strong interparticle repulsive forces.

Our purpose here is to describe the origins and measurement of interparticle forces, to demonstrate how this knowledge permits us to understand the properties of colloidal dispersions and, through several examples, illustrate how we may begin to probe crystallisation and coagulation behaviour in Bayer liquors.

To help us in our discussion, some basic terminology is useful (1,2).

Solids in suspension are considered to consist of:

- primary particles which are usually crystals with a diameter of a few tens of nm,
- aggregate particles and
- agglomerate particles.

An aggregate is a collection of primary particles sintered together so that their surface area is significantly less than the sum of the areas of their constituent particles. An agglomerate is formed from primary particles firmly joined at edges and corners with less loss of the surface area. Agglomerates and aggregates are porous and contain voids, however agglomerates have a higher fraction of voids than do aggregates. A colloidal dispersion is used to describe particles dispersed in a liquid when the particles are of colloidal size i.e. a 1 μm or so in diameter or less. The term "sol" (solid in liquid) is synonymous.

Flocculation describes the formation, under the influence of polymer, of relatively weak clusters or flocs from aggregates, agglomerates or individual particles. The term coagulation is used to describe this process when the clustering is dictated by electrolyte concentration, giving rise to coagulates.

Conditions of low shear, experienced during pouring or mild shaking, frequently disrupt coagulates and flocs. Crumbling of aggregates or agglomerates occurs under the action of large shear forces. Deflocculation and deaggregation are the terms used to describe the breakdown of flocs and coagulates into smaller entities. We now explore the forces which give rise to these effects.

2.0 INTERPARTICLE FORCES

2.1 van der Waals Forces

Any pair of identical atoms or molecules attract each other by van der Waals forces. The energy of this attraction u at a distance r is given by:

$$u(r) = -\frac{\beta}{r^6} \quad \dots(1)$$

where β is a constant related to the chemical nature of the molecules and r is the distance between the centres of the molecules. This theory has been developed in detail elsewhere (3). Suffice it to say that $u(r)$ falls off very rapidly with distance. For a pair of macrobodies, for example colloidal particles consisting of many identical molecules, the van der Waals energy, V_A can be calculated by integration of all interaction pairs.

$$V_A(r) \approx - \sum_{\text{all pairs}} \frac{\beta}{r^6} = - \iint_{V_1 V_2} \frac{\beta q^2}{r^6} dv_1 dv_2 \quad \dots(2)$$

where v_1 and v_2 represent the volumes of particles 1 and 2 and q represents the number of atoms per unit volume of the particle material. Independent of the geometry for two macrobodies of the same type, all solutions have the general form

$$V_A = -A f(\text{geometry}) \quad \dots (3)$$

where the proportionality constant A is known as the Hamaker constant. Its magnitude ranges from 1 to 100×10^{-20} J, depending on the nature of the material and the supporting medium. It is always positive for like materials, thus V_A is attractive (negative) in Equation 3, but may be negative for unlike materials, leading to a repulsive (positive) V_A . The latter case is less common. A is tabulated for many systems of interest (4) and may be calculated provided the correct optical data are available or can be measured (5). In passing one should note that A can vary with temperature, a change which may impact upon colloid stability.

When the interacting macrobodies consist of two flat, parallel plates or slabs with a thickness which is greater than the separation between the plates H (Figure 1a), the van der Waals energy of attraction V_A^{flat} between unit area of one plate and the other is given by (4):

$$V_a^{\text{flat}} = -A \frac{1}{12\pi H^2} \quad \dots (4)$$

which demonstrates that on approach the attraction energy increases with the square of the distance. Owing to the additive contribution of all the molecules in the macrobody, the decay of V_A with distance is much less pronounced than for the individual molecules, where the decay decreases with the sixth power of distance (see Equation 1).

For a pair of equal spheres with radius a (Figure 1b), particle centre to centre distance R , distance of closest approach between the spherical surfaces $H (= R-2a)$, with $S = R/a$, V_A is given by

$$V_A = -\frac{A}{6} \left(\frac{2}{S^2 - 4} + \frac{2}{S^2} + \ln \frac{S^2 - 4}{S^2} \right) \quad \dots (5)$$

Note that the geometrical function is dimensionless and that the dimensions of V_a^{sphere} are the same as those of the Hamaker constant A i.e. joules. V_a^{sphere} is a total energy and increases in magnitude with the radius a of the suspended particle at a given distance of separation. Hence it takes more energy to separate large particles than smaller ones, or alternatively the energy gain obtained on approach is larger for big than for small particles. This is even more clearly seen for short distances of approach where $H \ll a$, and Equation 5 becomes

$$V_a^{\text{sphere}} = -\frac{Aa}{12H} \quad (6)$$

In the case of attractive interactions, as soon as the energy of attraction becomes greater than that of the Brownian kinetic energy of the particles, attraction must inevitably result with the subsequent formation of doublets, triplets and higher multiplets (4).

The theory presented here is necessarily brief. It is wise to recognise that other subtle effects can modify these van der Waals interactions. For example van der Waals forces exhibit the quantum mechanical phenomenon of retardation, which leads to a stronger decay with distance at large distances (3, 4). This means that the change in energy occurring upon the approach of two particles becomes more sensitive to the interparticle distance. With big particles, which have larger attractive energies, the effects are particularly important and cause particle "bonding energies" to be dominated by the interactions of protrusions at the closest points of contact. This is a surface roughness effect another consequence of which is that protrusions cause particles in sediments to remain more separated than when they are smooth. Thus the average van der Waals "bonding energy" obtained at these more remote distances will be low, causing the particles to be more weakly held together. Small changes in the position of these particles, which reduce the particle separation, can then increase the van der Waals "bonding energy". The effects of surface roughness are dealt with in detail elsewhere (6).

2.2 Other Forces and Colloidal Stabilisation

We have seen that attraction by van der Waals forces causes an energetically favourable situation to occur when particles approach each other, as shown in Figure 2. For two like particles, the closer the surfaces approach, the larger is the reduction in energy. If at some distance from the surface of a particle, some "barrier" is created that hinders a closer approach, the energy at that distance is more favourable (lower) than at infinite separation. Both long (a) and short (b) range barriers are shown in Figure 2.

Such a repulsive barrier can markedly reduce the rate of coagulation of colloidal particles (2). For dispersed systems, there is always a very short range Born repulsion (4) which arises from the overlap of electron clouds on adjacent surfaces and is of too short range to prevent strong van der Waals attraction from taking place. Of much greater significance is the existence of barriers caused by electrostatic, steric or structural forces, or formed by combinations of these. The first effect is based on the creation of an electrostatic repulsive force and is discussed in more detail below, whilst the second arises from the formation of a barrier created by the presence of, say, an adsorbed, bulky polymer. Repulsion arises just as soon as the adsorbed layers begin to overlap, an unfavourable energy arising due to a decrease in entropy of the partially overlapped layers (7). Described in elegant detail elsewhere (7), the steric barrier is steep (simplistically it may be thought of as a "brick wall"), increasing sharply when $H < 2\delta$ where δ is the adsorbed layer thickness. Of much shorter range, extending over a few molecular diameters or so, are solvation forces, induced by the surface altering the nature of the fluid in the regions close to the surface. There is now direct experimental evidence for the existence of such forces (3) which permit many otherwise inexplicable colloid stability phenomena to be interpreted e.g. the swelling of dried clay minerals.

In recent years the surprisingly long range (up to tens of nms) distance dependence of attractive hydrophobic forces has been experimentally determined (3,8). Although their origin and theoretical interpretation remain obscure, they can be of key importance to particle interactions, particularly in mineral flotation.

We now turn to a more detailed consideration of electrostatic forces.

2.3 Electrical Double Layers and Electrostatic Repulsion

When a solid is introduced into an electrolyte solution, the solid surface becomes charged if there is an unequal adsorption of positive and negative ions at the surface. Coulombic forces caused by the adsorbed ions keep the counter ions near the surface and the co-ions further away whereas Brownian motion counteracts that effect and causes them to be distributed diffusely through the liquid phase. For the systems of interest here, surface charge arises as a result of the spontaneous dissociation of molecules present on the solid surface.

The combination of surface charge, counter ion and co-ion layers is referred to as the "electrical double layer", the formation and properties of which are dealt with in detail elsewhere (2, 3, 4).

The thickness of the electrical double layer around a charge can be characterised by the "Debye length", $\frac{1}{\kappa}$, where κ is the Debye-Hückel screening parameter. For a monovalent, symmetric 1:1 electrolyte (e.g. KNO_3), κ is defined as

$$\kappa = \sqrt{\frac{2e^2 n_i}{\epsilon_0 k_B T D}} \dots (7)$$

where ϵ_0 is the dielectric permittivity in vacuum, k_B is Boltzmann's constant, T the temperature in Kelvin, e the elementary charge, D the dimensionless dielectric constant and n_i the ionic number concentration (ions m^{-3}). A potential decay takes place from the surface as we move out into the electrical double layer. If the surface potential at the beginning of the electrical double layer is denoted as ψ_0 , for flat double layers it may be shown that

$$\tanh\left(\frac{e\psi}{4k_B T}\right) = \tanh\left(\frac{e\psi_0}{4k_B T}\right) \exp(-\kappa x) \dots (8)$$

where ψ is the potential at some distance x from the surface in the electrical double layer.

At small potentials

$$\psi = \psi_0 \exp(-\kappa x) \dots (9)$$

For spherical electrical double layers there is no general analytical solution. However at low potentials

$$\psi = \psi_0 \frac{a}{r} \exp(-k(r-a)) \dots (10)$$

where ψ is the potential at a distance r from the particle centre and a is the particle radius. From Equation 9, $\psi = \frac{\psi_0}{e}$ when $\frac{1}{\kappa} = x$ and, from Equation 7, noting that $n_i = N_A 10^3 C_i$ where C_i is the bulk molar ionic strength and N_A is Avogadro's constant, then

$$\frac{1}{\kappa} = \left(\frac{k_B T \epsilon_0 D}{2 \times 10^3 N_A e^2 C_i} \right)^{1/2} \dots (11)$$

Thus $\frac{1}{\kappa}$ decreases with increasing C_i and the potential ψ decays more rapidly as the electrolyte concentration increases.

Overlap of electrical double layers occurs when particles come close to one another under the action of shear, gravity or Brownian motion. Overlap of two double layers generally leads to the development of an electrostatic repulsive force if the particles are of like charge. The magnitude of this repulsion is linked to the extent of the overlap.

The repulsive forces and energies between, say, flat plates and spheres may be calculated. This is not a trivial exercise (2, 3, 4, 9) and only several important results are shown.

For conditions of weak overlap, where the potential at the halfway point between the two surfaces, $\psi_{H/2}$ is small, the repulsive energy between two flat plates is given by:

$$V_R^{\text{flat}} \approx 64 n_i k_B T \gamma^2 \frac{1}{\kappa} \exp(-\kappa H) \dots (12)$$

which reduces to

$$V_R^{\text{flat}} \approx 2\epsilon_0 D \psi_0^2 \kappa \exp(-\kappa H) \dots (13)$$

when both $\psi_{H/2}$ and ψ_0 are small; $\gamma = \tanh\left(\frac{e\psi_0}{4k_B T}\right)$

For two spheres, the equivalent expression becomes

$$V_R^{\text{sphere}} \approx \pi a 64 n_i k_B T \gamma^2 \frac{1}{\kappa^2} \exp(-\kappa H) \dots (14)$$

and, for small $\psi_{H/2}$ and ψ_0 ,

$$V_r^{\text{sphere}} \approx \pi a 2\epsilon_0 D \psi_0^2 \exp(-\kappa H) \dots (15)$$

In all cases (Equations 12 to 15) we can quickly observe that V_R is very sensitive to changes in electrolyte (or salt) concentration, decreasing quite sharply as the electrolyte concentration is increased. We are now in a position to consider the interplay of the van der Waals and electrostatic forces, embodied in the DLVO theory.

2.4 DLVO Theory

The magnitudes of attraction and repulsion can be conveniently represented by energy-distance or force-distance curves, where the distance refers to the separation, H , between the interacting surfaces. A simple addition of all these various energies or forces permits one to identify which effect dominates over any other at a specific distance. The additivity of van der Waals and electrostatic forces was first formulated by Derjaguin, Landau, Verwey and Overbeek (hence "DLVO" theory) some forty years ago. A general result is shown in Figure 3, where $V_{\text{total}} = V_A + V_R$.

Particles which are so close to each other that they are found at the distance of their primary minimum are in an energetically extremely favourable situation and are rigidly bound to each other. Suspensions consisting of such particles are rigid and unpourable. However, when only secondary minimum coagulation between particles occurs this gives rise to a more "liquid" behaviour of the suspensions. Thus, the strength of the interparticle attractions determines the physical properties of a suspension, as noted above.

The interparticle attractions can be strong or weak depending completely on the size and range of the repulsive barrier: a high repulsive barrier V_{max} kinetically inhibits strong primary minimum coagulation. A short range repulsive barrier causes a deeper secondary minimum. It induces an energetically more favourable position for the particles (in the secondary minimum) and gives faster coagulation to form loose and open coagulates. On the other hand a long range repulsive barrier causes a shallow secondary minimum at a relatively large interparticle distance, causing weak coagulation with dense packing.

3.0 MEASUREMENT OF INTERPARTICLE FORCES

Only a few of the available techniques are mentioned here, for there are very detailed descriptions available in the literature (2, 3).

One of the simplest and most informative techniques involves the measurement of coagulation rates i.e. the rate at which the colloid particle number decreases with time. This is normally measured by direct particle counting or turbidity measurements. Qualitative information as to the stability of the initial, dispersed system can be obtained. Does it remain kinetically stable or does it coagulate, reflecting a balance between repulsive and attractive forces? Can it be readily redispersed (or peptized), indicating the presence of a secondary minimum? Quantitatively, the ratio between measured and theoretically predicted coagulation rates, termed the stability ratio, is directly linked to the height of the potential energy barrier, V_{max} , shown in Figure 3.

It is possible to measure the force between two smooth surfaces using the surface forces apparatus (SFA). Although this technique has achieved prominence over the past decade or so, it is generally restricted to flat, smooth mica, silica and aluminium oxide surfaces in air or in a liquid. The atomic force microscope (AFM) has normally been used for imaging surfaces in air or in a liquid. The instrument can now be adapted so that the force between a small sphere (1 to 5 μm or so in diameter) and a flat surface or another sphere can be measured directly. These direct measurement techniques are very powerful indeed and enable the DLVO theory to be rigorously tested as well as the identification of non-DLVO solvation, steric and hydrophobic forces.

Whilst these techniques are very useful they are restricted to quite large macroscopic bodies. In Bayer liquors there is very strong evidence that very small species are detectable, with dimensions in the tens of nm range. Invisible to the naked eye the species do, however, scatter radiation. The technique for probing the particle size, concentration, particle interaction and wavelength dependence of this scattering process is termed "light scattering". For "particles" which are classed as Rayleigh scatterers, with a diameter less than circa one twentieth of the incident radiation wavelength,

$$\frac{Hc}{\tau} = \frac{1}{M} + 2BC \quad \dots 16$$

where C is the concentration of scatterers (gcm^{-3}), τ is the turbidity (cm^{-1}), M is the weight average molecular weight, H is an optical constant ($\text{mole cm}^2 \text{g}^{-2}$) and B is the second virial coefficient ($\text{mole cm}^3 \text{g}^{-2}$). Light scattering is a non invasive technique which permits the behaviour of a very large

number of scatterers, contained in the scattering volume (e.g. of dimension perhaps 1 cm^3) to be examined. The second virial coefficient, B , reflects the net excess (over the medium) attraction or repulsion between the scatterers and is directly linked to the interparticle forces discussed above. Let us now examine several examples which are pertinent to Bayer liquors.

4.0 EXAMPLES

(a) Colloid Stability of a Gibbsite Sol

Gibbsite particles have a point of zero charge of about 9.8 on the pH scale, below which their surfaces are positively charged, above which they are negative. The colloid stability of submicron sized gibbsite particles is shown in Figure 4. The change in turbidity, measured as an absorbance decrease, is shown as a function of pH where the background electrolyte is 10^{-4} M NaCl (10). From pH 7 to 9 the gibbsite sol is stable - there is a strong, electrostatic repulsive force between the particles. V_{max} in Figure 3 is large.

From around pH 9.5 to 10.5 the sol becomes unstable and coagulation occurs, for both ψ and ψ_0 are small (see Equation 8), V_R is small (Equation 15) and V_{vdw} is dominant (Equation 6). Above about pH 11, the sol becomes stable again as the particle surfaces become negatively charged and V_R exceeds V_A . This behaviour persists until about pH 12.5 where the sol becomes unstable again. The electrical double layer is compressed at this high pH, because the "salt" concentration or ionic strength is high, κ is correspondingly high (Equation 7) and $\frac{1}{\kappa}$ low, thus ψ (Equation 8) is low and V_R (Equation 15) is low. One would expect that this colloid instability to occur under the extreme conditions of Bayer process liquors e.g. $A/C = 0.7$, 6M NaOH . Surprisingly, however, colloidal gibbsite particles remain stable under these extreme conditions where V_R is essentially zero and V_A is strongly attractive. This stability persists for both dispersed particles as well as for those formed by precipitation from a supersaturated solution. This behaviour points to the existence of non-DLVO repulsive forces which are likely to be steric or structural (e.g. solvation) in origin. Interestingly particles which coagulate at lower pH appear to be relatively easily redispersed. Although this is only a preliminary observation, it hints that short range non-DLVO forces may operate at these pH values.

(b) Light Scattering Behaviour of Bayer and Near Bayer Solutions

The light scattering behaviour of fresh Bayer and near Bayer solutions containing dissolved aluminium III (from the metal) and 6.0M NaOH is shown in Figure 6 (11). The data are plotted according to Equation 16, noting that A/C can readily be converted to Al^{III} concentration in g cm^{-3} . Using this information it is possible to calculate the weight average molecular weight of the species from the intercept on the HC/τ axis. This yields a MW of $60 (\pm 40\%)$ which compares quite favourably with the MW of a single $\text{Al}(\text{OH})_4^-$ species of 95. Given the sensitivity required to obtain such data, along with the error involved, this is a quite remarkable result. The negative gradient in Figure 6 indicates that B (Equation 16) is negative and that scatterer-scatterer attractive interactions are dominant in this system i.e. that growth is favoured, a conclusion which was verified by the long time changes in the scattering intensities (11).

5.0 CONCLUSION

The measurement and interpretation of interparticle forces under and away from Bayer conditions can enhance our understanding of the process. Few measurements have been performed in such systems, with the result that gibbsite formation, growth and agglomeration are poorly defined.

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