ISM05

Properties of Colloids II
Topics

- DLVO theory
- Polymer adsorption/ steric stabilization
- Electrokinetic effects
- Special colloids: clay, foam, emulsions

Additional information from the book
*Intermolecular and surface forces*
Jacob Israelachvili
DLVO theory

Derjaguin-Landau-Verwey-Overbeek

\[ V = V_R + V_A \] potential energy

\[ V_R \] repulsive (electrostatics)

\[ V_A \] attractive (dispersion)

\[ V(h) = cst_1 e^{-\kappa h} - \frac{cst_2}{h^2} \] flat plates

\[ F(h) \equiv -\frac{dV}{dh} \] force
Potential energy curves

- a: high salt concentration
- b: intermediate
- c: low salt concentration

The system is unstable at high and intermediate salt concentration.

Notice the secondary minimum in curve b.

The system flocculates, but the aggregates are weak.

This may imply reversible flocculation.
Experiment

Colloidal suspension

Add salt

Flocculation (vlokjes)

Depending on density

cream

sediment
Experiment

Irreversible flocculation

Remove salt

Reversible flocculation
Surface force apparatus (Israelachvili)

Fig. 10.7. Surface Forces Apparatus (SFA) for directly measuring the force laws between surfaces in liquids or vapours at the ångstrom resolution level. With the SFA technique two atomically smooth surfaces immersed in a liquid can be brought towards each other in a highly controlled way (the surface separation being controlled to 1 Å). As the surfaces approach each other they trap a very thin film of liquid between them and the forces between the two surfaces (across the liquid film) can be measured. In addition, the surfaces can be moved laterally past each other and the shear forces also measured during sliding. The results on many different liquids have revealed ultrathin film properties that are profoundly different from those of the bulk liquids, for example, that liquids can support both normal loads and shear stresses, and that molecular relaxations can take $10^{10}$ times longer in a 10 Å film than in the bulk liquid. Only molecular theories, rather than continuum theories, can explain such phenomena. However, most long-range interactions are adequately explained by continuum theories.
Measured DLVO forces

(from Israelachvili’s book)

Notice logarithmic scale
DLVO theory

The derivation of the repulsive interactions in DLVO theory is … Something for later. But the attractive part we already know!

\[ V_R = 64kTc_0 A \tanh^2 \left( \frac{e\psi_0}{4kT} \right) e^{-\kappa h} \] (flat plates, surface area \( A \))

\[ V_R = 64kTc_0 R \tanh^2 \left( \frac{e\psi_0}{4kT} \right) e^{-\kappa h} \] (spheres, radius \( R \))

\( \psi_0 \) surface potential

when \( e\psi_0 < kT \) \((\psi_0 < 25 \text{ mV})\), this is simplified to

\[ V_R = \frac{2\sigma^2 A}{\kappa \epsilon} e^{-\kappa h} \] (flat plates)

\[ V_R = \frac{2\pi \sigma^2 R}{\kappa^2 \epsilon} e^{-\kappa h} \] (spheres)

\( \sigma \) surface charge density

(Hamley eq. 3.21 contains mistake, it misses \( \exp(-\kappa h) \))
Polymer adsorption/steric stabilization

The *advantage* of electrostatic stabilization is that it is easy to prepare: just introduce a few surface charges. A (very big) *disadvantage* of electrostatic stabilization is that it is highly sensitive with respect to surface charge (pH) and salt concentration.

Steric stabilization by surface bound polymers is:
1. not sensitive to surface charge and salt concentration
2. works also in non-aqueous media
3. (and works also in concentrated dispersions)

Disadvantage: more difficult to prepare
Types of polymer layers

Chemical adsorption (grafted polymers)
Types of polymer layers

Physical adsorption
Homopolymers
You need: Good solvent and a Bad surface
Types of polymer layers

Physical adsorption
*Block* copolymer

Best choice:
- no chemical synthesis required
- free design of anchoring block
Morphologies of grafted polymer layers

Figure 3.7  Polymer chains grafted at a planar interface: (a) brushes, at high grafting density, (b) mushrooms, at low grafting density
stabilization

**Good** solvent, adsorbed polymers

The chains are swollen
When the two layers come into contact
-the osmotic pressure rises,
because the concentration of monomers increases
-the configurational entropy decreases, because the polymers can sample fewer conformations
The two colloids are kept apart, on the scale of the swollen polymer layer.
When the van der Waals interactions of the colloids on this scale of separation is small
(depends on length of polymers, grafting density etc.)
The colloidal dispersion is stable

The higher the load with polymers,
The higher the repulsion
Free energy curves

Figure 3.8 Potential energy curves for a pair of sterically stabilized colloid particles, separated by a distance $h$. (a) Repulsive contribution to the free energy, (b) attractive contribution and total free energy. The grafting density decreases from i to iv.
Flocculation

Bad solvent, adsorbed polymers

The chains are collapsed, in order to avoid solvent-monomer interactions. When the polymer layers come into close contact, they will stick together.

The worse the solvent, the more unstable the colloidal dispersion.

Cross-over from stabilization to flocculation: $\theta$ solvent.
Bridging flocculation

Good adsorbers, good solvent, (very) low polymer density, (very) long polymers

The long polymers ‘bind’ the colloids together in open flocs. Application: water purification (in practice, a few ppm of cationic polyelectrolyte is added, since most natural colloid surfaces are negative)
Depletion flocculation

Good solvent, non-adsorbing polymers

When two colloids meet in close contact, the total amount of accessible volume (for the polymer) is increased, hence the translational entropy is increased, and thus the colloidal dispersion is destabilized.
Electrophoresis

\[ u = \frac{v}{E} \quad \text{mobility} \]
\[ v \quad \text{velocity} \]
\[ E \quad \text{electric field strength} \]

The surface bound ions pull the colloid along the electric field

\[ \mathbf{E} \equiv -\nabla V \]

\( V \) applied potential

\[ E = -\frac{dV}{dx} \quad \text{potential gradient in 1 dimension} \]
**Mobility**

Charge is in the center

\[ F_{\text{pull}} = qE \quad \text{small ions and spherical colloids} \]
\[ q = 4\pi R^2 \sigma \quad \text{colloids} \]

Charge is on the surface

\[ F_{\text{friction}} = 6\pi \eta R v \quad \text{Stokes} \]
\[ F_{\text{pull}} = F_{\text{friction}} \quad \text{stationary state} \]
\[ u = \frac{q}{6\pi \eta R} \]

Whether the charge is on the surface or in the middle, does not matter.
**Advanced topic: zeta-potential**

The colloid surface is hydrated, and the mobile ions do not penetrate the *Stern* layer (see ISM04)

The potential at the surface of the Stern layer is the zeta-potential $\zeta$

In the colloid and surface chemistry literature, electrokinetic phenomena are usually explained in terms of the zeta-potential. In the bio(chemical) literature, electrokinetics is explained with charges

**Bonus for exam: 0.5 point**

What is the relation between surface charge density and zeta-potential for a flat surface?
Application: SDS gel electrophoresis

Proteins: variable mass, variable charge

Denaturate with surfactant SDS

When the chain is completely unfolded

\[ q \approx q_{SDS} \approx cst. \times M \]

mmm….rather rough model
Gel electrophoresis

In the gel, the friction coefficient is (much) larger due to the physical polymer barriers. The net mobility is in first approximation a function of the protein mass only (and the pore size)

\[ q \approx q_{SDS} \approx \text{cst.} \times M \]

\[ F_{friction} = \eta f(M, gel) \]
\[ F_{pull} = F_{friction} \quad \text{stationary state} \]
\[ u = \frac{\text{cst.}}{\eta} \times \frac{M}{f(M, gel)} \]

In the experiments, the mobility (or distance traveled after given amount of time) is plotted versus logM: more or less a straight line, there is no satisfactory model why this should be so!
Electro-osmosis and capillary electrophoresis

Glass capillary, length 0.5 m, diameter 50 micron

The mobile positive counter-ions move in the applied electric field. They drag the solvent towards the anode. Hence the electric field generates a flow. The higher the surface charge, the more mobile counter-ions, and the larger the flow.
Capillary electrophoresis

Since the pull on the solvent is located at the boundaries (in the double layer O(1nm)), the flow-profile is that of a plug

\[ v_{EOS} = \frac{\overline{E} \epsilon \zeta}{\eta} \]

Compare with flow profile in response to pressure gradient (parabolic Poisseeuille profile)
Electro-osmotic velocity

Derived from combination of (Navier-)Stokes equation and Poisson Boltzmann equation
Very difficult!

We will try a simple dimensional analysis

\[ v_{EOS} = E \epsilon \zeta \frac{r_D}{\eta} \quad \text{m s}^{-1} \]

These are the factors we think are important

\[ v_{EOS} = E^\alpha r_D^\beta \sigma^\gamma \eta^\delta \]

\[ \alpha = 1 \]
\[ \beta = 1 \]
\[ \gamma = 1 \]
\[ \delta = -1 \]

Exercise: is the velocity dependent of the length of the capillary?
Capillary electrophoresis

Added charged analytes will
-move with the background solvent flow
-and on top of that, move faster or slower depending on the additional pull by the electric field

Very fast and efficient separation
Special colloids: clay

Diameter: O(microns)

Mica, Kaolinite, Betonite, Montmorillonite,...

Applications:
- bricks/ceramics
- fillers
- drilling muds
- clay ‘detergents’
- The Netherlands
Stacking of clays

Some clays may stack like a card house (or Mondriaan): positive edges in contact with negative plate surface with lots of open space for the solution

When softly shaken, such a structure behaves like a gel, ...but when vigorously shaken, it behaves like a fluid: catastrophic avalanche effect

In drilling mud, negative (poly)electrolyte is added to stabilize the edges, this is called ‘peptization’
Quick clay: very dangerous!

‘a type of clay formed by glaciers that loses its shape when shaken’

The quick clay landslide in Rissa, Norway
Available from NGI, Norway---
See this Web page for a browser video clip.
This is one landslide video you should see!
It was taken on the spot by someone who happened
to be there with a camcorder in his hand! Very dramatic scenes...
A tiny excavation triggered the slide
http://www.ejge.com/iGEM/videos.htm

Source: http://www.ngi.no/
Special colloid: casein micelles

Of, hoe je kaas maakt. Op het werkcollege!

This concludes file ISM05