Colloids and Surface Chemistry

What is a colloid?

- Finely-divided dispersion of one phase in another
- Size of dispersed ("solute-like") entity >> ordinary molecules
- Example: blood cell in water.

Solution: homogeneous particles are molecules
Suspension: heterogeneous particles settle out

Colloid
size 1-1000 nm
particles remain suspended

• Simplest: tiny particles dispersed in water

Examples

- Continuous phase is often water.
- Wide range of sizes:
  - bovine serum albumin: 3 nm;
  - cells: tens of microns
- Classify colloids as hydrophobic (e.g., carbon black) or hydrophilic (e.g., red blood cell).
- Stability of colloid: essential part of its function.
- E.g. blood cells:
  - normally colloidally stable, but
  - colloidally unstable when they clot
- Milk (oil in water emulsion) on edge of stability: it creams (some coalescence).

Characteristics of colloids

- Continuous phase and dispersed phase

- Thermodynamically unstable but kinetically stable (i.e. they are stable indefinitely)
- Classified in terms of dispersed substance (solid, liquid, gas) in dispersing medium (solid, liquid, gas)
- Dispersed phase 10-1000 nm particles:
  - Large surface area to volume ratio
  - Size appropriate for scattering light
  - May have charged surfaces
- The name: Greek kolla = glue, eidos = like
<table>
<thead>
<tr>
<th>Continuous phase</th>
<th>Dispersed phase</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas</td>
<td>liquid</td>
<td>aerosol</td>
<td>fog</td>
</tr>
<tr>
<td>gas</td>
<td>solid</td>
<td>aerosol</td>
<td>smoke</td>
</tr>
<tr>
<td>liquid</td>
<td>gas</td>
<td>foam</td>
<td>whipped cream</td>
</tr>
<tr>
<td>liquid</td>
<td>liquid</td>
<td>emulsion</td>
<td>milk</td>
</tr>
<tr>
<td>liquid</td>
<td>solid</td>
<td>sol</td>
<td>paint, blood, ink</td>
</tr>
<tr>
<td>solid</td>
<td>gas</td>
<td>solid foam</td>
<td>meringue</td>
</tr>
<tr>
<td>solid</td>
<td>liquid</td>
<td>solid emulsion</td>
<td>butter</td>
</tr>
<tr>
<td>solid</td>
<td>solid</td>
<td>solid sol</td>
<td>opal</td>
</tr>
</tbody>
</table>

**Polymer colloids**
- Paints, glues, ...

- Many long polymer chains
- Surfactant (soap)
- Water

**Kinetic vs. thermodynamic stability**
- Charges keep colloids apart indefinitely: very high activation energy for forcing them together (coalescence)
- However, the lowest free energy is when they are coalesced:
  - Higher entropy: polymer chains mix
- Hence kinetically stable (very high barrier, it takes “forever” to coalesce) but thermodynamically unstable

**What they look like**
- Electron micrograph of a polystyrene polymer colloid:
  - Often very monodisperse (all particles have same size)
They actually move

• Movie of light microscopic picture of large (~4 µm) polystyrene latex

Colloidal crystals

• The colloidal suspension can form regular arrays:
  Results in opalescence (diffraction because particles align with glass walls)

Surfactants

• Important in colloid and surface chemistry
• Surface-active agent: molecule with hydrophobic (= lipophilic) and hydrophilic (= lipophobic) portions.
  e.g. (a) sodium dodecyl sulfate
  \[\text{CH}_2(\text{CH}_2)_\text{OH} - \text{OSO}_3^-\text{Na}^+\]
  (b) salts of bile acids – sodium deoxycholate

• Can also be cationic, e.g. C_{14}\text{NH}_3^+\text{Br}^- (a common disinfectant)
Ionic surfactants

- Ionic surfactants: e.g. sodium dodecyl sulfate
- Adsorbs onto polymer colloid: hydrophobic part in (organic) polymer, hydrophilic part in water: thermodynamically advantageous.
- Colloidal stability through electrostatic repulsion

Negative charge from adsorbed surfactant attracts opposite charge: double layer
Repulsion between double layers keeps particles apart (colloidal stability)

Double-layer repulsion

- How it works

Micelles

- Fatty acids: $C_{12} = $ dodecyl, $C_{18} = $ stearic
- Ions have long nonpolar tail and polar head
- Soap solution:
  - individual fatty acid anions dispersed in water
  - groups of ions: micelles
  - hydrophilic part in water, hydrophobic tails: thermodynamically advantageous

End of Lecture 1
Revision - no need to copy

- Colloids: stable dispersion of one phase in another
e.g. paint and blood: tiny particles dispersed in water

- Surfactants: molecule with hydrophobic and hydrophilic part,
e.g. sodium dodecyl sulfate
- These adsorb on surface of (organic) colloid
  - colloidal stability through electrostatic repulsion
    - involves double layer of counter-ions

Micelles

- Fatty acids: $C_{12} = \text{dodecyl}, C_{18} = \text{stearic}$ (not $C_{14}$ – error in last transparency of previous lecture)
- Ions have long nonpolar tail and polar head
- Soap solution:
  - individual fatty acid anions dispersed in water
  - can group: micelles
  - hydrophilic part in water, hydrophobic tails with other hydrophobic tails: thermodynamically advantageous

Micelles form above Critical Micelle Concentration (CMC)

- Soap-water mixture: suspension of micelles in water.
- Relatively large micelles scatter light (colloidal) so soapy water looks cloudy

The CMC

- Bigger hydrophobic part:
  - more water-water hydrogen bonds it disrupts
  - more difficult to keep in aqueous solution
- Hence longer chain = lower CMC
The CMC

- Shape of surfactant also important → more difficult it is to pack the chains together, harder to form micelle

Hydrophobic interaction

- Water highly ordered around isolated surfactant molecule in solution.
- Lower free energy: hydrophobic tails together (e.g. in micelle), which increases entropy of external water.
- Will see: this is responsible for stability of membranes.

Light scattering

- Amount of scattering \( \propto (\text{particle diameter})^6 \cdot (\text{wavelength})^{-4} \)
- Scattering intensity also depends on viewing angle
- Demonstration: change in colour (which wavelength is scattered most) as colloidal sulfur is formed and particles increase in size
  - actual reaction is complex set of redox processes:
  - acidified \( \text{S}_2\text{O}_3^2- \rightarrow \text{S, SO}_4^{2-} \ldots \)

Surfactants

- “Dirt” is non-polar. Grease = long chain hydrocarbons
- However water is very polar and will not dissolve ‘greasy dirt’
- Soaps, detergents (e.g. sodium dodecyl sulfate): emulsifying agent
  - Suspends normally incompatible grease in water
  - Charges on outside from surfactant solubilise particle in water
- Hence called wetting agent or surfactant (= surface-active agent)
In biology

- Ionic surfactants include bile salts

- Break up fat into tiny emulsion droplets which can be more easily digested

Surface Tension

- Molecules in interior of liquid are surrounded by other molecules of the same kind
  - However, those at liquid surface see attractions only from one side and from below

- The effect of this uneven pull on surface molecules makes droplet become spherical – minimum surface area

Surfactants at the interface

- Surfactants have hydrophobic and hydrophilic parts
- Hence both parts “happy” in micelles (“happy” = low free energy)
- Hydrophobic part also makes them accumulate at air-water interface
  (hydrophobic part is at least out of the water)

- Hence they lower the surface tension of water
Surface Tension
- Molecules on the surface would rather be in bulk
- Resistance of liquid to increase in surface area: surface tension
- Polar solvent: high surface tension
- The liquid appears to have a skin over the surface—e.g., insect walking on water surface—"bends" surface under its weight

Detergents
- Disadvantage of soaps: anions form precipitates with some cations in hard water (Ca\(^{2+}\), Mg\(^{2+}\))
  - scum: precipitate e.g. Ca stearate = Ca (C\(_{17}\)CO\(_2\)\(^{-}\))
  - Reduces soap efficiency.
- Synthetic detergents (e.g. Na dodecyl sulfate): Ca, Mg salts are soluble, hence cleans in hard water

Ions and colloidal stability
- Another effect of ions: they cause shrinkage of double layer which gives electrostatically-stabilised colloids their stability
- Reduces electrostatic barrier
- Can cause coagulation

'Hardy-Schulze Rule'
- Trivalent cation (e.g. Al\(^{3+}\)) collapses double layer more than divalent …
- Hence adding alum or FeCl\(_3\) often causes coagulation
End of lecture 2
Colloids
• Surfactants
• Electrostatic stabilization of colloid: adsorption of charged surfactant onto surface.
• Adding salts: shrinks double layer, reduces electrostatic barrier, can cause coagulation

Surfactants

Polymeric surfactants
• Polymer with hydrophobic & hydrophilic parts
\[ \text{C}_9\text{H}_{19}\left(\text{OCH}_2\text{CH}_2\right)_n\text{OH} \]
Surrounds particle as “hairy layer”

A steric stabiliser

Blood cells: will see that they have colloidal stability through combination of electrostatic and polymeric stabilisers

Stabilisation of colloids
• Muddy water: a clay colloid
• Electrostatic stabilisation by charges on clay surface (clay is sodium aluminosilicate)
• Adding salts: shrinks double layer, reduces electrostatic barrier, can cause coagulation

Polymeric surfactants
• Polymer with hydrophobic & hydrophilic parts

\[ \text{C}_9\text{H}_{19}\left(\text{OCH}_2\text{CH}_2\right)_n\text{OH} \]

Colloidal stability because it is thermodynamically unfavorable to force chains together by compressing chains
Polymeric surfactants

- Polymer with hydrophobic & hydrophilic parts

\[ C_{9}H_{19}OCH_{2}CH_{2}OH \]

Colloidal stability because it is thermodynamically unfavorable to force particles together by compressing chains

Electrosteric stabilisation

- Some species can function as both electrostatic and steric stabilisers: polymer which can have charge in water phase.
- Commonest: proteins
  - long polymers, often water-soluble
  - both basic and acidic regions
- Examples:
  - mayonnaise stabilised by egg yolk
  - casein is polypeptide with many amino acids, phosphate, polysaccharide (\( \alpha \)-casein): stabilises the fat emulsion droplets in milk
  - cells: these colloids are electrosterically stabilized (discussed later)
  - paints

Coagulation

- Destabilisation of a colloid to form macroscopic lumps...
- Can be by:
  - Heating: forces particles together and/or changes nature of stabiliser
  - Stirring: forces particles together
  - Adding salt (electrolyte): shrinks double layer and/or neutralises inherent charge (e.g. on clay)
  - Changing pH: can flatten/desorb electrosteric stabilisers
  - Adding floculant (demonstration)

Flocculants

- Long-chain polymer for water purification: causes colloid particles to coagulate by "lassoing" them.
- For purifying potable water and also for flocculation of sewage.
Solid particulates are common

Particulates and health

Colloids and health

Example: overhead power lines?

Example: overhead power lines?

This has been shown, but whether any real link to cancer has not been proved...
Tutorials

- bonus tutorial next week, 6th November Wednesday 1 pm in LT4

- End of lecture 3
**Revision - no need to copy**

- Colloids
- Stabilisers: electrostatic and steric

Particles kept apart by:
- Electrostatic repulsion
- Electrosteric stabilizers: polymers whose water-soluble part includes charges

**Lipids**

- Water-insoluble substances that can be extracted from cells by non-polar organic solvents (benzene…)
  - fats
  - phospholipids
  - waxes
  - steroids

- Fats = esters of glycerol (OHCH\(_2\)-CHOH-CH\(_2\)OH): triglycerides
- Saponification: hydrolysis of triglycerides to glycerol + fatty acids.
  - Can be done with NaOH to form carboxylate salts = soaps

**Phospholipids**

- Similar to fats: esters of glycerol.
- Unlike fats: only two fatty acids. 3\(^{rd}\) ester linkage involves phosphate group:
  - long non-polar tail
  - polar substituted phosphate "head"

Phospholipids tend to form bilayers in aqueous solution:
- tails in interior, polar heads interfacing with polar water molecules

**Lipids bilayers**

- Bilayers of larger phospholipids can close to form vesicles
- These are cells!

- Colloidal stability partly from polysaccharides: polymers of sugar units (straight-chain and branched)
- Hydrophilic!
**Biological membranes**

- Complex structure:
  - Lipopolysaccharide
  - Lipid
  - Polysaccharide
  - Globular protein

- Colloidal stability: sterically stabilised

$P_2^+$

$P = \text{globular protein}$

$PL = \text{phospholipid}$

**Cells**

- Phospholipids form a significant portion of cell membranes

- Cell membrane:
  - Protects workings of cell from extracellular fluid
  - Allow nutrients etc. to enter cell and waste products to leave: semipermeable...

**Exams**

- Examinable part of syllabus and type of exam questions: as given in assignments
- Bonus tutorial next week, 6th November Wednesday 1 pm in LT4
- Remember extra duty tutor hours
- Studying for exam for these last 9 lectures:
  - learn what has been indicated in notes and on blackboard
  - do problems from lectures and assignments again until you can obtain right answer without looking at the notes

**Some paths forward**

- Two of the things that can be done with polymer colloids:
  -latexes for biomedical diagnostics
  -better barrier-protection products (surgical gloves, ...)
  -robust water-based paints for outdoors
- Made possible with a revolution:
  -controlled radical polymerization
    (developed by Ezio Rizzardo, CSIRO, Melbourne):
    - normally a single polymer chain grows only for a few seconds, but making polymer takes hours
    - hence cannot create block copolymer by starting with one monomer, letting it polymerize completely, then adding a second monomer
Controlled radical polymerization

- Instead of having a few growing chains with short lifetimes, add reagent which “caps” growing chains
- All chains are then “alive” and grow slowly over the whole polymerization process
- Normal: most chains dead, a few are growing
- Controlled: all chains growing slowly

- The “cap”: $\text{Ph-S=CH}_2\text{Ph}$

Latexes for biomedical diagnostics

- How agglutination tests work:
- Using controlled radical polymerization, we have put groups on surface which can be attached to wide variety of bioactive molecules in a completely controlled way

Natural rubber latex gloves

Natural rubber latex:
- Entirely cis-polyisoprene
- Hence becomes stronger on stretching
- Forms film with exceptional barrier properties, e.g., to passage of viruses
- Hence major uses: surgical gloves, condoms
- Renewable resource
- Properties cannot yet be duplicated synthetically
- But major allergy problem: the proteins which give it colloidal stability as electrosteric stabilisers cause allergic reactions (especially in medical professionals – sensitisation)