Characterization of colloidal materials by electrochemical, electrokinetic and rheological methods

Michael Bredol

Fachhochschule Münster - University of Applied Sciences

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Fields of Colloid Chemistry

Colloid chemistry is the chemistry of heterogeneous systems and thus dominated by interfaces

- Colloidal systems with “large” components: classical behaviour
- Very “small” particles are dominated by quantum physics
Thermodynamic and kinetic stability

- Dispersion colloids are unstable: positive interface tension
- Stabilization necessary for technical applications
- Ion adsorption on particles: electrostatic stabilization
- Polymer adsorption on particles: entropic stabilization
- Without stabilization: rapid (diffusion controlled) agglomeration
- Molecular colloids (hydrophilic polymers, proteins . . . ) are thermodynamically stable
- Association colloids (micelles, membranes . . . ) are thermodynamically stable
Particle, rigid adsorption layer and counter ion cloud

*Debye-Hückel* model: reduction into spherical system around one particle
Electric potential at shear plane: $\zeta$–potential
Thicknness of ion cloud

Electrostatic analysis yields expression for thickness of diffuse counter ion cloud:

\[ r_D = \sqrt{\frac{\varepsilon RT}{IF^2}} \quad I = \frac{1}{2} \sum z_i^2 c_i \]
Repulsive and attractive forces

Attraction between particles: *van-der-Waals*--forces
Repulsion: electrostatics, due to adsorbed ions
Sum curve: potential barrier against agglomeration

Global minimum on close contact, second local minimum before barrier!
Stabilization and ion strength

Ion strength is most important parameter for electrostatic stabilization
Steric / entropic stabilization

- Adsorption of polymers with high molecular mass results in repulsive interaction
- In contact area, number of conformations is restricted, thus entropy reduced, resulting in repulsion
- Correct concentration is critical!
Coagulation in stabilized and non-stabilized systems

- Unstabilized dispersions form irreversibly fluffy sediments with low density
- Stabilized dispersions form reversibly sediments with high density
- Sediments from stable dispersions may be redispersed by simple stirring and/or shaking
Measurement of $\zeta$–potentials

- Charging makes particles mobile in an electrical field
- $\zeta$–potential is measure for charging
- Either Brownian motion or shear at the shear plane are employed for measurement
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- Either Brownian motion or shear at the shear plane are employed for measurement.
- Absolute measurements often on individual particles, but technical dispersions are very concentrated.
- Practically, relative measurements are often sufficient.
- Linear phenomena without electrochemistry (at the electrodes) are desired.
- Electroacoustic methods allow for characterization of concentrated dispersions.
Electrophoresis

Drift velocity $v_w$ is directly proportional to $\zeta$–potential. Modern systems use laser tracking of individual particles.

\[ v_w = \frac{\epsilon E}{6\pi \eta_0} \zeta \]
Sedimentation potential

Popular method due to ease of measurement. Works also in turbid and coloured dispersions.

\[ E_S = \frac{\varepsilon \varepsilon_0 l g r^3 N}{3 \eta \kappa} (\rho - \rho_0) \zeta \]
Streaming potential

Important method in fibre and paper industry

\[ \frac{E_{St}}{\Delta P} = \frac{\epsilon}{6.75 \cdot 10^7 \cdot 4\pi \eta \kappa} \zeta \]

Automated systems collect fiber plug on funnel with electrodes
A current $I$ drives a volume stream:

\[
\frac{dV}{dt} = \frac{\epsilon I}{4\pi \eta \kappa \zeta}
\]

Not as convenient as streaming potential, since high voltage necessary
Coupling acoustic pressure with electric effect is a AC method and works well with concentrated dispersions.

Colloid vibration potential; inverse effect: electroacoustic sound amplitude ESA
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Debye-Hückel model
Electrokinetics
Kinetics / Rheology
Conjugation and Ligands

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ESA-setup

ESA measurements are very fast and can be performed online or during titration

Alternatively, probes can be inserted into stirred dispersions (large particles, unstable dispersions)
A useful way to characterize colloids is to assess the dependence of $\zeta$-potential on pH, here for colloidal silica (LUDOX):

The pH, at which no charging is measured, is called the \textit{point of zero charge} or the \textit{isoelectrical point}.
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ESA-example: adsorption of benzoic acid

Adsorption on colloidal particles can be followed by the ESA method. Titration of silica with benzoate at pH=9:

The surface charge is effectively reduced due to adsorption of benzoic acid replacing negative groups
ESA-example: coating of $\text{YF}_3$

Surface state (e.g. hydrolisis) and coatings can be followed by ESA as well:

Application: protection of sensitive surfaces of powder particles (protection against water, oxygen, radiation)
Shear stress

- Colloidal systems show Non-Newtonian flow: control through interface chemistry
- Basic quantities and situation:

  \[ \text{shear } \gamma = \frac{\Delta a}{b} = \tan \alpha \]
  \[ \text{shear rate } \dot{\gamma} = \frac{d\gamma}{dt} \]
  \[ \text{shear stress } \sigma = \frac{F}{A} \]
  \[ \text{viscosity } \eta = \frac{\sigma}{\dot{\gamma}} \]

Viscosities span several orders of magnitude (glaciers to gases)
Laminar flow

Situation for laminar flow (small *Reynold* number)

Viscosity may be defined as the coefficient of transport of momentum $p$ in a gradient of velocities $v$:

$$\frac{dp_x}{A dt} = -\eta \frac{dv_x}{dz}$$

$$[\eta] = \frac{kg}{m \cdot s} = Pa \cdot s$$
Viscosity measurement

Dispersions under test are sheared between rotator and stator.

- Measurement of torsional force together with fixed geometry yields stress applied
- Rotational speed defines shear rate
- Flow curves are determined by sweeping shear rates
- Viscoelastic properties are accessible by oscillating rotation
Basic flow types

Newtonian flow: viscosity is independent of shear rate

Pseudoplastic flow: viscosity decreases with shear rate ("shear thinning")
Dilatant flow: viscosity increases with shear rate
Thixotropic behaviour

Often flow equilibrium is not reached immediately: thixotropic behaviour

Area of hysteresis is characteristic for ratio of relaxation time and shear rate change
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Kinetics / Rheology Basics
Flow characteristics Examples
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Flow curves

Alternative plot: stress over shear rate
Newtonian flow then is depicted by straight lines

Critical yield stresses are displayed clearly in these plots
Flow control through additives relies on weak interaction, e.g. hydrogen bridges. Typical inorganic system (inks, varnishes...):

Characteristics may be modified by intercalation of complex ions and/or organic molecules.
Typical: polymers (if necessary, branched) with hydrophilic groups (OH, COOH, NH2, SO3H, ...) along the back bone

Examples: cellulose / starch, polymaleic acid, polyacrylic acid
Weakly interconnected polyacrylic acid (partially as salt) is used in “superabsorbers”
Viscoelasticity

Elastic (energy storage) and inelastic (flow) response to external stress

Description by complex viscosity with inelastic flow in the real part and elastic response in the imaginary part

\[ \eta = \eta' (\omega) + i \eta'' (\omega) \]

\( \omega \) is the frequency of oscillation (sign reversal of stress)
Inks in ball pens need a precisely defined yield stress and should not exhibit thixotropic hysteresis.

Typical modifiers: modified montmorillonites.
Example: wall paint

Applying wall paint produces a typical shear rate and stress

\[ \gamma' = \frac{0.5 \, \text{m/s}}{50 \cdot 10^{-6} \, \text{m}} = 10^{4} \, \text{s}^{-1} \]

Layer thickness: \( \sim 50 \, \mu\text{m} \)

Shear thinning (flow under stress, but not at rest) and some thixotropic component (film smoothening) have to be defined

Typical modifiers: cellulose (cheap), polyacrylic acids (expensive, but better defined)
Colloidal components in a system can be coupled by surface groups or adsorbed linkers

- Adsorption by covalent bonding or electrostatic attraction
- Bifunctional entities offer very flexible chemistry
- Spacers may deliberately decouple components
- Bifunctional silanes offer branching into inorganic or hybrid network
- Biochemical applications focus on drug delivery, signalling . . .
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Coated particles
Layers and films
Film formation
Resistivity

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Bio–conjugates

A: Bifunctional linkage
B: Silanization
C: Hydrophobic attraction
D: Peptides
E: Nanobeads

= Core/shell nanocrystal = Biomolecule
Y$_2$O$_2$S coated with Fe$_2$O$_3$

Functionalization and protection of surfaces are crucial for several applications.

Example: red emitting TV phosphor with colour filter protecting sulfidic substrate
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LaOBr:Tb coated with ZnS

Protection: Thick coatings to prevent hydrolysis

Example: green emitting projection TV phosphor coated with sulfidic barrier
Application of colloids in films

A huge number of applications uses colloidal systems in layers and films

- Film formation typically proceeds from liquid precursors
- Dipping, spinning, spraying, flooding, printing ... offer broad range of technological choices
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- Dipping, spinning, spraying, flooding, printing . . . offer broad range of technological choices
- During film consolidation, internal film structures are preformed
- Curing to solid films can be thermal or photochemical processes
- Self assembly is nature’s choice to fabricate complex film structures under ambient conditions
Dip–coating

Prototype of film formation process is dip–coating

Sequence: dipping $\rightarrow$ withdrawal $\rightarrow$ dripping $\rightarrow$ consolidation (evaporation, drying)
Wet film thickness depends on viscosity and withdrawal speed. Control of atmosphere necessary!
Spin–coating is standard technique in semiconductor processing

Example: nano-dispersions with luminescent nanoparticles on LED-chip
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Photonic structures

During film formation and consolidation, photonic structures may crystallize from colloidal particles:

Applications for electrooptical applications to be developed (e.g. photonic switches)

Generated polymeric templates may be converted to metamaterials of semiconductors, metals . . .
Layer-by-layer self assembly

Combining acidic and basic surface ligands allow for molecular recognition during film formation

Example: layer-by-layer self assembly of quantum dot / silica composites
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DC-conductivities

Sensor for nitric oxides

Excess conductivities
Concentration of nitric oxides derived from excess charge carries after adsorption
Impedance spectroscopy

Example: Mixed e/Ag\(^{+}\) conductor

Non-electron conductivity contributions can be characterized by AC methods.

Frequency-dependent conductivity measurement ("Impedance Spectroscopy") at small potential yields resistive and capacitive contributions without electrochemical effects.
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Interpreting results

Left: Complex plane, frequency as parameter
Right: Absolute impedance

Extraction of results by fit of measured data to electrical model
Non-local phenomena

Diffusion and reaction are included by special elements:

Warburg-impedance (imaginary impedance due to diffusion)

Typical form of Nyquist plot in the presence of Warburg-impedance
Non-destructive testing of inverted and coated metal substrates for quality assessment. Applications also for foils (packaging) between suited electrodes.
Application in fuel cells

Ion conductivities of membranes as well as three phase gas electrodes can be investigated by impedance spectroscopy.

Measurements can also be done under load (galvanostatic mode in contrast to potentiostatic mode).
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