Exercise 8

COAGULATION OF LYOPHOBIC COLLOIDS

Topics: colloidal state, classification of colloidal systems, diffusion in colloidal systems, Brownian motion, intermolecular interactions, double electric layer, stability of dispersive colloids, coagulation, light scattering in colloidal systems.

Colloidal particles are always in motion due to what is known as Brownian motion. This constant movement causes them to collide with each other. When they do, they can clump together, a process known as aggregation. How quickly this happens depends on the specific properties of the colloidal system. Sometimes, the process is so slow that it's almost impossible to notice, making the system appear stable, even if it's not truly stable in the long term. This phenomenon is called metastability. It suggests that there's some mechanism preventing the particles from spontaneously clumping together every time they collide.

The reason behind this metastability in lyophobic (water-repelling) colloidal systems is explained by the DLVO theory. This theory is named after its developers: Deriaguin, Landau, Verwey, and Overbeek. According to DLVO, there are different forces at play between colloidal particles. One of these forces is the London dispersion force, which is a common interaction found in matter. The strength of this interaction between colloidal particles increases as the distance between them decreases. This relationship is described by a factor known as the Hamaker constant. The value of this constant can change based on the structure of colloidal particles and the environment (including solvent). Another force to consider is the electrostatic force. When particles are suspended in a solution containing electrolytes, they usually carry an electric charge. The strength and distribution of the electric field around these particles depend on their nature and the concentration of the electrolyte ions in the surrounding medium. In simple terms, within a region called the diffusion layer, the electric potential drops off exponentially from a starting point known as the Stern potential. This rate of decrease is influenced by the concentration and charge of the electrolyte in the surrounding medium. The more charged and concentrated the electrolyte, the steeper this drop-off. A visual representation of a charged colloidal particle in an electrolyte solution, showing how the electric potential changes with distance from the particle, can be seen in Figure 1.

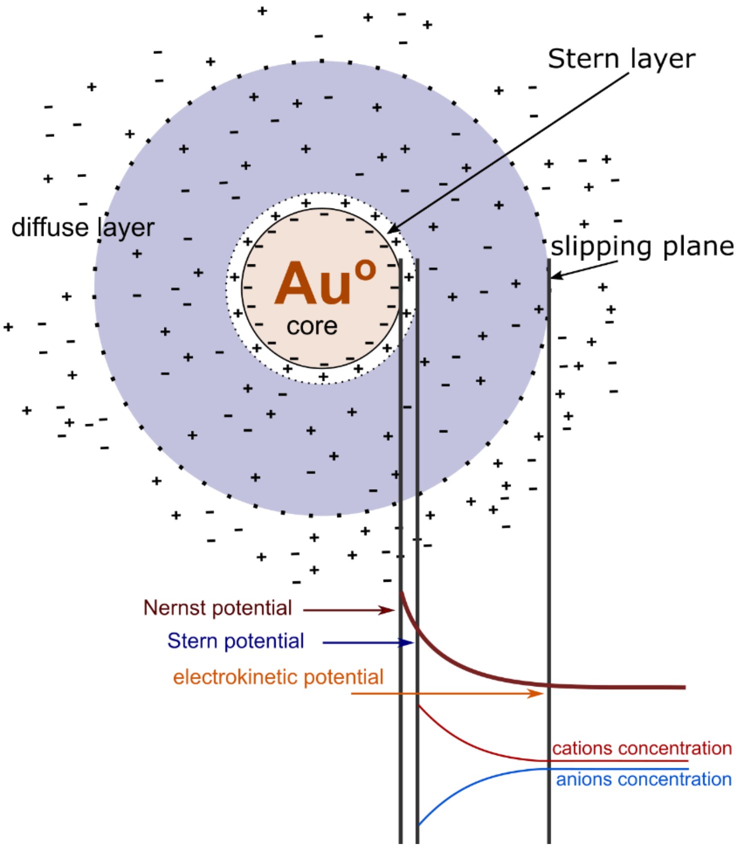

Fig. 1. Distribution of the electric field around a colloidal particle.

When two colloidal particles approach each other, an intervening force arises due to the previously mentioned interactions. This force's relationship to the distance between the particles is influenced by the Hamaker constant, the Stern potential, and the depth of the diffusion layer within the dispersion medium. Notably, only the latter two parameters are significantly influenced by the electrolyte concentration. If the electrolyte concentration remains relatively low, the energy relationship between the two colloidal particles based on their distance might resemble what's depicted in Figure 2. The shape of this curve graphically represents a function, which is a superposition of the London dispersion force attraction energy V_D , electrostatic repulsion energy V_E, and atomic repulsion energy V_A:

$$V = \mathrm{V}_D\left(\frac{H}{x}\right) + V_E\left(qe^{-\kappa x}\right) + \mathrm{V}_D\left(\frac{s}{x^n}\right) \tag{1}$$

where H, s, n are constants (with the exponent n ranging from 9 to 12), q, κ are constants dependent on the electrolyte concentration (specifically, from the Stern potential and the extent of the double electric layer), and xx represents the distance between the particles.

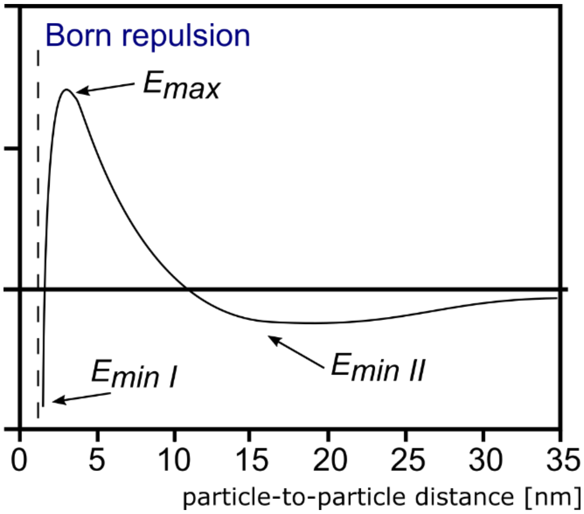

Fig. 2. Potential Energy Relationship of Two Colloidal Particles Based on Their Separation.

By analyzing Figure 2, one can infer the behavior of two colloidal particles as they spontaneously approach each other due to Brownian motion. If the absolute potential of the two-particle system in the II minimum exceeds the average translational kinetic energy of the particles, they tend to stabilize at a distance corresponding to this minimum. Colloidal particles might also settle in another potential well – at a distance corresponding to the I minimum on the energy chart. This occurrence is considerably less likely than the former, as it requires to overcome a high potential energy barrier. However, irrespective of its magnitude, there's always a finite probability that, due to fluctuations, the two-particle system will acquire the kinetic energy required to surmount this barrier. The formation of such aggregates (when the distance between particles corresponds to the I minimum), unless the approach of colloidal particles is obstructed for other reasons (e.g., their surfaces being coated with polymer molecules), always takes place, albeit sometimes at an exceedingly slow rate. Moreover, reversing this process – given the need to once again overcome of the potential energy barrier and the significant energy reduction within this position – is highly improbable. This process is, therefore, practically irreversible, especially since around the convergence point between particles, which are more or less regular shaped conglomerates, a recrystallization process is likely to ensue.

The formation of the above-described aggregates, consisting of two or more colloidal particles, is termed coagulation. The subsequent process, occasionally observed, which reduces the degree of dispersion by directly merging particles such that the interfacial surface separating them vanishes, is termed coalescence.

The curve's shape in Figure 2 is contingent upon the parameters of equation 1. An increase in electrolyte concentration results in a decrease in the values of parameters q and κ. Consequently, by increasing the electrolyte concentration, one can achieve a reduction in both the width and height of the potential barrier, and a deepening of the potential well in the I minimum. This leads to an increased likelihood of aggregate formation and a decreased probability of their eventual dissolution. Generally, an increase in electrolyte concentration tends to accelerate the coagulation process.

When the electrolyte concentration is sufficiently high, such that the potential barrier doesn't impede the particles approach, then every convergence within the action radius of the London forces results in aggregation. This phenomenon is termed rapid coagulation. Slow coagulation occurs when approaching particles encounter a potential barrier, or when the minimum on the potential curve is so shallow that a disaggregation process is also observable.

The kinetics of the coagulation process is detailed by the theory formulated by Smoluchowski. This theory portrays a colloidal system comprising identical spherical particles perpetually undergoing Brownian motion. These particles possess an attraction sphere with a specific radius, larger than the geometric one. Due to Brownian motion, particles can approach each other, and if one particle's center falls within the other's attraction radius, they irreversibly combine, or coagulate. Furthermore, if the colloidal system under consideration is dilute, it can be postulated that the ongoing process is analogous to a bimolecular reaction. The expression for this reaction's rate is:

$$\left(\frac{dN_1}{dt}\right) = k_1 N_1^2 \tag{2}$$

where k_1 denotes the rate constant of single particle disappearance, while, N_1 represents the number of single particles in the system. The coagulation process is multi-staged. Assuming that the rate constants for all stages are identical, we have:

$$-\frac{d\sum_i N_i}{dt} = \frac{1}{2}k\left(\sum_i N_i\right)^2 \tag{3}$$

where k denotes the rate constant of any aggregate's disappearance resulting from rapid coagulation, and N_i is the number of aggregates composed of *i* primary particles.

For the description of slow coagulation, the so-called coagulation inhibition coefficient is used:

$$W = \frac{k_p}{k} \tag{4}$$

where k_p represents the rate constant of slow coagulation, while k denotes the rate constant of rapid coagulation according to Smoluchowski.

The DLVO theory allows for deriving the relationship of the inhibition coefficient to the electrolyte concentration. Within the range of electrolyte concentrations corresponding to slow coagulation, the equation describing this relationship can be presented as:

$$\log W = a \log c_E + b \tag{5}$$

where *a* and *b* are constants dependent on the valency of the electrolyte ions, temperature, Stern potential, and average diameter of colloidal particles. c_E denotes the electrolyte concentration. At higher electrolyte concentrations, it naturally follows that:

$$\log W = 0 \tag{6}$$

The electrolyte concentration in the dispersion medium of the colloidal system, c_E^P, corresponding to the intersection point of the lines described by equations (5) and (6), is also the minimum electrolyte concentration inducing rapid coagulation. It is termed the coagulation threshold and is used as a parameter characterizing the resistance of the colloidal system to coagulating agents.

To observe the coagulation process, the Tyndall effect can be used. Using the theory developed for this process by Rayleigh, as well as conclusions derived from Smoluchowski's theory, a relationship can be derived between the apparent absorbance *A* of the colloidal system (where the attenuation of the incident beam is solely due to light scattering) and the coagulation time *t*, the initial number of particles in the system N_0, the rate constant of rapid coagulation *k*, and the inhibition coefficient *W*:

$$A = K(1 + WkN_0t)l \tag{7}$$

where *K* is a constant determined by the properties of the colloidal system and the wavelength of light, and *l* is the distance traversed by the light beam in the colloidal system. This equation can be used, with some approximation, even for systems where actual absorption occurs. Equation (7) can be used to determine the inhibition coefficient, based on determining three apparent absorbances of the examined colloidal system:

$A_{\min}$ – the apparent absorbance of the initial sol (where no coagulation has occurred), where $W = 0$ and $A_{min} = Kl$

$A_{\max}$ – the apparent absorbance of the sol, where during time tt, rapid coagulation occurred, so $W = 1$ and $A = (1 + WkN_0t)l$

as well as

A – the apparent absorbance of the examined system, where during time t, coagulation characterized by the inhibition coefficient W occurred.

The discussed equation thus takes the form:

$$W = \frac{A - Kl}{KkN_0tl} = \frac{A - Kl}{A_{max} - Kl} \tag{8}$$

Or finally:

$$W = \frac{A - A_{min}}{A_{max} - A_{min}}. \tag{9}$$

Exercise Execution

The aim of the exercise is to determine the coagulation threshold of gold hydrosol by potassium nitrate

Reagents

- 0.60% solution of chloroauric acid, $H[AuCl_4]$, m.w. 339.785 g/mol
- 0.10 g powdered gelatin
- 1.0% solution of sodium citrate, $C_3H_4(OH)(COONa)_3$, m.w. 258.07 g/mol
- 0.1 M aqueous solution of potassium nitrate(V), KNO_3, m.w. 101.10 g/mol

For this purpose, the gold hydrosol will undergo coagulation with KNO_3 solutions of varying concentrations. After a strictly defined time, the coagulation process will be halted by adding gelatin, a macromolecular substance (known as a protective colloid). This substance, by inducing steric stabilization of colloidal particles, prevents their further combination. This happens because the macromolecules adsorbed on the surface of colloidal particles, whose chain parts extend into the dispersion medium, lead to the steric repulsion of other chemical entities.

Subsequently, based on the results of apparent absorbance measurements, the degree of coagulation of the examined colloidal system will be estimated. Assuming that the increase in coagulation speed rises with the increase in electrolyte concentration, until this concentration reaches a critical value (at which the potential barrier becomes so small that it does not hinder the approach of particles), the value of the coagulation threshold will be estimated.

I. Preparation of Gold Hydrosol

- Pour 200 cm^3 of water into a clean (previously washed with aqua regia; rinse with distilled water at least three times) 300 cm^3 conical flask and add 3.0 cm^3 of a 0.60% solution of chloroauric acid.
- Heat the solution to boiling, then add 10 cm^3 of a 1.0% solution of sodium citrate to the boiling solution. After a moment, a gray hue from the reduced metallic gold can be observed. A few minutes after introducing the reducer, this hue gradually turns red. Before proceeding with coagulation, cool the sol to room temperature.

Note: If the final color of the obtained gold hydrosol has a hint of blue, it indicates that the used vessel was not clean.

II. Preparation of Gelatin Solution

- Mix 0.10 g of powdered gelatin into 100 cm^3 of water and leave it for 30 minutes to swell.

- Gently heat the vessel, stirring its contents until the gelatin is completely dissolved. Cool the solution to room temperature.

III. Coagulation

- Before starting the measurements, estimate the approximate value of the coagulation threshold. For this purpose, prepare 5.0 cm³ of aqueous KNO_3 solutions in several test tubes (clean and dry!) with concentrations increasing linearly (in steps of 0.02) ranging from 0 to 0.200 M.
- Add 5.0 cm³ of gold hydrosol to the test tubes containing KNO_3 solutions, mix immediately, and visually determine the approximate coagulation threshold after a moment. The coagulation threshold will corresponds to the electrolyte concentration in the first sample that turned blue. Remember that introducing the sol results in a twofold dilution of the electrolyte solution. Now determine the highest concentration, $c_{\max}$, in the series of electrolyte solutions that will be used for precise determination of the coagulation threshold - take the value of $c_{\max}$ as four times higher than the preliminarily estimated coagulation threshold.
- To precisely determine the coagulation threshold, prepare another series of KNO_3 solutions with a volume of 5.0 cm³ and concentrations changing linearly (in steps of 0.02) in the range from 0.0 to $c_{\max}$.
- Add 5.0 cm³ of gold hydrosol to each test tube every 15 seconds and mix immediately.
- 5 minutes after introducing the gold hydrosol to each test tube, add 1.0 cm³ of the previously prepared gelatin solution and mix quickly again. Ensure that coagulation occurs at the same time (5 minutes) in each test tube.
- Simultaneously, prepare a reference sample by mixing 5.0 cm³ of gold hydrosol, 5.0 cm³ of water, and 1.0 cm³ of gelatin solution. In this experiment, no measurable coagulation should occur, however adding gelatin is necessary due to the slight color change it causes in the system

IV. Spectrophotometric Measurements

Note: Before conducting a series of measurements, it is recommended to inspect purity of the cuvettes by measuring the absorbance of a reference sample.

- For samples of gold hydrosol prepared as described in point III, measure the apparent absorbance A at a wavelength of 660 nm, using water as a reference.
- Measure the apparent absorbance of the reference sample, $A_{\min}$.
- Compile the results in a table:

c_E [M]	A	W	$\log W$
0	....	....	....

Results Processing

- From the apparent absorbance A measurements obtained for the highest electrolyte concentrations, select values close to each other (in these samples, a distinct blue coloration is observed) and calculate their average value, A_{max}. It is necessary to assume that A_{max} is the apparent absorbance of samples in which rapid coagulation occurred, i.e., its rate does not depend on the electrolyte concentration.

- Then, for the remaining points, calculate the values of the coagulation inhibition coefficient W from equation (9).
- Present the obtained values graphically as $\log W = f(\log c_E)$. Then by using the least squares method, determine the linear regression which can be compared to equation (5). However if the calculated W for lowest electrolyte concentrations (for which the estimated error was the largest) doesn't agree with the regression line, they should be omitted.
- The coagulation threshold should be calculated by applying:

$$c_E^P = 10^{\frac{-b}{a}}$$

Where a and b respectively denote x-intercept, known points on the line and y-intercept of the linear equation $\log W = f(\log c_E)$.