

Module 8: "Stability of Colloids"

Lecture 40: ""

The Lecture Contains:

- ☰ Slow Coagulation
- ☰ Other Factors affecting Kinetics of Coagulation

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Slow Coagulation

As shown in figure 10.17, there is some energy is required for coagulation to occur. Due to this energy barrier the coagulation is slow. Energy barrier arises due to repulsive component in the force. As done for rapid coagulation, number of particles crossing a shell of radius 'r' towards a reference per second is

$$jA = -4\pi r^2 \left(D \frac{dN}{dr} + \frac{N}{f} \frac{d\phi}{dr} \right)$$

First term is trying to coagulate while the second term is driving the flux in opposite direction. So it makes the kinetic of coagulation slow. Removing the restriction that the reference is stationary (replacing D with 2D) we get:

$$jA = -8\pi r^2 D \left(\frac{dN}{dr} + \frac{N}{kT} \frac{d\phi}{dr} \right)$$

Or,

$$\frac{dN}{dr} + \frac{N}{kT} \frac{d\phi}{dr} = - \frac{jA}{8\pi r^2 D} \quad (10.25)$$

which is a first order homogenous equation. For steady state, flux (jA) is constant so this differential equation can be solved with appropriate boundary conditions. As $r \rightarrow \infty$, energy (ϕ) = 0 and $N = N_\infty$ and at $r = 2R$, energy (ϕ) = $-\infty$ and $N = 0$. So equation (10.25) has solution as

$$N \exp(\phi/kT) \Big|_{N=0, \phi \rightarrow -\infty}^{N_\infty, \phi=0} = \left[\int \frac{-jA}{8\pi r^2 D} \exp\left(\frac{\phi}{kT}\right) dr + c \right] \Big|_{r=2R}^{\infty}$$

Above equation can be written as

$$jA = -8\pi D N_\infty \left(\int_{2R}^{\infty} \frac{\exp(\phi/kT)}{r^2} dr \right)^{-1}$$

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Number of particles crossing the spherical shell would be same as number of particles coagulating with respect to reference particle. Thus total number of particles coagulating per unit time is equal to product of flux (jA) and number of particles. Rate of coagulation for slow coagulation is equal to (jA) N_∞ .

$$\text{Rate of coagulation, } R_s = jAN_\infty = -8\pi D N_\infty^2 \left(\int_{2R}^{\infty} \frac{\exp(\phi/kT)}{r^2} \right)^{-1} = K_s N_\infty^2 \quad (10.26)$$

where K_s is the rate constant for slow coagulation. Stability ratio (w) is defined as the ratio of rate of rapid coagulation to rate of slow coagulation. From equation (10.18) and equation (10.26) we can write stability ratio as:

$$\text{Stability ratio} = w = \frac{R_f}{R_s} = 2R \int_{2R}^{\infty} \frac{\exp(\phi/kT)}{r^2} dr \quad (10.27)$$

Stability ratio is always greater than 1 as rapid coagulation is faster than slow coagulation. From equation (10.18), rate of slow coagulation can be written as

$$R_s = -\frac{K_r}{w} N_\infty^2$$

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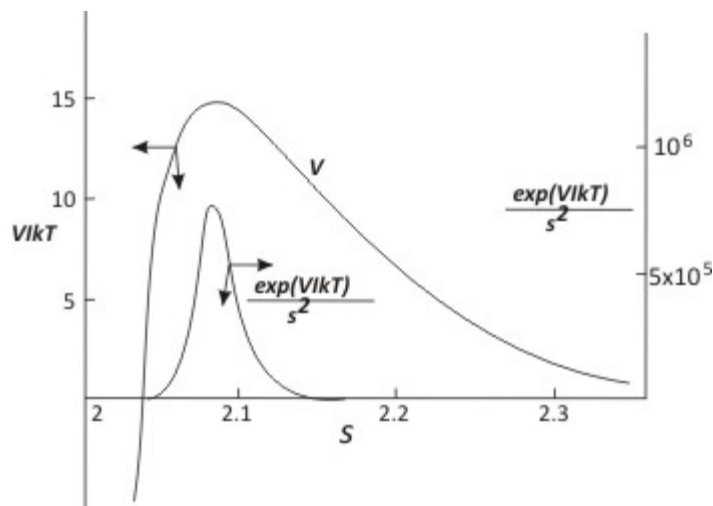


Fig.10.11: Comparison of V curve vs stability ratio curve

Stability factor being given by

$$W = \frac{R_f}{R_s} = \frac{J_f}{J_s} = 2 \int_2^{\infty} \exp\left(\frac{V}{kT}\right) \frac{ds}{s^2} \quad s = r/a$$

Let r_m be the separation distance between 2 particles at which the maxima in energy occurs. It can be approximated that centre to centre distance (r) between particles is the sum of r_m and radii of the 2 particles. Thus,

$$r = 2R + r_m \quad (10.28)$$

Expanding u by Taylor series about u_m the maximum of energy we get

$$\phi = \phi_m + \left. \frac{\partial \phi}{\partial r} \right|_{r_m} (r - r_m) + \left. \frac{\partial^2 \phi}{2 \partial r^2} \right|_{r_m} (r - r_m)^2 + \dots \quad (10.29)$$

$(\partial \phi / \partial r)|_{r_m} = 0$ as r_m is the point where the energy is maximum. Substituting the values from equation (10.28) and (10.29) in equation (10.27) we get

$$W = \frac{2R \exp(\phi_m/kT)}{r_m^2} \int_{2R}^{\infty} \exp\left(\frac{\phi_m''}{2kT} (r - r_m)^2\right) \quad (10.30)$$

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Higher terms in the Taylor series have been neglected. Let $x = r - r_m$ and $p^2 = \phi''_m/2kT$, ϕ''_m would be negative as the energy is maximum at that point, so p^2 would be always positive.

$$w = \frac{2R \exp(\phi_m/kT)}{r_m^2} \int_0^\infty \exp(-p^2 x^2) dx \quad (10.31)$$

The integral term can be calculated directly as it is definite integral and p^2 is positive. Thus,

$$w = \frac{2R \exp(\phi/kT)}{r_m^2} \frac{\sqrt{\pi}}{p} \quad (10.32)$$

where $\sqrt{\pi}/p$ is the value of integral term and $p = \sqrt{-\phi''/kT}$. Substituting the value of w in

$$\text{equation } K_s = \frac{K_r}{w} = \frac{16\pi RD}{w}$$

we get the approximate value of K_s as function of temperature.

$$K_s = \frac{8\pi D r_m^2 p \exp(-\phi_m/kT)}{\sqrt{\pi}} \quad (10.33)$$

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The validity of the basic findings of the Smoluchowski analysis of colloidal coagulation rates has been tested many times. The stability factor 'W', being experimentally accessible, has played a vital role in the development of the notion of colloidal stability. The $\log(W)$ - $\log(c)$ plot is of a bilinear nature and allows for determination of a kinetic c.c.c. (critical coagulation concentration), and a great amount of literature is available on the interpretation of W for a variety of colloids.

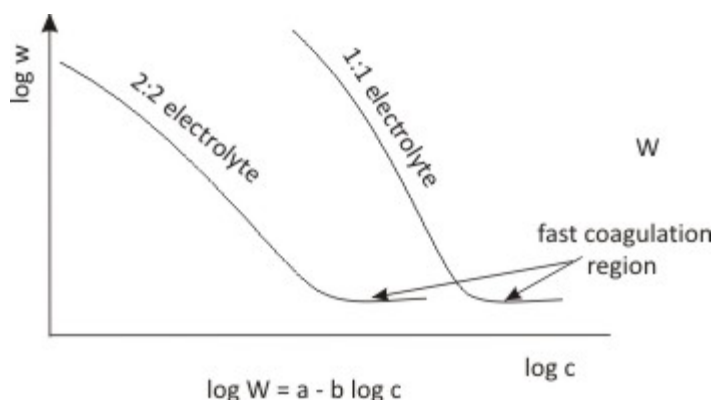


Fig.10.12: The above plot shows the bilinear nature of the $\log W$ plot, $\log W = a - b \log c$

The ccc is the critical salt concentration at which there is a change from coagulation, limited by the presence of a primary maximum to coagulation which has no barrier. At this point there is a distinct change in the coagulation rate. Measurement techniques for the coagulation rate can be broadly classified into two categories:

1. directly – by counting the number of particles, measuring the number of particles as a function of time, best suited for large particles
2. indirectly – by experimental techniques such as light scattering, best suited for small particles, for which direct counting becomes difficult.

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In each case we are observing the change in the number of aggregates with time, which tells us about the loss of primary particles from the system. A simple experiment for this would be to observe the concentration at which aggregation becomes apparent using tubes containing different electrolytes. This can also be quantified using the percentage transmission of the system as a measure of the number of particles in suspension. The measurement of rate of aggregation provides a more precise determination of ccc. At higher electrolyte concentrations the rate increases to the plateau value (as seen in Fig. 10.13) representing the fast or diffusion limited rate.

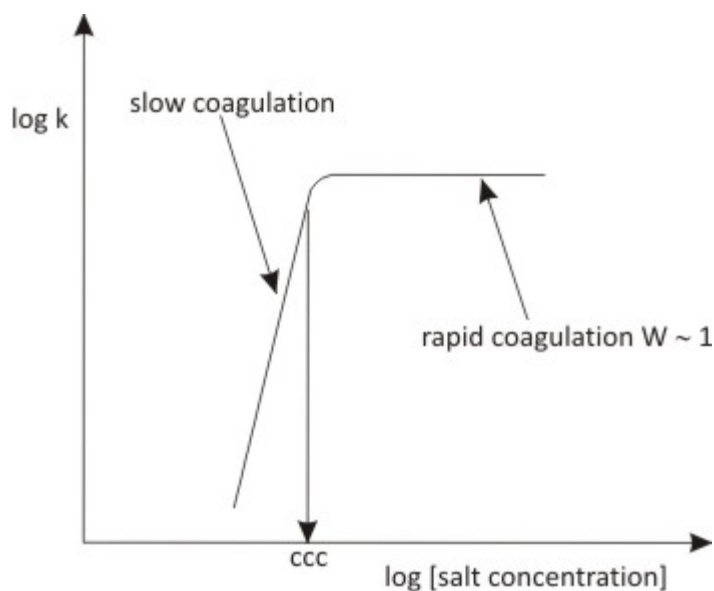


Fig. 10.13: Rate of coagulation against salt concentration (indicating c.c.c.)

Again, it should be noted that the analysis of the rate constant in terms of the diffusion of single particle is strictly the initial rate. As we progress into the coagulation process the particle number changes and the mechanism changes to one where the large much less mobile aggregates get larger by adding singlets and accurately describing the rates becomes quite complex.

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Other techniques, such as scattering techniques, involving radiation sources like neutrons, x-rays and light are also widely used in this field. These scattering experiments study the scattered intensity as a function of the scattering angle and provide useful insight into the particle distributions within clusters.

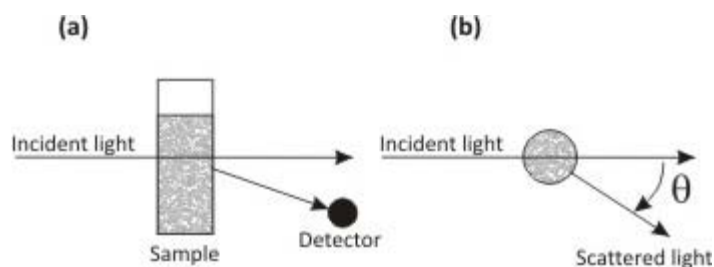


Fig. 10.14: Schematic of a scattering experiment. (a) side view, (b) top view

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Other Factors affecting Kinetics of Coagulation

The effect of external forces (such as gravity, electric/ magnetic and other field forces) on the kinetics of coagulation has been a widely researched field. The particle in this case is "directed" rather than (purely) Brownian; this affects the collision frequency, and hence the rate of coagulation is affected. Other factors such as the building up of the concentration when particles hit a "boundary" (e.g. a wall or electrode), also need to be accounted for. Flow forces (such as applied shear) also have their effect on the rate coagulation/aggregation. The particle motion is now hydrodynamically controlled (rather than Brownian), i.e. orthokinetic rather than perikinetic coagulation. For laminar flows, the rate constant is now a function of the shear rate, and a stronger function of particle size.

As mentioned earlier, the above derivation ignored hindered diffusion. Hydrodynamic correction factor, which was first introduced by Deryaguin (1966) takes into account that in the final stages of approach of two particles, they are slowed down because it is increasingly difficult for the remaining film to escape. If this hydrodynamic interaction is introduced, the following changes are made:

$$D(u) = D_0/\beta(u)$$

$$jA = -8\pi DN_\infty \left(\beta(u) \int_{2R}^{\infty} \frac{\exp(\phi/kT)}{r^2} dr \right)^{-1} \quad (10.34)$$

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Where $D(u)$ is the diffusion coefficient of a particle at a distance u from another particle, D_0 is that of a particle in an infinitely dilute solution, $\beta(u)$ is the coefficient of hydrodynamic retardation, reflecting the influence of the hydrodynamic interaction of the approaching particles on their diffusivity, given by Honig et al. [10]:

$$\beta(u) = \frac{6(u)^2 + 13(u) + 2}{6(u)^2 + 4(u)} \quad (10.35)$$

The theoretical computations by Honig et al.^[10] predict that hydrodynamic interaction changes the rate of fast coagulation by a factor of about 0.4 to 0.6 in general.

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References

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