CHAPTER II

THEORY AND BACKGROUND

Particles dispersed in liquid media, with a size from 10^{-9} m (nanometer) to 10^{-6} m (micrometer), are, in general, called "colloidal particles". Numerous papers have been investigated the different aspects and the phenomena of colloidal systems (the detail as in the introduction part). The fundamentally important questions need to be answered in order to further understand the general colloidal behaviors including "How does the particle move in liquid media?", "How does the flocculation of particles occur?" etc. To answer these questions, the dynamics of the colloid particle movement in the solution is described first. In the absence of external force, e.g. shaking or stirring, the motion of colloidal particles proceed a continuous random movement, called "Brownion motion", due to their random collisions with solvate molecules in the suspending medium [19]. The answer for the flocculation phenomena in the stabilization of the colloidal system can be explained by the well known classical theory "DLVO theory", Derjaguin, Landau, Verwey, and Overbeek[20, 21], that explain the colloid system in quiescent media. This theory describes the stability of colloidal particles in solution in terms of the balance between the attractive van der Waal force and the repulsive electrostatic force between particles.

$$V = V_A + V_R \qquad\qquad (2.1)$$

V_A = Attractive energy

V_R = Repulsive energy

The van der Waal force is a short-range attractive force between colloidal particles major from the summation of van der Waal force between the particles and surrounding fluid. The van der Waal attractive force can be described using the Hamaker constant concept[22] which is based on the

interaction of molecular pairs and is assumed to be additive. The attractive energy between two atoms is receiprocal to the power of six of the distance(h) between them as shwon in equation (2.2)

$$V_A = -\frac{\beta}{h^6}$$ (2.2)

β = van der Waals constant which depends on the type of atoms

The equation describing attractive force has shown in equation (2.3)

$$V_A = -\frac{A}{12}\left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2\ln\left(\frac{x(x+2)}{(x+1)^2}\right)\right]$$ (2.3)

A = Hamaker constant

x = H/2a

For two identical spheres of radii $a_1 = a_2 = a$, and shortest distance between their Stern layers = H, the equation for the attractive force is

$$V_A = -\frac{A}{12} \cdot \frac{1}{2X} = -\frac{Aa}{12H}$$ (2.4)

Other methods that can be used to calculate the Hamaker constant is shown [23, 24, 25, 26].

The repulsive force between two particles is mainly due to the overlapping of the diffusive electrical double layers. The interacting distance can be calculated by Gouy Chapman and Debye-Huckel theory which is clearly explained[27]. Overbeek[28] concluded that the rate of double layer overlap in a typical Brownian motion encountered between particles was too fast to maintain the adsorption equilibrium. Thus the real situation might

lie somewhere between constant potential and constant charge. For equal spheres, the repulsive interaction can be written as :

$$V_R = 2\pi \varepsilon a \psi_d^2 \ln(1 + \exp[-kH])$$
(2.5)

ε = Permitivity of dispersion medium

$1/k$ = Thickness of the diffuse double layer

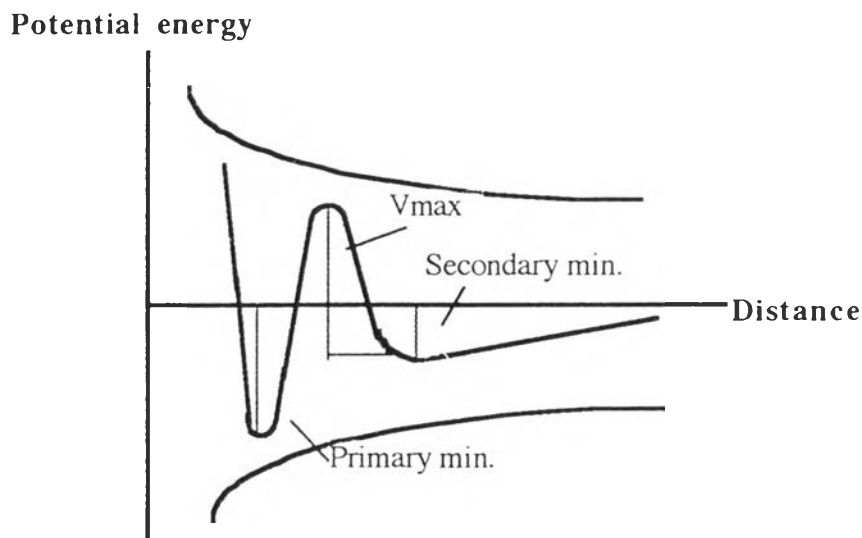ψ_d = Stern Potential

Potential energy

Figure 2.1 Potential energy curve between two particles [29].

When two particles come closer (for large particles), the flocculation occurs because the attractive force overcome the Brownian motion at "secondary minimum" (Figure 2.1). At this point the flocs are easy to be redispersed (by stirring or tumbling). On the other hand, if the colloid has sufficient energy to overcome the energy barrier (V_{max}), the particle will attract each other strongly at the primary minimum and the flocculation at this point is irreversible. The sharp increase in repulsive energy is observed when two particles come so close as the repulsion between the electron cloud of the particles becomes significant or which can be called "born repulsive energy".

The flocculation rate depends on the frequency of the collision which has sufficient energy to overcome the repulsive potential energy

barrier. The electrostatic barrier can be eliminated by adding electrolyte solution. Smoluchowski[30] developed the rapid coagulation theory which calculated the degree of stability in the system (stability ratio, W). The stability is calculated from the ratio between the presence and the absence of an energy barrier in the system. The rapid flocculation process occurred in the absence energy barrier process so that the rate of flocculation is controlled by diffusion-limitation.

Diffusion coefficient : $$D = \frac{KT}{6\pi\eta a}$$ (2.6)

η = Viscosity

T = Temperature

a = Particle radius

The equation of doublets for the aggregation of single particle is

$$n = \frac{n_0}{1 + 8\pi D a n_0 t}$$ (2.7)

The rate of particle aggregation is

$$-\frac{dn}{dt} = k_2 n^2$$ (2.8)

With equation (2.6), (2.7), and (2.8), k_2^0 can be determined as

$$k_2^0 = \frac{4kT}{3\eta} = k_r$$ (2.9)

$k_2^0 = k_r$ = second order rate constant for rapid flocculation

The stability's equation is

$$W = \frac{k_r}{k_s} \qquad\qquad (2.10)$$

k_s = Slow flocculation rate constant.

The stabilization of the system can be explained based on two effects

1. Electrostatic Effect : Electrostatic effect stabilizes the system by electronic charge at the particle surface. The electrostatic energy of repulsion between like charge surfaces arises from the overlap of electrical double layer on two particles.

2. Steric Effect : This effect is due to the physical barrier from the adsorbed layer. The amphiphile that has lyophobic part or the anchor group can be a stabilizer. The system is stable when the particle surface is fully covered so that there is no amphiphile to penetrate to the surface. The stability of the system can also be explained by the osmotic effect taking place by the loop and tail of polymer extruding into the solution [31].

The best condition for steric stabilization is when one group of adsorbed molecule has limited solubility in the liquid phase, thereby promoting its adsorption in the solid phase. Therefore, the other(long) group will interact with the liquid phase, assisting its extension [32].