

CHAPTER 3

THEORETICAL CONSIDERATION

3.1 Clay Suspension and Colloidal system ^(18,19,20)

When clay is dispersed in water, a colloidal solution of clay in water has been formed. Colloid particles have dimension within the range of 1 nm to 1 μm that they settle extremely slowly and result suspension to be cloudy. In order to understand the behavior of clays, it is necessary to study colloidal system. Simple colloidal dispersions are two-phase systems. The particulate substance is known as the *dispersed phase* and *dispersion medium* as the continuous phase. The characteristic of colloidal dispersion is the large area-to-volume ratio for the particles involved. At the interfaces between dispersed phase and medium characteristic surface properties and determine the physical properties of the system.

The ability of colloidal suspensions is to remain indefinitely in suspension. Stokes' law states that the velocity of sedimentation, v , of a spherical particle suspended in a liquid is given by the equation.

$$v = \frac{2r^2(d_1 - d_2)g}{9\eta} \quad (3.1)$$

where r = Radius of particle

d_1 = Density of solid

d_2 = Density of liquid

g = Acceleration due to gravity

η = Viscosity of the liquid

However, small particles suspended in a liquid exert an outward pressure like gas molecule in a diffusion effect according to Fick's law of steady state diffusion, the amount dw of substance diffusion across unit area in time dt is given by.

$$dw = -D \frac{dc}{dx} dt \quad (3.2)$$

where D = Diffusion coefficient
 $\frac{dc}{dx}$ = Concentration gradient

At constant temperature and viscosity, D is proportional to $1/r$, where r is the radius of particle diffusion the limiting size for r where diffusion is sufficiently rapid to prevent degree of sedimentation is around $0.2 \mu\text{m}$

Colloidal systems

Lyophilic colloids or emulsoids (liquid-loving) and Lyophobic colloids or suspensoids (liquid-hating) are the general groups of colloids used to describe the tendency of a surface to become wetted or solvated (phenomenon of surface activity). If the liquid medium is aqueous, the terms of hydrophilic and hydrophobic are used.

The distinction between Lyophobic and Lyophilic is not evident, some substances are intermediate. Whole clays are lyophobic but some, like the montmorillonites, possess some lyophilic properties.

Colloidal suspensions exhibit *Tyndall effect* when a beam of light viewed at right angles and passed through a colloidal suspension, the light is scattered by the particles. If the beam of light is examined with a microscope, the colloidal particles appear as bright points of light at the right angles. In this way, particles are seen motion rapidly and randomly, known as *Brownian motion* caused by molecules of the dispersion medium striking the colloidal particles and causing them to move in a similar manner.

The origin of the electric charge of the particles.

When an electric field is applied to a hydrophobic sol, the particles move toward one of the electrodes. To reverse the electric field, the particles immediately change direction and move to the other electrode. For particles in clay sols are negative charges that move toward the positive electrode. This transportation of particle in an electric field is called *electrophoresis*.

The hydrophobic sol does not have a net electric charge, the particle charge must be internal balance in the sol as the *electrical double layer*. An inner region is the layer which includes adsorbed ions. An another layer is diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion. There are many scientists who describe models of electrical double layer. Gouy and Chapman¹⁹ simplified quantitative treatment of diffuse part of double layer (Fig. 3.1) based on Poisson-Boltzmann distribution as ;

$$\psi = \frac{2kT}{ze} \ln \left(\frac{1 + \gamma \exp [-Kx]}{1 - \gamma \exp [-Kx]} \right) \quad (3.3)$$

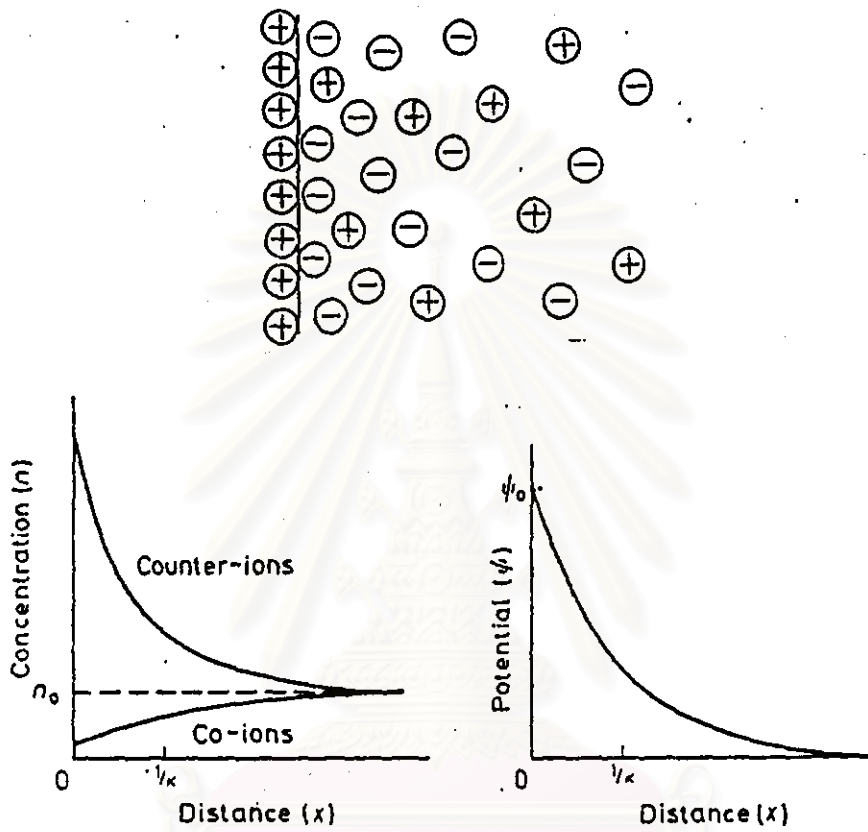


Fig. 3.1 Schematic representation of the diffuse electric double layer.⁽¹⁹⁾

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where $\gamma = \frac{\exp [ze \Psi_0/2kT] - 1}{\exp [ze \Psi_0/2kT] + 1}$ (3.4)

and $K = \left(\frac{2e^2 N_A c z^2}{\epsilon kT} \right)^{1/2}$ (3.5)

- Ψ = Electrical potential at distance x from the surface of electrolyte solution
 Ψ_0 = Electrical potential at flat surface
 k = Boltzmann's constant
 T = Absolute temperature
 z = Valence of the counterion
 e = Electron charge
 N_A = Avogadro's constant
 c = Concentration of electrolyte
 ϵ = The permittivity

With Debye-Huckel approximation, These can be made equation (3.3) and (3.4) simplified to

$$\Psi = \Psi_0 \exp [Kx] \quad (3.6)$$

At low potentials, the potential decreases exponentially with distance from the charged surface. The potential, Ψ_0 , can be related to the charge density at the surface, σ_0 , by equating the surface charge with the net space charge in the diffuse part of the double layer and applying the Poisson-Boltzmann distribution.

$$\sigma_0 = (8n_0 \epsilon kT)^{1/2} \sinh \frac{ze \Psi_0}{2kT} \quad (3.7)$$

At low potential reduces to $\sigma_o = \epsilon K \Psi_o$

Therefore, the surface potential, Ψ_o , depends on both the surface charge density, σ_o , and on the ionic composition of the medium. If the double layer is compressed (K increased) then either σ_o must increase or Ψ_o must decrease or both.

Stern¹⁹ proposed a model in which the double layer is divided into two parts separated by the Stern plane located at about a hydrated ion radius from the surface. (Fig 3.2) Adsorbed ions are attached to the surface by electrostatic and/or van der Waals forces strongly enough to overcome thermal agitation. The potential changes from Ψ_o (the surface or wall potential) to Ψ_d (the stern potential) in the stern layer and decays for Ψ_d to zero in the diffuse double layer. In the absence of specific ion adsorption, the charge density at the surface and at the stern plane are equal and capacity of the Stern layer (C_1) and diffuse layer (C_2) are given by

$$C_1 = \frac{\sigma_o}{\Psi_o - \Psi_d} \text{ and } C_2 = \frac{\sigma_o}{\Psi_d}$$

From which
$$\Psi_d = \frac{C_1 \Psi_o}{C_1 + C_2} \quad (3.8)$$

Treating the stern layer as a molecular condenser of thickness δ and with a permittivity ϵ' , the charge density at the particle surface σ_o is

$$\sigma_o = \frac{\epsilon'}{\delta} (\Psi_o - \Psi_d) \quad (3.9)$$

Overall electrical neutrality throughout the whole double layer

$$\sigma_{\text{surface}} + \sigma_{\text{stern}} + \sigma_{\text{diffuse}} = 0 \quad (3.10)$$

(σ_{surface} from (3.7) and σ_{diffuse} from (3.9))

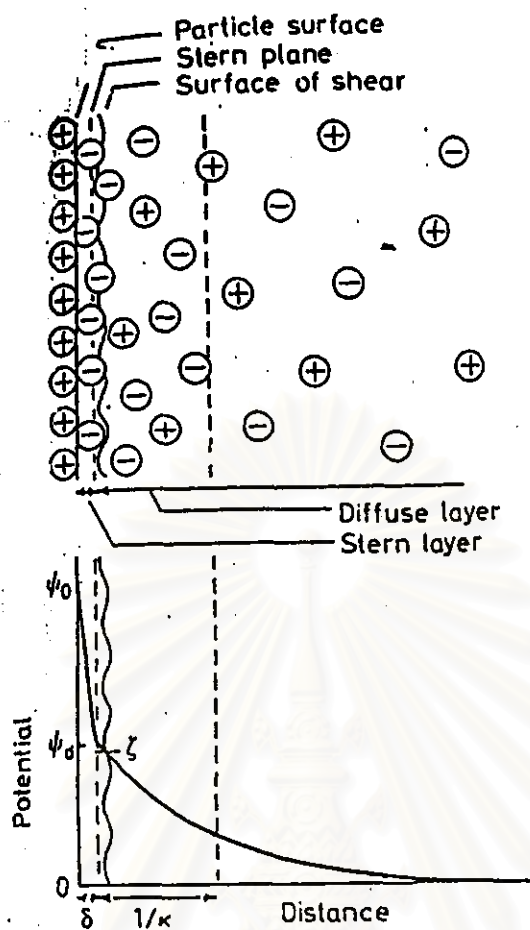


Fig. 3.2 Schematic representation of the structure of the electric double layer according to stern's theory.⁽¹⁹⁾

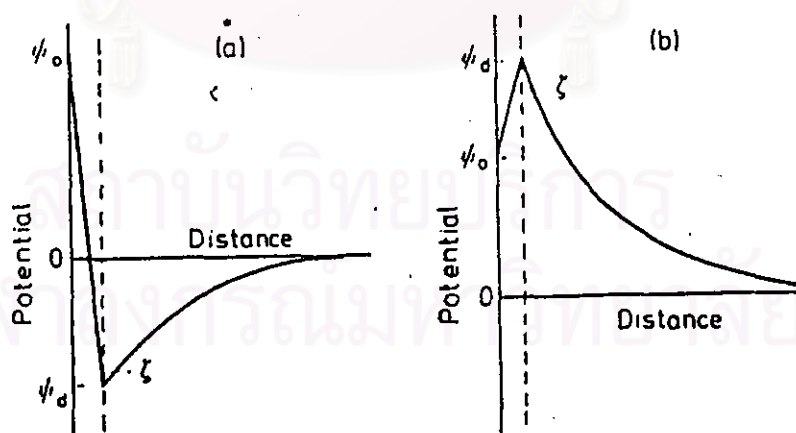


Fig. 3.3 (a) Reversal of charge due to the adsorption of surface-active or polyvalent counterions (b) Adsorption of surface-active co-ions.⁽¹⁹⁾

Zeta potential (ζ) or electrokinetic potential is the potential at surface of shear between the charged surface and the electrolyte solution the shear plane usually located at a small distance further out from the surface than the stern plane, the next hydrate cation layer, which is sufficiently attached to the particle to travel with it and form the boundary between hydrated particles and the bulk medium.

The theory of colloidal stability was developed by DeJaguin and Landau in Russia and Verwey and Overbeek in Holland during the 1940s, called *DLVO theory*.^(5,19) This involves an estimate of the relative magnitude of the two forces that act on the particles in a suspension. Two forces are the attractive Van der Waals and the repulsive electrical force (electrostatic force). Deflocculated and flocculated suspensions can be described by considering the total potential energy of interaction (V_T) as a function of particle separation distance.

$$V_T = V_A + V_R \quad (3.11)$$

$$V_A = \text{The attractive energy}$$

$$V_R = \text{The repulsive energy}$$

A deflocculated slurry will result when V_T is positive potential energy maximum at the intermediate particle separation (Fig.3.4(A)). A flocculated system is negative (Fig.3.4(B)).

The shape of total interaction is determined by V_R because V_A is fixed. Therefore, the stability of system is a function parameters that control V_R : the particle surface charge and the particle double thickness ($1/K$).

$$\frac{1}{K} = \left[\frac{\epsilon_0 \epsilon_r RT}{4\pi F^2 \sum c_i z_i^2} \right]^{1/2} \quad (3.12)$$

ϵ_0	=	The permittivity of a vacuum
ϵ_r	=	The dielectric constant
R	=	The gas constant
T	=	The absolute temperature
F	=	The Faraday constant
c_i	=	Concentration of the counterion
z_i	=	Charge of the counterion

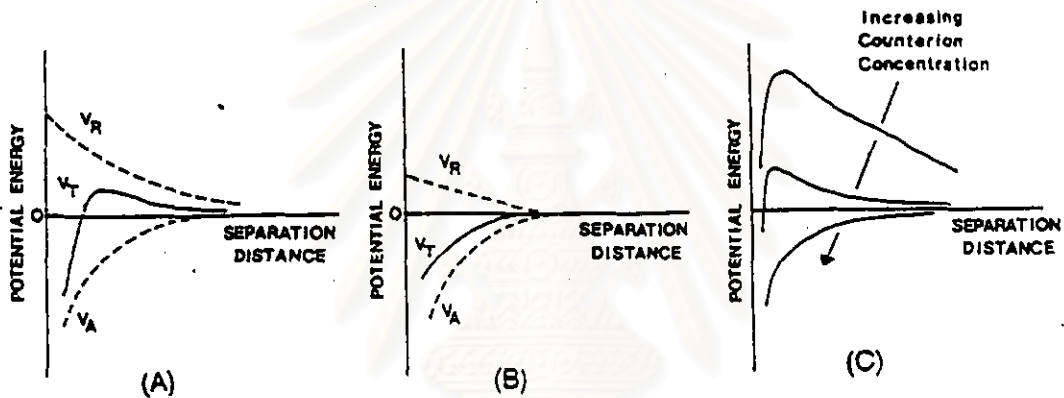


Fig. 3.4 Potential energy curve for the Van der Waals attraction and the electric repulsion between particles suspended in an aqueous medium.⁽⁵⁾

(A) Deflocculated system (B) Flocculated system (C) Effect of the counterion concentration on the net energy of interaction (V_T)

From the equation (3.12), the double layer thickness ($1/K$) is inversely proportional to the valence of the counterions and to the square root of their concentration. The DLVO theory predicts that a compression of the double layer results in a decreased energy barrier to flocculation, a deflocculated slurry requires the low content of the valence and concentration of the solution counterion. Flocculation can occur upon the much addition of soluble ionic content.

3.2 Rheology of slurry ^(20,21)

Rheology is the science of the change in form and flow of matter. Rheology of dispersed system is essential when designing or selecting equipment for storing, pumping, transporting, milling, mixing, atomizing and forming a ceramic slurry. Rheological properties of dispersed systems depend on the following factors⁽²⁰⁾ :

- (1) The viscosity of the fluid medium
- (2) The concentration of the suspended matter
- (3) The size and shape of the suspended particles
- (4) The forces of interaction between the particles, i.e., the state of stability or flocculation of the suspension

3.2.1 Viscosity^(22,23)

Viscosity is the measurement of the internal friction of a fluid. This friction (shear) becomes apparent when a layer of fluid is made to move in relation to another layer. Issac Newton defined viscosity by considering the model represented in Fig.3.5. Two parallel planes of fluid of equal area "A" are separated by distance "dx" and are moving in the same direction at different velocity "v₁" and "v₂". Newton assumed that the force required to maintain this difference in speed through the liquid (velocity gradient; $\frac{dv}{dx}$). That can be expressed as equation (3.13)

$$\frac{F}{A} = \eta \frac{dv}{dx} \quad (3.13)$$

η = The viscosity constant for a given material

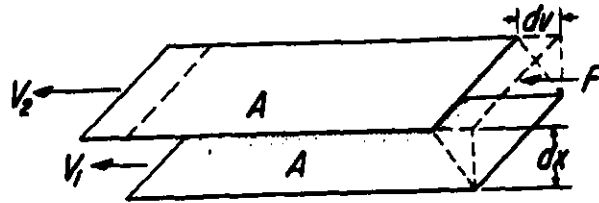


Fig. 3.5 Model of viscous flow.⁽²²⁾

Velocity gradient, $\frac{dy}{dx}$, is a measurement of the speed at which the intermediate layers move with respect to each other. It describes the shearing of the liquid and is called “shear rate”, γ' or symbolized as S in the figures. Its unit is reciprocal second (sec^{-1}). F/A is the force per unit area required to produce the shearing action, that refers to “shear stress” (τ or symbolized as F' in the figures) and unit of measurement is “dyne/cm²”

$$\eta = \frac{F'}{S} = \frac{\tau}{\gamma} = \frac{\text{shear stress}}{\text{shear rate}}$$

The unit of viscosity is $\frac{\text{dyne}}{\text{cm}^2 \text{sec}}$ or poise and is equal to dPa.s

3.2.2 Type of flow

The flow behavior can be separated into two main groups. One is Newtonian flow and the other one is Non-Newtonian flow.

Newtonian flow

In this flow type, viscosity of a material is a constant. The relation between shear stress and shear rate is a straight line and viscosity is

independent of shear rate. When shearing Newtonian liquid at constant rate, time has no effect on the viscosity if the temperature is constant. Examples of Newtonian liquids are water, oils and organic solvent.

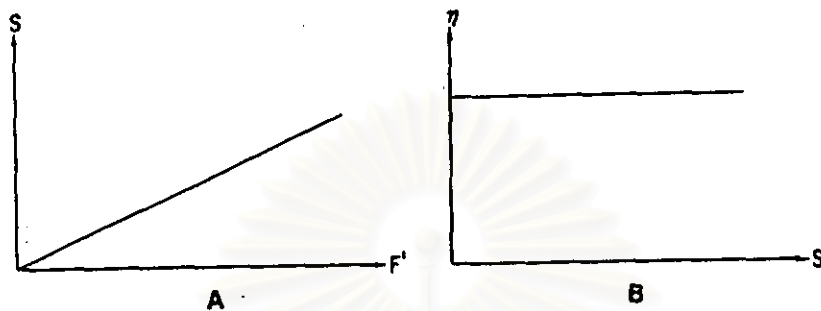


Fig. 3.6 Flow curve and viscosity of Newtonian liquid.⁽²²⁾

Non-Newtonian flow

A non-Newtonian fluid is widely defined as one for which the relationship F'/S is not constant. When shear rate is varied, the shear stress doesn't vary in the same proportion.

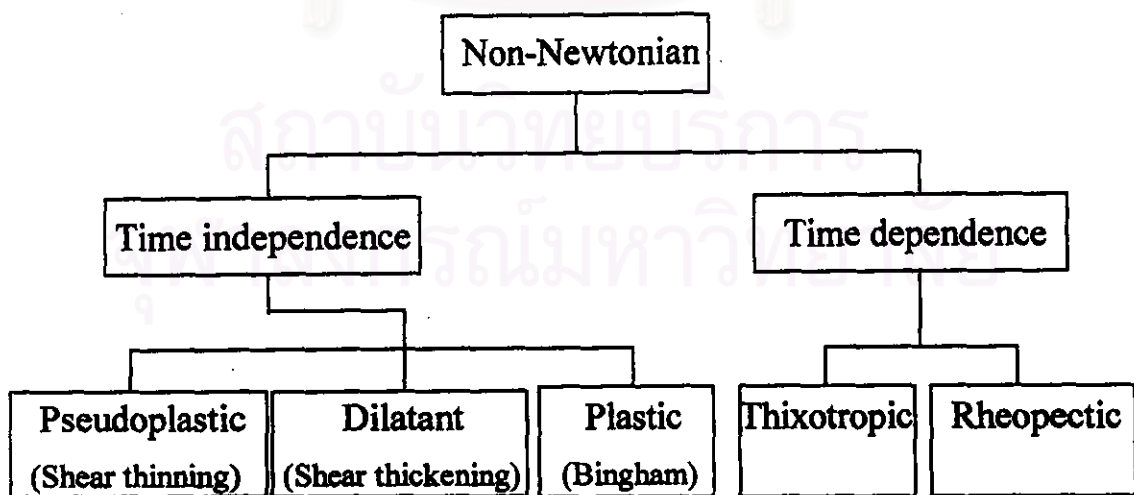


Fig. 3.7 Types of non-Newtonian behavior

Pseudoplastic flow (shear thinning)

Pseudoplastic fluid will display a decreasing viscosity with an increasing shear rate (Fig. 3.8) and will be found in paint, emulsion and dispersions.

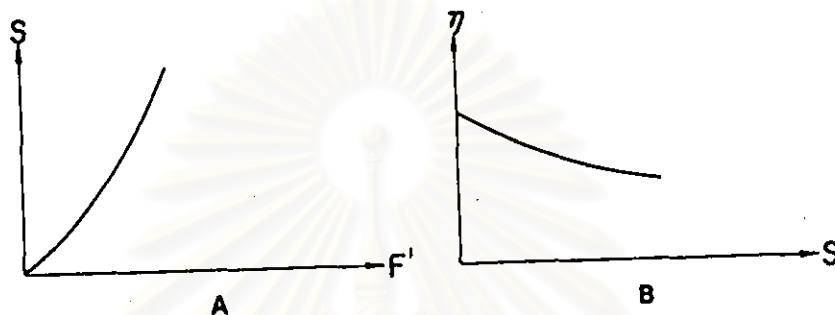


Fig. 3.8 Pseudoplastic flow.⁽²²⁾

Dilatant flow (Shear thickening)

Characteristic of dilatant flow is increasing viscosity with an increase in shear rate as Fig. 3.9. Dilatancy is frequently observed in fluids containing with high level of deflocculated solid such as starch, sand- water mixture and some clay slurries.

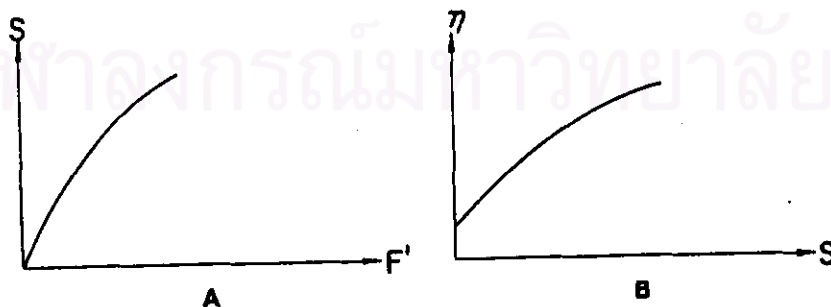


Fig. 3.9 Dilatant flow.⁽²²⁾

Plastic flow

Materials with plastic flow behavior have a yield stress τ_0 . They behave as a solid when the shear stress is smaller than the yield value and start to flow at a stress bigger than τ_0 .

Bingham flow is one type of Plastic flow that has relation between shear rate and shear stress in linear like Newtonian but Bingham flow has a yield stress. Another type of plastic is 'casson' that is similar to pseudoplastic with a yield stress.

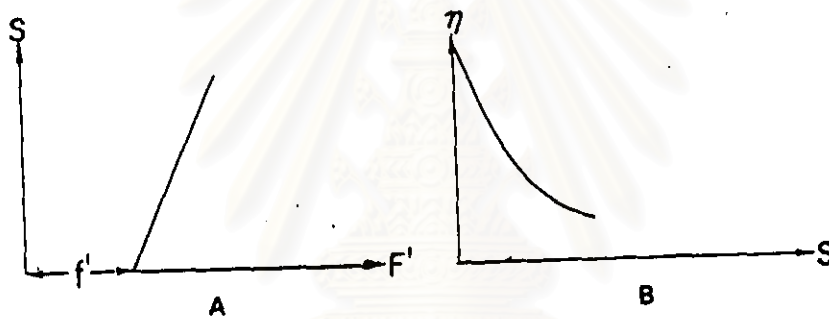


Fig. 3.10 Plastic flow.⁽²²⁾

Thixotropy

Thixotropy is the time dependent type of shear-thinning and plastic behavior. This system is allowed to stand is then sheared at a constant rate, the apparent viscosity decreases with time until a balance between structural breakdown and structure reformation is reached.

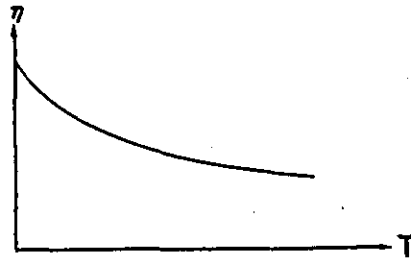
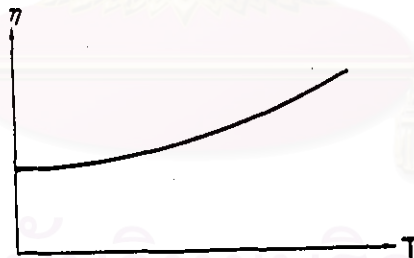


Figure 4-6

Fig. 3.11 Thixotropic flow.⁽²²⁾

Rheopectic

The fluid's viscosity increases with time as it is sheared at a constant rate. For example, bentonite clay suspension often sets only slowly on standing but quite rapidly when gently disturb.

Fig. 3.12 Rheopectic flow.⁽²²⁾

Both thixotropy and rheopecty may occur in combination with any of flow behavior or only at certain shear rate. Time is extremely variable, some fluids will reach the final viscosity in a few seconds while others may take up to several days under condition of constant shear.