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A Thermodynamic Theory of Suspension II. Kinetic Theory for Viscosity of Suspension

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A dispersion is prepared by vigorous agitation for large particles of radius r or volume v larger than its critical r_c or v_c. The viscosity η is several Pa s and will be large compared with the viscosity of the solvent η_0 of 10^{-3} Pa s. As a typical case, cement paste was studied by Hattori–Izumi who showed a gradual increase in η with time t. It was explained by collisions followed by cohesion, but gradual sedimentation seems more likely to be the origin. The author proposes a dynamic theory of viscosity.

The static viscosity is proportional to the energy of sedimentation W_{sed}, whereas dynamic viscosity η is expressed as exponential functions of W_{sed}. Molar concentration W_{sed}/v increases with the density of particles ρ, but decreases with the viscosity of solvent. The η value decreases by addition of water and fly ash. ζ-potential promotes dispersion. Contrary to an ordinary concept, cohesion heat may not act except in the coagulated state.

Time-dependent viscosity is caused by the relaxation of agitation energy W_{ag} through three stages: rapid stage relaxation by collision of particles, slow stage relaxation by the consumption of W_c i.e., internal sedimentation energy due to viscous resistance and finally relaxation by coagulation. The second stage is expressed as $\ln \eta \approx \phi\ (W_c/v_cRT)(t/\tau)$, where $W_c/v_cRT = 1$, $v_c = (r_c/r)^3$, $r_c = 30$ nm, $r = 1$ µm, $\tau = C^{0.5}(r_c/r)^2$, $C = \eta_0^{0.5}/\Delta\rho^{3/4}$ and τ is about 1 h.

For the case of very large particles e.g., fluidized bed, the relative volume v of the bed expands with the velocity of gas stream u_0 like thermal expansion with a coefficient β and η is expressed as $\eta = A \exp(W_{\mathrm{sed}}/\beta u_0RT)$. This type of equation for polymeric material is known as Doolittle's equation, $\eta = A \exp(B/v_f)$, v_f being a free volume fraction.

In Part I, the author proposed a thermodynamic theory of the stability of colloidal suspension and emphasized that the stability is greatly affected by the effect of gravity on the particles of large size. The size effect may be more obvious in the time-dependent viscosity. As a typical case, viscosity of cement paste is discussed in this paper.

Cement is composed of particles of sodium and calcium silicates. The sizes of particles are distributed in the vicinity of 1 µm and exceed the critical size for sedimentation i.e., 0.03 µm. Cement reacts with about 10% of water to give a rigid material and concrete is used after being mixed with sand and gravel. In ordinary case, 20—50 weight% water is added to cement to give a plastic paste. These plastic states are suitable for working clay in ceramic industry as well as pasting and built-up processes for construction.

The plastic cement paste becomes liquid-like lowering its viscosity by vigorous agitation, but it is unstable and viscosity increases gradually to become a sticky paste after several hours. This is a physical hardening and by agitation it can be redispersed. Such time-dependent viscosity is a serious problem for transportation and pouring of concrete. To protect against physical hardening a kind of sulfonic acid of polymer or oligomer is often added. The viscosity of suspension is explained by various theories involving cohesion and hydrogen-bonding of silicate. But the time-dependent viscosity is a problem which has not yet been elucidated. Partial coagulation by cohesion is often assumed. Hattori and Izumi[1] studied the cement pastes and explained the physical hardening as coagulation due to cohesion of particles based on the DLVO–Hamaker theory.

However, cohesion energy acts only at the contact points of particles and is active only in the static state but may not occur in dilute suspension. The effect of cohesion is so little that the introduction of other factors than cohesion is necessary. The author proposed the effect of partial sedimentation for relatively large particles like cement or clay, which decreases the uniformity of dispersion and causes the formation of a muddy state containing domains of particles and water. Size of particles determines the time-dependency of viscosity.

For dilute colloidal solution the viscosity η is given by Einstein's equation[2] as

$$\eta = \eta_0(1 + 2.5\phi), \tag{1}$$

which was derived by a tensor analysis of mechanical loss of particles rotating by shear. The η value increases with increasing volume fraction of the particles ϕ with a coefficient of 2.5 regardless of size and time. However, it is valid only for the small and uniform spherical particles.

The author proposes here a theory of viscosity of disper-

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sion of large particles based on the theory of the viscosity of liquid proposed by Eyring. The theory contains the following assumptions: Particles possess micro-Brownian motion and the dispersion behaves as liquid molecules. Viscosity is expressed as an exponential function of temperature and the activation heat E^*. As E^*, the energy of internal sedimentation W_c is taken as well as the electric repulsion, if the particle is charged, but cohesion heat is neglected except for the final stage for dynamic state or the static state.

Theory

1. Static Viscosity of Large Particles. In the case of solid particles of large sizes, the suspension is prepared by vigorous agitation but it is unstable and gradually becomes a muddy dispersion containing an agglomerate of particles and water domains. For manufacturing ceramic materials of industrial or art products, the technology for a potter's wheel is employed for which such a muddy dispersion is very important. The static viscosity is caused by the friction of particles and the coefficient of friction μ is proportional to the contact area as well as to the cohesion heat H. For spherical particles the ratio of contact area to the volume of particle is almost constant and is equal to the coordination number z for molecules. For non-spherical particles the Stokes law is to be modified but may be proportional to the increase of the number of contact points or to the surface area or to $v^{2/3}$. Static viscosity η_{st} is expressed as

$$\eta_{st} \approx \mu \approx \phi v^{2/3}(H + W_{sed}). \tag{2}$$

In fact, μ of plastics is proportional to H.[3] Hydrogen-bonding, if it occurs, is the important factor.

In relation to the friction of particles, it may be interesting to note that rubber possesses very small cohesion heat H but it exhibits μ of high value. According to the concept of pseudo cross-links of multi-size proposed by the present author,[3] the friction of plastics is caused by the dissociation of the smallest pseudo link A which forms between plastics and the slider, whereas the friction of rubber is caused by repeating cohesion and peeling of the largest pseudo links B. The sizes A and B in the theory are 4 and 16 segmental units, respectively.

The size of pseudo links runs parallel to the area of contact points. Thus, viscosity is proportional not only to the cohesion heat but also to the size and number of pseudo links. For plastics the size of pseudo links is small and the contact area as well as μ is small, whereas those of rubber are large and μ is large. These properties are important for the stability of an emulsion. An emulsion of polymers of low softening temperature T_s or low glass-transition temperature T_g, e.g., rubber latex, possesses a high ability of tacky adhesion and is vulnerable to agitation, because collision of particles induces thixotropic coagulation.

On the contrary, with suspensions of solid particles, e.g. cement paste and suspension of polystyrene, μ is very small due to the small number and small area of contact points. For the emulsion of oily particles or particles of polymer of low T_m like rubber latex, a thixotropic change occurs by fusion induced by vigorous agitation. Clay gives also a tacky suspension perhaps due to the formation of hydrogen-bonding between particles, but coagulation is slow because it does not fuse. The author takes the effect of sedimentation as the formation of muddy paste.

2. Dynamic Viscosity. For particles of small size, the suspension viscosity η is small. Its dynamic state is stable due to the micro-Brownian motion; the effect of internal sedimentation, if it occurs, is compensated by the micro-Brownian motion.

For large particles, η is expressed as an exponential function of the cohesion, gravity and electric repulsion as well as of the of energy of Brownian motion, i.e., RT per mole. Cement paste also possesses micro-Brownian motions of various degrees and free volumes of various sizes depending on the size of particles. In this case, the dynamic viscosity is explained more easily by kinetics than by mechanics or potential energy.

A suspension resembles an ordinary liquid which shows flow property. The author proposes here the kinetics based on the concept that the suspension is regarded as a kind of liquid including large particles and the theory of viscosity of a liquid is extended to that of a suspension.

According to Eyring,[4] the coefficient of viscosity of a simple liquid is given as

$$\eta = (N_A h/V)\exp(-S^*/R + E^*/RT\}, \tag{3}$$

where N_A is the Avogadro's number, i.e. 6×10^{23} per mole, h is the Planck constant, i.e. 3×10^{-27} erg s and V is the molar volume given in cm^3, one erg being 10^{-7} J.

In the viscous flow, the activation heat E^* is necessary for production of a hole for translation of a molecule. E^* is usually equal to one-third the heat of vaporization H_{vap} (Appendix in Part I). H_{vap} is equal to the product of cohesion heat H times the coordination number z. z is 8—10 and H_{vap} is about 6 kcal for hydrocarbon and 10 kcal for water having hydrogen-bonds and the exponential factor $\exp(E^*/RT)$ is $10^{2.3}$ and $10^{3.2}$, respectively. S^* is the entropy for activation and it is mainly concerned with factors of conformation of a molecule and its activated state. Hydrocarbons and water are used often as a solvent for colloid: their viscosity η is low, for example 10^{-3} and 10^{-2} poise, or 10^{-4} and 10^{-3} Pa s, respectively.

For a colloidal solution, Eq. 3 is extended simply. Then,

$$\eta = (N_A h/vV_0)\exp(vH_{vap}/3RT), \tag{4a}$$

but it is too large compared with the Einstein equation. Actually, a hole for translation of a particle is formed in the solvent and so a large hole is not necessary when a particle translates successively with v-times steps. In this case,

$$\eta = (N_A h/vV_0)v \exp(H_{vap}/3RT) = \eta_0, \tag{4b}$$

which seems too small.

There may be another factor for viscosity of suspension. The term of gravity is introduced in the way that rotational energy is introduced in Einstein's equation. The dynamic viscosity is caused by the micro-Brownian motion and the energy factors are expressed by their exponential functions. As activation energy the energy of internal sedimentation W_{sed} is considered, because the energy W_{sed} acts to decrease the uniformity of supension and so the energy of the same amount is necessary to recover the uniformity. The energy of sedimentation of the critical size can be involved in the system. On the other hand, the cohesion heat H is very small except for the condensed or static system, as explained in Part 1, and is neglected in the dynamic state. Then, the viscosity of large particles η becomes

$$\eta = \eta_0 \exp(\phi W_{\mathrm{sed}}/vRT). \tag{5}$$

When W_{sed}/vRT is larger than 1, the energy absorbed in the system is limited to 1 and a large part of the eneygy may form a heterogeneous mixture containing domains of particles and water.

For a stable suspensions, the relative radius r or volume v is below the critical values r_{c} or v_{c} for sedimentation, respectively. At the critical state, η becomes

$$\eta = \eta_0[1 + a\phi + b\phi^2 + \cdots]. \tag{6}$$

The coefficients a and b involve energies of sedimentation, cohesion heat, electric repulsion as well as the rotational energy and is larger than a of 2.5 of Einstein's equation Eq. 1.

For a suspension of large size, agitation is necessary to achieve a dynamic state. Collision of particles occurs and promotes dispersion against sedimentation but does not induce coagulation by cohesion, except for the cases of emulsions of oil or polymer of low T_{g} which are vulnerable toward fusion and aggregation.

In this case, viscosity may be expressed as exponential functions of W_{sed}, cohesion heat H and electric energy W_{el} as

$$\ln \eta \simeq \ln(N_{\mathrm{A}}h/vV_0) + [\phi W_{\mathrm{sed}} + \phi^2 H - \phi^2 W_{\mathrm{el}}]/vRT, \tag{7}$$

where H does not increase as v increases and is inactive except for ϕ of 1.

3. Time-Dependent Viscosity of Large Particles. When the particles have a radius r which is larger than r_{c}, the energy of sedimentation W_{sed} is larger than the kinetic energy of Brownian motion $R\ T$. By vigorous agitation, particles are dispersed, but the dispersion is unstable; thus, after stopping agitation, sedimentation occurs gradually. A part of a sedimentation energy is absorbed in the system as the internal sedimentation, but this is limited and the remaining energy $W_{\mathrm{sed}}(r/r_{\mathrm{c}} - 1)$ causes a heterogeneous or muddy dispersion. This causes an increase in the viscosity to give a time-dependent viscosity. There are various states of motion of particles.

In the initial state, the motion of particles is violent due to the energy of agitation W_{ag}. The state A corresponds, as it were, to a gaseous or super-heated state of particles. Viscosity η of the gaseous state is proportional to the number of collisions of particles, but η is small compared with the viscosity of a liquid and the viscosity of the dispersion at the state A, η, is proportional to W_{ag}.

After agitation is stopped, W_{ag} decreases rapidly due to the friction of collision of particles. At the state B, W_{ag} decrease to the kinetic energy of Brownian motion in a liquid, i.e. $W_{\mathrm{c}}/v_{\mathrm{c}}RT = 1$. Then it decreases gradually by the friction of particles with solvent molecules to the state C or a kind of glassy state, where $W_{\mathrm{c}} = v_{\mathrm{g}}RT$ and the free volume is decreased from v_{c} of 10% to v_{g} of 2.5%. The Brownian motion is lost at the state D or static state.

According to the above concept, the changes in the dynamic viscosity can be shown in Fig. 1, where the states and the stages for changing states are expressed as follows:

$$\text{State A}: \ln \eta_{\mathrm{A}} = \ln \eta_0 + \phi^2(W_{\mathrm{sed}} - W_{\mathrm{ag}}/vRT), \tag{8a}$$

$$\begin{aligned}\text{State B}: \ln \eta_{\mathrm{B}} &= \ln \eta_{\mathrm{A}} + \phi(W_{\mathrm{sed}}/vRT)\\ &= \ln \eta_0 + \phi^2(r/r_{\mathrm{c}})^4,\end{aligned} \tag{8b}$$

$$\text{State C}: \ln \eta_{\mathrm{C}} = \ln \eta_{\mathrm{B}} + \phi(W_{\mathrm{c}}/v_{\mathrm{c}}RT) \simeq \ln \eta_0 + \phi, \tag{8c}$$

$$\text{State D}: \eta\,(\text{static}) = \mu \backsim W + H. \tag{8d}$$

Changes of states are rate processes proceeding through the stages of different relaxation times τ's and can be expressed as follows:

$$\text{Stage AB}: \ln \eta_{\mathrm{AB}} = \ln \eta_{\mathrm{A}} + \phi^2(r/r_{\mathrm{c}})(1 - \mathrm{e}^{-t/\tau_{\mathrm{AB}}}), \tag{9a}$$

$$\text{Stage BC}: \ln \eta_{\mathrm{BC}} = \ln \eta_{\mathrm{B}} + \phi(t/\tau_{\mathrm{BC}}), \tag{9b}$$

$$\text{Stage CD}: \ln \eta_{\mathrm{CD}} = \ln \eta_{\mathrm{C}} + \phi^2(H/vRT)(t/\tau_{\mathrm{CD}}). \tag{9c}$$

4. Relaxation Times of Each Stage. Relaxation times

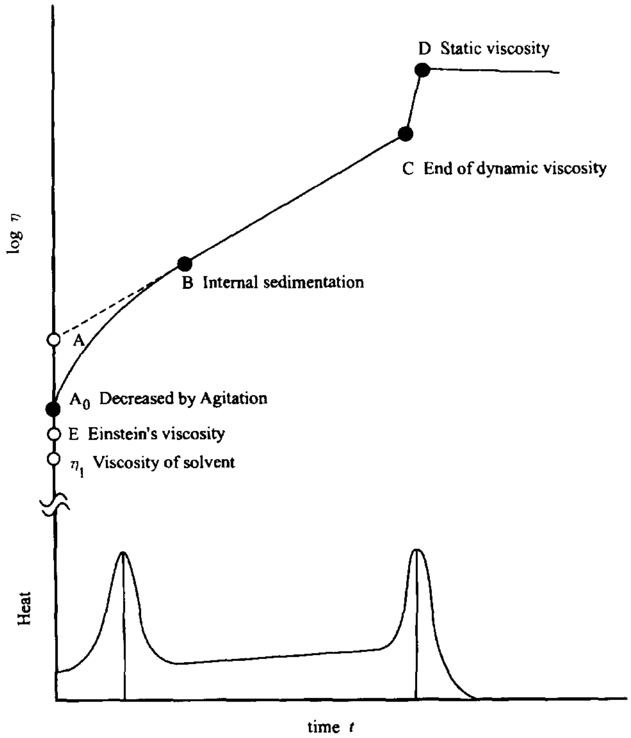

Fig. 1. Schematic diagram of the dynamic viscosity and thermal change. η_1 : Viscosity of solvent, E : Einstein's viscosity, A_0 : Agitation, B : Internal sedimentation, C : End of dynamic viscosity, and D : Static viscosity.

are estimated from the degree of Brownian motion as follows:

The state A is a quasi-gaseous state and the viscosity is almost equal to that of suspension of large particles with strong Brownian motion. In the stage AB, W_{ag} is converted to the energy of suspension, i.e. W_{sed}. It is consumed by the friction of particles; the relaxation time τ_{AB} is very short and may be inversely proportional to W_{ag}.

The states A and B are muddy where the main part of W_{sed} is not accepted in the dispersion except a critical value W_c equal to v_cRT. The viscosity is directly propotional to a static work of gravity or $\phi(r/r_c)$.[4]

In the stage BC, the energy of internal sedimentation W_c, equal to v_cRT, decreases to RT with the relaxation time τ_{BC} as expressed by Eq. 9b. On lowering the degree of Brownian motion, the uniformity of the dispersion decreases and the dispersion becomes a muddy mixture, which involves muddy masses as well as liquid-voids. The relaxation time τ_{BC} may be given by the sedimentation time of the particle of the radius r.

The state C is the end of the dynamic state or a glass transition state and D is a static solid state. According to the concept of glass transition, the free volume fraction decreases from 10 to 2.5% at the glass-transition state (See: Appendex in Part I) The time for transition τ_{CD} may be one fourth of τ_{BC} and is short.

As a result, the time-dependent viscosity can be expressed as

$$\ln \eta(t) = \ln(\eta_A) + \phi(t/\tau_{BC}) + \phi^2(H/vRT)(t/\tau_{CD}). \tag{9}$$

The stage BC is important for the stability of muddy or plastic state of dispersion. The relaxation time τ_{BC} may be given by the reciprocal of the stationary gravity velocity of particles u, as $3/u$, because relaxation of the energy is caused by the gravity acting in the perpendicular direction and therefore, it is of one-dimension. For Brownian motion it is multiplied by 3.

$$u = (2/9)g(\Delta\rho/\eta_0)r^2,$$

and τ_{BC} is equal to

$$\tau_{BC} = 3/u = 0.014(\eta_0/\Delta\rho r^2). \tag{10}$$

Thus, τ_{BC} increases with increasing η_0 and decreasing $\Delta\rho$ and r. A lyophilic surfactant may be used as a stabilizing agent to enhance viscous resistance.

5. Effect of Ionic Surfactant. Ionic surfactants are often used for the stabilization of a suspension of large size particles. For example, cement paste is stabilized by addition of a special kind of surfactant such as sulfonic acids of lignin or various oligomers, e.g. condensates of naphthalene–formaldehyde, aliphatic hydrocarbon of a short chain, etc. They exhibit marked effects on the dispersion and stabilization of suspensions without coagulation by calcium ions and without foaming, unlike ordinary soap.

The surfactants react with cement particles to introduce many sulfonic acid groups to particles. Sulfonic acid is much stronger than the silanol or silicate group of cement and is dissociated to form a layer of strong ions, which induces the strong electric repulsion between cement particles.

The electric force acting between particles is inversely proportional to the distance; the effective range is very long compared with the cohesion force. In the lattice model, the particles bearing an electric charge interact with each other not only in the coordination site but also in many other sites.

6. Viscosity of Polymer Solution. Emulsion and suspension of polymers are widely used. The viscosity of a dilute colloidal solution follows the Einstein equation Eq. 1. However, for a polymer solution a chain molecule forms a coil and it is often swollen by the solvent. The actual volume fraction of the polymer particles is increased. In the θ-solvent,[5] a coil involves one polymer chain and the diameter of a coiled polymer is $n^{0.5}$, n being the chain length or the degree of polymerization. The molar volume of the coil or particle is $n^{1.5}/n$ or $n^{0.5}$-times larger than that of solvent.

The viscosity of solution is much increased depending on the chain length n and the equation of Staudinger is obtained:

$$\eta = \phi n^m \eta_0, \tag{11}$$

m being 1, but 0.5—1 according to Sakurada, Mark and Flory depending on the stiffness of polymer chain.[2,5]

For a concentrated solution of polymer or a molten polymer, the coil is entangled with other coils to form links due to cohesion of the segments. These links slip by shear to give viscous flow.

The present author proposed a theory of pseudo links of multi-sizes[3] and extended the theory to the above problems. For a molten polymer or highly concentrated polymer solution

$$\eta = \phi^{4.6} n^{3.5}(N_A h/V)\exp(E^*{}_B/RT), \tag{12}$$

is obtained theoretically.[3] Equation 12 becomes important for the case of the suspension in polymer. In the case of a polymer blend, the matrix polymer acts as a solvent in which the other polymer particles act as a filler. The thermoplastic elastomer is a special case where particles are linked with many rubber chains and act as the bulky crosslink.

7. Effect of Shear Rate on Viscosity. Viscosity is much decreased by shear or shear rate. This is shown in the equation of viscosity derived by Eyring.[4] The rate constant of flow k_{vis} is enhanced by mechanical work, because

$$\eta = f\lambda/\Delta u, \tag{13}$$

where λ is a distance between particles. According to Eyring the velocity difference Δu is

$$\begin{aligned}\Delta u &= \lambda k(\mathrm{e}^{fv/2kT} - \mathrm{e}^{-fv/2kT}) \\ &= \lambda k[(fv/2kT) + (fv/2kT^3/6 + \cdots] \approx (fv/2kT)^m \end{aligned} \tag{14}$$

where f is a the applied force. Therefore, at large f

$$\eta = f\lambda/\Delta u = f\lambda/(fv/2kT)^m \approx \eta_0 f^{-m+1}. \tag{15}$$

In the case when the stable suspension of τ is less than τ_c, the decrease in viscosity by high shear was reported. Induced orientation of particles may occur depending on the aspect ratio or specific surface area. High shear γ and high shear rate $\dot{\gamma}$ may decrease the activation energy of flow by orientation of particles, especially for non-spherical particles. These effects decrease the dynamic viscosity η from the standard viscosity $\eta_{(0)}$. η may be expressed as

$$\eta = \eta_{(0)}\exp(-\delta\eta_{(0)}\dot{\gamma}^2), \tag{16}$$

where δ is a coefficient concerning orientation, shape and uniformity of the size distribution of particles. It was sometimes called a *structural viscosity*. The effect of shear is closely correlated with geometrical or mechanical properties such as size, aspect ratio, roughness, and hydrogen-bonding of particles.

These properties also change the free volume at the activated state in the rheological phenomena. In the dilatancy, the shear decreases the free volume and increases viscosity. It is correlated with the aspect ratio as well as with the state of close packing.

8. Fluidization of Very Large Particles. Grain and sand include very large particles whose radii are larger than 1 mm, but they become fluid-like in transportation due to mechanical agitation. They are mostly dealt with by mechanics but for the dynamic states the thermodynamical treatment may be more simple. The author[6] investigated previously the viscosity of the fluidized bed. Fluidization occurs when a stream of gas is passing through the bed of particles and the bed expands and becomes fluid-like. The bed is in a dynamic state caused mechanically but not thermally.

Viscosity measured by a Stomer-type viscometer is found to be expressed by an Andrade-type equation with respect to the velocity u_0 of the gas stream:

$$\eta = A\exp(B/u_0). \tag{17}$$

In this case v_f is not changed thermally but expands thanks to the velocity of the stream of gas u_0. In fact, the bed expands with increasing u_0, because u_0 is the volume of gas passing through the bed in a unit time and the expansion is proportional to the volume of the bed.

$$\eta = A\exp[W_{\mathrm{sed}}/v(1+\beta u_0)RT], \tag{18}$$

where β is an expansion coefficient. Doolittle[7] proposed for viscosity of a material an equation involving a free volume fraction v_f

$$\eta \backsim \exp(B/v_f). \tag{19}$$

The equation is used by Ferry[8] for introduction of the temperature shift factor for the dynamic relaxation spectrum of polymers.

9. Suspension and Emulsion of Polymer. Matsumoto–Hachisu–Horie[9] and Ise et al.[10] found the formation of an ordered structure of particles in the suspension of polystyrene prepared without any emulsifier. It looks like a crystal. It evolves iridescent light and its wave length may depend on the size of particles. Unlike an emulsion, the solid suspension without soap does not fuse below T_m of polymer particles on coagulation. When particles are uniform in size, an ordered structure is formed like a crystal.

For the suspension of polystyrene, the density ρ is 1.05 $\mathrm{g\,cm^{-3}}$ and it forms a coil of diameter of about 250—1600 nm or $n^{0.8-1}$, n being the length of the polymer in a segmental unit. Thus, the diameter of the polymer coil or the particle is of the order of 100 nm. The particles are uniform in size and form domains of an ordered structure. They involve many large voids but such voids are assumed by the present author to be formed by the formation of muddy masses during the slow internal sedimentation. In the above case, polystyrene was prepared by the method of living polymerization without any soap and has no electric charge except for the polymer end and the melting point is high enough to prevent thermal or mechanical coagulation.

It is noticed that emulsion of liquid particles is vulnerable towards collision by agitation and paricles are united to cause thixotropy. An emulsion is dispersed with the aid of surfactants, which is important for electric repulsion. The number of ions of a particle depends on the chain length of soap and ions are necessary for the stability of a soap micelle as well as the emulsion.[11] The electro-neutrallization occurs by the reaction of ions of the added salts with particles and it is very rapid.

An emulsion coagulates immediately witout direct collision of particles. Emulsion of oily particle or rubber latex coagulates by the destruction of ionic emulsifier followed by fusion of particles. Emulsions also coagulate by vigorous agitation and fusion of particles, i.e., thixotropy.

10. Effect of Cohesion. Cohesion acts at the contact points of particles. Ionic particles coagulate very rapidly by the addition of a salt of a strong acid and base.[12] For example, cement paste coagulates by addition of sodium chloride. It has been known that the critical amounts of salts inducing coagulation of the aqueous suspension: For example, for suspension of As_2S_3 and Al_2O_3, the critical amount is 50 $\mathrm{mmol\,dm^{-3}}$ for NaCl, KNO_3, K_2 SO_4, but 0.3— 0.7 $\mathrm{mmol\,dm^{-3}}$ for $MgCl_2$, $MgSO_4$, $CaCl_2$, K_2SO_4, K_2CrO_4, and 0.1—0.06 $\mathrm{mmol\,dm^{-3}}$ for $AlCl_3$, $Ce(NO_3)_3$, $Al_2(SO_4)_3$ and K_3 $Fe(CN)_6$. Addition of common ions of a large valency retards electric dissociation of the colloid salt of a weak acid such as silanol or silicate.

This process may be induced by the migration of the counter metal ions but not the direct collision of colloid particles. Salt of di- or tri-valent acids are very effective This is neutralization by a strong acid dissociated from a salt but not the coagulation due to collision of particles followed by cohesion.

11. Stability of Colloid and Relaxation Time. As explained in Parts I and II, gravity affects the condition of equilibrium as well as rate processes. The critical radius r_c for sedimentation, and the stationary velocity u_c are summarized for cement paste (Cp) of ρ ($\mathrm{g\,cm^{-3}}$) and polystyrene–water suspension (Ps) of ρ of 1.05, ρ_0 being 1.

$$u_c = (kT/\Delta\rho)^{0.5}, \tag{20}$$

which is 1.4 $\mathrm{nm\,s^{-1}}$ (Cp) and 8.8 $\mathrm{nm\,s^{-1}}$ (Ps).

$$r_c = [(9/2g)^{1/2}(kT)^{1/4}](\eta^{1/2}/\Delta\rho^{3/4}), \tag{21}$$

which is 13 nm (Cp) and 2.1 μm (Ps).

On the other hand, the relaxation time for a particle of the radius r is given by Eq. 9. For r of 10^{-4} cm, $\Delta\rho$ of 2 g cm^{-3}, and η of 10^{-2} poise or 10^{-3} Pa s, and g of 980 dyn s^{-1} or 9.8 10^{-3} N s^{-1}, τ is about 1 h. τ indicates a stability of dispersion which runs parallel to $\Delta\rho/\eta r^2$.

For a charged dispersion, salts of a strong acid destruct the emulsifier-layer and induces the coagulation or agglomeration of particles.

Discussion

Partial Sedimentation of Cement Paste. Hattori and Izumi[1] studied cement paste of particles of the large radius r of 1—10 μm, specific density ρ of 3 and ϕ of 26— 60%. The paste is a plastic mass in the static state. By vigorous agitation it becomes a liquid-like suspension and its viscosity η_A is about 1—2 Pa s, which is thousand times larger than the viscosity of water.

After agitation is stopped, η increases again with the time t. Viscosity increases with increasing density of particles, specific surface area and ionic strength, while it decreases by the addition of water of ρ of 1 and fly ash of ρ of 2. Dynamic viscosity η becomes 5—10 Pa s. η is much decreased with increasing the ζ-potential and slightly decreased with decreasing the ion number.

These authors ascribed the time-dependence of viscosity to the formation of aggregates of particles due to collision followed by cohesion of particles. The viscosity is proportional to the surface of aggregates. They expressed the time-dependent viscosity as follows:

$$\eta(t) = (\phi/v)[kt/(1+kt)]^{2/3}, \qquad (22)$$

where k is the rate constant of coagulation by collision followed by cohesion of particles. They calculated the value of k based on the DLVO theory[13] and by using the equations of Verwey–Overbeek and Hamaker.[14] The reports are very important for the chemistry of suspension.

The present author checked their data and found that when plots are taken between log η and the time t the relation is expressed by straight lines of the same slope as shown in Fig. 2, t and η being expressed in min and Pa s, i.e. 0.1 poise, respectively. The following relation is obtained:

$$\log \eta_{BC} = \log \eta_B + (t/\tau_c)/5, \qquad (23)$$

where τ_c is a relaxation time. The relation seems to be compatible with the theoretical Eq. 9b transformed into

$$\log \eta_{BC} = \log \eta_B + (t/\tau_c)/2.3 \times 3. \qquad (24)$$

At the initial point A_0 or t of 0, η is about 1 Pa s and η increases rapidly until 20 min i.e. the point B, and from B to C it gives a straight line. The slope is constant in all cases despite different values of η_A. The relaxation time τ_{BC} estimated from the point C is about 40—50 min and is compatible with the value obtained from Eq. 10.

The point C may be the point of the close packing state and the factor of 0.5—0.75 is to be multiplied. The real relaxation time is to be estimated from the point D in the thermogram. It is not the beginning of chemical coagulation contrary to their proposal, because the heat evolution is small and short in time.

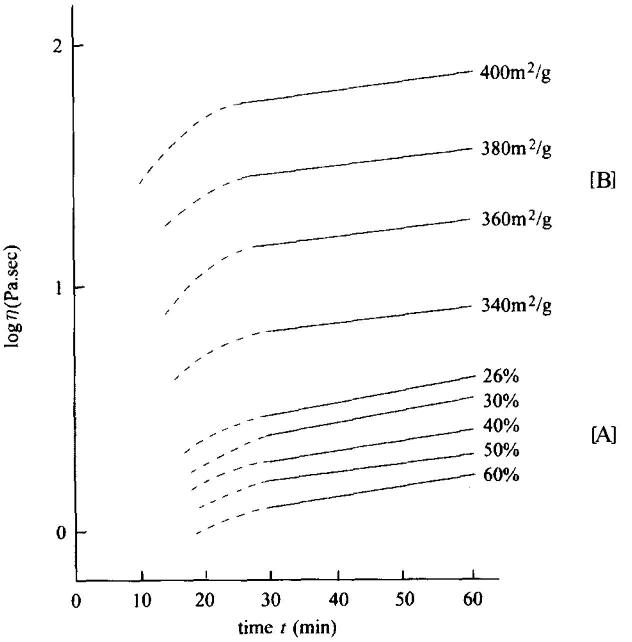

Fig. 2. Increase in the logarithmic viscosity η with time t for [A] cement paste of different amount of added water (%) and [B] of different specicific surface area of particles (m^2 g^{-1}).

Interestingly, log η and various properties give also straight lines, as shown in Figs. 3, 4, and 5, where η is expressed in Pa s: The effect of concentration of particles acts as an exponential function as

$$\log \eta = \log \eta_B + \phi(W_{sed}/vRT)$$
$$\approx (w/c)/[(w/c)+1] \approx (w/c) \qquad (25a)$$

where w and c are the weight fraction of water and cement, respectively, and w/c is the weight ratio (Fig. 3A).

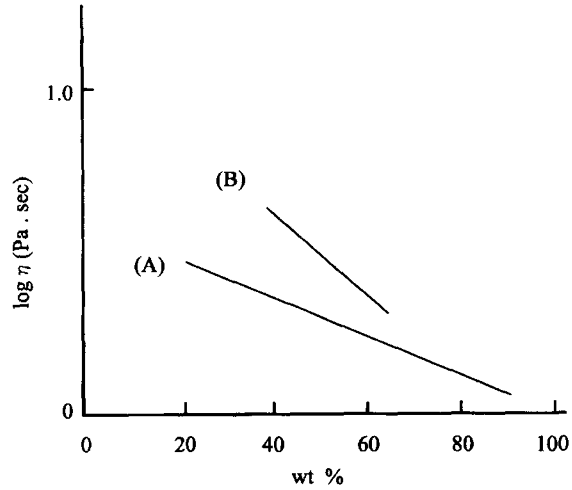

Fig. 3. Linear relation between the logarithmic viscosity η and the weight fraction (wt%) of water (A) and fly ash (B).

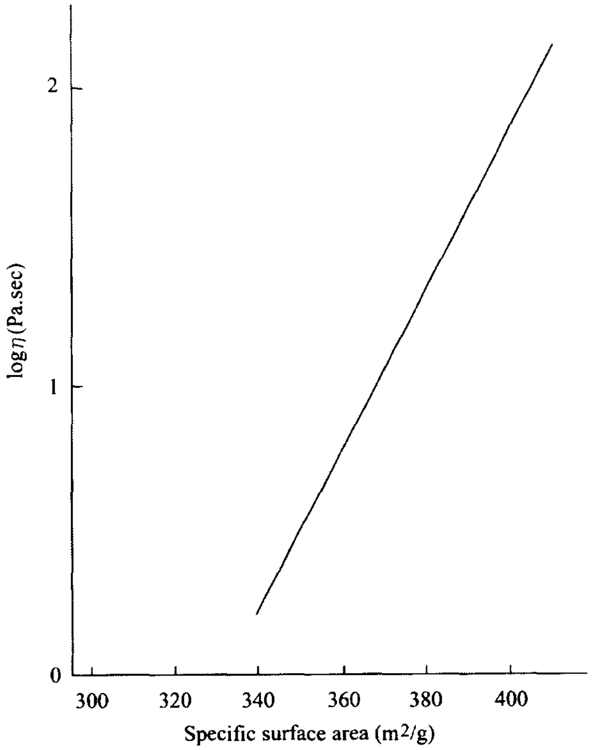

Fig. 4. Linear relation between the logarithmic viscosity η and the specific surface area.

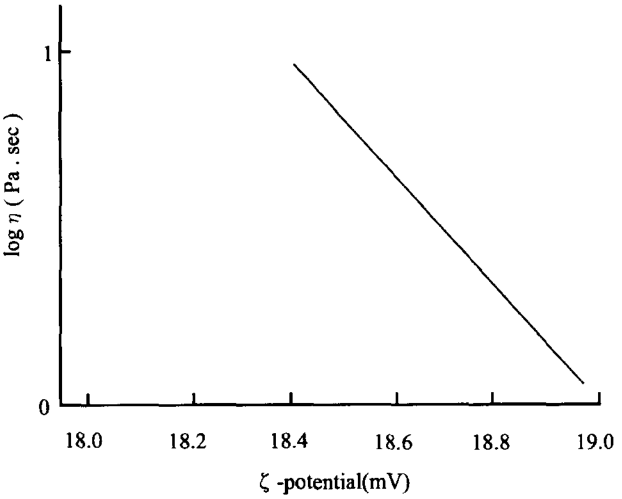

Fig. 5. Linear relation between the logarithmic viscosity η and the ζ-potential.

The addition of fly ash is a kind of silica fume of large specific area (400 $m^2\,kg^{-1}$), and small density ρ (2 $kg\,m^{-3}$), lower than that of cement of ρ of 3 $kg\,m^{-3}$. Silica fume or fly ash seems to play a minor role and it acts merely as a diluent as well as water, perhaps because of the low density of these particles. Figure 3 the line B indicates that

$$\log \eta \sim \text{vol\%fly ash}. \tag{25b}$$

Specific surface area (SSA) showed a very large effect on viscosity. η is 80 Pa s for SSA of 400 $m^2\,kg^{-1}$ and it is extremly large compared with 10 Pa s for ordinary case. Nevertheless, log η increases linearly with SSA for a small range of 300—400 $m^2\,kg^{-1}$ (Fig. 4). In this case the radius is constant and SSA is concerned with the aspect ratio or roughness of the particles. The time-depndency is the same as other effects, as shown in Fig. 2 the line A. The explanation may need some reason other than the gravity effect. For a muddy dispersion, viscosity may involve not only the dynamic property but also the static one.

η increases as the density of cement of ρ of 3.35—2.95 or its difference $\Delta\rho$ with water of ρ of 1. The linear relation,

$$\log \eta \backsim \Delta\rho^3 \tag{25d}$$

is obtained as expected.

The viscosity of solvent η_0 is controlled by the thicking agent and increases the viscosity of dispersion η. This is expected from Eq. 9 in Part I, although the decrease seems to be smaller than that of Eq. 9.

$$W_{\rm sed} = \rho u^2 = \Delta\rho\{(\Delta\rho/\eta_0)(2/9)g\}^2 \approx \Delta\rho^3/\eta_0{}^2. \quad \text{Part I (9)}$$

The other effect of thicking agent on the density of solvent is to be examined. Figure 5 indicates

$$\log \eta \backsim \zeta - \text{potential} \tag{25e}$$

In all cases, the pastes are subjected to the measurements without agitation. Nevertheless, the viscosity is small, perhaps because the pastes may exist still in dynamic states caused by the remaining effect of the agitation provided on the occasion of the preparation.These relations are explained by the theory of dynamic viscosity. The effects on viscosity are expressed in their exponential functions. This is characteristic for the dynamic state.

For the temperature effect of viscosity, the Arrhenius equation holds and the activation energy of viscous flow was reported to be 2.8 kcal, which seems to be close to that of the solvent water.

Their thermogram indicates exothermic peaks at the points A and D. The peaks may indicate some small thermal changes: A caused by the agitation and D caused by coagulation due to cohesion of particles but not chemical hardening. The region BC and CD are athermal without any peak and viscosity increases gradually. The process is expected from the concept of the internal sedimentation and the decrease in the degree of the Brownian motion.

In cement industry, the slump-time $\tau_{\rm BC}$ is used conventionally as a measure of stability of cement paste: Cement paste placed in a cone-shaped container can flow when the container is removed. The height of sedimented cement mass increases with time. The time giving the height becoming half that of container is called the slump-time $\tau_{\rm sl}$. Accordingly, $\tau_{\rm sl}$ is inversely proportional to the viscoaity η rather than the the relaxation time $\tau_{\rm BC}$ and is affected by the chemical and physical nature of cement paste. In fact, $\tau_{\rm sl}$ is found by Hattori[1] to be proportional to r^2 and w/c.

Conclusion

The author proposed a new kinetic theory for coagulation of colloid of large particles as well as electrical repulsion. Viscosity of cement paste is very high and by vigorous agitation it decreases to 1 Pa s. But dispersion is unstable and viscosty increases with time due to sedimentation, giving a muddy mass.

Viscosity of cement paste is varied by the chemical and physical properties of particles and viscosity is time-dependent. They shows linear relationships between logarithmic viscosity and poperties as well as time. Viscosity changes through three stages: the relaxation of agitation energy, the relaxation of internal sedimentation and coagulation. The critical radius for sedimentation runs parallel to $\eta/\Delta\rho$. The rate of sedimentation is proportional to $\Delta\rho/\eta r^2$. Electrical repulsion enhances stability. Cohesion may affect the coagulation.

This work was initiated by the suggestion of Hattori and Izumi since they sent to the present author a large number of publications of their works. The author expresses his sincere thanks.

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