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Measurement of Sedimentation Velocity of Titanium Dioxide Particles in Aqueous Suspensions in an Electric Field(1)

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An attempt was made to determine an approximate formula for sedimentation velocity of a solid particle, when a potential difference is applied between two electrodes, from statistical analysis.

The powder used was Al-modified rutil type titanium dioxide. Sedimentation velocities of this particle adsorbed by sodium metaphosphate were measured when an electric force affected this suspension.

When the strength of electric field, E, affects the powder particle placed between two electrostatic charges, the equation for the sedimentation velocity of a particle can be written as:

$$\frac{\pi}{6}d_{\mathrm{p}}{}^{3}\rho_{\mathrm{p}}g\downarrow - \frac{\pi}{6}d_{\mathrm{p}}{}^{3}\rho_{\mathrm{e}}g\uparrow + f(E,\, d_{\mathrm{p}})\downarrow = 3\pi d_{\mathrm{p}}u_{\mathrm{e}}\eta\uparrow$$

where $f(E,d_{\mathrm{p}})$ is the function concerned with an electric field, E, and particle size, d_{p}. This function $f(E,d_{\mathrm{p}})$ is given as,

$$f(E,\, d_{\mathrm{p}}) = \frac{3\pi\eta h}{950}\cdot d_{\mathrm{p}}{}^{2.662}\cdot 10^{1.468E}$$

From the above equation, values of both sedimentation velocity and particle size distribution can be predicted beforehand when a powder particle exists between two electrodes.

Keywords——disparsing agent; electric field; electrical double layer; particle size distribution; stability; sedimentation; suspension; turbidity

The modern fundamental work on the theory of Stokes concerned with the sedimentation velocity of suspended particles has been devoted to the question of how far the theory of suspension stability, developed by many workers,(3–5) goes towards explaining the measurement of particle size. It is important to recognize at the outset that the Stokes theory was developed primarily to deal with the relation of sedimentation velocity to particle size.(6–8) Caution must be exercised in applying the Stokes theory to analyze the sedimentation of a microscopic size solid particles, surrounded by a dispersing agent, when a potential difference is applied between two electrodes. The crux of the theory is the concept that dispersed solid particles are subject to two kinds of long-range force which can influence the sedimentation velocity of particle.(9,10) The two forces concerned are the gravitational force and the

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1) T. Kubo, A. Takamura, and S. Noro, Presented at the 98th Annual Meeting of the Pharmaceutical Society of Japan, Okayama, April, 1978.

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electric force between electrostatic charges. As the origin of these force is entirely independent, they should be evaluated separately. The net interaction force between particles is obtained by summing the interaction forces for each size range of particles. If the electric force affects the solid particle on which dispersing agent adsorbs, the electrical double layer[11,12] must be considered as one of the important factors concerned with the sedimentation velocity of particle. Under such a condition, the electrical double layer that is established can be characterized by the following three parameters; surface charge density, surface potential, and thickness of the diffuse part of the double layer.[13-15]

In the present work, particle size distribution was measured by a turbidimeter because turbidimetry has several advantages compared with other methods.[16,17] For example, the particle size distribution can be exactly measured by using only a small amount of powder.[18] The powder of titanium dioxide, the size distribution of which had already been found by other measurements, was selected as the standard sample and examined by a turbidimeter when the gravitational force alone affected this suspension. After changes of relative turbidity with time were measured, sedimentation velocity was indirectly calculated and evaluated from the Stokes equation. In succession, sedimentation velocities of solid particles were measured in the case that the electric force affected this suspension.

Furthermore, the approximate formula of sedimentation velocity of a particle, when potential difference is applied between two electrodes, was determined from the aspect of statistical analysis. Consequently, the strength of electric force on solid particles, surrounded by dispersing agents, in an electric field was calculated.

Theory

When a powder particle in the size range of 1 to 100 μm falls into a fluid, sedimentation velocity of the particle increases with increasing force of the gravitational acceleration at a very early stage in the course of sedimentation.[19] However, viscous force, which is in the direction opposite to that of particle movement, increases with increasing sedimentation velocity of particle. Accordingly, the sedimentation velocity of a particle gradually becomes constant.

$$\frac{\pi}{6}d_p{}^3\rho_p g\downarrow - \frac{\pi}{6}d_p{}^3\rho_c g\uparrow = 3\pi d_p u_0 \eta_c\uparrow \tag{1}$$

where d_p is the particle size, g is the acceleration of gravity, u is the sedimentation velocity, η_c is the viscosity of continuous phase, ρ_p is the density of particle, and ρ_c is the density of continuous phase. By arranging Eq. (1), the sedimentation velocity of particle is given by following equation,

$$u = \frac{(\rho_p - \rho_c)g}{18\eta_c} d_p{}^2 \tag{2}$$

Equation (2) is, in general, named the Stokes law concerning the sedimentation velocity of a particle and applies to the particles suspended in a dispersion medium.

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11) A.M. James, *J. Colloid Interface Sci.*, **29**, 696 (1969).
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13) H. Gouy, *J. Phys.*, **9**, 457 (1910).
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The sedimentation velocity of particles is considered when powder particle having a charge on its surface is placed between two electrostatic charges. Now, the theory of Millikan[20] which has already been proved for the measurement method of electron quantum, can be applied to the above experimental system. When the strength of an electric field, E, affects the powder particle placed between two electrostatic charges, equation for the sedimentation velocity of the particle can be written as:

$$\frac{\pi}{6}d_p{}^3\rho_p g\downarrow - \frac{\pi}{6}d_p{}^3\rho_c g\uparrow + f(E,\, d_p)\downarrow = 3\pi d_p u_e \eta\uparrow \qquad (3)$$

where $f(E, d_p)$ is the function concerned with an electric field, E and particle size, d_p. Equation (3) means that the four forces such as gravity, buoyancy, intensity of electrostatic field, and viscosity, affect the particle. Under the above consideration, sedimentation proceeds steadily and its velocity has a constant value. Now, the sedimentation velocity u is defined as a transfer distance h of a particle in unit time interval T and indicated as

$$u = h/T \qquad (4)$$

By substitution of Eqs. (4) and (1) into Eq. (3), the term of f(E, d_p) can be represented by the function of two sedimentation periods.

$$f(E,\, d_p) = 3\pi d_p \eta h[(1/t_e) - (1/t_0)] \qquad (5)$$

where t_e is the sedimentation time of a particle placed between two electrostatic charges and t_0 is the sedimentation time of a particle in the gravity force alone. Equation (5) can be rewritten as Eq. (6).

$$\frac{f(E,\, d_p)}{3\pi d_p h \eta} = \frac{1}{t_e} - \frac{1}{t_0} = k\cdot f(E)\cdot f(d_p) \qquad (6)$$

Here, k is constant value at Eq. (6). Thus, if t_0 and t_e are measured from the sedimentation time of a particle under two different conditions by turbidimetry, the term of $k\cdot f(E)\cdot f(d_p)$ can be experimentally determined.

Figure 1 shows a model for the movement of charged particles placed between two oppositely charged platinum plates in the presence of the dispersing agent. Since both gravity and electric forces affect the powder particle, sedimentation velocity becomes faster than that of natural sedimentation under the gravity force alone.

Figure 2 gives the diagram for the analysis of sedimentation velocity of particles by turbidity measurement.[21]

First, in the absence of an electrostatic field, the values of sedimentation time, t_0, can be converted to the particle size, d_p, by calculation from Eqs. (2) and (4).

Second, in the presence of an electrostatic field, a few curves of the relative turbidity with time are experimentally measured and the values, t_e, are determined. In these cases, it is thought that the same relative turbidity means the same particle size distribution, as already described in our previous report.[22] Accordingly, the term of $f(d_p)$ can be determined by calculation of the value of $[(1/t_e)-(1/t_0)]$ at optional particle size, d_p, when the electric field is kept constant. Furthermore, the term of $f(E)$ can also be determined by calculation of the value of $[(1/t_e)-(1/t_0)]$ at an optional electron field when particle size is maintained constant. Consequently, the function of $k\cdot f(E)\cdot f(d_p)$ can be calculated from the both above terms of $f(d_p)$ and $f(E)$.

The following qualified conditions such as (1) to (4) terms are employed in order to simplify the theoretical analysis for sedimentation behavior of suspended particles: (1) The shape of particle is a sphere.[22] (2) Electric charges are homogeneously distributed on the

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[20] R.A. Millikan, *Phys. Rev.* (London), 32, 349 (1911).

[21] M. Kerker, "The Scattering of Light and Other Electromagnetic Radiation," Academic Press, New York, 1969, p. 5.

[22] A. Takamura, S. Noro, and M. Koishi, *Chem. Pharm. Bull.* (Tokyo), 25, 2144 (1977).

particle surface.[23,24] (3) Electrostatic layer is thinner than the particle size.[25] (4) The particle size distribution of titanium dioxide is the same under all experimental conditions.[18]

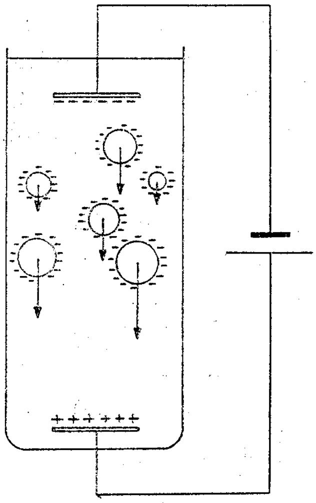

Fig. 1. Schematic Representation for the Movement of Negative Charged Particles Placed between Two Oppositely Charged Platinum Plates

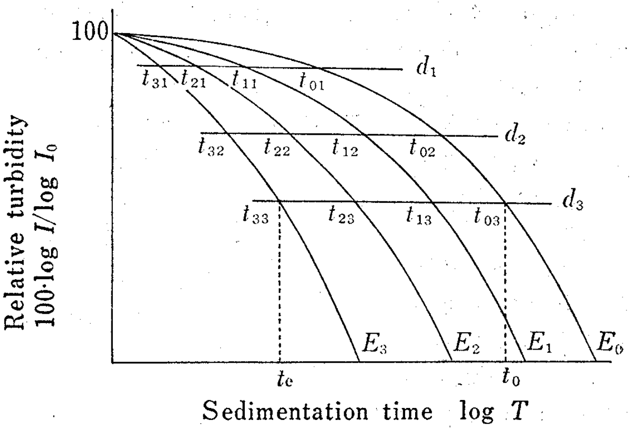

Fig. 2. Diagram for the Analysis of Sedimentation Velocity of Particle by the Measurement of Turbidity

Experimental

The specimen used in our work was Al-modified rutil type titanium dioxide, designated SR-1, of Sakai Chemical Co., Tokyo. The density, ρ_p, of TiO_2 was 4.10 (g/cm^3). The specific surface area, S, of TiO_2 was 7.0 (m^2/g).

TiO_2 was sufficiently dried at 105° and kept in a desiccator before use. The suspension was diluted with distilled water until the concentration was about 30 mg/liter. Then, sodium metaphosphate was added as a dispersing agent and its concentration was determined as 100 mg/liter by the measurement of zeta potential, as shown in Fig. 4. Total volume of suspension was adjusted to 500 ml with distilled water. An ultrasonic beam (30 kHz) was emitted on the suspension for 50 min in order to disperse powder particles homogeniously into distilled water.

A sketch of the apparatus employed is shown in Fig. 3. The turbidimeter used was PT-201 type of Nihon Seimitsu Kogaku Co., Tokyo. The cell used was made of a special coated glass (80 mm × 14 mm). Two spherical platinum plates (10.0 mm × 5.0 mm) were used as electrodes, and the distance between electrodes was kept constant at about 60 mm. The depth from a liquid surface to an optical axis of the turbidimeter was 15.0 mm to keep measurement position of turbidity constant.

After 30 sec of sedimentation time from preparation, measurement of turbidity was started. The specimen box was surrounded and circulated with the air controlled at 25.0° by a thermostat in order to keep the temperature of stable suspension constant for preventing thermodynamic flow. Changes in turbidity and temperature with time were recorded simultaneously on Model B-281H type recorder of Rika Denki Co., Tokyo. Then,

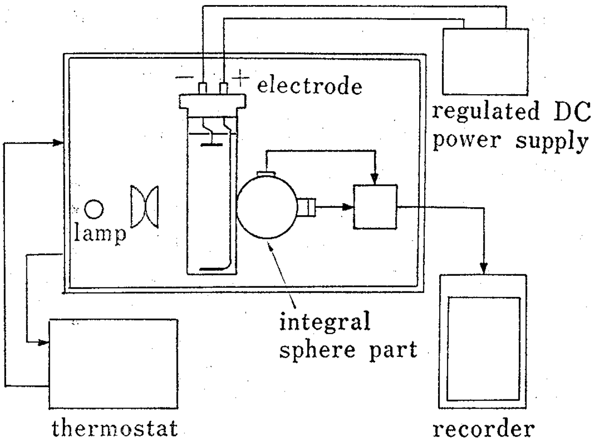

Fig. 3. Apparatus of Turbidity Measurement

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[25] F. Kitahara and A. Watanabe, "Interfacial Electric Phenomena," Kyōritsu Shuppan, Tokyo, 1972, p. 21.

these data were analyzed and the approximate formula of sedimentation velocity was calculated by using a Seiko Model S-301 electronic computer.

Results and Discussion

Figure 4 shows the relation between zeta potential and concentration of sodium metaphosphate. The particle of Al-modified titanium dioxide had the positively charged sites on its surface, and the zeta potential measured was +32.9 mV. Sodium metaphosphate (Kantō Kagaku Co., Tokyo) as a diapersing agent was dissociated into the negatively charged metaphosphate ion and sodium ion in water. As the number of metaphosphate ion adsorbed on titanium dioxide surface increased with increasing concentration of the dispersing agent, zeta potential changed from positive to negative values, as can be seen in Fig. 4. The plots of zeta potential gave a concave curve with a minimum value, −50.94 mV, at the characteristic concentration of 100 ppm. In the high concentration of sodium metaphosphate, the negative value of zeta potential decreased and approached the zero value gradually. The reason for these results is considered

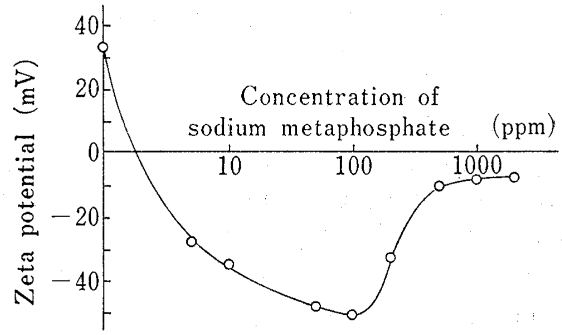
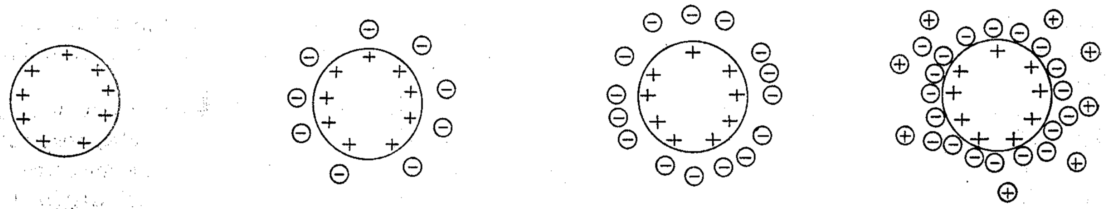


Fig. 4. Relation between Zeta Potential of Titanium Dioxide and Concentration of Sodium Metaphosphate as Dispersing Agent



(1) bare particle surface

(2) particle surface adsorbed of metaphosphate anion at lower degree

(3) particle surface adsorbed of metaphosphate anion at intermediate degree

(4) particle surface adsorbed of metaphosphate anion at higher degree

Fig. 5. Adsorption Model of Dispersing Agent to Titanium Dioxide Particle

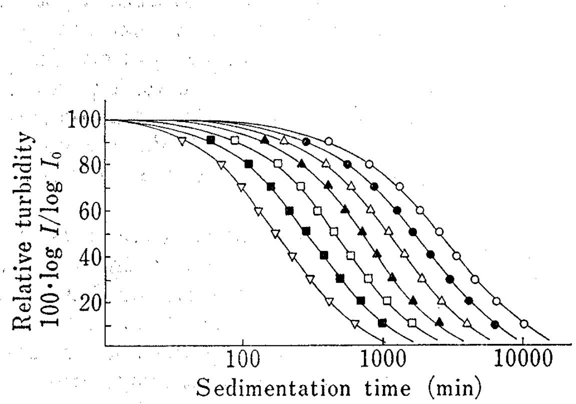


Fig. 6. Changes of Relative Turbidity with Sedimentation Time

○: 0 V, ●: 1 V, △: 2 V, ▲: 3 V,
□: 4 V, ■: 5 V, ▽: 6 V.

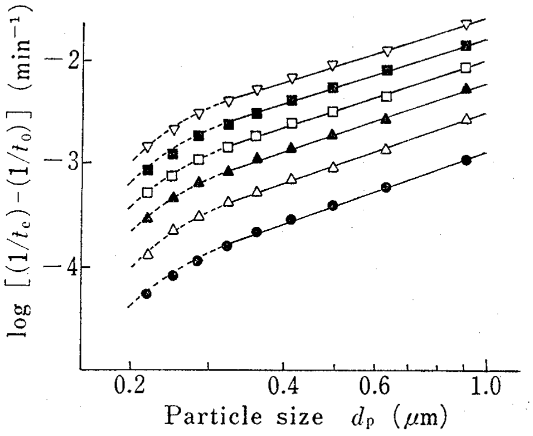


Fig. 7. Relation between $\log[(1/t_e)-(1/t_0)]$ and $\log d_p$

●: 1 V, $\alpha=1.580$, △: 2 V, $\alpha=1.667$,
▲: 3 V, $\alpha=1.642$, □: 4 V, $\alpha=1.691$,
■: 5 V, $\alpha=1.696$, ▽: 6 V, $\alpha=1.760$.
$\bar{\alpha}=1.672\pm0.054$.

as follows: When the dispersing agent concentration becomes high, the anions adsorbed on the particle surface are fixed with sodium ions, and the electrical double layer around the particles became thinner because the ionic strength reached over 10^{-3}.

From these results, sedimentation experiments were carried out under a constant concentration of 100 ppm of sodium metaphosphate. As a reference, the schematic representation of the adsorption of metaphosphate anions on the surface of titanium dioxide particle is shown in Fig. 5.

The effect of electric force on the sedimentation velocity of powder particle is shown in Fig. 6. The values of relative turbidity is given on the Y-axis, and logarithmic values of sedimentation time on the X-axis. As can be seen in Fig. 6, it is obvious that the sedimentation velocity of a particle increases as the electric potential became higher in the range of 1 to 6 V. Each curve in this graph consisted of the average of 10 individual measurements.

Log-log plots of the values of $[(1/t_e)-(1/t_0)]$ against particle diameter, d_p, of titanium dioxide for the six different electric potentials are shown in Fig. 7. It was clearly found, as seen in this graph, that the points fitted very well on a straight line with the data of suspension. The mean of slope by means of the least squares method was equal to 1.672. Therefore, the following calibration equation was obtained.

$$f(d_p) \propto d_p^{2.672} \qquad (7)$$

It was noteworthy that the individual value of gradients in Fig. 7 agreed with the average gradient within 5.5% error for these suspension systems with particle size in the range of 0.3 to 1.0 μm.

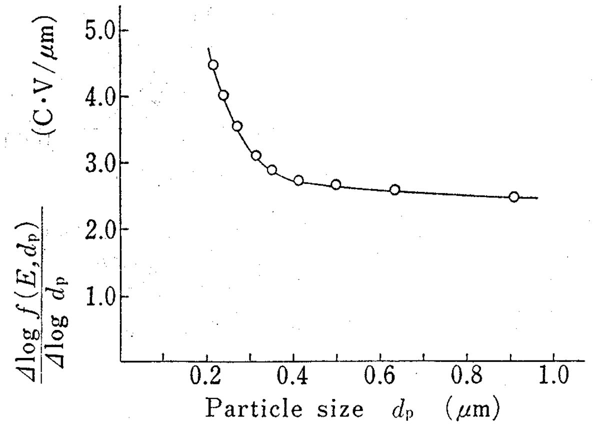


Fig. 8. Relation between $\Delta\log f(E,d_p)/\Delta\log d_p$ and Particle Size d_p

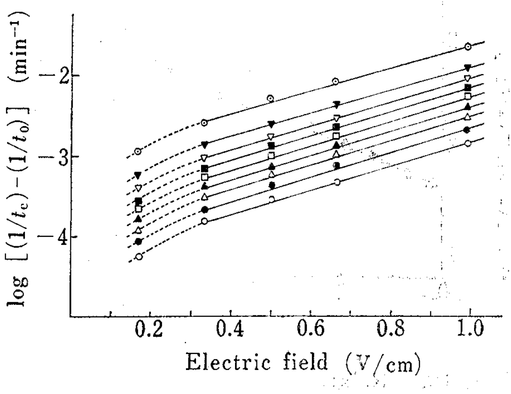


Fig. 9. Relation between $\log[(1/t_e)-(1/t_0)]$ and Electric Field

○: $d_p=0.214$ μm, $\beta=1.482$, ●: $d_p=0.240$ μm, $\beta=1.443$,
△: $d_p=0.270$ μm, $\beta=1.519$, ▲: $d_p=0.307$ μm, $\beta=1.486$,
□: $d_p=0.352$ μm, $\beta=1.485$, ■: $d_p=0.411$ μm, $\beta=1.496$,
▽: $d_p=0.497$ μm, $\beta=1.507$, ▼: $d_p=0.634$ μm, $\beta=1.471$,
⊙: $d_p=0.914$ μm, $\beta=1.409$,
$\overline{\beta}=1.477\pm0.04$.

Figure 8 gives the relation between $[\Delta\log f(E,d_p)/\Delta\log d_p]$ and particle size, d_p, calculated from the slope in Fig. 7. The values of $[\Delta\log f(E,d_p)/\Delta\log d_p]$ were constant at 2.672 in the range of 0.3 to 1.0 μm particle size, but these values increased markedly as the particle size, d_p, decreased below 0.3 μm.

The relation between $\log[(1/t_e)-(1/t_0)]$ and electric field, E, is shown in Fig. 9. Values of both t_e and t_0 were calculated from the data in Fig. 6. The electric field ranged from 0.167 to 1.000 (V/cm). For this suspension system, it was found experimentally as seen in Fig. 9 that the values of $\log[(1/t_e)-(1/t_0)]$ against electric field were linear with a constant slope. The values of gradients for nine points of particle size were calculated by the least squares method. The average of gradients was 1.477, hence, a calibration equation for these lines can be written as,

$$f(E) \propto 10^{1.477E} \tag{8}$$

By combining Eqs. (7) and (8), the term of $f(E, d_p)$ for this suspension can be represented as a function of particle size, d_p, and electric field, E. In order to determine the term of $f(E)$, the relation between $\log[(1/t_e)-(1/t_0)]$ and $\log d_p^{1.672} \cdot 10^{1.477E}$ was plotted in Fig. 10. These plots fitted well into a straight line, and the slope had nearly a constant value. The average of these lines yielded the following calibration equation by means of the least squares method.

$$\log[(1/t_e)-(1/t_0)] = 0.9937 \log(d_p^{1.672})(10^{1.477E}) - 2.978 \tag{9}$$

By substituting Eq. (9) into Eq. (6), the term of $f(E,d_p)$ is given as follows:

$$f(E, d_p) = \frac{3\pi\eta h}{950} \cdot d_p^{2.662} \cdot 10^{1.468E} \tag{10}$$

Experimental data and the values calculated from Eq. (10) are compared in Fig. 11. The experimental and calculated lines are shown by a solid and broken lines, respectively, under the condition where the electric field was 0.5 (V/cm). There were a few discrepancies between experimental and calculated data when the particle size became below 0.3 μm. On the contrary, the curve calculated from Eq. (10) was in very close agreement with the experimental values when the particle size was in the range of 0.3 to 1.0 μm.

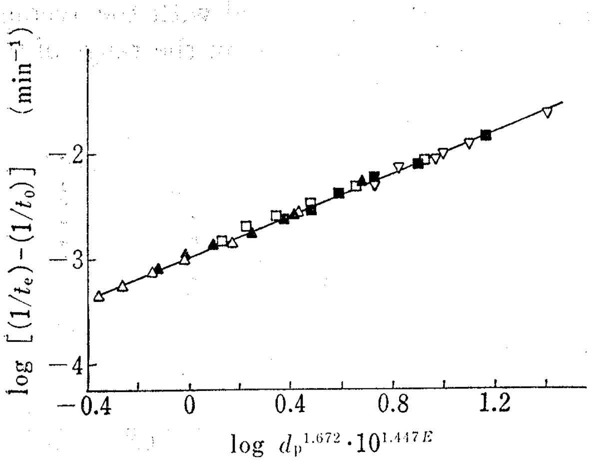


Fig. 10. Relation between $\log[(1/t_e)-(1/t_0)]$ and $\log d_p^{1.672} \cdot 10^{1.447E}$

△: 2 V, ▲: 3 V, □: 4 V, ■: 5 V, ▽: 6 V.

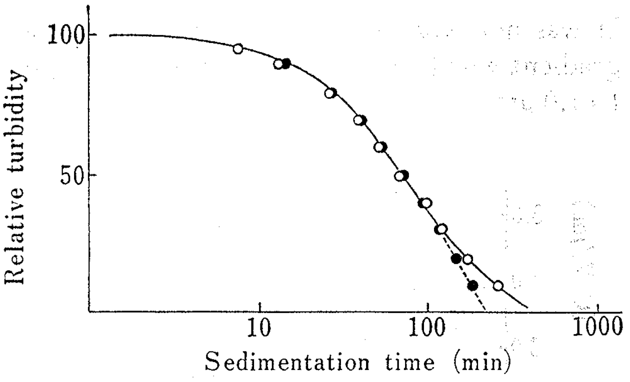


Fig. 11. Comparison of the Experimental Data with the Calculated Values from Equation for the Sedimentation Velocity of Particle

○: experimental data ●: calculated value
E: 0.5 V/cm.
$f(E, d_p) = \frac{3\pi\eta h}{950} d^{2.662} \cdot 10^{1.468E}$

It was interesting that the term of $f(E,d_p)$, which was affected by the electric force, was directly proportional to 2.662 powers of the particle size. The electrical charge quantum was influenced by both the surface area (d_p^2) and volume of particles (d_p^3), and this effect resulted in $f(E,d_p) \propto d_p^{2.662}$ when the particle size was in the range of 0.3 to 1.0 μm.

The electric force affecting the particle is generally considered to be proportional to the strength of an electric field, but its value in this experiment was a complicating feature, as $10^{1.467E}$. It can therefore be presumed that the above result is due to the electrical complexity of the electrical double layer on the particle surface having a zeta potential. Further, there will be an electro-viscous effect between two particles. When a very dilute suspension containing electrically charged particles undergoes sedimentation, symmetry of the electrical double layer around each particle is distorted. The interaction between anions in the electrical double layer and electrical charge on the particle surface is affected, this leads to an extra dissipation of energy and an increased viscosity. If the experimental data are introduced into Eq. (10), values of both sedimentation velocity and particle size distribution can be predicted beforehand when a powder particle exists between two electrodes and settles on the top and bottom in the cell. However, the function concerned with the electric field, E, is complex, equal to $10^{1.467E}$, so that the surface charge density or the charge circumstances distributed at the interface and in the interior of electrical double layers cann't be presumed from the present work. To clarify the many electrical problems on the particle surface, the micro and precise measurement method should be established for the suspension system.