Apparent Extinction Coefficient for a Scanning Photosedimentometer

Junichi Takahashi* and Akinori Muta
Department of Inorganic Materials, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
(Received February 6, 1982)

Synopsis. Particle-size distributions of subdivided samples were analyzed independently with electron microscopy and a scanning photosedimentometer. Apparent extinction coefficient for the optical scanning system was estimated by the comparative examination of the distributions.

In light transmission methods for particle-size distribution analysis, the effect of the extinction coefficient, which is defined as the effective particle cross section divided by its geometric cross section, must be taken into account when a sample under examination contains particles of a size comparable to the wavelength of the incident light. It has been confirmed by Rose[1] that, at any given particle diameter, an increasing solid angle was associated with a decreasing value of extinction coefficient, and for a solid angle of about 10°, deviations from unity in the value of the extinction coefficient were small at particle diameter larger than 3 μm. Therefore it was expected that significant errors as seen in the theoretical treatment of light-scanning properties of fine particles might be eliminated in the determination of particle-size distribution using an apparatus with white light and a large solid angle.

A scanning photosedimentometer has been developed by Muta and co-workers.[2,3] In this optical scanning system, a white light beam can be moved up and down by a specially-designed cam through the sedimentation tank in which steady-state settling conditions have been achieved. The cam has been designed so that the analyst can calculate the particle-size distribution of a sample from the graph of optical density versus square root of depth of the sedimentation tank, which can be easily converted to particle diameter using Stokes equation, in a simple manner. Thus a single quick continuous scan of the concentration gradient set up in the sedimentation tank gives enough information to enable the analyst to establish the particle-size distribution. This apparatus (*PSA*-2) is also characterized by a large solid angle subtended by the photo-sensitive receiver. Few data, however, are available on the examination of particle-size distribution by *PSA*-2 for a sample containing a number of fine particles.[4] Hence an attempt was made in this work to represent that the size distribution estimated using *PSA*-2 for a sample consisting of very small particles could be accepted without any special correction.

For particles with sizes ranging from d_1 to d_2, the energy removed from the forward beam by the particles is related to their cross-sectional area as follows:

$$S_m = \frac{1}{K_m C}(\log I_1 - \log I_2), \qquad (1)$$

where S_m is the total cross-sectional area of the particles, I_1 and I_2 is the intensity of transmitted light for each particle of size d_1 and d_2, respectively, C is a constant, and K_m is the extinction coefficient for the particles. Thus the apparent extinction coefficient for *PSA*-2 could be evaluated by comparing the cross-sectional area analyzed independently with both *PSA*-2 and electron microscopy for subdivided samples. The solid material used in this study was Kanto loam JIS 11. Suspensions of the material were prepared by dispersing uniformly a definite amount of the powder in distilled water containing 0.1 wt% sodium *cyclo*-hexaphosphate as a dispersing agent. The original particle-size distribution of Kanto loam JIS 11 was evaluated by electron microscopy. The direct images of deposited particles on electron microscope grids covered with specimen support collodion film were observed with a transmission electrom microscope. The raw data obtained by examining about 3000 particles in electron micrographs were collected in the form of a number distribution and converted to a surface distribution. In Fig. 1 the percentage of particles per micrometer, $d\phi/dD$, is plotted against the projected area diameter which is the diameter of a circle having the same area as the particle. The distribution curve in Fig. 1 indicates that the sample is composed of fine particles smaller than 7 μm with a narrow-ranged size distribution. For the estimation of the apparent extinction coefficient for *PSA*-2, suspensions with the powder concentration of 0.05 vol% were subdivided into several portions, in which particle size ranged as narrow as possible, by a centrifugal withdrawal method described below.

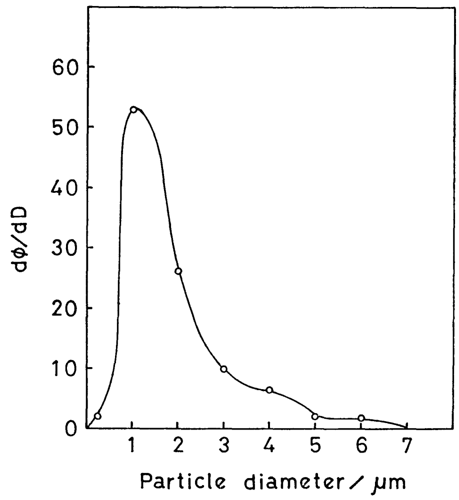

Fig. 1. The relative percentage frequency distribution of the original sample.

For a homogeneous suspension, a particle in a centrifugal field theoretically settles according to the equation,[5]

$$S = R\exp(-kD^2t) \quad k = \frac{\rho_s - \rho_f}{18\eta}\omega^2, \qquad (2)$$

where t is the time for a particle of size D and density

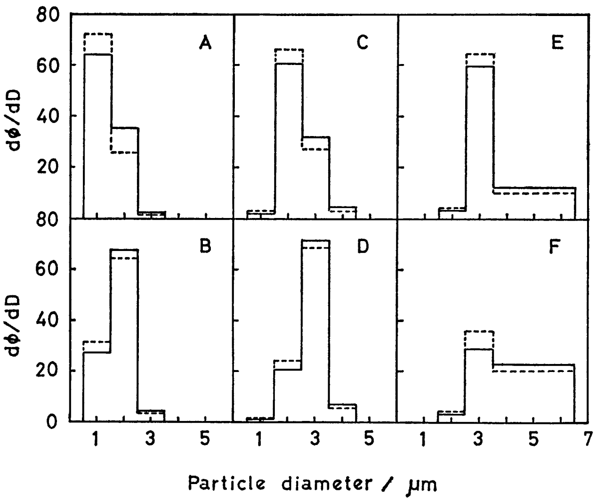

Fig. 2. The particle-size distribution of subdivided samples analyzed independently by *PSA*-2(——) and electron microscopy (----).

ρ_s to settle from the surface of the liquid with density ρ_f and viscosity η at distance S to the bottom of the tube at distance R, both S and R being distances from the axis of the centrifuge rotating at ω in radians per second. After t seconds, all particles greater than D will have settled out to the bottom of the tube with simultaneous partial sedimentation of all particles smaller than D. For each of these smaller sizes, Eq. 2 may be rewritten:

$$x_0 = R\exp(-kD^2t), \tag{3}$$

where x_0 is a starting point beyond which all the smaller particles will have reached R. The volume fraction of the suspension lying between R and x_0 for a cylindrical tube is equal to

$$\frac{R-x_0}{R-S} = \frac{R}{R-S}\{1-\exp(-kD^2t)\}. \tag{4}$$

Firstly, particles smaller than 0.5 μm were removed from the original samples because the presence of these particles yielded experimental errors due to the breakdown in the laws of geometric optics in the submicrometer particle-size range. This was carried out by repeated withdrawals of a definite amount of suspension from a cylindrical tube after centrifugal sedimentation. Electron microscopic observation of the residue after the operation indicated that it contained small amounts of submicron particles, which led to a negligible disturbance in the results obtained in the present study.

Experimental operations necessary for the subdivision of the sample into several portions with different size ranges were determined using Eqs. 2—4. To avoid an agglomeration of particles caused by centrifugal force, suspension of particles which remained at the bottom of the tube after a single withdrawal were placed in the ultrasonic bath prior to a subsequent centrifugal sedimentation. In the series of centrifugal withdrawal experiments, particle-size distribution of withdrawn portions or remaining portions was roughly checked with *PSA*-2, whenever required. Consequently, suspensions with the intended particle-size range, which were required for the estimation of the apparent extinction coefficient for *PSA*-2, were prepared by subdividing the original sample and mixing the subdivided samples up to a fixed particle concentration suitable for size distribution analysis.

Dristributions of the narrowly classified particles were measured using *PSA*-2 for the samples prepared by the procedure mentioned above. Fractional intensities of transmitted light for each sample are plotted against particle diameter in Fig. 2. An independent analysis by electron microscopy of the same sample was made and fractional projected areas of each sample are also included in Fig. 2. Now let the fractional intensity be dI_1, dI_2, dI_3, dI_5, fractional projected area dS_1, dS_2, dS_3, dS_5, and apparent extinction coefficient K_1, K_2, K_3, K_5, where each subscript indicates the corresponding particle diameter. Then from Eq. 1, both measured quantities can be correlated with each other using the apparent extinction coefficient. For instance, from sample A shown in Fig. 2,

$$dI_1 = \frac{K_1 dS_1}{K_1 dS_1 + K_2 dS_2 + K_3 dS_3}$$

$$dI_2 = \frac{K_2 dS_2}{K_1 dS_1 + K_2 dS_2 + K_3 dS_3},$$

and $K_1(dS_1/dI_1) = K_2(dS_2/dI_2)$, hence $K_1/K_2 = (dI_1/dI_2 \cdot dS_2/dS_1)$. In this way, the relative extinction coefficient of K_1/K_2, K_2/K_3, and K_3/K_5 was calculated from samples A and B, C and D, E and F, respectively, being $K_1/K_2 = 0.72$, $K_2/K_3 = 0.80$, and $K_3/K_5 = 0.75$.

On the basis of the result reported by Rose[1] for the solid angle subtended by the photo-cell of about 10° and that by Muta[2] on the comparative examination of particle-size distribution for several powders, the extinction coefficient for particles ranging from 4 to 6 μm, K_5, was assumed to be 1.3. Therefore the apparent extinction coefficients were evaluated, in turn, as $K_3 = 1.0$, $K_2 = 0.8$, and $K_1 = 0.6$. This result suggests that particle-size distribution of powder with a minimum size of about 1 μm could be accurately analyzed by the scanning photosedimentometer, *PSA*-2, without any substantial error.

References

1) H. E. Rose, *J. Appl. Chem.*, **2**, 80 (1952).
2) A. Muta, *Hitachi Rev.*, **14**, No. 11, 1 (1965).
3) A. Muta, N. Saito, and Y. Uehara, Presented at Symposium on Particle Size Analysis, Loughborough Univ., England, (1966).
4) A. Muta, *Hitachi Sci. Instrum. Tech. Data*, **1969**, 1.
5) T. Allen, "Particle Size Measurement," 2nd ed, Chapman and Hall, London (1975), p. 274.