Small Angle X-Ray Scattering Study for Determining the Particle Size of Colloidal Materials

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ABSTRACT

The average particle size of two monodispersed colloidal silica HS-40 and SM-30 and one polydispersed colloidal ferrite has been estimated from the small angle X-ray scattering (SAXS) data using four methods proposed by Guinier, Fankuchen, Hosemann and Porod. The same information was also obtained by the transmission electron microscope (TEM) and calculated from the specific surface area (SSA) data measured by the nitrogen gas adsorption technique.

The values of the average particle size of colloidal silica and colloidal ferrite estimated from the SAXS data using four methods were found to be of the same order of magnitude. These SAXS values of colloidal silica HS-40 and SM-30 also agree well with those determined by both the TEM and SSA measurements. However, it should be noted that in the case of colloidal ferrite the SAXS and TEM are almost the same, whereas a significant difference is found when comparing the value estimated from the SSA data. This can be attributed to the strong agglomeration of ferrite particles after drying.

1. INTRODUCTION

Small-angle X-ray scattering (hereafter referred to as SAXS) has been extensively used to characterize various types of systems including colloidal materials /1-3/.

SAXS studies are known to provide valuable information about the internal structure of particles /4/. More recently, an anomalous small-angle X-ray scattering technique using the synchrotron radiation source has been applied in order to obtain the origin of heterogeneities that give rise to a broad scattering at the small-angle region /5,6/.

The main purpose of this work is to estimate the average particle size of colloidal materials in suspension based on the SAXS data using four methods proposed by Guinier, Fankuchen, Hosemann and Porod. The results are compared to the particle size determined by the transmission electron microscope (TEM) and calculated from the specific surface area (SSA) measured by the nitrogen gas adsorption technique based on the BET method.

2. MATERIALS AND EXPERIMENTAL METHODS

Three kinds of commercially available colloidal materials in suspension were used in this work. Two are monodispersed colloidal silica named HS-40 and SM-30 (Ludox; Du Pont, Japan Ltd.) suggested to have a particle diameter of about ~14 nm and ~8 nm respectively; and one is colloidal ferrite (magnetic fluid, Taiho Kogyo Ltd.) composed of ferrite particles of about 10 nm in diameter.

SAXS measurements in the step-scan mode were carried out by a goniometer of three slits system (SASG, Rigaku) using Fe$K\alpha$ radiation with a filter of manganese-oxide and a pulse-height analyzer. Corrections for absorption and slit-height smearing effect must be made *a priori* in order to obtain any structural information from the measured SAXS data. The background scattering intensities from slits and sample holder were experimentally estimated. The slit-height smearing correction is an important factor, because the measured intensity is a convolution of the intensities as a function of scattering angle with the intensity distribution along the slit height of the primary beam when the slit system is employed. Nevertheless, it may be notified that this correction is not necessary for obtaining some characteristic constants such as a radius of gyration R_g for Guinier's and Fankuchen's methods /7,9/ and the correlation length, l_c for Porod's method /8/, when the infinite slit-height approximation is applied.

X-ray scattering intensity measurements were carried out by preparing diluted samples because a sample with higher concentration induces so-called interparticle interference phenomena, which prevents us from estimating the accurate particle size /7/. The colloidal silica solutions were diluted with distilled water up to 6×10^{-3} kg/l and the dilution for colloidal ferrite was made with kerosene up to 1.3×10^{-3} kg/l. It is also worth mentioning that the window of a sample holder for liquid solutions was made of kapton film of 7.5 μm on acrylic resin thin plate of 500 μm in thickness.

The average particle size estimated from the SAXS data was compared with those observed by the transmission electron microscope (JEM-2010, JOEL).

The values of average particle size of colloidal silica and colloidal ferrite were also estimated from the SSA measured by nitrogen gas adsorption technique based on the BET method (Flow Sorb 2300, Micromeritics Instruments Corp.). For determining the SSA, the colloidal solutions of silica were freeze-dried and colloidal solution of ferrite was dried in air after precipitation by adding acetone to the solution. In order to calculate the average particle size, the density values should be known. The pellets were prepared and the density measurements were made by Archimedes' method with toluene. Furthermore, to obtain additional information, the dried materials were also subjected to the ordinary X-ray powder diffractometry using Cu$K\alpha$ radiation with the pyrolytic graphite monochromator in the diffracted beam path (RAD-B, Rigaku). As a result of X-ray powder diffractometry, silica samples appear to be amorphous and the ferrite sample is considered to be crystalline. The diffraction patterns are shown in Fig. 1. The profiles of diffraction peaks of ferrite particles are broad and then the accurate identification of crystalline phases is difficult. However, the present authors maintain the view that the present diffraction pattern agrees well with the γ-hematite and/or magnetite ones compiled by the JCPDS cards No. 24-81 and 19-629, respectively.

3. RESULTS AND DISCUSSION

3.1. Small-angle X-ray scattering

The average particle size of colloidal materials in suspension were estimated from the SAXS data according to the methods proposed by Guinier /7/, Fankuchen /9/, Hosemann /7/ and Porod /7,8/. For the sake of convenience of discussion, the essential points of each method are given below.

3.1.1. Guinier's method: According to Guinier /7/, the SAXS intensity from a low concentrated solution is well approximated by the following exponential function in terms of a radius of gyration R_g.

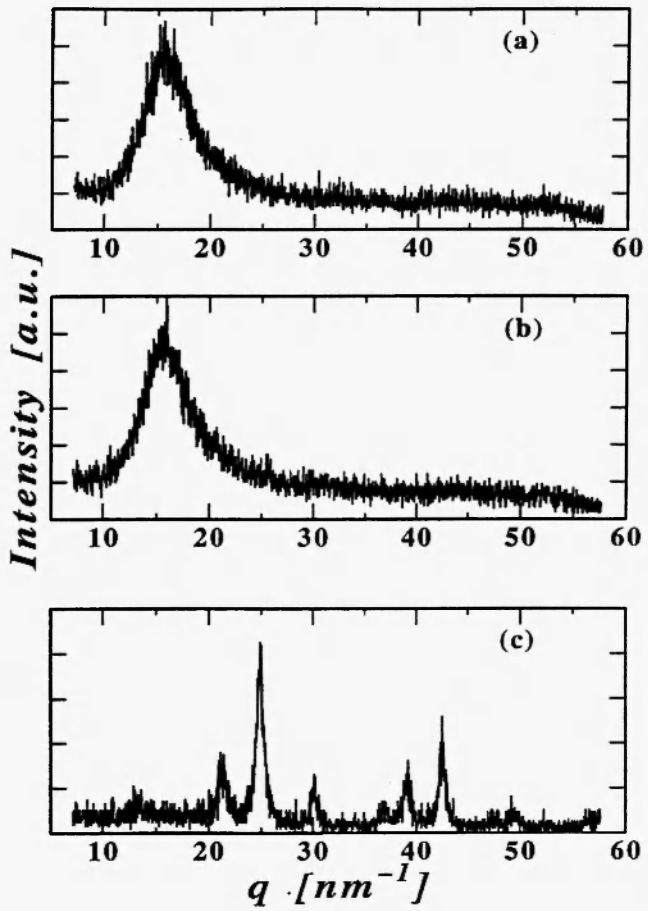

Fig. 1: Wide angle X-ray diffraction patterns of dried colloidal materials, (a) colloidal silica HS-40, (b) colloidal silica SM-30 and (c) colloidal ferrite.

$$I(q)=N.I_e.\ n^2.\exp(-q^2R_g^2/3) \qquad (1)$$

where I_e is the intensity scattered by a single electron, N is the number of particles, n is the number of electrons in a particle, q is the wave vector ($q = 4\pi\sin\theta/\lambda$), θ is half of the scattering angle and λ is the wavelength of the incident X-rays. In practice, the values of R_g can be obtained from the relation of the quantity of $\ln I(q)$ versus q^2 (Guinier plot).

Figure 2 shows the SAXS intensities as a function of the wave vector for colloidal silica of SM-30 and HS-40, and colloidal ferrite. A good linear correlation is observed in the cases of monodispersed colloidal silica

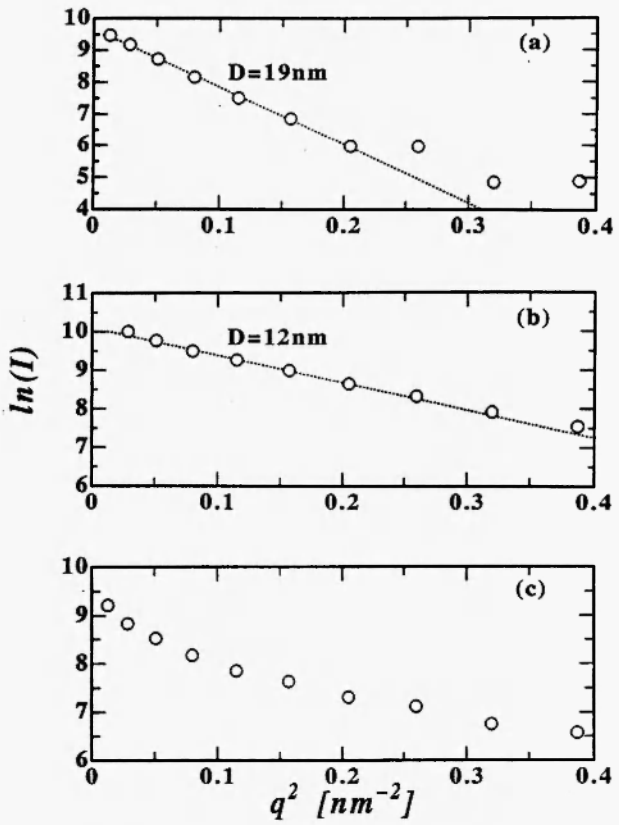

Fig. 2: $I(q)$ versus q^2 plots for colloidal materials, (a) colloidal silica HS-40, (b) colloidal silica SM-30 and (c) colloidal ferrite.

of HS-40 and SM-30. The particle sizes of these silica samples were estimated to be 19 nm and 12 nm in diameter from the gradient of the straight line, respectively, assuming the spherical shape for the radius of gyration applying the relation $D_G = (5/3)^{1/2}2R_g$. On the other hand, such linear correlation is not obtained in the SAXS intensity for colloidal ferrite. This is usual, because the colloidal ferrite sample is suggested to be in the polydispersed state. In this case, the average diameter should be determined using another method mentioned in the following section.

3.1.2. Fankuchen's method: There are several methods for estimating the average particle size of polydispersed materials from the SAXS data /9-12/. The average value of diameter of colloidal ferrite was estimated by applying Fankuchen's method /9/. This method is based

on an assumption that particles with different size in a specimen independently scatter X-rays at the small-angle region and the intensity may be expressed by the following equations:

$$I(q) \quad (= \text{constant } \Sigma\, W(R_{g,i}) R_{g,i}^3 \exp(-q^2 R_{g,i}^2/3) \qquad (2)$$

$$W(R_{g,i}) = M(R_{g,i})(R_{g,i} - R_{g,i-1}) \qquad (3)$$

where (R_{gi}) is the distribution function of particles. The graphical analysis proposed by Fankuchen for determination of particle size is shown in Fig. 3, as an example. The average value of diameter given by $D_F = \Sigma 2R_{gi}W(R_{gi})/\Sigma W(R_{gi})$ was estimated as 10 nm for colloidal ferrite.

3.1.3. Hosemann's method. In Hosemann's method /7/, the average particle size determination is based on the assumption that particles scatter X-rays at the small-angle region and their intensities are given by equation (1). Hosemann also uses the assumption that the distribution of a radius of gyration R_g is represented by a Maxwellian distribution. In this case, the scattering intensity is given by the following relation:

$$I(q) = \text{constant}/[1+(q.r_o)^2/3]^{(m+4)/2} \qquad (4)$$

where r_0 and m are the parameters for describing the Maxwellian distribution.

When plotting a curve $q^2 * I(q)$ as a function of q this curve always presents a maximum at some position q_M greater than zero as shown in Fig. 4 using the result of colloidal silica HS-40 as an example. The quantity q_T is defined as the intersection with the q-axis of the tangent to the curve at the inflection point P on the higher angle side of the curve. Hosemann proposed the following relation:

$$[q_T/(2.q_M)]-1 \cong 1/\{[2(m+1)]^{1/2}\} \qquad (5)$$

Equation (5) provides the parameter m, which defines the sharpness of the distribution. The average diameter can be determined by the following relation:

$$D_H = (2/q_M).\{[10/(m+2)]^{1/2}\}. \{\Gamma[(m+2)/2]\}/\{\Gamma[(m+1)/2]\} \qquad (6)$$

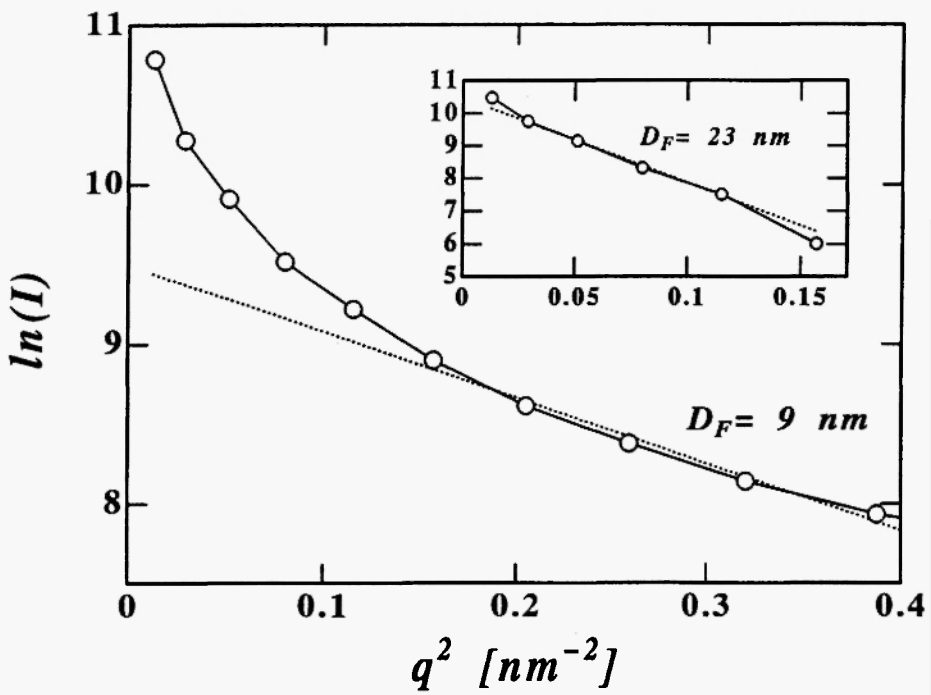

Fig. 3: Guinier plot with Fankuchen graphic analysis for colloidal ferrite.

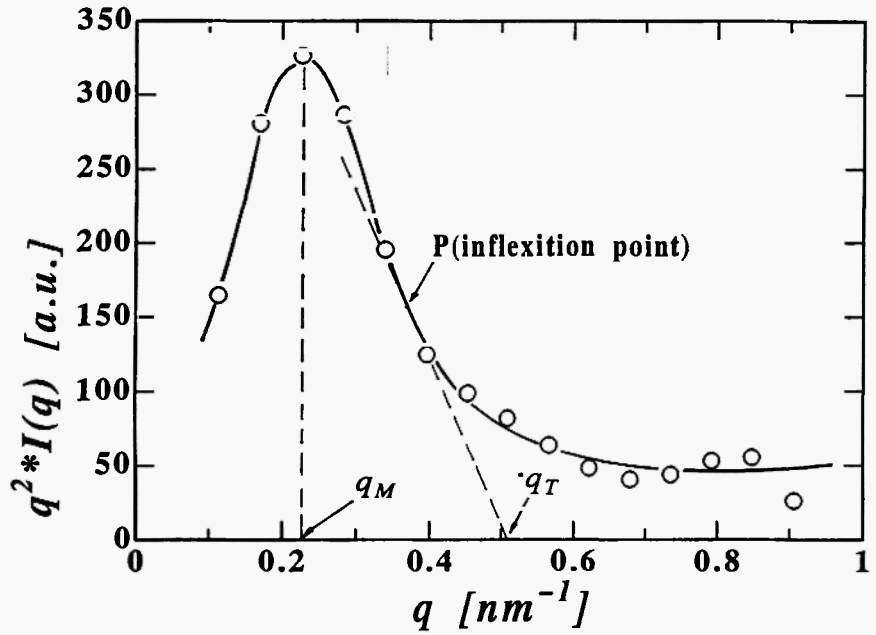

Fig. 4: Hosemann plot for colloidal silica HS-40.

This method was applied to the SAXS data of colloidal silica and colloidal ferrite and the results are summarized in Table 1.

3.1.4. Porod's method: According to Porod's theory /7,8/, the X-ray scattering intensity can be expressed at the small angle region by the following integration:

$$I(q)=I_e.V.\rho^2.c.(1-c)\int_0^\infty [\gamma(r)\sin(qr).4\pi r^2/qr]dr \quad (7)$$

where V is the total volume of the specimen irradiated by X-ray, ρ is the mean electron density in the particles, c is the packing density of the specimen, and $\gamma(r)$ is the characteristic function of the specimen. When the infinite slit-height approximation is employed, a distance of inhomogeneity l_c introduced by Porod is given as follows:

$$l_c = 2\int_0^\infty I(q)dq / \int_0^\infty qI(q)dq \quad (8)$$

Table 1

Particle size of colloidal silica HS-40, SM-30 and colloidal ferrite determined by SAXS, TEM and SSA. D_G, D_F, D_H and D_P correspond to the diameter determined by Guinier's, Fankuchen's, Hosemann's and Porod's methods; respectively. l_c correspond to distance of inhomogeneities.

Material	D_G	D_F	D_H	l_c	D_P	D_{TEM}	D_{SSA}
Silica HS-40	19	–	19	17	23	19	13
Silica SM-30	12	–	11	7	9	10	9
Ferrite	–	11	10	9	–	10	793

The evaluation of the integrals frequently involves some experimental errors because of the unknown small-angle part of the X-ray scattering intensity curve. If the SAXS increases rapidly with decreasing the scattering angle, the reservation should be stressed for the extrapolation of the curve to zero-angle. However, it may be suggested that the devised method proposed by Warren /13/ could be used when the sample scatters X-rays rather strongly. The present results are included in this category. The resultant values of the distance of inhomogeneity l_c for both colloidal silica and ferrite are given in Table 1. The diameter can be calculated from this equation: $D_p = (4/3)l_c$ and also listed in Table 1. Nevertheless, this equation is applicable only to spherical and monodispersed particles /7/.

3.2. Transmission electron microscopy and specific surface area measurement

Figure 5 shows the micrographs of colloidal particles of silica HS-40, SM-30 and colloidal ferrite taken by TEM. It is observed that the shape of three samples is almost sphere-like. This supports the validity of the present analysis for estimating the particle size from the SAXS data using the spherical shape approximation. Furthermore, particles size of silica of HS-40 and SM-30 appears to be homogeneous. This contrasts with the case of the colloidal ferrite. The average particle sizes directly estimated from the transmission electron micrographs are listed in Table 1. The average values of particle size of colloidal silica and colloidal ferrite measured by TEM agree well with those determined by the SAXS data.

Specific surface areas (SSA) of dried colloidal particles of silica HS-40, SM-30 and colloidal ferrite were also measured by nitrogen gas adsorption technique. The average particle size can be estimated from the SSA data using the following simple equation assuming the spherical shape.

$$D_{SSA}=6/(d.S) \qquad (9)$$

where D_{SSA} is the diameter, S is the specific surface area and d is the density. The values of D_{SSA} calculated in this procedure are also listed in Table 1. In the case of colloidal silica either for HS-40 or SM-30, the

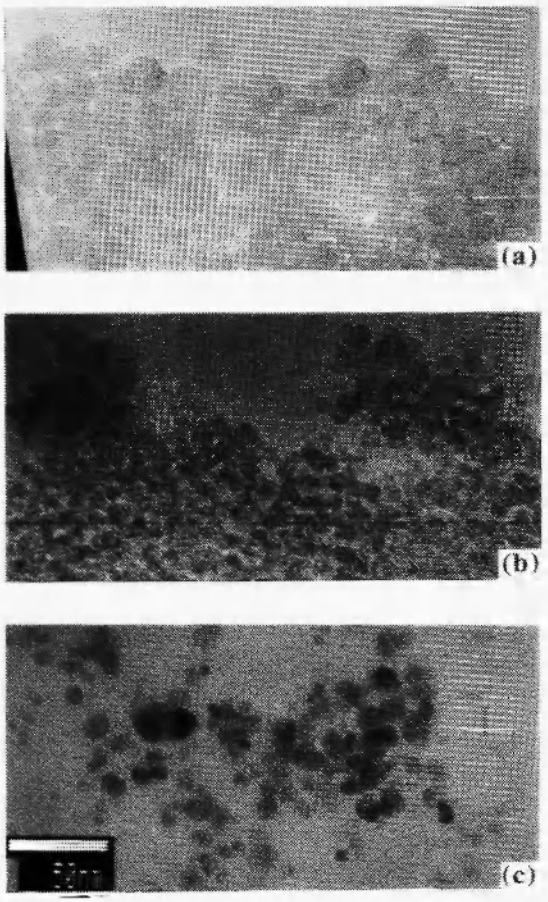

Fig. 5: Transmission electron microscopic micrographs of colloidal materials, (a) colloidal silica HS-40, (b) colloidal silica SM-30 and (c) colloidal ferrite.

average particle sizes estimated from the SSA data show the same order of magnitude as those obtained by SAXS and TEM. However, the value of average particle size of colloidal ferrite differs considerably from those estimated by SAXS. This should be attributed to the fact that the ferrite particles strongly agglomerate after drying.

4. CONCLUDING REMARKS

In the present study, four methods proposed by Guinier, Fankuchen, Hosemann and Porod were tested to determine the particle size from the SAXS data of two monodispersed colloidal silica and one poly-

dispersed colloidal ferrite. By comparing the results determined by TEM and calculated from the SSA measurement, it is reasonably concluded that the SAXS method is a powerful tool for determining the particle size of any colloidal system because this method can be applied directly to suspensions or solutions including particles and the constituent particles are free from the state; crystalline or amorphous. Both the shape and size of visible particles can be straightforwardly determined by TEM methods. However, the sample must be dried before it is placed in a vacuum. This contrasts with the SAXS method, which is known to be an easy way to prepare samples, only requiring a suitable dilution in order to reduce the interparticle interference effect.

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