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Estimation of Particle Size of Synthetic Latices by Turbidity Measurements

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A method for estimating the particle size of synthetic latices from the ratio of turbidities measured at two distinct wavelengths was discussed. The particle sizes of various synthetic latices obtained by this method agreed with those obtained by using electron microscope. A method proposed by Heller et al. to estimate the particle size empirically from changes in absorption coefficient with wavelength was also discussed.

INTRODUCTION

Teorell¹⁾ has first suggested the "dispersion quotient" (DQ) to be related to particle size of colloidal dispersion, which is defined as the ratio of turbidities at two different wavelengths. Evva²⁾ has applied this DQ method to colloidal dispersion of silver halides, with the aid of the tables of light scattering functions presented by La Mer and co-workers^{3,4)}.

This method can be applied for estimation of the particle size of synthetic latices. The application, however, could not be studied in detail because of the lack of pertinent tabulation of Mie functions corresponding to relative refractive indices (in water) of synthetic latices. Sakurada and Hosono⁵⁾, in connection with turbidometric study of polyvinyl alcohol have obtained by numerical calculation a relationship between DQ and particle radius for the range of relative refractive indices 1.20 and 1.0 which covers over the m values of various synthetic latices. In the present paper, it is intended to check the the validity of this relationship by comparing the values of particle size calculated from the ratio of turbidity with those obtained by electron microscopy. The method proposed by Heller^{6,7)} will be discussed also.

THEORETICAL

As Sinclair and La Mer¹⁾ have generally stated, the method for determination of the particle size of colloidal dispersions from light scattering measurements is based in principle on the electromagnetic theory by Mie. One present method for determination of the particle size from turbidity or transmission measurement is a special case of the general theory.

(a) Relationship between turbidity and particle radius

As is well-known, the transmission T is related to absorption coefficient k and turbidity τ by the following relation

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$$T = I/I_0 = e^{-kcl} = e^{-\tau l} \tag{1}$$

where I_0 and I are the incident and emergent intensities of light of wave length λ , respectively, c is the mass concentration and l is the length of path traversed by the light. The quantity τ is related to scattering coefficient K by

$$\tau = KSN \tag{2}$$

where S is the sectional area of the particle and N is the number of particles in a unit volume. In the case of nonabsorbing sphere, K can be expressed in a general form such as

$$K_s = \frac{2}{a^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |P_n|^2), \tag{3}$$

where

$$a_n = \frac{\alpha \psi_n(\alpha) \psi_n'(\beta) - \beta \psi_n'(\alpha) \psi_n(\beta)}{\alpha \zeta_n(\alpha) \psi_n'(\beta) - \beta \zeta_n'(\alpha) \psi_n(\beta)}$$

$$P_n = \frac{\alpha \psi_n'(\alpha) \psi_n(\beta) - \beta \psi_n(\alpha) \psi_n'(\beta)}{\alpha \zeta_n'(\alpha) \psi_n(\beta) - \beta \zeta_n(\alpha) \psi_n'(\beta)}$$

$$\psi_n(\alpha) = \left(\frac{\pi\alpha}{2}\right)^{1/2} J_{n+1/2}(\alpha), \quad \chi_n(\alpha) = (-1)^n \left(\frac{\pi\alpha}{2}\right)^{1/2} J_{-n-1/2}(\alpha)$$

$$\zeta_n = \psi_n + i\chi_n$$

$$\alpha = 2\pi r/\lambda^*, \quad \beta = ma, \quad \text{and} \quad \lambda^* = \lambda/m_0$$

The primes attached to ψ_n and ζ_n represent the derivatives, and J represents the Bessel function of half order. r is the radius of sphere, λ^* the wavelength of the light in the surrounding medium, λ the wavelength in vacuum, m the relative refractive index, and m_0 the refractive index of medium.

For $r \ll \lambda$, Eq. (3) reduces to well-known Rayleigh's equation,

Table 1. Scattering function.

$m=1.20$			$m=1.10$		
α	K_s	K_s/α	α	K_s	K_s/α
0.25	0.00018	0.0003	—	—	—
0.50	0.0027	0.0054	0.5	0.001	0.002
0.75	0.0127	0.0169	—	—	—
1.00	0.0319	0.0319	1.0	0.010	0.010
1.50	0.111	0.0740	1.5	0.030	0.020
2.00	0.238	0.119	2.0	0.080	0.040
3.00	0.666	0.222	3.0	0.25	0.085
4.00	1.216	0.304	4.0	0.44	0.110
5.00	1.775	0.355	5.0	0.60	0.140
6.00	2.360	0.393	—	—	—

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$$K_s = \left(\frac{1}{\pi r^2} \right) 24\pi^3 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \frac{V^2}{\lambda^8}, \quad (4)$$

where V is the volume of the sphere equal to $4\pi r^3/3$. In the case of absorbing sphere (scattering plus absorption), one obtains

$$Ke = \frac{1}{a^2} Re \left[\sum_{n=1}^{\infty} (2n+1) (a_n + P_n) \right] \quad (5)$$

where Re stands for the real part of the expression in the bracket.

As is clear from Eqs. (3) and (5), the scattering coefficient is a function of the wavelength, λ , relative refractive index, m and radius of sphere, r . In Table 1, the values of K_s for $m=1.20$ and $m=1.10$ are given.

The tabulation for $m=1.20$ was obtained by numerical calculation with the use of Eq. (3), whereas the scattering function for $m=1.10$ was computed approximately by extrapolation of the results for $m=1.44$ and $m=1.33$ obtained by La Mer et al.³⁾ and those for $m=1.20$ obtained by us.

b) Relationship between DQ and particle radius

From Ep. (2), the ratio of turbidities DQ measured at two wavelengths λ_1 and λ_2 is given by

$$DQ = \tau(\lambda_1)/\tau(\lambda_2) = K_s(\lambda_1)/K_s(\lambda_2), \quad (6)$$

(For simplicity, in the following, attention is paid to the case of nonabsorbing sphere.) When the wavelength is small compared with the radius of sphere (Reyleigh scattering), the equation (6) reduces to

$$DQ = (\lambda_2/\lambda_1)^4 \quad (7)$$

with the aid of Eq. (4), and the quantity DQ becomes independent of the particle radius. However, as shown in Fig. 1, DQ is a function of the particle radius, when the latter quantity is the same order of magnitude as the wavelength. Fig. 1 shows the relation between DQ and particle radius, which was obtained from Table 1 for $\lambda_1=430 \text{ m}\mu$, $\lambda_2=700 \text{ m}\mu$, $m_0=1.33$ (water), $m=1.20$ and $m=1.10$.

c) Method for determination of particle radius from turbidity measurement

Two methods may be developed for determination of particle radius from turbidity measurement. Using Eqs. (2) and (3), we can express the turbidity in the form :

$$\tau = \frac{3\pi m_0}{2} \frac{c}{\lambda} \frac{K_s}{a} = f(c, \lambda, m, r) \quad (8)$$

Firstly, one can determine particle radius by turbidity measurement at known wavelength, m_0 , m and concentration. In connection with this method, La Mer et al.⁴⁾, making use of the fact that $\tau\lambda$ is a function of λ only as is clear in Eq. (8), have suggested an interesting method. Secondly, when the concentration is unknown, it is possible to estimate particle radius by the following procedure : one first determines the ratio of turbidities (DQ)

at two different wavelengths, and then reads r -value corresponding to the DQ from the $DQ-r$ relation theoretically obtained (for example, Fig. 1). In this paper, this second method was applied.

EXPERIMENTAL

a) Materials

Measurement were made using the following five kinds of synthetic latices.

- 1) Polystyrene latex (LS-040-A) : from the Dow Chemical Company.
- 2) Polymethylmethacrylate latex (M-1, M-3, M-5) : furnished by courtesy of Dr. T. Motoyama, the Kobunshikagakukogyo Company.
- 3) Acrylonitrile-butadiene copolymer latex (Hyear Latex No. 1571) from the B. F. Goodrich Chemical Company
- 4) Polyacrylonitrile latex (PAN-K) : prepared by Dr. R. Kitamaru
- 5) Polyvinyl acetate latex (Polysol SH-3) : furnished by the Kobunshikagakukogyo Company.

b) Apparatus

Turbidity Measurements were carried out with a photometer Type 7 of the Tokyokoden Company at room temperature.

c) Estimation of radius of sphere from DQ

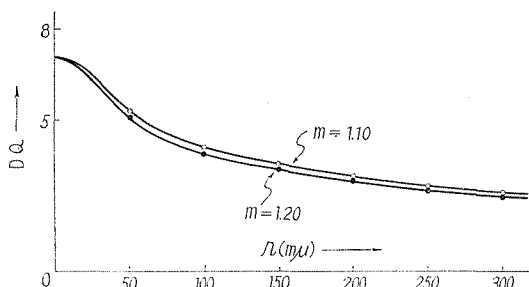


Fig. 1. Dispersion quotient DQ versus radius r . Curves are obtained at wavelengths in vacuo 430 $m\mu$ and 700 $m\mu$.

Using the $DQ-r$ relation given in Fig. 1, the radius of sphere was estimated graphically from DQ obtained by turbidity measurements. For all latices, relative refractive index was taken to be 1.20, the validity of which will be mentioned below.

d) An example of measurements

Fig. 2 shows the result of measurements for monodisperse polystyrene latex (LS-040-A).

The apparent concentration (c') of a solution was defined to be unity, which was obtained by diluting the parent solution about 1000-fold with water. The apparent turbidity τ' is τl . A linear relation between $\tau' - c'$ in Fig. 2 indicated that the measurements were carried out in a concentration

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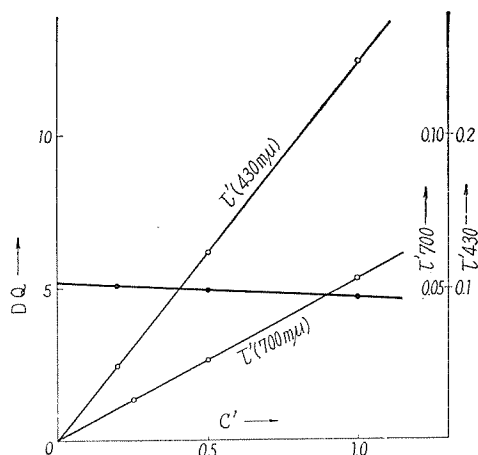


Fig. 2. DQ and apparent turbidity (τ') at wavelengths 430 $m\mu$ and 700 $m\mu$ as a function of apparent concentration (c'). Sample : Dow polystyrene latex (LS-040-A).

range, where the Lambert-Beer equation held. DQ was found to vary slightly with concentration. This was the case for other latices as well. The value of DQ at infinite dilution was found to be 5.10, corresponding to an r value of 480 Å according to Fig. 1. The particle radius, which was determined for the same latex by Bradford and Vanderhoff⁸⁾, by using electron microscopy, was 440 Å.

RESULTS

In Table 2, the values of particle radius obtained from the DQ method (r) for various synthetic latices are compared with those of particle radius estimated by electron microscopy (R).

Table 2. Particle radius obtained from the DQ-method (r) and particle radius obtained from electron microscopy (R) for various synthetic latices.

Sample	DQ	$r(\text{Å})$	$R(\text{Å})$
Polystyrene (LS-040-A)	5.10	480	450*
Polymethylmethacrylate (M-1)	5.70	370	350
Polymethylmethacrylate (M-3)	5.30	440	410
Polymethylmethacrylate (M-5)	5.60	380	290
Acrylonitrile-Butadiene (Hycar No. 1571)	4.10	870	810
Polyacrylonitrile (PAN-K)	3.30	1500	1260
Polyvinyl acetate (Polysol SH-3)	2.70	2240	2080

* According to the measurement by Bradford and Vanderhoff, R is 440 Å.

From this table, it is seen that r is in a good agreement with R , indicating

the validity of the DQ-method.

DISCUSSION

a) Relative refractive index m

In Table 3, relative refractive indices m of some synthetic polymers in the medium of water are tabulated. As is seen from the table, the relative

Table 3. Relative refractive indices m of various synthetic polymers.

Polymer	Refractive index	m
Polystyrene	1.58	1.19
Polymethylmethacrylate	1.49	1.12
Polyvinyl acetate	1.46	1.10
Polyvinyl chloride	1.60	1.20
Acrylonitrile-styrene copolymer	1.57	1.18
Acrylonitrile-butadiene copolymer	1.52	1.14

indices of polymers composing the synthetic latices in question lie between 1.10 and 1.20, when the medium is water. Taking into account the experimental error associated with the apparatus employed, the difference between the DQ- r relation for $m=1.10$ and that for $m=1.20$ is thought to be negligible, as Fig. 1 shows. Therefore, in the present paper, the particle radius was estimated tentatively using $m=1.20$ for all samples. Also the refractive index was assumed to be independent of the wavelength.

b) Concentration dependence of DQ

Recently Deželić et al.⁹⁾ reported the same kind of treatment as the present one, in which they estimated by the DQ-method the particle radius of monodisperse polystyrene latices of the Dow Chemical Company using $m=1.20$ at $\lambda_1=405\text{ m}\mu$ and $\lambda_2=546\text{ m}\mu$. They have not noticed concentration dependence of DQ. However, we found that DQ depended on concentration for all synthetic latices (as is shown for example in Fig. 2). Presumably turbidity measurements in the present paper have been carried out in a higher concentration range than that in Deželić et al.'s experiments. The observed concentration dependence appears to be due to secondary scattering, which becomes important as the inter-particle distance becomes small.

c) Comparison of the DQ-method with Heller et al.'s method

Heller et al.^{6,7)} have proposed a method (H-method) to determine empirically the particle radius by utilizing an approximate relation between absorption coefficient k and wave length λ ,

$$k = a\lambda^{-n}, \quad (9)$$

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which holds when the wavelength does not appreciably change. a is a factor depending on the particle radius and relative refractive index, and n is an exponent being related to the particle radius. The relation between n and particle radius can be empirically determined by correlating particle radius obtained, for example, from electron microscopy with n . The determination of particle radius of polystyrene latex LS-040-A by the H-method gave $n=3.50$ and $r=450 \text{ \AA}$ which agrees with that obtained by the DQ-method.

Let us consider the relation between the DQ-method and H-method. One obtains from Eqs. (1), (8) and (9),

$$\begin{aligned} DQ &= \tau(\lambda_1)/\tau(\lambda_2) = f(\lambda_1, \lambda_2, m, r) \\ &= k(\lambda_1)/k(\lambda_2) = (\lambda_1/\lambda_2)^{-n}. \end{aligned} \quad (10)$$

which shows that $f(\lambda_1, \lambda_2, m, r)$ is replaced by $(\lambda_1/\lambda_2)^{-n}$. Therefore, n is a function of r and m . This means that, in the determination of the particle size by the H-method, an empirical relation between n and r has to be known for any values of m . As is shown in Table 3, the values of m of many kinds of synthetic polymers are nearly the same (1.10~1.20), so that the H-method can be said to be useful to some extents. However the values of n with comparatively small experimental errors range from 2.10 to 3.9, corresponding to particle radius $r=350 \text{ \AA}$ and 1200 \AA , respectively; whereas, in the DQ-method, those of DQ for $\lambda_1=430 \text{ m}\mu$ and $\lambda_2=700 \text{ m}\mu$ are 2~6, corresponding to particle radius=300 A and 3000 A, respectively.

Thus the DQ-method, one may say, has an advantage that it can be applied for particles of a broader range of radius, besides an advantage that the determination of particle radius can be carried out theoretically.

d) Average value of particle radius when latices are not monodisperse

From Table 2, one notices that the value of particle radius obtained by the DQ-method (r) is always slightly larger than that obtained from electron microscopy (R). This discrepancy is thought to be partly due to the experimental errors and partly due to a possibility that the used latices are not monodisperse. In this connection, Loebel⁷⁾ has empirically found that the average value of particle radius determined by the H-method can be approximately given by $R_L = \sum N_i r_i^5 / \sum N_i r_i^4$, where N is the number of the particle. On the other hand, the average value of the particle radius determined from electron microscopy is usually given by the number average, i.e., $R_N = \sum N_i r_i / \sum N_i$. Mathematically $R_L \geq R_N$ can be proved. From the values of a and K_S in Table 1, one notices that $K_S \propto a^{2.8}$ holds to a rough approximation in the case of $m=1.20$ and $a=0.5\sim 5.0$. (This range of a corresponds to particle radius=250~4000 A for a range of wavelength=430~700 m μ .) Therefore, using Eq. (2) and this proportionality, one obtains $\tau \propto N r^5$ to a rough approximation. This means that the average particle radius determined by the turbidity measurement is, roughly, $R_5 = (\sum N_i r_i^5 / \sum N_i)^{1/5}$, which is nearly equal to R_L .

The fifth power of average particle radii of M-1, and M-5 estimated from

electron microscopic photograph, are 360 Å and 340 Å, respectively, which are found to be in a better agreement with the value obtained by the DQ-method. However, the samples used in this work are comparatively uniform in size so that they might not be suitable for the discussion of whether the particle radius obtained by the DQ-method is the fifth power of average value. It is hoped to carry out further experimental check concerning this problem in future.

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