Optical Properties of Colored Colloidal Systems. II. Apparent Refractive Index and Extinction Coefficient of the System of Small Spherical Particles

By Masayuki NAKAGAKI* and Tomiko FUJII

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In the preceding paper of this series[1], the extinction of light by the system of colored small spheres were theoretically calculated. As a result, it was concluded that the scattering of light by colored spheres is affected by the absorption of light, the latter being expressed by the imaginary part of the refractive index of the dispersed phase. In the present paper, the calculation will be extended to the apparent refractive index of the system. The result thus obtained will be applied to the system of infinitesimally small particles, and will be used to discuss the optical properties of a dyestuff solution as an example.

Theoretical Calculations

Principle of the Calculation. — The relation between the refractive index of a colloidal system or a solution, μ_{12}, and the refractive indices and compositions of the components is usually given by the following equation called a mixture rule,

$$\mu_{12}=\mu_1\varphi_1+\mu_2\varphi_2 \tag{1}$$

where μ_1 and μ_2 are the refractive indices of the solvent and dispersed phases, respectively, and φ_1 and φ_2 are the volume fractions of the respective phases. If the concentration of the dispersed phase, c, is given in mol./l. unit, Eq. 1 may be rewritten as,

$$\mu_{12}=\mu_1+(M/1000\rho_2)(\mu_2-\mu_1)c \tag{2}$$

where M is the molecular weight of the material of the dispersed phase and ρ_2 is the specific gravity of the same phase. The linear relationship between μ_{12} and c as predicted by Eq. 2 has been verified experimentally by many investigators, but the value of μ_2 is not equal[2] to the refractive index in bulk of the dispersed phase, μ_2 (bulk). Therefore the value of μ_2 obtained experimentally on the basis of Eq. 2 is an apparent refractive index of the dispersed phase. If the apparent relative refractive index m' defined by

$$m'=\mu_2/\mu_1 \tag{3}$$

is used, the inclination of the straight line to give the variation of μ_{12} with the concentration c is expressed as

$$\partial\mu_{12}/\partial c=(M\mu_1/1000\rho_2)(m'-1) \tag{4}$$

This equation is to be used to determine the value of m' experimentally.

On the other hand, $(m'-1)$ is given theoretically by the equation[2],

$$m'-1=(3/2)\mathrm{R}[j_\perp(180)]/\alpha^3 \tag{5}$$

where α is a parameter defined by

$$\alpha=2\pi a/\lambda \tag{6}$$

Here, a is the radius of the sphere and λ is the wave length of light in the medium. The sign R in Eq. 5 means the real part of a complex function $j_\perp(180)$, the latter being

$$j_\perp(180)=\frac{m^2-1}{m^2+2}\alpha^3+\left(\frac{m^2-1}{m^2+2}\right)^2 \times\frac{(m^4+27m^2+38)}{15(2m^2+3)}\alpha^5 -i\frac{2}{3}\left(\frac{m^2-1}{m^2+2}\right)^2\alpha^6 \tag{7}$$

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* Present address: Faculty of Pharmacy, Kyoto University, Sakyo-ku, Kyoto.

1) M. Nakagaki, This Bulletin, 31, 980 (1958).

2) M. Nakagaki and W. Heller, *J. Appl. Phys.*, 27, 975 (1956).

as already given in the previous paper[1], where m is a complex quantity in the case of colored particles:

$$m=\mu_2^*(\text{bulk})/\mu_1=m_0-ik_0 \tag{8}$$

where μ^* means the complex refractive index.

Apparent Refractive Index as a Function of Particle Size.—If $k_0 \ll m_0$, the theoretical equation may be expanded in a power series,

$$m'-1=M_1-M_2k_0+M_3k_0^2+\cdots\cdots \tag{9}$$

where

$$\left.\begin{aligned} M_1&=(3/2)(X_1+Y_1\alpha^2)\\ M_2&=(3/2)Z_2\alpha^3\\ M_3&=(3/2)(X_3-Y_3\alpha^2)\end{aligned}\right\} \tag{10}$$

Here,

$$\left.\begin{aligned} X_1&=\frac{m_0^2-1}{m_0^2+2}\\ Y_1&=\frac{1}{15}\left(\frac{m_0^2-1}{m_0^2+2}\right)^2\frac{(m_0^4+27m_0^2+38)}{(2m_0^2+3)}\\ Z_2&=8m_0\frac{m_0^2-1}{(m_0^2+2)^3}\\ X_3&=\frac{3(3m_0^2-2)}{(m_0^2+2)^3}\\ Y_3&=\frac{\left\{\begin{aligned}&4m_0^{18}+66m_0^{16}-1104m_0^{14}-5033m_0^{12}\\&+12966m_0^{10}+105525m_0^8+218152m_0^6\\&+182376m_0^4+37824m_0^2-16176\end{aligned}\right\}}{15(m_0^2+2)^6(2m_0^2+3)^3}\end{aligned}\right\} \tag{11}$$

The results of the numerical computation are shown in Fig. 1. Crosses in the figure are the values for colorless particles calculated on the basis of the Mie theory without any approximation[2]. The agreements between these Mie values and the values obtained from Eqs. 9, 10 and 11 and shown with open circles for colorless particles are very good, although a small discrepancy can be seen in the case where both α and m_0 are large ($\alpha=0.8$, $m_0=1.3$). When k_0(which shows the absorption of light) is small, the apparent relative refractive index m' increases with α (or particle size), but when k_0 is large, the value of m' decreases (after passing a flat maximum when m_0 is large) with the increase of α.

Optical Properties of Infinitesimally Small Particles.—The equation used in the preceding paper as well as in the preceding paragraphs of this paper are for small values of k_0. In the present paragraph, equations for infinitesimally small particles ($\alpha\rightarrow 0$) are examined without any restriction on k_0. The equations are

$$m'-1=\frac{3}{2}-\frac{9}{2}\times\frac{(m_0^2+2-k_0^2)}{(m_0^2+k_0^2+2)^2-8k_0^2} \tag{12}$$

and

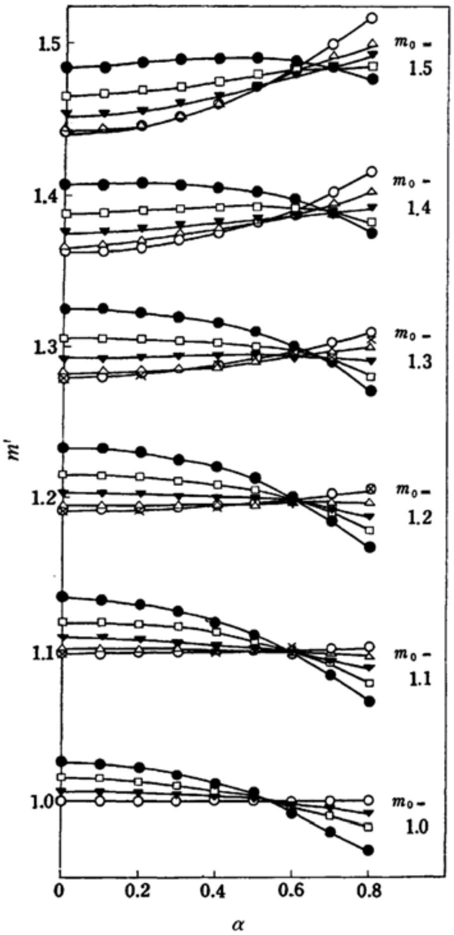

Fig. 1. $m'-\alpha$ relation for $k_0=0$ (○); 0.1 (△); 0.2 (▼); 0.3 (□); 0.4 (●). Mie's values are shown with (×).

$$\left.\begin{aligned} x&\equiv(\lambda\rho_2/3\pi)\varepsilon=\frac{12m_0k_0}{(m_0^2+k_0^2+2)^2-8k_0^2}\\ x(\text{bulk})&=(4/3)k_0\end{aligned}\right\} \tag{13}$$

where x is a quantity proportional to the extinction coefficient ε as already introduced in the preceding paper[1].

The numerical values of m' as a function of k_0 were calculated for various values of m_0 from 0.88 to 1.24 with the interval of 0.02. A part of the results is shown in Fig. 2. Although the apparent relative refractive index m' and the relative refractive index in bulk m_0 are parallel when k_0 is small, the sequence is inverted when k_0 is larger than about 1.4. The smaller m' the larger is the m_0. Moreover, the value of m' approaches 2.5 when k_0 becomes infinitely large. These results shown in Fig. 2 have not been expected by any previous investigator.

The numerical values of x as a function of

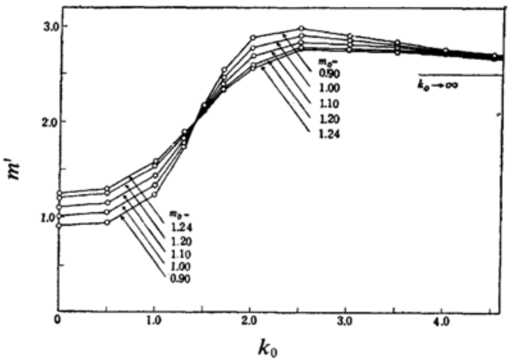

Fig. 2. $m'-k_0$ relation calculated theoretically.

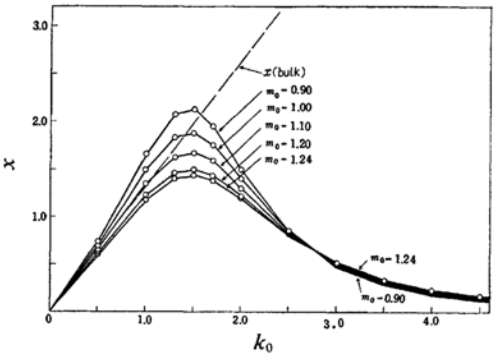

Fig. 3. $x-k_0$ relation calculated theoretically.

k_0 were calculated for various values of m_0 from 0.88 to 1.24 with the interval of 0.02. A part of the results is shown in Fig. 3. The curves have the maximum at the k_0 value of about 1.5. The apparent extinction coefficient or x decreases for the larger value of k_0 and approaches zero when k_0 becomes infinitely large.

These results, too, have not been expected by any previous investigator[3].

An Example for the Treatment of Experimental Data

Materials.—It is generally believed that acid dyes dissolve in water monomolecularly, showing a small tendency to form micelles in contradistinction to direct cotton dyes which form micelles when the temperature is not high. Therefore, an acid dye solution is used as a model of the system of colored infinitesimally small particles.

The acid dye used in this experiment was Acid Orange R (C. I. 15575, Acid Orange 8) purified by the sodium acetate-alcohol method. The purity determined by titanium trichloride titration was 96.32%.

3) In Figs. 2 and 3, theoretically calculated points were connected with straight lines for the convenience of the drawings. The actual theoretical curves should, of course, be curved smoothly.

Determination of Refractive Index.—The difference of the refractive index between the solution and the solvent was measured by using a differential refractometer of modified Brice type as shown in Fig. 4. Light from a

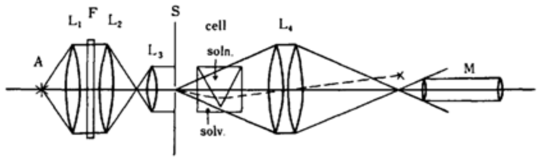

Fig. 4. Schematic diagram of differential refractometer of modified Brice type.

tungsten lamp A was collimated with lenses L_1 and L_2 ($f_1=6$ cm., $f_2=6$ cm.), filtered with a gelatine filter F, made parallel with a lens L_3 ($f_3=3$ cm.) and projected to a slit S. The image of the slit focused by a lens L_4 ($f_4=$ 15 cm. lens for a slide projector was used) was observed with a microscope M of the magnification of 40 times (4×10). The location of the image of the slit was shifted when a solution was put in the prism cell containing solvent outside the prism in the cell. The shift of the image of the slit was measured by a micrometer in the eyepiece of the microscope M. The reading θ is proportional to the difference of the refractive index,

$$\mu_{12}-\mu_1=K\theta \tag{14}$$

The proportionality constant K was determined to be $K=4.15\times10^{-5}$ by using potassium chloride solution as a standard, the refractive index of the latter being cited in the literature[4]. The value of μ_1 is also given in the literature[5].

In order to convert the experimental values of $(\partial\mu_{12}/\partial c)$ to m' according to Eq. 4, the value of the density of dye, ρ_2, should be known. The density was assumed to be 1.5 by Robinson[6] and to be 1.0 by Atherton et al.[7] Since the accurate value of the density for the dispersed state can not be known, calculations were made here for both these density values. The results are shown in Fig. 6 with broken lines. A typical anomalous dispersion was observed as already reported for some other dye solutions[7]. In Fig. 6 and also Fig. 7, λ_0 is wavelength in vacuum.

Determination of Extinction Coefficient.—The extinction coefficient was determined by Shimazu spectrophotometer QR-50. The results were recalculated to x by Eq. 13 for $\rho_2=1.0$ and $\rho_2=1.5$. The results are shown in Fig. 7 with broken lines.

4) "International Critical Tables", VII, 13, 75 (1930).
5) "International Critical Tables", VII, 13 (1930).
6) C. Robinson, *Trans. Faraday Soc.*, **31**, 245 (1935).
7) E. Atherton and E. Cowill, *J. Soc. Dyers Colorists*, **70**, 116 (1954).

Calculation of m_0 and k_0. — The quantities obtainable by experiments are m' and x, but the fundamental quantities of theoretical interest are m_0 and k_0. To determine m_0 and k_0 from m' and x, a graphical method is shown in Fig. 5. The $m'-x$ relation calculated theoretically for systematically varied values of parameters m_0 and k_0 make a network. A

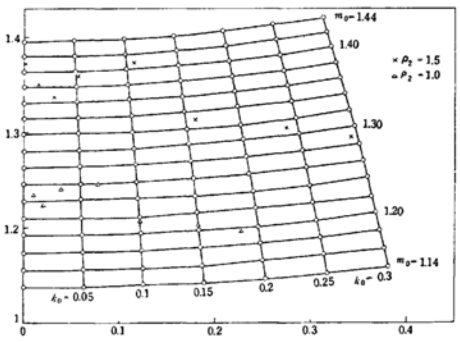

Fig. 5. $m'-x$ relation. Network shown with (○) is theoretical. Experimental data for $\rho_2=1.0$ (△) and for $\rho_2=1.5$ (×) are also ploted.

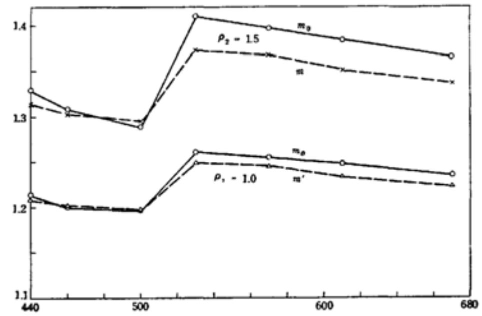

Fig. 6. Dependencies of m_0 and m' on λ_0.

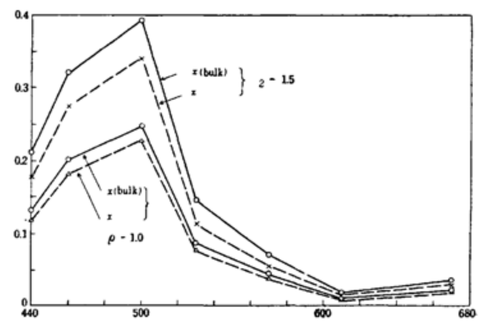

Fig. 7. Dependencies of x(bulk) and x on λ_0.

pair of experimental values of m' and x give one plot on this chart. Then, the values of m_0 and k_0 corresponding to this plot can be read off by interpolation. The values of m_0 thus obtained are shown in Fig. 6 with solid lines, and the values of x(bulk) calculated by Eq. 13 from the values of k_0 thus obtained are shown in Fig. 7 with solid lines.

The discrepancies between solid curves and broken curves in Fig. 6 and Fig. 7 show the error committed if one assume that the experimental m' and x values are equal to m_0 and x(bulk)—the latter is equal to $(4/3)k_0$—of the dispersed phase in bulk. The errors in this sense are given in Table I for the present solutions. The table shows that the error in m' is less than 2.6% at the greatest, but the error in x reaches as far as 21% at the greatest.

TABLE I. ERRORS COMMITTED BY IGNORING THE PRESENT THEORY

λ_0	$\rho_2=1.5$		$\rho_2=1.0$	
mμ	Δm %	Δx %	Δm %	Δx %
440	−1.27	−15.7	−0.43	− 9.6
460	−0.37	−14.4	−0.24	− 9.0
500	0.55	−13.1	0.08	− 8.0
530	−2.56	−20.6	−0.96	−11.5
570	−2.51	−19.6	−1.10	−10.4
610	−2.41	−19.5	−1.05	− 8.1
670	−2.10	−17.7	−0.91	− 8.7

Summary

The theoretical values of apparent relative refractive index m' of colored particles was calculated as a function of particle size for various values of m_0 and k_0.

The theoretical values of m' as well as x were calculated for infinitesimally small particles. It was shown that m' increases and, after passing a maximum point, approaches a limiting value of 2.5 with the increase of k_0, and that x approaches zero, after passing a maximum, with the increase of k_0.

The values of m' and x of Acid Orange R solutions were measured by a modified Brice type differential refractometer and by a spectrophotometer. A method to convert m' and x values into m_0 and k_0 values was illustrated. The errors committed by assuming experimental m' and x values as m_0 and $(4/3)k_0$ values of bulk phase are estimated for the dye solution. The error of x reached 21%, while the error of m' was not larger than 2.6%.

Faculty of the Science of Living
Osaka City University
Nishi-ku, Osaka