Optical Properties of Colored Colloidal Systems. I. Theoretical Studies on the Extinction of Light by the System of Small Spherical Particles

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Recently the light scattering of colorless systems has been studied quite extensively by many investigators. However, the light scattering of the colloidal systems of colored particles has had little systematic study, although the papers by G. Mie[1] and R. Gans[2] concerned with the optical properties of metal colloids.

In the present paper, theoretical expressions for the extinction, scattering and absorption by a system of colored spherical particles are derived and the numerical values are calculated for systematically varied values of the particle size, refractive index and absorption coefficient of the dispersed phase.

Theoretical Derivations

Definitions.—Consider a system of colored spherical particles dispersed in a colorless medium whose refractive index is μ_1. The refractive index, μ_2, of the colored particle is complex and may be written as follows:

$$\mu_2 = \mu_0(1 - ik) \tag{1}$$

Then, the relative refractive index, m, is

$$m = \mu_2/\mu_1 = m_0 - ik_0 \tag{2}$$

where

$$m_0 = \mu_0/\mu_1 \quad \text{and} \quad k_0 = m_0 k \tag{3}$$

1) G. Mie, *Ann. Phys.*, (4), **25**, 377 (1908).
2) R. Gans, *Ann. Phys.*, (4), **37**, 881 (1912); **62**, 331 (1920).

Here the physical meaning of the quantities, μ_0, k and k_0 are as follows. If the homogeneous phase of the material which composes the colloidal particles is considered, the refractive index of the phase is μ_0, and

$$-\ln(I'/I_0')/l' = 4\pi\mu_0 k/\lambda_0 = 4\pi k_0/\lambda \tag{4}$$

where l' is the thickness of the phase, I_0' and I' are the intensity of the incident and transmitted light, respectively, and λ and λ_0 are the wave lengths, in the medium and in vacuum, respectively. Therefore, k and k_0 are both zero if the phase is colorless.

Now consider a colloidal system of thickness l, the unit volume of which contains N particles of radius a. A parameter α defined by

$$\alpha = 2\pi a/\lambda \tag{5}$$

is used in the studies of light scattering. If the density of the particle is ρ_2, the concentration c in g./cc. is

$$c = \alpha^3\lambda^3\rho_2 N/6\pi^2 \tag{6}$$

If the intensities of the incident and transmitted light are I_0 and I, respectively, the quantity E defined by

$$E = -\ln(I/I_0)/l \tag{7}$$

will be called extinction. It is equal to the turbidity, τ, if the particles are colorless, while it is equal to the product of the specific extinction coefficient, ε, and the concentration, c, if the particles are colored and the turbidity of the system is small and negligible. In general cases,

$$E/N = R + A \tag{8}$$

where R and A are the energy of light scattered and absorbed, respectively, by one particle par unit time.

Scattering *R*.—The total of the energy of light scattered in all directions by one particle par unit time, R, is

$$R = 2\pi \int_0^{\pi} J(\gamma) \sin\gamma \, d\gamma = (\lambda^2/2\pi)\Sigma \tag{9}$$

where $J(\gamma)$ is the intensity of light per unit solid angle[3] scattered in the direction designated by the scattering angle, γ, when the intensity of the incident light is unity, and Σ is a dimensionless quantity defined by[4]

$$\Sigma = \sum_{n=1}^{\infty} (|A_n|^2 + |B_n|^2) n^2 (n+1)^2 / (2n+1) \tag{10}$$

where A_n and B_n are complex functions expressed by combinations of Bessel's functions, as shown by the Mie theory[1]. If α is small compared to unity, A_n and B_n can be expanded as a power series in α and the results are[5]

$$\left.\begin{aligned} A_1 &= \frac{m^2-1}{m^2+2}\alpha^3 + \frac{3}{5}\frac{(m^2-1)(m^2-2)}{(m^2+2)^2}\alpha^5 \\ &\quad - i\frac{2}{3}\left(\frac{m^2-1}{m^2+2}\right)^2\alpha^6 + \cdots \\ B_1 &= -\frac{1}{30}(m^2-1)\alpha^5 + \cdots \\ A_2 &= -\frac{1}{18}\frac{m^2-1}{2m^2+3}\alpha^5 \cdots \end{aligned}\right\} \tag{11}$$

Neglecting the term higher than the eighth power of α,

$$\Sigma = \frac{4}{3}\left|\frac{m^2-1}{m^2+2}\right|^2 \alpha^6 \tag{12}$$

This is the well known equation by Rayleigh[6].

In the case of $k \ll 1$ (that is $k_0 \ll m_0$), Σ can be expanded as a power series in k_0 as follows:

$$\Sigma = \frac{4}{3}\left(\frac{m_0^2-1}{m_0^2+2}\right)^2 \alpha^6 + 8\frac{(3m_0^4 + m_0^2 + 2)}{(m_0^2+2)^4}\alpha^6 k_0^2 + \cdots \tag{13}$$

The quantity R obtained from Eqs. 9 and 13 is the total scattering by one particle, and RN is the scattering by the unit volume of the colloidal system. It is, however, not adequate to call RN turbidity, because the turbidity is extinction in case of colorless systems. The extinction by a colored system should include the contribution of absorption as well as that of scattering. In order to take the absorption into account, it is not sufficient to use complex refractive index in the Rayleigh equation, because the term of k_0^2 in Eq. 13 is not the term of absorption but is the term which expresses the effect of absorption on the scattering.

Now RN/c is set as κ. Then,

$$\kappa = RN/c = (3\pi/\lambda\rho_2)(\Sigma/\alpha^3) \tag{14}$$

In the case of a colorless system, κ is the specific turbidity (τ/c), which can be determined experimentally by the measurement of transmittancy. In the case of a colored system, however, what is obtained by the measurement of transmittancy is not the turbidity but it containes the effect of absorption as well. Therefore, there exists no handy experimental method to determine the value of κ. It may, however, be worth-while to mention that there should exist, at least principally, an experimental method to determine the value of κ, although the method is very tedious and almost impossible to practice. It will be done by measuring the intensity of scattered light as a function of the angle of observation in all ranges and integrating the results in all possible directions.

According to Eq. 13, R and Σ are zero if k_0 is zero and m_0 is unity. That is, the scattering does not occur in a colorless system if the refractive index of particles and the medium are equal. In the case of a colored system, however, the scattering occurs even when m_0 is equal to unity. Generally, there exists no value of m_0 which makes R equal to zero when k_0 is not equal to zero.

Extinction *E*. — The extinction by one particle, E/N, can be calculated theoretically by the equation

$$E/N = -(\lambda^2/\pi) I[j_\perp(180)] \tag{15}$$

where $I[j_\perp(180)]$ indicates the imaginary

3) In order to avoid the use of photometric distance, the intensity is defined here per unit solid angle, instead of per unit area in the usual definiton of the intensity.

4) See, e. g., W. J. Pangonis, W. Heller and A. Jacobson, "Tables of Light Scattering Functions for Spherical Particles", Wayne State Univ. Press, Detroit, U. S. A. (1957).

5) See, e. g., H. C. van de Hulst, "Optics of Spherical Particles", Chapter 4(a), Holland (1946). His notation is different from that used here. A_n and B_n are $(-1)^n i a_n (2n+1)/n(n+1)$ and $(-1)^{n+1} i b_n (2n+1)/n(n+1)$, respectively, in van de Hulst's notation.

6) Lord Rayleigh, *Phil. Mag.*, (5), **47**, 375 (1899).

part of $j_{\perp}(180)$, and the latter is the quantity which appeared in the expression[7]:

$$J_{\perp}(\gamma)=(\lambda^2/4\pi^2)|j_{\perp}(\gamma)|^2 \tag{16}$$

Therefore, $j_{\perp}(\gamma)$ is proportional to the amplitude of the light scattered at the direction γ and vibrating perpendicularly to the observation plane, the proportionality constant being $(\lambda/2\pi)$. According to the Mie theory,

$$j_{\perp}(\gamma)=\sum_{n=1}^{\infty}[A_nP_n^1(\cos\gamma)/\sin\gamma + B_n\mathrm{d}P_n^1(\cos\gamma)/\mathrm{d}\gamma] \tag{17}$$

where $P_n^1(\cos\gamma)$ is Legendre's function of the first kind. In the forward direction, or in the case of $\gamma=180$,

$$j_{\perp}(180)=A_1-B_1-3A_2+\cdots = \frac{m^2-1}{m^2+2}\alpha^3+\left(\frac{m^2-1}{m^2+2}\right)^2\frac{(m^4+27m^2+38)}{15(2m^2+3)}\alpha^5 - i\frac{2}{3}\left(\frac{m^2-1}{m^2+2}\right)^2\alpha^6+\cdots \tag{18}$$

can be obtained using Eq. 11 if $\alpha \ll 1$.

In order to be analogous to the relation between R and $\sum$ in Eq. 9, $\sum_f$ is introduced by

$$E/N=(\lambda^2/2\pi)\textstyle\sum_f \tag{19}$$

Then,

$$\textstyle\sum_f=-2I[j_{\perp}(180)] \tag{20}$$

Using Eq. 18 for $j_{\perp}(180)$ and expanding it as a power series in k_0,

$$\sum\nolimits_f=\frac{4}{3}\left(\frac{m_0^2-1}{m_0^2+2}\right)^2\alpha^6+2\left(\frac{6m_0}{(m_0^2+2)^2}\alpha^3+F\alpha^5\right)k_0 + 8\frac{(3m_0^4-11m_0^2+2)}{(m_0^2+2)^4}\alpha^6k_0^2+\cdots \tag{21}$$

where,

$$F=\frac{2m_0}{15}\times\frac{(m_0^2-1)(2m_0^8+20m_0^6+349m_0^4+935m_0^2+674)}{(m_0^2+2)^3(2m_0^2+3)^2} \tag{22}$$

If the particles are colorless and k_0 equals to zero, E/N is equal to R, and E is equal to τ, indicating that the attenuation of the light is due to the scattering only.

By analogy with the colored system of no scattering, the specific extinction coefficient in a wider sense, ε, is defined here by E/c and it is to be understood that this quantity containes the contribution of both scattering and absorption. Then,

$$\varepsilon=E/c=(3\pi/\lambda\rho_2)(\textstyle\sum_f/\alpha^3) \tag{23}$$

This is the quantity obtained by the measurement of the intensity of transmitted light.

Absorption A.—The absorption by the colored colloidal system can be obtained directly neither by theoretical calculation nor by experimental determination. It is, however, theoretically obvious that the absorption is the difference of extinction and scattering, as already shown by Eq. 8. Thus, the absorption per one particle, A, is given by

$$A=(\lambda^2/2\pi)(\textstyle\sum_f-\sum) \tag{24}$$

Using Eqs. 13 and 21,

$$\sum\nolimits_f-\sum=2\left[\frac{6m_0}{(m_0^2+2)^2}\alpha^3+F\alpha^5\right]k_0 - \frac{96m_0}{(m_0^2+2)^4}\alpha^6k_0^2 \tag{25}$$

Then, using the symbol ε_a for the specific extinction coefficient due to the absorption,

$$\varepsilon_a=AN/c=(3\pi/\lambda\rho_2)(\textstyle\sum_f-\sum)/\alpha^3 \tag{26}$$

or

$$\varepsilon_a=\varepsilon-\kappa \tag{27}$$

For the homogeneous phase of the material which composes the colloidal particles, the value of ε and ε_a obtained from Eq. 4 is

$$\varepsilon(\mathrm{bulk})=\varepsilon_a(\mathrm{bulk})=4\pi k_0/\lambda\rho_2 \tag{28}$$

since no scattering occurs and the concentration in g./cc. is equal to the density, ρ_2, for the bulk phase.

Numerical Computations

The numerical values of ε, κ and ε_a could be calculated if the values of density, ρ_2, and the wave length of light to be used, λ, are assigned. In order to make, however, the results of the computation applicable more widely, the quantities x, y and z are defined by

$$x=(\lambda\rho_2/3\pi)\varepsilon=\textstyle\sum_f/\alpha^3 \tag{29}$$

$$y=(\lambda\rho_2/3\pi)\kappa=\textstyle\sum/\alpha^3 \tag{30}$$

and

$$z=(\lambda\rho_2/3\pi)\varepsilon_a=x-y \tag{31}$$

The values of x, y and z for systematically varied values of α, m_0 and k_0 are calculated by using these equations together with Eqs. 13 and 21. For the bulk phase,

7) The derivation of Eq. 15 was shown, e. g., by H. C. van de Hulst (loc. cit.) although his notation is different from that used here. In the case of colorless particles, B. H. Zimm and W. B. Dandliker (*J. Phys. Chem.*, **58**, 644 (1954) have also shown the derivation of a similar equation in which the turbidity was used instead of the extinction E. However, the negative sign was dropped in their equation by a typographical mistake.

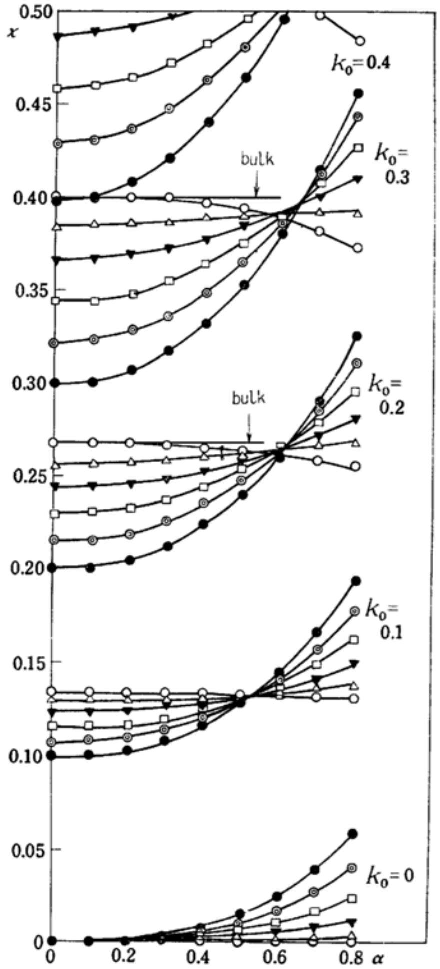

Fig. 1. $x-\alpha$ Relation for $m_0=1.0$ (○); 1.1 (△); 1.2 (▼); 1.3 (□); 1.4 (◎); 1.5 (●).

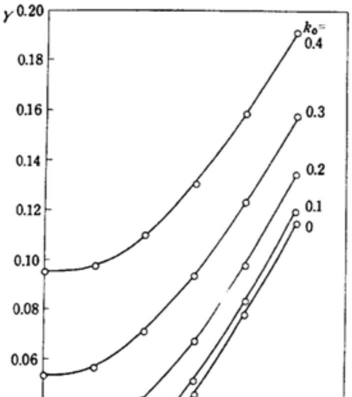

Fig. 2. $Y-m_0$ Relation.

$$\left.\begin{array}{l} x(\text{bulk}) = z(\text{bulk}) = (4/3)k_0 \\ y(\text{bulk}) = 0 \end{array}\right\} \qquad (32)$$

The value of x thus computed as a function of α is shown in Fig. 1, the complex relative refractive index (m_0-ik_0) being the parameter. The rather complicated nature of the curves will be explained as the sum of y and z in the succeeding figures.

As readily understood from Eqs. 30 and 13, the quantity y, a quantity proportional to the specific turbidity in the case of colorless particles, is proportional to α^3. As the consequence, the value of y increases with α so rapidly that it is not convenient to show it in a figure. Therefore, the proportionality constant, Y, in

$$y = Y\alpha^3 \qquad (33)$$

is shown in Fig. 2. The figure shows that

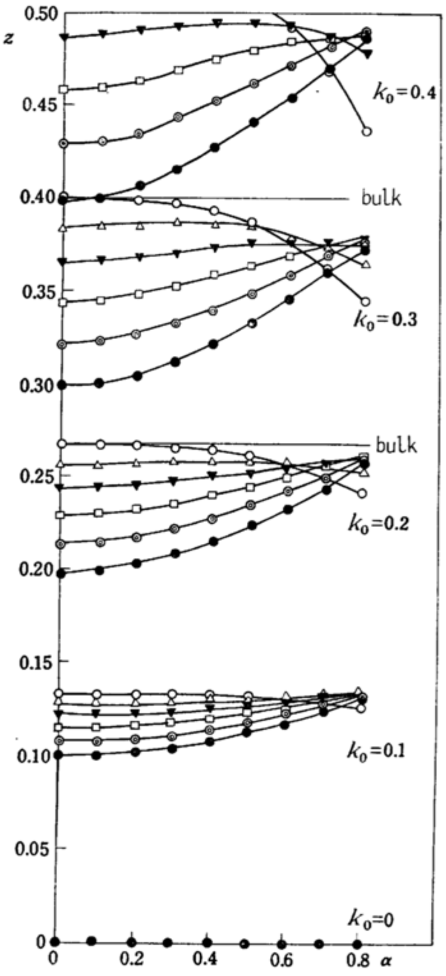

Fig. 3. $z-\alpha$ Relation for $m_0=1.0$ (○); 1.1 (△); 1.2 (▼); 1.3 (□); 1.4 (◎); 1.5 (●).

the value of Y increases with k_0 as well as with m_0. The value of Y is not equal to zero even when m_0 is equal to 1, if the value of k_0 is not zero. This means that the scattering occurs not only by the difference of refractive index, but also by the absorption.

The value of absorption, z, against α is shown in Fig. 3. The values corresponding to the bulk phase are shown by horizontal lines. It may be worth-while to mention that the value of z is equal to the value of the bulk phase only when m_0 is equal to unity and the particles are very small. If the relative refractive index is not equal to unity, the value of the absorption is, even for very small particles, not equal to the value of the bulk phase but is smaller than the latter. The absorption by colloidal particles is the smaller, the larger the value of m_0. With the increase of the particle size, α, the value of z at first increases and then decreases after passing a maximum. The value of α corresponding to the maximum is zero for m_0 is equals 1 and increases with the value of m_0.

Considering again the value of x, its α-dependence can be understood on the basis of the α-dependence of y and z since x is the sum of them. The value of x decreases with the increase of α if m_0 is small, because the absorption decreases while the scattering is not significant. On the other hand, the value of x increases rapidly if m_0 is large, because both the scattering and the absorption increase.

Check of the Results of Computation

The scattering coefficient of colored particles is considered here. Both the extinction per one particle, (E/N), and the total scattering, R, have the dimension of the area. Therefore, the quantity R is called the scattering cross section, and its ratio to the geometrical cross section is called the scattering coefficient, K. The extinction and the scattering are the same for colorless particles, but they are different for colored particles. The quantity usually measured is the extinction. Therefore, using the word "scattering coefficient" in its wider sense, K may be defined by[8)]

$$K = (E/N)/\pi a^2 = 2\textstyle\sum_f/\alpha^2 \tag{34}$$

8) National Eureau of Standards (U. S. A.), "Tables of Scattering Functions for Spherical Particles", Washington, U. S. A. (1948).

for colored particles.

Now, the people in the National Bureau of Standards of the U. S. A.[8)] expanded K as a power series in k_0,

$$K = C_0 + C_1 k_0 + C_2 k_0^2 + \cdots \tag{35}$$

and calculated the values of the coefficients, C_0, C_1 and C_2 on the basis of the Mie theory for the m_0-values between 1.44

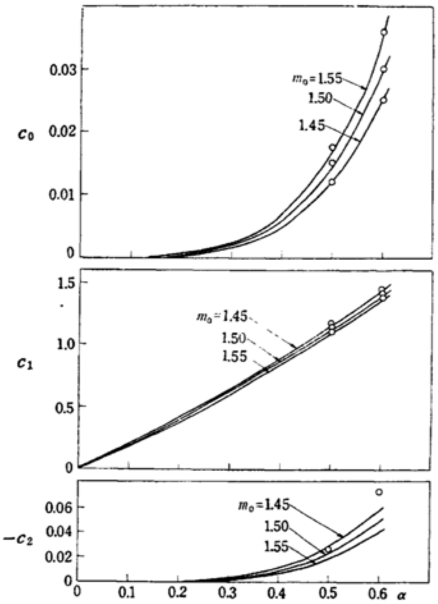

Fig. 4. Comparison with Mie theory.

and 1.55 and for the α-values of 0.5, 0.6, 1.0 and so forth. The values of C_0, C_1 and $-C_2$ by the Mie theory are plotted in Fig. 4 with open circles, while the results by the approximate equations derived in the present paper are shown with solid lines for m_0=1.45, 1.50 and 1.55. The agreements are excellent for C_0 and C_1 in the range of α up to 0.6. As for $-C_2$, the computation by the National Bureau of Standards neglected its dependence on m_0, so that the accuracy of their computation is probably rather poor. Taking this into consideration, the agreement between their values and the values by the present paper is sufficient.

Summary

The extinction, scattering and absorption of light by the colored colloidal systems of small spherical particles have been discussed. Approximate equations for these quantities have been derived for a case where the size of particles and the absorption coefficient of the dispersed

phase are relatively small. Using these equations, the numerical values of the quantities have been computed for the systematically varied values of the relative refractive index, $(m_0 - ik_0)$, and of α.

It is shown by the results of the computation that the values of the extinction and the absorption by the colloidal systems of small colored spheres (whose α-value is smaller than about 0.5) are the smaller, the greater the value of m_0. On the other hand, the scattering increases with m_0, k_0 and α.

The values of the scattering coefficient calculated by the approximate equations showed sufficient agreement with the values by the Mie theory as far as α is smaller than 0.6.

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