The Optical Properties of Colored Colloidal Systems. III. A Theory of Spherical Particles, with Especial Attention to Systems Dispersed in Colored Media*

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In a previous paper,[1] the extinction, scattering and absorption of light by a colloidal sytem of colored spherical particles dispersed in a colorless medium was studied theoretically; it was concluded that the scattering is affected by the absorption, and that the absorption is affected by the scattering. In another paper,[2] the apparent refractive index of the same system was studied theoretically, and the results were applied to a solution of dye, Acid Orange R, the system being treated as a dispersed system of infinitesimally small particles. In the present paper, the theoretical treatment will be extended to cases where either the particle or the medium is colored, or both; the results will be discussed in detail for the case of a relatively small absorption.

Theoretical

Complex Refractive Index.—The refractive index of a colored phase is usually expressed by a complex quantity. For the dispersion medium;

$$\mu_1 = \mu_{10}(1 - ik_2) \tag{1}$$

and for the dispersed phase;

$$\mu_2 = \mu_{20}(1 - ik_2) \tag{2}$$

may be used, where μ_{10} and μ_{20} are the usual refractive indices of the respective bulk phases, while k_1 and k_2 are related to the optical densities per unit of thickness, E_i', of the respective bulk phases by the following equation,[3] with $i=1$ or 2;

$$E_i' = -[\ln(I_i'/I_0')]/l_i' = 4\pi\mu_{i0}k_i/\lambda_0 \tag{3}$$

Here l_i' is the thickness of the phase i, I_0' and I_i' are the intensities of the incident and transmitted light, and λ_0 is the wavelength of the light in a vacuum.

When phase 2 is dispersed as small spherical particles in phase 1, the optical properties of the dispersed system are determined by the relative radius, α, the relative refractive index, m, the number of particles in a unit volume, N, and the wavelength of light in the medium, λ. The relative radius is defined by:

$$\alpha = 2\pi a/\lambda \tag{4}$$

where a is the radius of the sphere and where

$$\lambda = \lambda_0/\mu_{10} \tag{5}$$

If the concentration c (g./ml.) is used instead of N;

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

where ρ_2 is the density of the dispersed phase.

The relative refractive index, m, defined by:

$$m = \mu_2/\mu_1 \tag{7}$$

is also a complex quantity in our case; it is separated into real and imaginary parts as follows:

$$m = m_0 - ik_0 \tag{8}$$

where i is $\sqrt{-1}$ and

$$m_0 = (\mu_{20}/\mu_{10})(1+k_1k_2)/(1+k_1^2) \tag{9}$$

$$k_0 = (\mu_{20}/\mu_{10})(k_2-k_1)/(1+k_1^2) \tag{10}$$

or

$$k = k_0/m_0 = (k_2-k_1)/(1+k_1k_2) \tag{11}$$

If the medium is colorless and the particles are colored,

$$\left.\begin{array}{c} m_0 = \mu_{20}/\mu_{10} \\ k_0 = m_0k_2 \text{ or } k = k_2 \end{array}\right\} \text{(if } k_1=0) \tag{12a}$$

Therefore, m_0 is equal to the ratio of the usual refractive indices and k_0 is positive. This is the case discussed in the previous papers.[1,2]

On the contrary, if the medium is colored and the particles are colorless,

$$\left.\begin{array}{c} m_0 = (\mu_{20}/\mu_{10})/(1+k_1^2) \\ k_0 = -m_0k_1 \text{ or } k = -k_1 \end{array}\right\} \text{(if } k_2=0) \tag{12b}$$

Therefore, m_0 is smaller than the ratio of the usual refractive indices (μ_{20}/μ_{10}) and k_0 is negative. Finally, if both the medium and the particles are colored, the situation is different depending on whether k_1 or k_2 is the greater. If $k_1<k_2$, then $m_0>(\mu_{20}/\mu_{10})$ and $k_0>0$, but if $k_1>k_2$, then $m_0>(\mu_{20}/\mu_{10})$ and $k_0<0$. The case when $k_1=k_2$ is especially interesting because $m_0=\mu_{20}/\mu_{10}$ and $k_0=0$. This means that the effect of the particles on the optical properties of the dispersed system for which $k_1=k_2$ can be treated theoretically as if the system is colorless, although actually the system is colored.

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

2) M. Nakagaki and T. Fujii, ibid., **34**, 433 (1961).

3) The optical density is usually defined by a common logarithm, but the natural logarithm is used throughout this paper.

Optical Density, Absorption and Scattering.—The optical density per unit layer thickness of the colored colloidal system is set as E_0, which may be measured, for example, by a Beckman-type photometer, using distilled water as the reference for an aqueous colloidal system. The difference in the optical densities per unit layer thickness between the colored colloidal system, E_0, and the colored medium, E_1, is set at E, which may be measured by using the colored medium (instead of distilled water) as the reference solution. Therefore,

$$E=E_0-E_1=-[\ln(I/I_1)]/l \tag{13}$$

where l is the layer thickness, I is the transmitted light through the colloidal system, and I_1 is the transmitted light through the dispersion medium. On the other hand,

$$E_0=-[\ln(I/I_0)]/l=E+4\pi k_1/\lambda \tag{14}$$

where I_0 is the intensity of the incident light and where the last term is obtained from Eqs. 3 and 5. The quantity E means the increment in the optical density as a result of the existence of the colloidal particles. In the special case where the medium is colorless ($k_1=0$), E is equal to E_0. When $k_0<0$ (that is, $k_2<k_1$), E will take a negative value, as will be shown later, except when the effect of scattering is sufficiently large.

The optical density increment per particle, E/N, is considered to be the sum of the scattering, R, and the absorption, A.

$$E/N = R + A \tag{15}$$

The parameters ε, κ, and ε_a will, however, be used because the concentration, c, is experimentally more convenient than the number of particles, N. Here,

$$\left.\begin{aligned} \varepsilon &= E/c \\ \kappa &= RN/c \\ \varepsilon_a &= AN/c \end{aligned}\right\} \tag{16}$$

The parameters x, y and z will be used, as in a previous paper.[1]

$$\left.\begin{aligned} x &= (\lambda\rho_2/3\pi)\varepsilon \\ y &= (\lambda\rho_2/3\pi)\kappa \\ z &= (\lambda\rho_2/3\pi)\varepsilon_a=x-y \end{aligned}\right\} \tag{17}$$

The theoretical values of the parameters x, y and z can be calculated according to the Mie theory.[4] The equations expanded in a power series of α and k_0 have already been given in a previous paper.[1] Numerical calculations according to these equations have been made for $\alpha=0$ (0.2) 0.8, $m_0=0.50$ (0.05) 1.50 and $k_0=-0.3$ (0.1) 0.3. The m_0-values smaller than 1.00 were included because, first, those values may be smaller than unity if k_1 is sufficiently greater than k_2 (cf. Eq. 9), even when (μ_{20}/μ_{10}) is greater than unity, and, second, (μ_{20}/μ_{10}) itself may be smaller than unity in such a case, as when, for examples, bubbles are dispersed in a liquid. The negative k_0-values were included because sometimes the medium is colored, as has been mentioned before. The results are shown in Fig. 1 for x, in Fig. 2 for y, and in Fig. 3 for z, although only the results for $m_0=1.50$, 1.00,

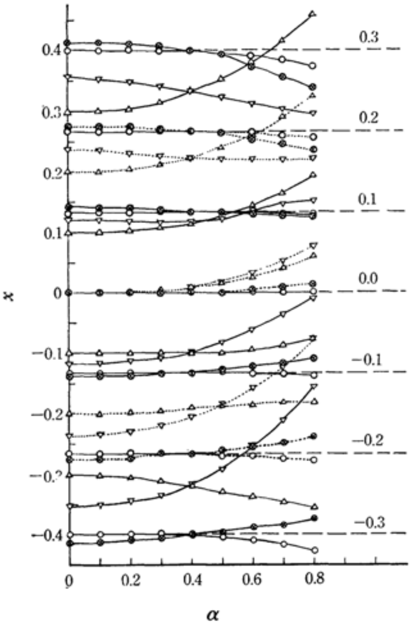

Fig. 1. Relation between x and α.
Parameter: k_0. $m_0=1.50$(△), 1.00(○), 0.8165 (⊗) and 0.50(▽). $k_0=0$ and $\pm$ 0.2(···); $\pm$ 0.1 and $\pm$ 0.3(—)

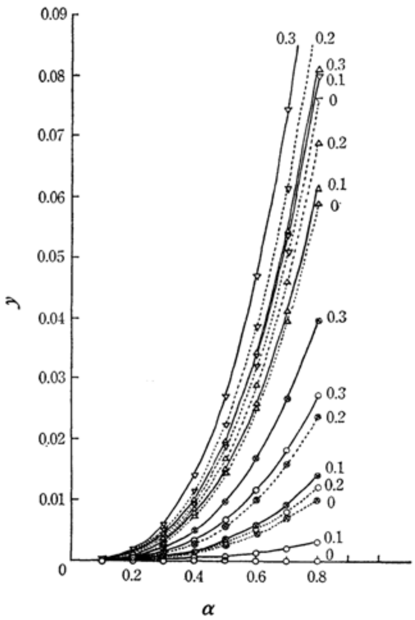

Fig. 2. Relation between y and α.
Parameter: $|k_0|$. $m_0=1.50$(△), 1.00(○), 0.8165 (⊗) and 0.50(▽). $|k_0|=0$ and 0.2(···), 0.1 and 0.3(—)

4) G. Mie, *Ann. Phys.*, (4), **25**, 377 (1908).

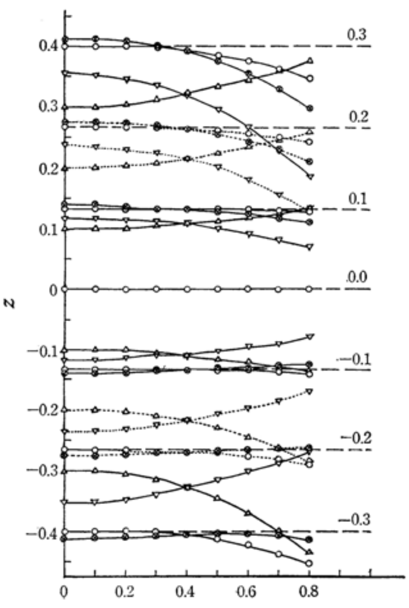

Fig. 3. Relation between z and α.
Parameter: k_0. $m_0=1.50(\triangle)$, $1.00(\bigcirc)$, 0.8165 $(\otimes)$ and $0.50(\bigtriangledown)$. $k_0=0$ and $\pm$ 0.2(⋯), $\pm$ 0.1 and $\pm$ 0.3(—)

0.8165 (corresponding to the maximum of ζ_0, as will be discussed later) and 0.5 will be shown in order to keep the figures simple. The horizontal broken lines in Figs. 1 and 3 are the limitting values where m_0 is 1.00 and α is sufficiently small; that is:

$$\left.\begin{aligned} x(m_0=1.00;\ \alpha=0)=z(m_0=1.00;\ \alpha=0)=(4/3)k_0 \\ y(m_0=1.00;\ \alpha=0)=0 \end{aligned}\right\} \tag{18}$$

When the medium is colorless, these values are equal to the values for the bulk phase of the dispersed material;

$$\left.\begin{aligned} x_2(\text{bulk})=z_2(\text{bulk})=(4/3)\,(\mu_{20}/\mu_{10})k_2 \\ y_2(\text{bulk})=0 \end{aligned}\right\} \tag{19}$$

but when the medium is colored, the limiting value of Eq. 18 is not equal to the values of Eq. 19 for the bulk phase.

After the author had published a previous paper,[1] Chromey[5] made computations based on the exact Mie theory for $\alpha=0.2$ (0.2) 2.0; $m_0=0.50$ (0.25) 3.00, and $k=(k_0/m_0)=0.0$ (0.1) 1.0. The results agree with each other in the range discussed in the present paper as far as comparison is possible, although Chromey never treated the case of $k_0<0$.

The effect of k_0 on the quantities x, y and z

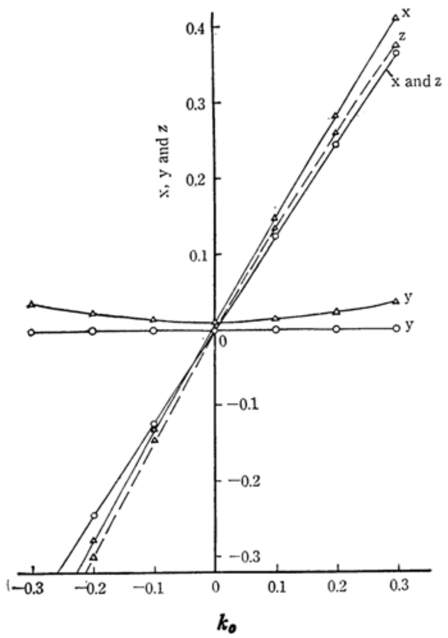

Fig. 4. Relation between x, y and z vs. k_0
$\alpha=0(\bigcirc)$ and $0.8(\triangle)$; $m_0=1.20$

can be seen from Fig. 4. The figure illustrates the case of $m_0=1.20$, which is close to the m_0-values for a polymer latex dispersed in an aqueous solution. In the range of small k_0-values, both x and z are approximately linear with regard to k_0. The line for z passes the origin, but the line for x does not, because x is the sum of y and z, and y is not zero, even when k_0 is zero, if $\alpha\neq0$.

If k_0 is small, the value of z is proportional to k_0. The proportionality constant, ζ, is defined by:

$$\zeta\ =\ \lim_{k_0\to0}(z/k_0) \tag{20}$$

If there were no effect of scattering, ζ should be equal to 4/3, as is shown in Eq. 18. The actual

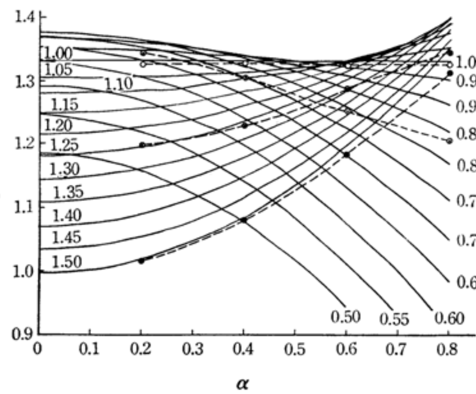

Fig. 5. Relation between ζ and α.
Parameter: m_0. Chromey's date for $m_0=0.75$ $(\odot)$, $1.00(\bigcirc)$, $1.25(\otimes)$, $1.50(\bullet)$

5) F. C. Chromey, *J. Optical Soc. Am.*, **50**, 730 (1960). The symbols Ω, $(\Omega-\Omega')$, Ω' and x in his paper correspond, respectively, to x, y, z and k in our notation, although he erroneously states that Ω' is pure scattering.

ζ-value, however, depends on both the relative particle size, α, and the relative refractive index, m_0, as is shown in Fig. 5. The results of the numerical calculation may be compared with the values obtained by extrapolating Chromey's data.[6] Fairly good agreement is observed, except when α exceeds 0.6. The value of ζ for very small particles, ζ_0, depends on m_0, as is shown in Fig. 6. ζ_0 takes a maximum value ($\zeta_0(\max)=1.377838$)

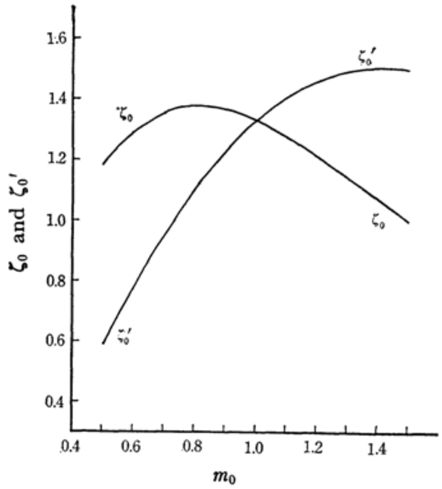

Fig. 6. Relation between ζ_0 and ζ_0' vs. m_0.

at $m_0=\sqrt{2/3}$. Sometimes the quantity k, instead of k_0, is taken as the variable. Then:

$$\zeta_0' = \lim_{\substack{k\to 0\\ \alpha\to 0}} (z/k) \tag{21}$$

should be used instead of ζ_0. The value of ζ_0', too, is shown in Fig. 6, which takes a maximum value ($\zeta_0'(\max)=3/2$) at $m_0=\sqrt{2}$. The values of ζ_0 and ζ_0' are the same and are equal to 4/3 at $m_0=1$, since $k_0=m_0k$.

The scattering (expressed by the quantity y as has already been shown in Fig. 2) is proportional to the cube of the relative particle radius, as far as the present approximation is concerned.

$$y = Y\alpha^3 \tag{22}$$

The coefficient Y depends on both m_0 and k_0, as is shown in Fig. 7, and its value is the greater, the greater $|m_0-1|$ is and the greater $|k_0|$ is. The scattering is, thus, caused by the refraction and absorption. The Y-value for $k_0=0$ is considered to represent the scattering caused by the refraction and is expressed by Y_m, while the Y-value for $m_0=1$ is considered to represent the scattering caused by the absorption and is expressed by Y_k. The actual Y-value is, however, not equal to the sum of Y_m and Y_k; a cross term, Y_{mk}, is also required.

$$Y = Y_m + Y_k + Y_{mk} \tag{23}$$

6) His data for $m_0=1.25$, $k=0.2$ and $\alpha=0.2$ are in error. These values were, therefore, disregarded in the extrapolation.

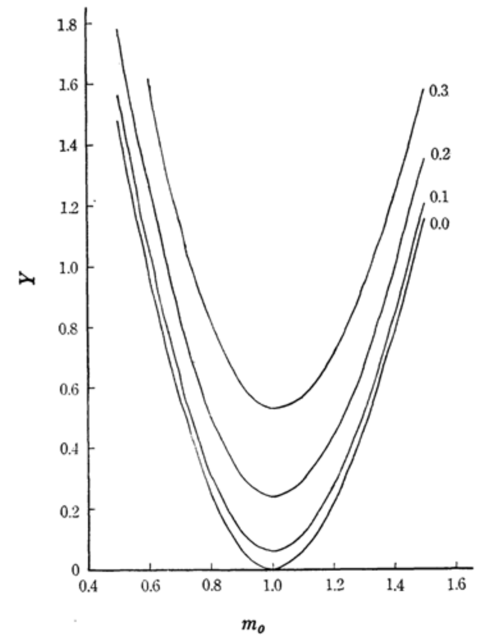

Fig. 7. Relation between Y and m_0. Parameter: $|k_0|$

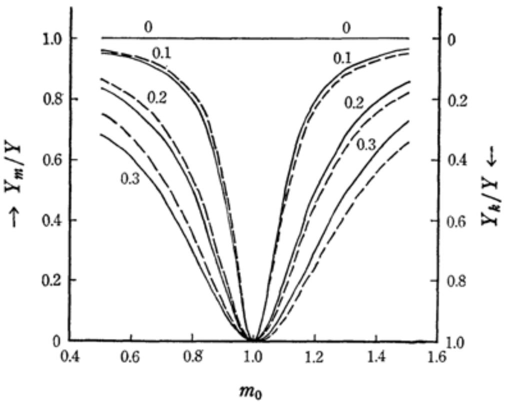

Fig. 8. Dependence of Y_m/Y(—) and Y_k/Y(⋯) on m_0. Parameter: $|k_0|$

In Fig. 8, the ratio Y_m/Y (solid lines) is shown on the left ordinate in an upward direction, while the ratio Y_k/Y (broken lines) is shown on the right ordinate in a downward direction. It may be seen from Fig. 8 that the cross term, Y_{mk}, is negative when $m_0>1$ and positive when $m_0<1$. The value of Y_{mk}/Y is not large, although it is not equal to zero except when $m_0=1$ or $k_0=0$.

The Refractive Index of the Dispersed System.—It has been well established experimentally that the refractive index of a dispersed system, μ_{12}, is linear to the concentration, c, (g./ml.), at least within the concentration range of the usual experimental conditions. This can be explained by the mixture rule:

$$\mu_{12} = \mu_{10}\varphi_1 + \mu_{20}'\varphi_2 \quad (24)$$

because the rule yields the following equation, which states that $\partial\mu_{12}/\partial c$ is constant:

$$\partial\mu_{12}/\partial c = (\mu_{20}' - \mu_{10})/\rho_2 \quad (25)$$

where φ_1 and φ_2 are the volume fractions of the medium and the dispresed phase respectively, and where ρ_2 is the density of the dispersed phase. The apparent refractive index of the particle μ_{20}' is, however, not equal to the refractive index of the dispersed phase, μ_{20} (the real part of the complex refractive index as defined by Eq. 2) because the refractive index is affected by light scattering, as has already been stated by the author and Heller.[7]

The value of the apparent relative refractive index

$$m' = \mu_{20}'/\mu_{10} \quad (26)$$

can be calculated on the basis of the Mie theory, as has been stated in previous papers.[2,7] In the case of $\alpha \ll 1$ and $|k_0| \ll m_0$, the equation was expanded in a power series of k_0 and the coefficients of the power series were expressed[2] as known functions of m_0 and α. Numerical calculation has been made for $\alpha = 0$ (0.1) 0.8, $m_0 = 0.85$ (0.05) 1.50 and $k_0 = -0.3$ (0.1) $+0.3$. The m_0-values smaller than unity and the negative k_0-values were included in order to consider the case where the medium is colored. Only some of the results, for $k_0 = -0.3$, 0 and $+0.3$, are shown in Fig. 9 in order to keep the figure simple. When k_0 is equal to zero, or when the system is colorless,

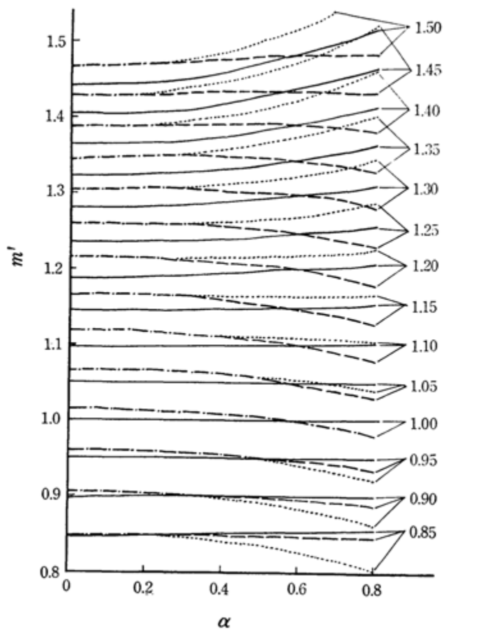

Fig. 9. Relation between m' and α.
Parameter: m_0. $k_0 = +0.3$(---), 0(—), -0.3(···)

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

the value of m' increases[8] with the α, and the increment is the greater, the greater $|m_0 - 1|$ is. When k_0 is not equal to zero, or when the system is colored, the value of m' increases or decreases with α, depending on the values of m_0 and k_0. When α approaches zero, the value of m' depends on the absolute value of k_0. When α is not so small, the value of m' depends not only on the absolute value but also on the sign of k_0. If k_0 is so small that the term k_0^2 can be neglected, then:

$$m' = m_0'(1 - fk_0) \quad (27)$$

where m_0' is the m'-value for $k_0 = 0$. The value of the coefficient f is shown in Fig. 10. The value

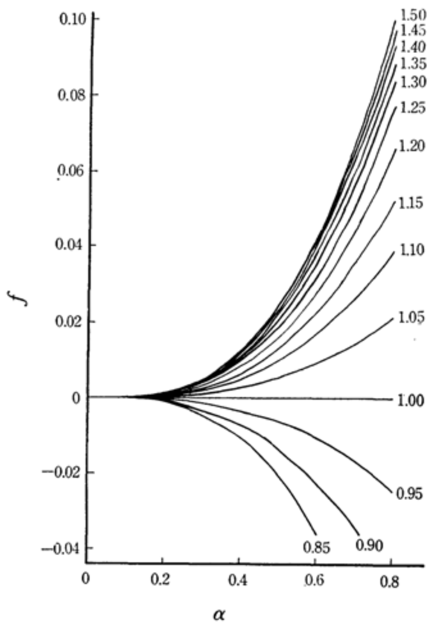

Fig. 10. Relation between f and α.
Parameter: m_0

of f is positive for $m_0 > 1$ and negative for $m_0 < 1$, and the absolute value of f increases with the α.

A Note on the Usual Experimental Conditions for the System of a Colored Medium.— The value of k_0 may be very large if the particles are colored. It may even be infinitely large if the particles are made of a good conductor, but the extinction of the dispersed system as a whole can be made as small as possible in experimental work by diluting the dispersed system. If, however, the medium is colored and the particles are colorless, the absolute value of k_0 cannot be very large, because a certain detectable amount of light must pass through the layer of the dispersed system. If k_0 is not small, an extremely strong light source is needed.

Considering a layer of a colored medium, the value of, for example, $k_1 = 0.76 \times 10^{-4}$ is obtained

8) The value of m' passes a maximum point when α increases further. (Cf. Ref. 7)

according to Eq. 3, if the optical density $-\log (I_1'/I_0')$ is 3.00, the layer thickness is 0.30 cm., the refractive index of the medium is $\mu_{10}=1.333$ (water), and the wavelength of the light is $\lambda_0=555$ mμ (the most sensitive wavelength for the human eye). This gives the result that $k_0=-0.91\times 10^{-4}$ if $k_2=0$ and if $\mu_{20}/\mu_{10}=1.20$. Therefore, extremely small k_0-values are interesting experimentally.

The scattered-light intensity of a colored colloidal system, of course, decreases by the term $\exp.(-E_0 l)$ according to the Lambert law, where l is the path length of light in the colloidal system. However, after this decrease in light intensity ash been corrected properly, the scattered-light intensity of a colored colloidal system should be almost exactly equal to that of a colorless system which has the same m_0 and α values. This is obvious because, according to Fig. 4, the x, y and z values for such small k_0 value as 10^{-4} are practically equal to those for $k_0=0$. According to Eq. 27 and the f value shown in Fig. 10, it is obvious that the value of the refractive index of the colored system is also practically equal to that of the colorless system if k_0 is as small as 10^{-4}.

Summary

In the expression of the complex refractive index of a colored colloidal system ($m=m_0-ik_0$), the value of m_0 may be smaller than unity and k_0 may be negative if the medium is colored. Including these cases, the values of x (corresponding to the optical density), y (scattering) and z (absorption) have been calculated for relatively small α and k_0 values. The values of the apparent relative refractive index, m', have been calculated also. These results have been discussed in detail in order to show the effect of the scattering and absorption on the scattering, absorption and apparent refractive index. It has been concluded that the data of a system in which colorless particles are dispersed in a colored medium will be practically equal to those in a colorless medium if the extinction of light according to the Lambert law is corrected properly.

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