Theoretical Studies of Light Scattering by Polydispersed Colloidal Systems of Spherical Particles[1]

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Recently light scattering has been widely used as a useful method to determine the size of colloidal particles. The method has become available as a result of the extensive improvement of experimental techniques and the development of theoretical information, at least, for monodispersed systems. Actual colloidal systems are, however, polydispersed, and their particle-size distribution is yet to be determined. For this purpose, it is, of course, desirable to determine the entire shape of the distribution curve experimentally, but that would require a great deal of experimental data of a very high precision. Therefore, one must often be satisfied with the determination of the values of a few parameters in an approximate presupposed equation and with the determination of a kind of average particle size. This approximate method is not unsatisfactory if the actual distribution curve has one maximum only. Heller et al. assumed a special shape of the distribution

1) Presented before the 14th Discussion of Colloid Chemistry, Ueda, October, 1961, and the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

function containing two parameters and studied the polarization ratio[2] and the turbidity.[3] Dettmar et al.[4] calculated the specific turbidity for the log-normal distribution of two parameters.

In the experiments of light scattering, howvever, the specific scattering intensity and the dissymmetry factor are frequently measured. Therefore, the effect of polydispersity on these quantities is of interest. The results obtained by using a three-parameter distribution function will be reported here.

Theoretical

Presupposed Distribution Curve.—If the distribution curve of the particle size has one maximum point, the distribution maximum, the width of the distribution and the dissymmetry of the distribution curve will be of main interest. A modified Gaussian curve containing the above-mentioned three parameters was used in the present experiment.

In the study of light scattering by colloidal spheres, the relative particle size:

$$\alpha = 2\pi r/\lambda \tag{1}$$

is used, where r is the particle radius and λ is the wavelength of light in the dispersion medium. The particle-size distribution in weight, $W(\alpha)$, is assumed to have its maximum point at α_m, and for $\alpha<\alpha_m$ the function $W(\alpha) = W_1(\alpha)$ is a Gaussian function with the standard deviation of $\varDelta\alpha_1$, and for $\alpha<\alpha_m$ the function $W(\alpha)=W_2(\alpha)$ is that with $\varDelta\alpha_2$. Therefore, by using the average width of the distribution,

$$\langle\varDelta\alpha\rangle = (\varDelta\alpha_1+\varDelta\alpha_2)/2 \tag{2}$$

and the dissymmetry of the distribution,

$$\varDelta = \varDelta\alpha_1 - \varDelta\alpha_2 \tag{3}$$

the distribution in weight will be;

$$\left.\begin{array}{l} W_1(\alpha) = (1/\langle\varDelta\alpha\rangle)\phi(x_1) \\ x_1 = (\alpha-\alpha_m)/\varDelta\alpha_1 \end{array}\right\} \text{ for } \alpha>\alpha_m \tag{4}$$

and

$$\left.\begin{array}{l} W_2(\alpha) = (1/\langle\varDelta\alpha\rangle)\phi(x_2) \\ x_2 = (\alpha_m-\alpha)/\varDelta\alpha_2 \end{array}\right\} \text{ for } \alpha<\alpha_m \tag{5}$$

where the function ϕ is the normalized Gaussian function;

$$\phi(x) = (1/\sqrt{2\pi})\exp(-x^2/2) \tag{6}$$

Mathematically, the function $W_2(\alpha)$ extends to the negative of α, and the $W(\alpha)$ given above by the combination of Eqs. 4 and 5 is normalized over the range from $-\infty$ to $+\infty$. Actually, however, the size distribution function should tend to zero when the α value approaches zero and should be meaningless for a negative value of α. Therefore, Eq. 5 is to be used only for $0<\alpha<\alpha_m$, and the functions of Eqs. 4 and 5 are to be re-normalized by dividing them with a factor $(\varDelta\alpha_1/2\langle\varDelta\alpha\rangle + f\varDelta\alpha_2/2\langle\varDelta\alpha\rangle)$, where

$$f = 2\int_{-\alpha_m/\varDelta\alpha_2}^{0}\phi(x)\mathrm{d}x \tag{7}$$

In this method, the value of $W_2(0)$ is not equal to zero. This discrepancy, is, however not serious in practice because the scattered light intensity rapidly decreases to zero when α decreases to zero.

Calculation of Mean Values. — The mean value, $\langle G\rangle$, of a quantity, G, for the presupposed distribution of the particle size can be calculated by the equation:

$$\langle G\rangle = (g_1+g_2)/(\varDelta\alpha_1+f\varDelta\alpha_2) \tag{8}$$

where

$$\left.\begin{array}{l} g_1 = 2\langle\varDelta\alpha\rangle\displaystyle\int_{\alpha_m}^{\infty}GW_1(\alpha)\mathrm{d}\alpha \\ g_2 = 2\langle\varDelta\alpha\rangle\displaystyle\int_{0}^{\alpha_m}GW_2(\alpha)\mathrm{d}\alpha \end{array}\right\} \tag{9}$$

For the numerical calculation of g_1 and g_2 in this paper, the entire range of α is divided into equal intervals of $(\delta\alpha)=0.2$ and approximate summations instead of integrations were made because the numerical values of the scattered light intensity were available only at this interval of α. Therefore

$$\left.\begin{array}{l} g_1 = 2(\delta\alpha)\displaystyle\sum_{x_1=0}^{\infty}G\phi(x_1) \\ g_2 = 2(\delta\alpha)\displaystyle\sum_{x_2=0}^{\alpha_m/\varDelta\alpha_2}G\phi(x_2) \end{array}\right\} \tag{10}$$

In these summations, the terms for $x_1=0$ and $x_2=0$ were multiplied by 1/2 because the same term is included in both summations, g_1 and g_2.

The Specific Scattering Intensity and Dissymmetry Factor. — The quantities measured most often in the study of colloidal systems are the specific scattering intensity,[5] J_θ/I_0c, and the dissymmetry factor, z, where J_θ is the intensity per unit solid angle of the light scattered at the angle,[6] θ; I_0 is the intensity of the incident beam, and c is the concentration of the dispersed phase in g./100 ml. The

2) A. F. Stevenson, W. Heller and M. L. Wallach, *J. Chem. Phys.*, **34**, 1789 (1961); W. Heller and M. L. Wallach, *J. Phys. Chem.*, **67**, 2577 (1963).

3) M. L. Wallach, W. Heller and A. F. Stevenson, *J. Chem. Phys.*, **34**, 1796 (1961).

4) H.-K. Dettmar, W. Lode and E. Marre, *Kolloid-Z.*, **188**, 28 (1963).

5) The value extrapolated to the infinite dilution should be compared with the theoretical value.

6) The scattering angle, γ, usually used in the case of a colloidal system according to Mie is related to the angle, θ, used here by the equation: $\gamma=180°-\theta$.

specific scattering intensity can be expressed theoretically by

$$J_\theta/I_0c=(N/c)(\lambda^2/4\pi^2)i_\theta \qquad (11)$$

where N is the number of particles per unit of volume and i_θ is the function defined elsewhere.[7] If the system is polydispersed, the observed specific scattering intensity should be an average value defined by:

$$\langle J_\theta\rangle/I_0c=(\lambda^2/4\pi^2c)\langle Ni_\theta\rangle \qquad (12)$$

or, by using Eq. 1;

$$\langle J_\theta\rangle/I_0c=(3/200\lambda\rho_2)\langle i_\theta/\alpha^3\rangle \qquad (13)$$

where ρ_2 is the density of the dispersed phase. For the sake of the simplicity of numerical computation, a quantity, Y_θ, is used, which is to be determined experimentally by:

$$Y_\theta=(200/3)\lambda\rho_2\langle J_\theta\rangle/I_0c \qquad (14a)$$

and computed theoretically by;

$$Y_\theta=\langle i_\theta/\alpha^3\rangle \qquad (14b)$$

The dissymmetry factor, z, is:

$$z=Y_{45}/Y_{135}=\langle i_{45}/\alpha^3\rangle/\langle i_{135}/\alpha^3\rangle \qquad (15)$$

Results and Discussion

Numerical Values of Y_θ and z.—Numerical values of Y_{45}, Y_{90}, Y_{135} and z for unpolarized light have been calculated according to Eqs. 8, 10, 14b and 15 for $m=1.20$ and $\alpha_m=0$ (0.2) 3.0, and for $\varDelta\alpha_1=0$ (0.2) 1.0 and $\varDelta\alpha_2=0$ (0.2) 1.0. For the calculations, the values of i_θ/α^3 were taken from the table published by Pangonis and Heller[8] for $\alpha=0$ (0.2) 7.0 for monodispersed systems. Some of the results of the computation are shown in the following figures.

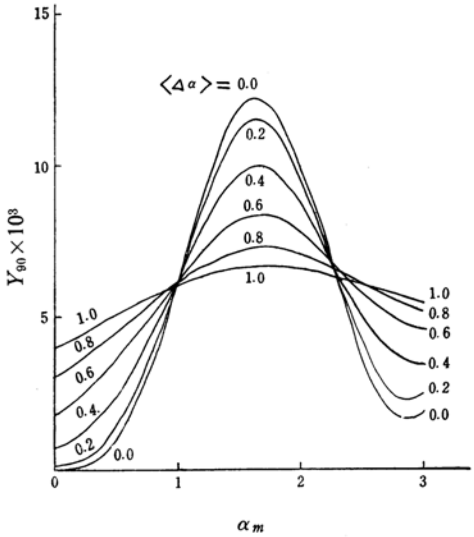

Fig. 1. Relation between Y_{90} vs. α_m for $m=$ 1.20, $\varDelta=0$ and for various $\langle\varDelta\alpha\rangle$ values.

Figure 1 shows the relation between Y_{90} and α_m when $\varDelta=0$ and $\langle\varDelta\alpha\rangle=0$ (0.2) 1.0. Each curve of Y_{90} vs. α_m has a maximum point at about $\alpha_m=1.6\sim1.7$; this curve becomes less steep as the $\langle\varDelta\alpha\rangle$ value increases. The value of Y_{90} is mostly independent of $\langle\varDelta\alpha\rangle$ at about $\alpha_m=0\sim1.0$ and $\alpha_m=2.3$. According to a figure (not shown here) designed to illustrate the relation between Y_{45} and α_m for $\varDelta=0$ and $\langle\varDelta\alpha\rangle=0$ (0.2) 1.0, it is concluded that the Y_{45} increases monotonously in the range of $\alpha_m=3.0$. The curves become less steep as the

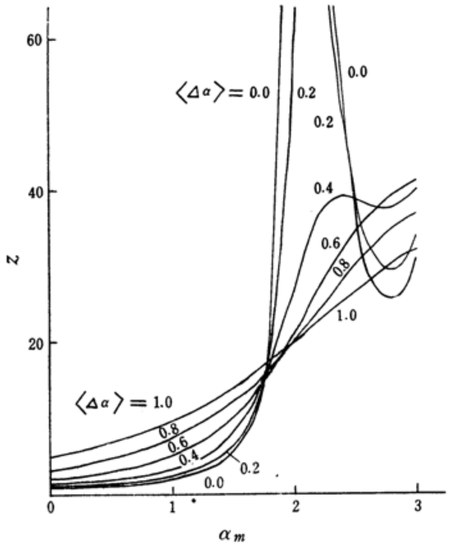

Fig. 2. Relation between z and α_m for $m=$ 1.20, $\varDelta=0$ and for various $\langle\varDelta\alpha\rangle$ values.

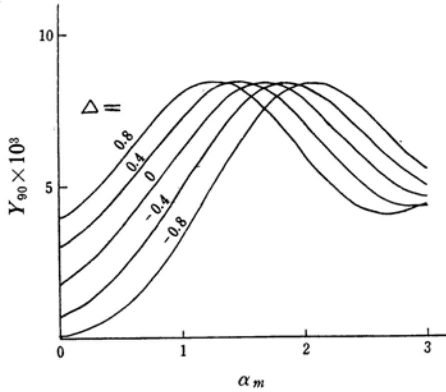

Fig. 3. Relation between Y_{90} and α_m for $m=$ 1.20, $\langle\varDelta\alpha\rangle=0.6$ and for various $\varDelta$ values.

7) E. g., W. Heller, M. Nakagaki and M. L. Wallach, *J. Chem. Phys.*, 30, 444 (1959).

8) W. J. Pangonis, W. Helleer, "Angular Scattering Functions for Spherical Particles," Wayne State University Press, Detroit, U. S. A. (1960).

$\langle \Delta\alpha \rangle$ values increase. The value of Y_{45} is mostly independent of $\langle \Delta\alpha \rangle$ at about $\alpha_m=1.85$. According to a figure (not shown here) designed to illustrate the relation between Y_{135} and α_m for $\Delta=0$ and $\langle \Delta\alpha \rangle=0$ (0.2) 1.0, it is concluded that each curve of Y_{135} vs. α_m has a maximum point at about $\alpha_m=1.3$, a minimum point at about $\alpha_m=2.15$, and another maximum point at about $\alpha_m=2.8$, when $\langle \Delta\alpha \rangle$ is not too large. The curves become less steep as the $\langle \Delta\alpha \rangle$ values increase. The values of Y_{135} at about $\alpha_m=0.75$, 1.75, and 2.5 are mostly independent of $\langle \Delta\alpha \rangle$.

The dissymmetry factor, z, for $m=1.20$ is shown in Fig. 2 for $\Delta=0$ and $\langle \Delta\alpha \rangle=0$ (0.2) 3.0. In the range of $\alpha_m=0\sim3.0$, the z value has a maximum point at about $\alpha_m=2.2$ and a minimum point at about $\alpha_m=2.8$. The greater the $\langle \Delta\alpha \rangle$, the lower the maximum point becomes; at last the curve comes to increase monotonously with α_m when $\langle \Delta\alpha \rangle \geq 0.6$. The variation of z with $\langle \Delta\alpha \rangle$ is small at about $\alpha_m=1.75$.

The change in the quantities due to the variation of $\Delta=-0.8(0.4)+0.8$ were then studied. As is shown in Fig. 3, the curve of Y_{90} vs. α_m for $m=1.20$ and $\langle \Delta\alpha \rangle=0.6$ has one maximum in the range $\alpha_m=0\sim3.0$; the curve is shifted to the left when $\Delta>0$, and to the right when $\Delta<0$, with the increase in $|\Delta|$. Similar shifts of curves were also observed in the cases of Y_{45} vs. α_m, Y_{135} vs. α_m and z vs. α_m (not shown here).

A Method to Determine the Parameter Values of the Distribution Functions. — The distribution function of the particle size presupposed previously had three parameters, α_m, $\langle \Delta\alpha \rangle$ and Δ. The three parameters can, in principle, be determined experimentally if three independent quantities, for example, Y_{90}, Y_{45}

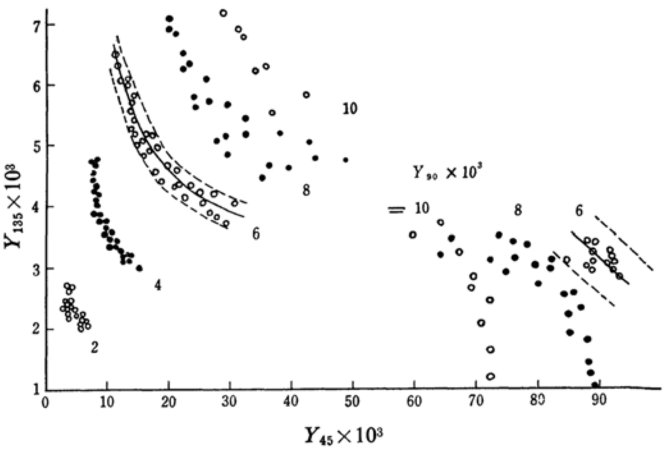

Fig. 4. Relation between Y_{45} and Y_{135} for various Y_{90} values of $m=1.20$.

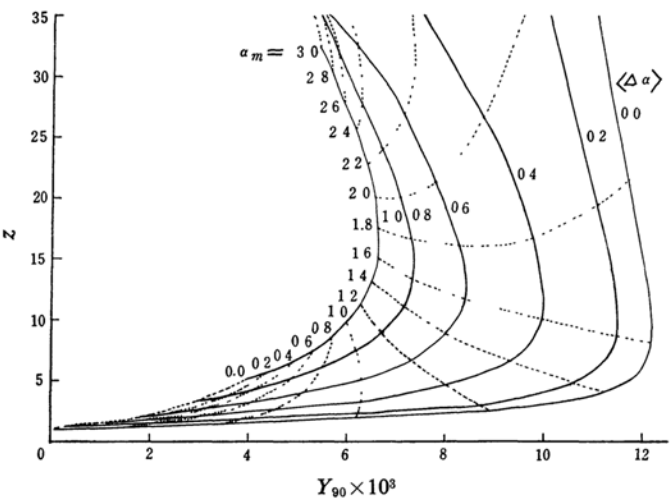

Fig. 5. Relation between z and Y_{90} for $m=1.20$.

and Y_{135}, are measured with sufficient accuracy. In practice, however, the extent of the accuracy required for the procedure should be examined. In this connection, the values of Y_{45} and Y_{135} corresponding to several fixed values of Y_{90} are plotted[9] in Fig. 4 on the basis of the previously-computed values of Y_{90}, Y_{45} and Y_{135} for various α_m, $\langle \Delta\alpha \rangle$ and Δ values. The points for a given Y_{90} value are located in two separate regions, because the Y_{90} vs. α_m relation has a maximum. If the three quantities Y_{90}, Y_{45} and Y_{135} are entirely independent of each other and if all of three parameters α_m, $\langle \Delta\alpha \rangle$ and Δ can be determined experimentally, the points for a given Y_{90} value should be distributed over a sufficiently wide region on the $Y_{45}-Y_{135}$ plane. The actual distribution of the points, however, is not extended over a region, but is collapsed mostly on either one of two lines, as is shown in Fig. 4. If one assumes lines as drawn arbitrarily for the sake of illustration in Fig. 4, for example, for $Y_{90}=6\times10^{-3}$, one should be able to determine accurately the distance of points from these lines in order to be able to estimate the three parameter values experimentally. If the experimental errors of both Y_{45} and Y_{135} are as much as $\pm5\%$, the experimental values would be scatterd between the dotted lines in Fig. 4. This makes the experimental determination of the distance from the lines impossible when $\langle \Delta\alpha \rangle$ is smaller than 1.0 and $|\Delta|$ is smaller than 0.8. The accuracy of the experiment should be better than $\pm0.2\%$ in order to be able to determine three parameters with an accuracy of about $\pm4\%$.

If the accuracy of the experiment is not very good, as is described above, one must be satisfied with a distribution function of two parameters. The parameters to be adopted would be α_m and $\langle \Delta\alpha \rangle$ by assuming $\Delta=0$. This means that the distributsion of the particle radius is approximated by the usual Gaussian function. The two parameters, α_m and $\langle \Delta\alpha \rangle$, can be determined by measuring two independent quantities, for example, Y_{90} and z as in the usual light-scattering studies, on the basis of a chart such as Fig. 5 for $m=1.20$, constructed by using the results of the theoretical computation. The multivaluedness of α_m for a given Y_{90} value or the existence of a maximum point in the Y_{90} vs. α_m relation as shown in Fig. 1 or 3 does not make the analysis ambiguous if the maximum is only one or if the α_m value is less than 3.0, because the z values corresponding to the ascending and descending branches of the $Y_{90}-\alpha_m$ curve are different each other. In Fig. 5, the line for $\alpha_m=1.0$ is almost vertical because the dependence of Y_{90} on $\langle \Delta\alpha \rangle$ is small for this α_m value, and the line for $\alpha_m=1.8$ is almost horizontal because the dependence of z on $\langle \Delta\alpha \rangle$ is small for this α_m value, as has been described above.

Weight-averaged Particle Radius. — As a measure of the particle size, the α_m value corresponding to the most probable particle radius has been used so far. In light-scattering studies, however, the weight-average molecular weight is usually determined, especially for high polymer solutions. In the case of

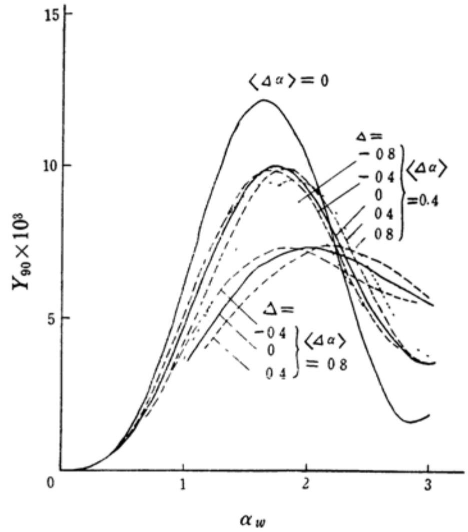

Fig. 6. Relation between Y_{90} and α_w for $m=1.20$.

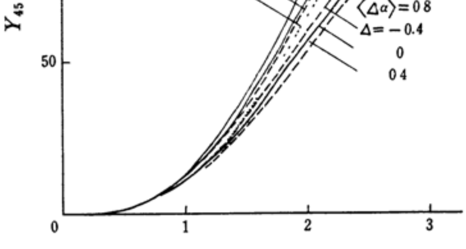

Fig. 7. Relation between Y_{45} and α_w for $m=1.20$.

9) A given value of Y_{90} corresponds to one or two (since Y_{90}-α_m relation has a maximum) values of α_m for each set of ($\langle \Delta\alpha \rangle$, Δ), and each set of (α_m, $\langle \Delta\alpha \rangle$, Δ) gives the corresponding Y_{45} and Y_{135} values.

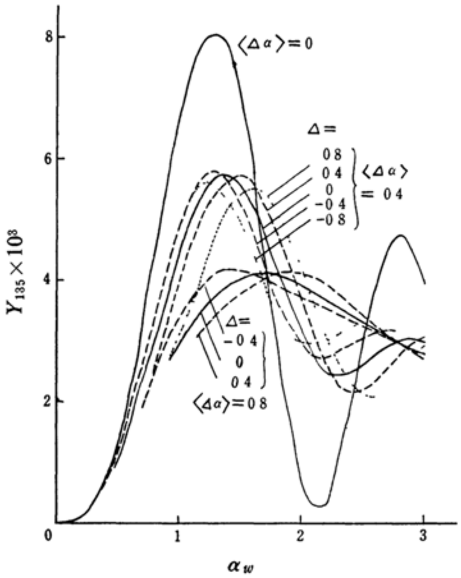

Fig. 8. Relation between Y_{135} and α_w for $m=1.20$.

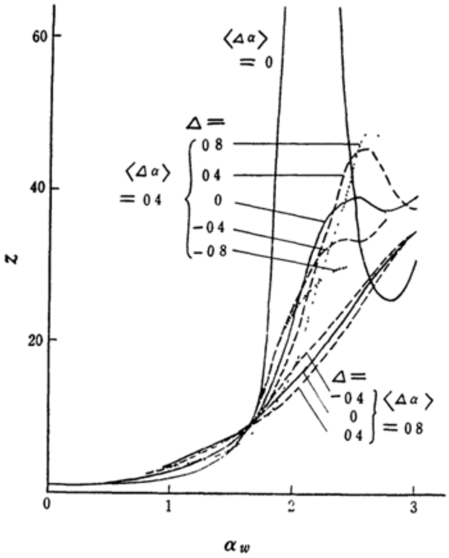

Fig. 9. Relation between z and α_w for $m=1.20$.

colloidal systems, too, the weight-averaged α^3 value may be preferable. Therefore, the cubic root of the weight-averaged α^3 value:

$$\alpha_w=\sqrt[3]{\langle\alpha^3\rangle} \tag{16}$$

may be used as a measure of the particle size of a polydispersed system. The theoretical value of $\langle\alpha^3\rangle$ for the presupposed distribution function was calculated according to Eqs. 8 and 10 for various α_m, $\langle\Delta\alpha\rangle$ and Δ values, and the previously discussed Y_θ and z vs. α_m relations were redrawn to Y_θ and z vs. α_w relations. The results of Y_{90} vs. α_w are shown in Fig. 6, those for Y_{45} vs. α_w in Fig. 7 those for Y_{135} vs. α_w in Fig. 8, and those for z vs. α_w in Fig. 9 for $m=1.20$ and for several combinations of $\langle\Delta\alpha\rangle$ and Δ. From these figures, it may be concluded: (1) the curves are mostly dependent on neither $\langle\Delta\alpha\rangle$ nor Δ if α_w is small. They coincide with the curve of $\langle\Delta\alpha\rangle=0$, although the deviation from the latter becomes the greater, the larger the α_w value; (2) the shape of the curves is determined mainly by the value of $\langle\Delta\alpha\rangle$; (3) the curves are shifted to either side when the Δ value comes to be different from zero, but the effect of Δ is not as great as that of $\langle\Delta\alpha\rangle$.

The fact that the curves coincide with each other when α_w is small is a natural consequence of Rayleigh's theory. Therefore, the value of α_{obs} obtained experimentally from the observed Y_θ values on the basis of the theoretical Y_θ vs. α relation of a monodispersed system is equal to α_w for a polydispersed system when the α_{obs} is smaller than about 0.6. When the value of α_{obs} is greater than about 0.6, however, another method is required to obtain the α_w value from the experimental Y_θ and z values.

An Empirical Method to Determine α_w.— When the Y_{90} value of a polydispersed system is measured, the values of α_{90} and z_{90} are determined where α_{90} and z_{90} are the α and z values of a monodispersed system having the same Y_{90} value as the polydispersed system.

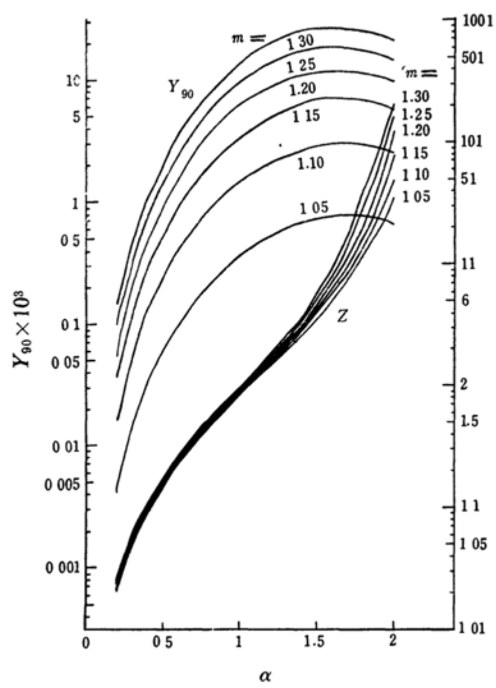

Fig. 10. Relations between Y_{90} and Z vs. α.

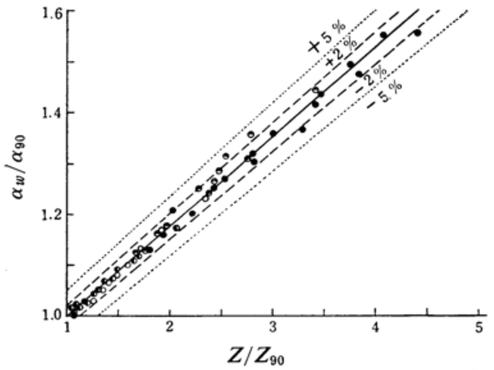

Fig. 11. Relation between α_w/α_{90} and Z/Z_{90} for $m=1.20$ and for $\langle\Delta\alpha\rangle=0.4$, $\Delta<0$ (◐), $=0$ (○), <0 (◓) and for $\langle\Delta\alpha\rangle=0.8$ (●).

For this purpose Fig. 10 may be used. In it the theoretical Y_{90} value is plotted on the left-side ordinate in a log scale, while the theoretical z value is plotted on the right-side ordinate in a $\log(z-1)$ scale, for various m-values of the monodispersed system. From Fig. 10, the values of α_{90} and z_{90} corresponding to the Y_{90}(obs) can be read off by using the curve for the m value of the system.

The Y_{90} and z values supposed to be measured for various polydispersed systems of $m=1.20$ can be obtained from the theoretical results described in the preceding paragraphs of this paper. By using these values and Fig. 10, it may be empirically concluded, as is shown in Fig. 11, that a linear relation holds approximately between α_w/α_{90} and z/z_{90}, at least within the range of $\langle\Delta\alpha\rangle$ and Δ values examined in this paper. Therefore, the following empirical equation:

$$\alpha_w/\alpha_{90}=1+k(z/z_{90}-1) \quad (17)$$

is obtained with $k=0.176$ for $m=1.20$. This relation can then be used in order to determine the α_w value from the experimentally-determined Y_{90} and z values. In order to see the extent of the error arising in this method, the curves corresponding to errors of $\pm2\%$ and $\pm5\%$ are drawn on Fig. 11. Almost all points are located within the range of $\pm2\%$ precision. It was estimated, further, that the error was within 2% for $\alpha_w<1.2$ if $\langle\Delta\alpha\rangle=0.4$ and $\Delta=\pm0.8$ or if $\langle\Delta\alpha\rangle=0.8$ and $\Delta=\pm0.4$, and within 5% for $\alpha_w<1.5$ for the same $\langle\Delta\alpha\rangle$ and Δ values.

Similar studies have been made for other m values; the values of k thus obtained are shown in Table I. The error was not very dependent on the m values and was within 2% for $\alpha_w<1.5$ and within 5% for $\alpha_w<1.6$ if $\langle\Delta\alpha\rangle=0.4$ and $\Delta=0$.

TABLE I. COEFFICIENTS k FOR VARIOUS m-VALUES

m	k	m	k
1.05	0.207	1.20	0.176
1.10	0.192	1.25	0.172
1.15	0.182	1.30	0.169

Summary

In order to study the light scattering of polydispersed colloidal systems of spherical particles, a weight distribution function, $W(\alpha)$, of the relative particle radius α has been assumed to be a modified Gaussian function with three parameters: the most probable α-value, α_m; the width of the distribution, $\langle\Delta\alpha\rangle$, and the dissymmetry of the distribution, Δ. The values of Y_θ, which is proportional to the specific scattering intensity, for $\theta=45°$, 90° and 135°, and the dissymmetry factor, $z=Y_{45}/Y_{135}$, have then been computed.

In principle, it should be possible to determine three parameters of the particle size distribution, α_m, $\langle\Delta\alpha\rangle$ and Δ, from the observed values of three independent quantities, Y_{45}, Y_{90} and Y_{135}. It has, however, been concluded that practically the method requires very precise experiments. If one is satisfied with a distribution function of two parameters, α_m and $\langle\Delta\alpha\rangle$, the values of these parameters can be determined from the experimentally-obtained Y_{90} and z values on the basis of a chart constructed theoretically.

The value of α_w, which is the cubic root of weight-averaged $\langle\alpha^3\rangle$, is equal to the α value obtained from the measured specific scattering intensity by assuming that the system is monodispersed when α is small. If α is not small, the value of α_w can be obtained according to the empirical equation:

$$\alpha_w/\alpha_{90}=1+k(z/z_{90}-1)$$

The error will be within about 5% if $\alpha_w<1.5$.

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