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Experimental Investigations on the Light Scattering of Colloidal Spheres. VI. Determination of Size Distribution Curves by Means of Turbidity Spectra[1]

by Morton L. Wallach and Wilfried Heller

Department of Chemistry, Wayne State University, Detroit, Michigan *(Received August 13, 1963)*

Spectra of turbidity exhibited by polystyrene latices were investigated and the results were used to derive the size distributions in these systems. The turbidity spectra method was found to be equivalent in performance to that based upon the study of spectra of the scattering ratio (depolarization) provided the spectral turbidity maximum is within or near the spectral range investigated. Turbidity spectra were determined for systems showing a negatively skewed, a positively skewed, and a gaussian-type distribution. The distribution curves derived from the spectra were compared with electron microscopic distribution curves obtained on the same systems. Simplifications of the method proposed here are outlined which may be sufficient if the objective is merely a determination of the modal and/or mean particle diameter or if the concentration of the scattering material is not exactly known.

Introduction

The preceding paper in this series[2] dealt with a method for determining size distribution curves in heterodisperse systems of colloidal spheres by means of the spectra of the scattering ratio. An alternate method may be based upon the use of turbidity spectra. The theory of this alternate method was given some time ago.[3] The present paper is concerned with the experimental test of this alternate method, using again heterodisperse polystyrene latices as model systems. The distribution curve is again assumed to be of the type

$$\begin{aligned} \mathrm{f}(r) &= (r - r_0)e^{-[(r-r_0)/s]^2} \qquad (1) \\ &= 0,\ r < r_0 \end{aligned}$$

Here, $C\mathrm{f}(r)\,\mathrm{d}r$ is the number of particles per unit volume of a system containing particles with radii between r and $r + \mathrm{d}r$, s is a parameter proportional to the width

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[1] This work was supported by the Office of Naval Research. The results given in the present paper were presented at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

[2] 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).

of the distribution, and r_0 is the radius of the smallest particles present in consequential numbers. Particles with a radius smaller than r_0 are quantitatively defined here as those having a radius smaller than 99% of all the particles present in the system. This definition, for the present systems, is based upon electron microscopic histograms.

Experimental

The systems investigated were the same latices as used previously.[2] They represent a positively skewed distribution (H.D. 1) in line with eq. 1, a negatively skewed distribution (H.D. 2), and a gaussian distribution (H.D. 3). The apparatus used and preparation and treatment of the latex samples were the same as in the preceding investigation.[2] Details of the optical setup were on the whole the same as before when turbidity measurements were carried out on monodisperse systems.[4] Modifications already described[2] were taken advantage of. In addition, the following changes were introduced: (1) Since it was desirable to have radiation of the highest possible spectral purity, the radiation emerging from the incandescent light source was passed through interference filters supplemented by colored glass filters prior to entry of the light beam into the monochromator proper. (2) The solid angle was decreased to 1.1×10^{-4} steradian in order to eliminate, as much as possible, the contribution of forward scattering.[5]

Turbidity measurements were carried out at each wave length at systematically varied concentrations, the lowest concentration within a series being given by $\phi = 0.24 \times 10^{-5}$ (ϕ, volume fraction of the polymer). The specific turbidity, $\lambda\tau/\phi$ (λ, the wave length in the medium; τ, the turbidity), was then plotted against concentration and extrapolated to infinite dilution. The turbidity spectra to be given apply therefore to infinitely dilute systems. The respective $\lambda\tau/\phi$ values are differentiated from those actually measured by a subscript, *viz.* $(\lambda\tau/\phi)_0$.

Results

Figure 1 summarizes the specific turbidity spectra derived from experiment for the three systems. The width of the rectangles represents the maximum uncertainty in λ_0; their height is the maximum uncertainty in $(\lambda\tau/\phi)_0$. The data indicated by the black dots are the most probable values. In the case of H.D. 3, the combined use of a Hg-vapor lamp (instead of the Pointolite lamp used in the other two cases), a monochromator, and interference filters reduced the former uncertainty to a negligible value at two of the three wave lengths used.

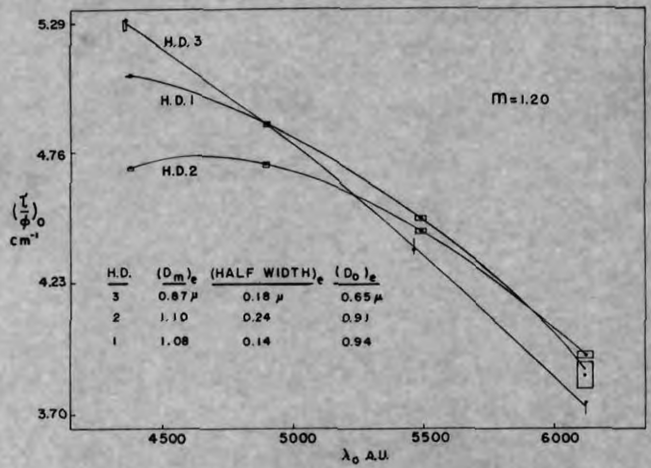

Figure 1. Actual $(\tau/\phi)_0$ spectra of the heterodisperse systems H.D. 1 and 3 investigated. Numerical data identifying the three characteristic parameters of the distribution curves are due to electron microscopy (subscript e): dots, most probable values; height of rectangles, total width of spectral band entering apparatus. (In two instances, use of Hg-vapor lamp, instead of incandescent source—in combination with monochromator, interference filters, and color filters—reduced width of rectangle to practically zero.)

The shapes of the curves differ characteristically. The turbidity maximum is seen to move toward shorter wave lengths in the direction H.D. 2 → H.D. 1 → H.D. 3. This indicates, as will be seen, a decrease, in this direction, of the modal diameter, D_{m}. The direction in the shift is therefore qualitatively the same as that expected in monodisperse systems.

In order to derive distribution curves, the experimental spectra are compared with a series of theoretical spectra until that theoretical spectrum is found which fits the experimental spectrum in a satisfactory approximation. These theoretical spectra are constructed by varying systematically the p_{R} and q_{R} values defined as

$$p_{\mathrm{R}} = p\lambda/\lambda_{\mathrm{R}} \tag{2}$$

$$q_{\mathrm{R}} = q\lambda/\lambda_{\mathrm{R}} \tag{3}$$

where

$$p = 2\pi r_0/\lambda \tag{4}$$

$$q = 2\pi s/\lambda \tag{5}$$

$$s = (r_{\mathrm{m}} - r_0)\sqrt{3} \tag{6}$$

The quantity p depends on the radius of the smallest

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(4) R. M. Tabibian, W. Heller, and J. N. Epel, *J. Colloid Sci.*, **11**, 195 (1956).

(5) For a discussion of this effect, see R. M. Tabibian and W. Heller, *ibid.*, **12**, 25 (1957).

particles present in consequential numbers, r_0; and the quantity q is a measure of the spread of the distribution curve, r_m being the modal radius. These quantities are related to the $(\lambda\tau/\phi)_0$ value by the equation

$$(\lambda\tau/\phi)_0 = \frac{3\pi \int_p^\infty \Sigma(\alpha)(\alpha - p) \exp\{-[(\alpha - p)/q]^3\}\mathrm{d}\alpha}{\int_p^\infty \alpha^3(\alpha - p) \exp\{-[\alpha - p]/q]^3\}\mathrm{d}\alpha} \quad (7)$$

In these equations, r is the particle radius, $\mathrm{d}r = (\lambda/2\pi)\mathrm{d}\alpha$, and $\alpha = 2r\pi/\lambda$. The electronically computed theoretical values of $(\lambda\tau/\phi)_0$ have been given[3] for a wide range of p and q values for $m = 1.05(0.05)1.30$, where $m = (\mu_2/\mu_1)$, μ_2 being the refractive index of the particles and μ_1 that of the medium. In contradistinction to p and q, p_R and q_R are normalized with respect to the reference wave length λ_R which, in the present work (the medium being water at 25°), is 4093.57 Å. (the corresponding vacuum wave length is the green Hg line, 5460.73 Å.). The procedure followed in finding the best theoretical spectrum is as follows: The values of q_R, p_R pairs are varied first within large intervals. Having come reasonably close to the normalized experimental spectra, the intervals in the numerical values of q_R and p_R are reduced to 0.4 or 0.2. (After some experience, the first step of wide variations in q_R and p_R can be eliminated). Four (Fig. 2) or three (Fig. 3) theoretical spectra are reproduced for each of the three systems investigated. They cover the entire range of acceptable q_R, p_R combinations. The best q_R, p_R pair is obtained subsequently. This final selection may be made by simply picking that theoretical spectrum which comes closest to the experimental one. Instead, one may, for a still better approximation, obtain the best q_R, p_R pair by interpolation between the two or three closest fitting theoretical spectra. The spectra used for such interpolations are identified in Fig. 2 and 3 by the symbols i_1 and i_2, respectively. In order not to crowd Fig. 2 and 3, only three or four instead of the larger number of actually considered theoretical spectra are shown. The i_2 curve in Fig. 2, pertinent to H.D. 3, is omitted ($q_R = 1.8$, $p_R = 5.6$). Similarly, an i_3 curve in Fig. 3 (1.8, 7.2) is omitted.

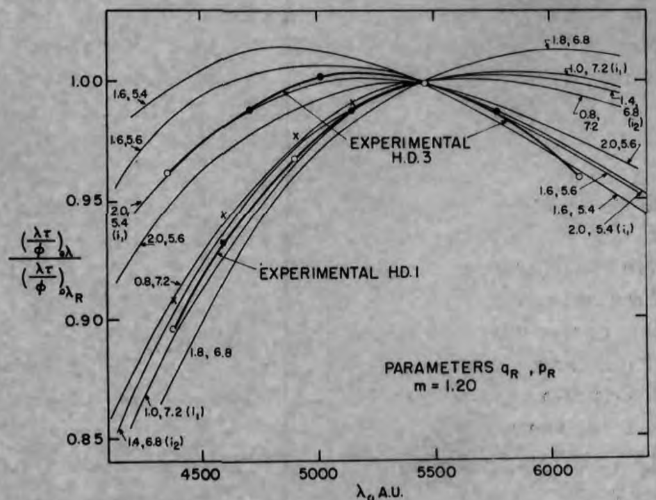

Figure 2. Normalized experimental and theoretical $(\lambda\tau/\phi)_0$ spectra of H.D. 1 and H.D. 3: heavily drawn curves, spectra derived from experiment; other curves, theoretical spectra.

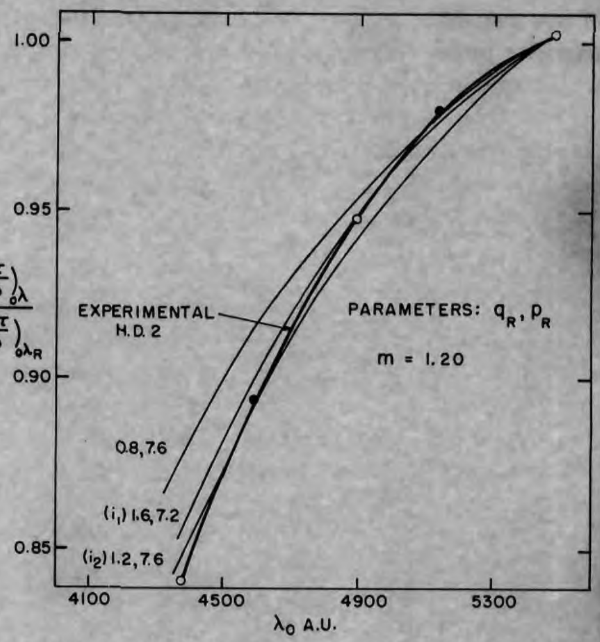

Figure 3. Normalized experimental and theoretical $(\lambda\tau/\phi)_0$ spectra of H.D. 2. A third theoretical curve (i_3) is omitted (see text for details).

The experimental spectra are also normalized by plotting $(\lambda\tau/\phi)_{0,\lambda}/(\lambda\tau/\phi)_{0,\lambda_R}$. This eliminates uncertainties connected with concentration determinations and corrections in the numerical values associated with the use of a finite solid angle.[6] It also allows one to accommodate several spectra in a single graph.

The normalized experimental $(\lambda\tau/\phi)_0$ spectra are represented by the heavily drawn curves in Fig. 2 and 3. The open circles correspond to the most probable experimental values given in Fig. 1. The black circles are obtained by interpolation by means of the curves in Fig. 1.

Figures 4, 5, and 6 give the optical distribution curves and electron microscopic histograms obtained for H.D.

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(6) Electronic computation would, of course, carry out automatically the equivalent of such interpolations.

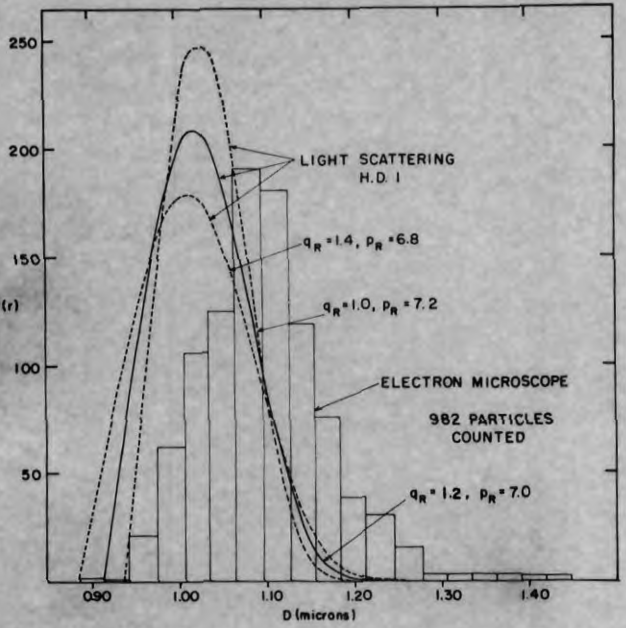

Figure 4. Size distribution curves derived from turbidity spectra and comparison with electron microscopic histogram. System (H.D. 1) with positively skewed distribution conforming to eq. 1: fully drawn curve, using interpolated q_R, p_R values; dotted curves, using the two q_R, p_R pairs which come closest to achieving spectral fit on using Δq_R and Δp_R intervals of 0.4.

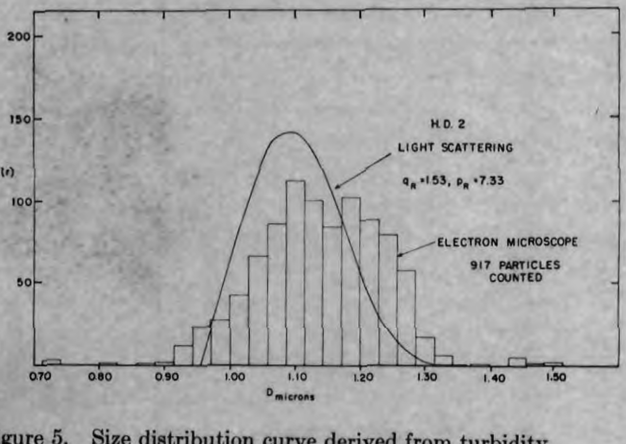

Figure 5. Size distribution curve derived from turbidity spectra and comparison with electron microscopic histogram. System (H.D. 2) with negatively skewed distribution curve (interpolated q_R, p_R values used).

1, H.D. 2, and H.D. 3, respectively. (The procedure used for the electron microscopic determinations of the size distribution has been described previously.[2]) The fully drawn curve in Fig. 4 (H.D. 1) results from the interpolated q_R and p_R values intermediate between those of the i_1 and i_2 spectra in Fig. 2.[6] The dotted curves pertain to the i_1 and i_2 spectra themselves.

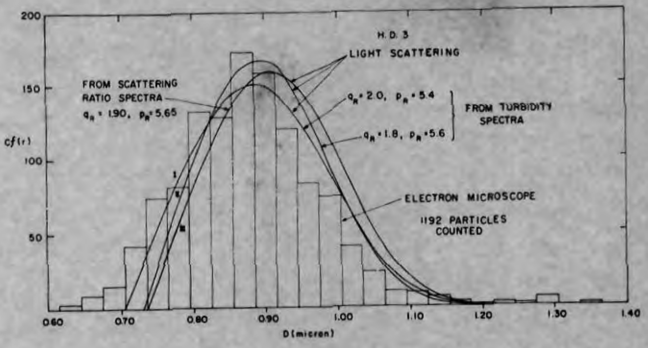

Figure 6. Size distribution curves derived from turbidity spectra and comparison with curves obtained from spectra of scattering ratio and with electron microscopic histogram. System (H.D. 3) approximating gaussian distribution: I and II, using turbidity spectra and the two q_R, p_R pairs which came closest to achieving spectral fit on using Δq_R and Δp_R intervals of 0.2. (Interpolation of q_R and p_R values would yield curve within area bounded by curves I and II); III, using σ-spectra and interpolated q_R and p_R values.

The modal diameter is hardly affected by the interpolation. On the other hand, the peak height of the curve is improved by it. Figure 5 (H.D. 2) contains only the curve obtained by interpolation among the i_1, i_2, and i_3 curves (see Fig. 3). Figure 6 gives two distribution curves (I, II) derived for H.D. 3 from the i_1 and i_2 pairs of q_R, p_R values (see Fig. 2). The distribution curve which would result from an interpolation between the i_1 and i_2 pairs is omitted. It would be intermediate between the curves I and II.

Instead of extrapolating the experimental spectra to zero concentration it may be sufficient to operate at a single reasonably small concentration if optimum accuracy is not required for the distribution data. Although the individual $(\lambda\tau/\phi)$ values are then slightly different from the extrapolated $(\lambda\tau/\phi)_0$ values, the shape of the normalized $(\lambda\tau/\phi)$ *vs.* λ_0 curve is not materially affected. This is tested for H.D. 1. Normalized data of $(\lambda\tau/\phi)$ obtained at the very small concentration of 0.827×10^{-3} g. of solids/100 g. of latex are identified by crosses in Fig. 2. They agree throughout to within 1% with those obtained by extrapolation to zero concentration (circles). The q_R, p_R pair satisfying these alternate data (1.0, 7.0) would give a distribution curve very similar to that of the pair 1.0, 7.2 except for a slightly lower modal diameter. On using this approximation method, it is really not necessary to know the absolute concentration provided that one has proof that one operates within a "safe" range of low concentrations. The safe range is defined by the fact that τ varies, within it, linearly with the degree of dilution at all wave lengths used (negligible multiple scattering).

Table I: Summary of Numerical Results[a]

System	$\bar{D}_n$	D_m	D_0	W
H.D. 1	1.02_8 (6.5)	1.02_0 (5.6)	0.91_2 (3.3)	0.14_1 (~1)
H.D. 2	1.10_2 (3.3)	1.09_3 (0.6)	0.95_5 (4.5)	0.18_0 (26)
H.D. 3	0.90_0 (2.5)	0.88_8 (2.1)	0.71_7 (6.5)	0.22_3 (27)

[a] All data are in μ except bracketed data which represent % deviations relative to electron microscopic data.

Table I gives a comprehensive survey of the numerical results obtained for the number average diameter, $\bar{D}_n$; modal diameter, D_m; diameter of the smallest particles present in consequential numbers, D_0; and half-width, W. (The half-width W considered here is twice the half-width, w, defined previously.[2] The latter would apply if the independent variable were the particle radius, r, rather than the diameter used here.) In each instance, the % deviation with respect to the electron microscopic data is given in parentheses. The quantities enumerated being those of principal importance, it can be stated from the results obtained here that the present method for determining size distribution curves is very satisfactory in those cases where the actual distribution curve does not differ much in type from that assumed (eq. 1). If the distribution curve is not of this type then the results for $\bar{D}_n$, D_m, and D_0 are still satisfactory, but the half-width W is obviously very much in error. If better results are to be obtained for the half-width in such a case, it is necessary to use the two term equation or other procedures discussed previously.[2] It is, fortunately, easy to ascertain when this contingency arises A major departure of the distribution curve from that assumed by eq. 1 is indicated by the fact that it is impossible to obtain good agreement with experiment for any q_R, p_R pair. In Fig. 2 the experimental curve for H.D. 1 which satisfies eq. 1 is nearly parallel to any of the best fitting theoretical curves. On the other hand in Fig. 3, no theoretical curve can be found which fits more than $^1/_3$ or $^1/_2$ of the spectral range considered. This indicates at once that the system investigated does not possess the distribution assumed. For the gaussian distribution in Fig. 2 (H.D. 3) the situation is intermediate. Here, it is seen from the degree of agreement between experimental and theoretical spectra that the distribution curve differs, but not as much as in the preceding case from that assumed. The rather poor partial fit in Fig. 3 leads to the distribution curve in Fig. 5 which has the wrong skew, but does not—except for this feature—differ radically from the actual distribution curve. It therefore depends on the objective as to whether or not in such cases use of the more time consuming two term equation or of other procedures is warranted.

Approximation Methods for Attaining Limited Objectives

Less exacting procedures are warranted if the objective is merely the determination of $\bar{D}_n$, D_m, and D_0. The reason is that the numerical value of these quantities changes relatively little on varying q_R and p_R within modest limits. Thus, the agreement between the electron microscopic D_m value and that derived from *any* of the theoretical spectra in Fig. 2 and 3 is within at least 7, 3, and 2% for H.D. 1, H.D. 3, and H.D. 2, respectively. Similarly, the agreement between the electron microscopic D_0 values and those derived from any of the theoretical spectra in Fig. 2 and 3 is within at least 5%, 12%, and 9%, respectively. An approximate fit of theoretical and experimental spectra is therefore sufficient if one is satisfied with a determination of these three quantities.

If the objective is even more limited, *i.e.*, if one is merely interested in determining an *approximate* value of D_m or $\bar{D}_n$, one may dispense with spectra entirely and operate at a single wave length. The diameter thus obtained is an *apparent* quantity since the system is treated as if it were monodisperse. It is of interest to evaluate the error committed by using such a very simple technique on heterodisperse systems. Choosing, for this purpose, the data obtained at the green mercury line, the theoretical specific turbidities would yield a particle diameter of 1.196, 1.214, and 0.736 μ for H.D. 1, H.D. 2, and H.D. 3, respectively. The differences between these diameters and the modal diameters obtained from the optical distribution curves are 15, 10, and 21%, respectively. The numerical error would be larger in systems more heterodisperse than those used here and smaller in the reverse case. Similarly, in a given system, the error would obviously vary with the wave length. Therefore, the ratio of the apparent diameters obtained at two wave lengths—treating the system as if it were monodisperse ($q = 0$)—can provide a rough measure of the relative degree of heterodispersion. It is clear that the apparent diameter should increase with decreasing wave length if the spectral range considered comprises wave lengths larger than that at which the turbidity maximum occurs. It should decrease with decreasing wave length in the inverse case.

Probable Range of Usefulness of Turbidity Spectra

The usefulness of turbidity spectra (within the visible spectral range) for determining size distribution curves and the sensitivity of the spectra to changes in the degree of heterodispersion have been investigated in the present work for size distributions extending from particle diameters of about 0.7–1.4 μ and for half-widths from 0.14–0.24 μ. It can be anticipated (see Fig. 1 in ref. 3) that the sensitivity to heterodispersion for systems with particles smaller than 0.7 μ and with larger half-width is similar to that found here. While experiments in this lower range of particle diameters and with wider distributions are desirable, the situation which one is bound to find if D_0 is as small as 0.26 μ ($p_R = 2.0$) can be derived from an inspection of Fig. 3 of ref. 3. An increase of q_R from 1.0 to 4.0 changes the normalized $(\lambda\tau/\phi)_0$ spectrum just as profoundly no matter whether p_R has the value 6.0 ($D_0 \sim 0.8$ μ) or the value 2.0. Finally, it should be noted that the method described here, like any other light scattering method, will, of course, be wholly insensitive to particle size distributions if all the particles are so small compared to the wave length that Rayleigh scattering applies.

Turbidity spectra will become quite insensitive to particle size distributions if the particles are large relative to the wave length. Inspection of Fig. 1 and 2 in ref. 3 shows that the range of sensitivity terminates for slightly heterodisperse systems at $p \sim 16$ and for moderately heterodisperse systems ($q = 4.0$) at $p \sim 12$. Thus a system with a distribution half-width W of 0.5 μ will not respond well to the analysis if D_0 is about 2 μ. Work done by Wu in continuation of the present work shows that the sensitivity within the visible range of the spectrum begins in fact to fall off seriously if the distribution extends appreciably into the microscopic range.

On being faced with systems in which the particles are too small (Rayleigh range) or too large (upper microscopic range) to apply turbidity spectra usefully within the visible spectral range, one may, of course, in favorable instances (no true absorption), resolve the problem by making use of turbidity spectra in the ultraviolet or intermediate infrared, respectively.

Comparison of the Present Method With That Based on the Spectra of the Scattering Ratio

On comparing the results presented here with those given previously,[2] it is clear that the method of determining size distribution curves from turbidity spectra is, for the systems investigated, comparable in performance to that based upon spectra of the scattering ratio. A specific example is given in Fig. 6. The size distribution curve obtained for H.D. 3 from σ-spectra (curve III) is compared to that obtained by the method described in this paper. The curves are in satisfactory agreement. For a closer check, the results given in Table I may be compared with the results obtained for the same systems by the alternate method (see Table I, ref. 2). An advantage of the present method is its relative experimental simplicity inasmuch as any properly modified spectrophotometer may be used. A further advantage is the fact that the sensitivity of turbidity spectra to heterodispersion is preserved even at very high degrees of heterodispersion (a half-width of 0.5 μ) provided $D_0 < 1$ μ. In addition, owing to their monotonic character, theoretical $(\lambda\tau/\phi)_0$ *vs.* λ curves can be derived and constructed faster. Also, a high brightness of the light source is not as imperative here as in the case of scattering ratio spectra.

On the other hand, an advantage of the method based upon the scattering ratio is that the spectra of the latter are more profoundly affected by changes in p_R (by the smallest particle size at which the distribution curves effectively begin). The larger the quantity p_R is, the larger is the number of maxima and minima exhibited by the spectra. Thus, giving a q_R value of 1.4, one has one maximum if $D_0 \sim {}^1/_3$ μ, one maximum and one minimum if $D_0 \sim {}^2/_3$ μ, and two maxima and one minimum if $D_0 \sim 1$ μ on investigating a spectrum extending from the vacuum wave length of 4500 Å. to 6000 Å.[7] There is, therefore, no upper limiting p_R value beyond which the method is not applicable except that the occurrence of many maxima and minima in the upper microscopic range may make the resolution of the spectra a difficult task. This may well be the most important advantage of scattering ratio spectra over turbidity spectra, the latter of which should, as stated, become rather insensitive to size distributions if D_0 is in the microscopic range. As regards the sensitivity of the spectra of the scattering ratio, σ, to heterodispersion, it will most likely exceed that of the turbidity spectra as long as the degree of heterodispersion is small or moderate. This is due to the strong effect of q_R upon the amplitude of the σ *vs.* λ oscillations.[7]

Some of these differences between the two types of spectra also lead to differences in the ease with which one may find, for a given system, the best q_R, p_R combination. The number of maxima and minima observed in a σ-spectrum, within a given spectral range, suggests at once the range of p_R values to be examined. The amplitude of the spectral oscillations suggests the range of q_R values to be examined (see, *e.g.*, Fig. 4, 5, and 6 in ref. 7). In the case of the turbidity spectra, on the other hand, the number of possible maxima is reduced to one. A quick analysis is therefore possible

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(7) A. F. Stevenson, W. Heller, and M. L. Wallach, *J. Chem. Phys.*, **34**, 1789 (1961).

only if the $(\lambda\tau/\phi)_0$ maximum occurs within the visible range. The presence of such a maximum immediately limits the number of p_R values that may be considered. The degree of shallowness of the maximum is a reliable indicator of the approximate q_R range to be considered. The absence of a maximum within or very close to the experimental spectrum of $(\lambda\tau/\phi)_0$ increases the labor of finding the best q_R,p_R pair; it does, however, not interfere with the applicability of the $(\lambda\tau/\phi)_0$ method. Only one of the three systems investigated here exhibited a $(\lambda\tau/\phi)_0$ maximum.

The availability of both the $\sigma(\lambda)$ and $(\lambda\tau/\phi)_0$ *vs.* λ methods provides a welcome opportunity to check the results obtained with one against those obtained with the other. It allows one to make a quicker decision as to the proper q_R and p_R combination than with one spectrum alone. Furthermore, a combination of the two methods and, if necessary, consideration of a third (variation of lateral scattering with the angle of observation) may allow one to derive distribution curves without having to make any assumption about its basic type. This possibility which appears very promising—provided the degree of heterodispersion is not so large as to wipe out spectral and angular maxima and minima completely—is being explored at the present time.

In conclusion, it may be noted that with systems which show a strong dispersion (of the refractive index), the dispersion should be taken into account in the calculation of the theoretical spectra on applying the method described here. With the systems investigated here, these corrections proved to be negligible.

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