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Experimental Investigations on the Light Scattering of Colloidal Spheres. VII. Resolving Power of the σ-Spectra Method for Determining Size Distribution Curves[1]

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The resolving power of a previously described method for determining size distribution curves in colloidal dispersions of spheres was examined. The method is based upon use of the spectra of the scattering ratio or of the depolarization of scattered light. The systems used were two of those Dow latices of polystyrene which have a distribution curve so narrow that they are often referred to as monodisperse. The spectra of the scattering ratio showed that these systems are not strictly monodisperse and, in addition, allowed one to derive this distribution curve. The half-width of the distribution curve thus determined differed by 2.6 and 0%, respectively, from that obtained by electron microscopy. Similar good agreement with electron microscopic data was found for the mean and modal diameters and other quantities of statistical interest. Since the half-width was, in the systems investigated, one order of magnitude smaller than the modal diameter, the resolving power of the method can be stated to be most satisfactory.

Introduction

In two preceding papers the theory[2] and experimental test[3] of a method were given which allows one to determine the size distributions of spherical colloidal particles from spectra of the scattering ratio. It was found that the modal diameter D_m can be obtained with a high degree of accuracy, the % deviation with respect to electron microscopic results being at the most 5% no matter whether or not the particular type of distribution curve agreed or disagreed with that assumed. This is just within the range of uncertainty of electron microscopic data. If the distribution was of the type assumed,[2] the diameter of the smallest particles present in consequential numbers, D_0, and the "half-spread" ($D_m - D_0$), of the distribution curve were obtained with an error not in excess of 6% and 2%, respectively. For other types of distribution, the error in D_0 and ($D_m - D_0$) was somewhat but not appreciably larger. The same applied to the number average diameter, $\bar{D}_n$. Only the result for the half-width of the distribution curve proved to be quite sensitive to the type of distribution actually present. A question not explored previously was the sensitivity of the method to deviations of a system from strict monodispersity. This problem of the resolving power of the method, based upon σ-spectra, is the subject of the present paper.

It may be recalled[3] that $\sigma = I_{||}/I_{\perp}$ where $I_{||}$ is the intensity of light scattered from an incident polarized beam of unit intensity whose electric vector vibrates parallel to the plane of observation. Similarly, $I_{\perp}$ refers to the light scattered from an incident polarized beam vibrating perpendicular to the plane of observation. The angle of observation with respect to the incident beam is again 90°.

Experimental

Electron microscopy gave the following information on the number average diameter, $\bar{D}_n$, and the standard deviation, S, of the two "monodisperse"

(1) This work was supported by the Office of Naval Research.

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

(3) M. L. Wallach, and W. Heller *J. Phys. Chem.*, **68**, 924 (1964).

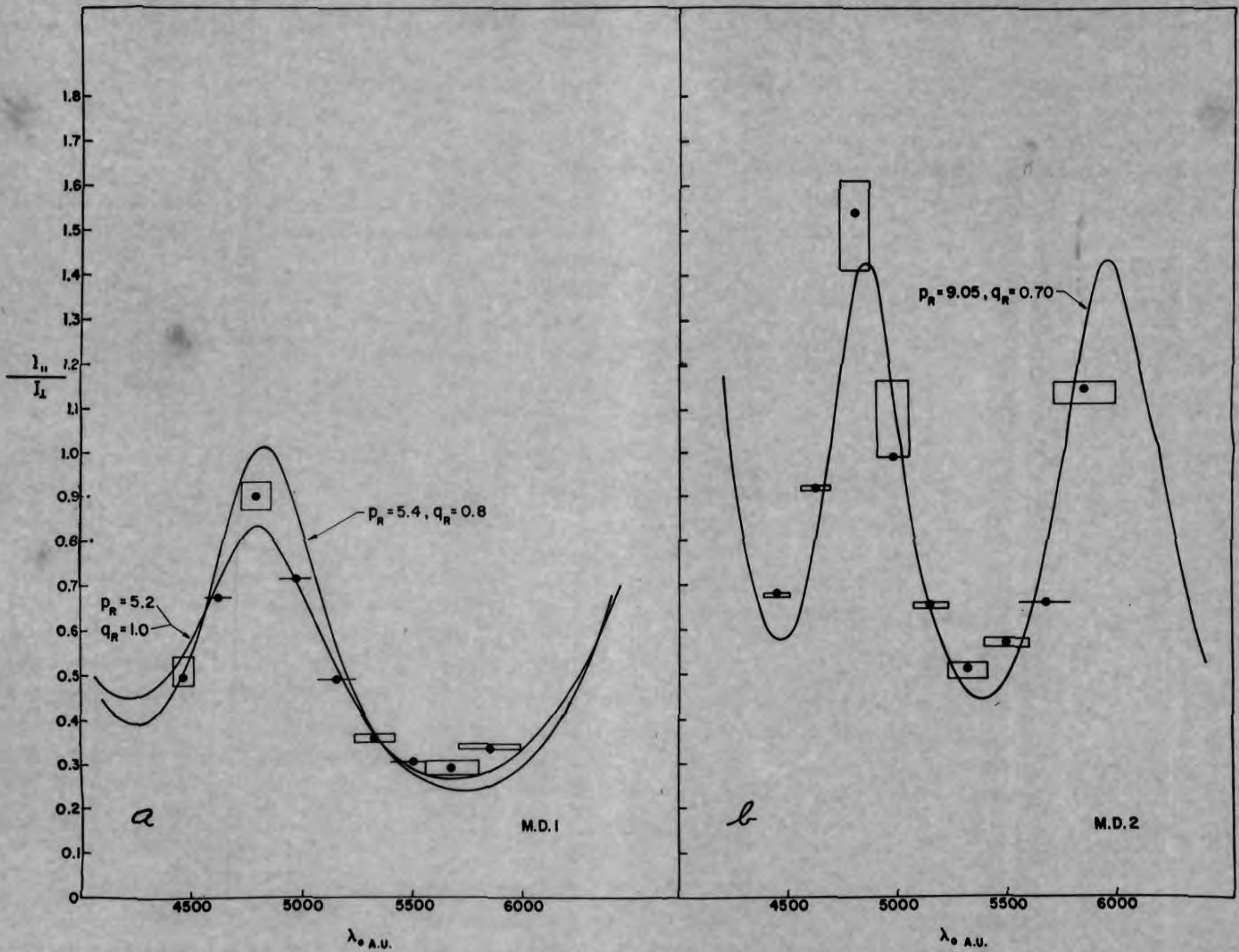

Figure 1. σ-Spectra of "monodisperse" latex M.D. 1 (part a) and M.D. 2 (part b). Part a: black circles, most probable experimental value; rectangle, range of experimental uncertainty; two curves, theoretical curves which satisfy experimental data best on varying p_R and q_R in intervals of 0.2. Part b: curve represents result of interpolation between four p_R and q_R values.

Dow latices investigated, both $\bar{D}_n$ and S being expressed in μ: M.D. 1, $\bar{D}_n = 0.761$; $S = 0.039$; M.D. 2, $\bar{D}_n = 1.230$; $S = 0.042$. The use of quotation marks for "monodisperse" means here, as is customary, that the size distribution curve in these latices, though remarkably narrow, is finite; *i.e.*, the systems are not ideally monodisperse.

The apparatus used for the optical studies, the treatment of the systems prior to the light scattering measurements, and all of the experimental details including electron microscopy were throughout the same as in the preceding investigation.[3]

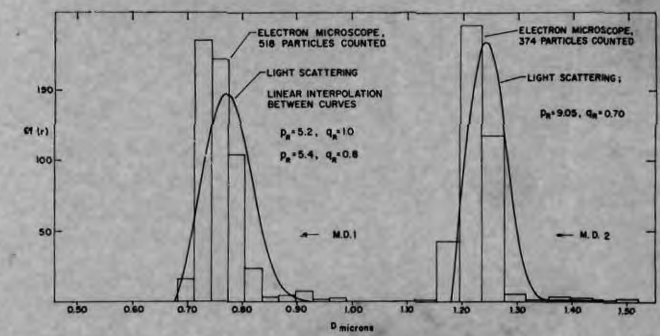

Figure 2. Size distribution curves of M.D. 1 and M.D. 2. M.D. 1: Curve obtained by linear interpolation between two distribution curves derived from the two spectra in Fig. 1, part a. M.D. 2: Curve derived from interpolated spectrum in Fig. 1, part b.

Results

The spectra of the scattering ratio are given in Fig. 1. Two theoretical curves which come closest to satisfying the experimental data of M.D. 1 are traced in Fig. 1, part a; only one is given in Fig. 1, part b, for M.D. 2.

In the case of M.D. 1, separate distribution curves were derived from the two theoretical spectra. The distribution curve actually given in Fig. 2 is the result of interpolation between these two primary distribution curves. This technique approximates the performance of the two-term distribution function.[3] It will be noted that by virtue of this interpolation procedure the rigidity in form of the basic distribution assumed is removed as documented particularly by the appearance of a curvature near the lower end of the distribution curve.[4]

The single $\sigma(\lambda)$ spectrum of M.D. 2 in Fig. 1, part b, was obtained by using the previously described procedure of interpolating between the p_R and q_R values pertinent to the four best fitting theoretical spectra (p_R, q_R pairs: 9.0, 0.6; 9.0, 0.8; 9.2, 0.6; 9.2, 0.8).[5] From the resulting single theoretical $\sigma(\lambda)$ spectrum of M.D. 2, the distribution curve in Fig. 2 was derived.

It may be recalled that

$$p_R = p\lambda/\lambda_R \quad (1)$$

$$q_R = q\lambda/\lambda_R \quad (2)$$

where

$$p = 2\pi r_0/\lambda \quad (3)$$

$$q = 2\pi s/\lambda \quad (4)$$

λ_R is the reference wave length, in the medium, used for normalization (it corresponds to the vacuum wave length 5460.73 Å.); λ is the wave length, in the medium, used in a given experiment; r_0 is the radius of the smallest particle present in consequential numbers (still smaller particles accounting for not more than 1% of the total number); s is a quantitative measure of the spread of the distribution, *i.e.*, it is a measure of the degree of departure from monodispersity. The defining relation is

$$s = (r_m - r_0)/\sqrt{3} \quad (5)$$

where r_m is the modal radius.

The electron microscopic histograms, also given in Fig. 2, agree very well with the distribution curves derived from the σ-spectra.

Table I gives the numerical values for the modal diameter, $\bar{D}_m$; number average diameter, $\bar{D}_n$; and diameter of the smallest particles present in consequential number, D_0. In addition, the half-width W is given.[6] The values in parentheses represent the % deviation of these data relative to those obtained from the electron microscopic histograms.[7] The agreement of the numerical data obtained by electron microscopy, on the one hand, and from the σ-spectra, on the other, is excellent. The deviations are throughout within the limits of the combined uncertainty of the two methods.

Table I: The Diameters, D_0, D_m, $\bar{D}_n$,[a] and the Half-Width, W,[b] as Derived from the σ-Spectra of "Monodisperse" Latices M.D. 1 and M.D. 2, and Comparison with the Apparent Diameter, D_a, Obtained at 5460.73 Å. on Assuming Strict Monodispersity[c]

	M.D. 1			M.D. 2	
D_0	678	(0.9)	D_0	1179	(3.0)
D_m	773	(5.9)	D_m	1242	(1.0)
$\bar{D}_n$	776	(2.0)	$\bar{D}_n$	1246	(3.0)
W	106	(2.6)	W	82	(0.0)
D_a	800	[3.4]	D_a	1213	[−2.4]

[a] D_0, D_m, and $\bar{D}_n$ are in mμ. [b] See ref. 6. [c] Data in parentheses, % deviation from electron microscopic data; data in brackets, % deviation from D_m value.

It is of interest to note the large difference in the frequencies and amplitudes of the oscillations in the $\sigma(\lambda)$ curves of Fig. 1a and 1b. This illustrates well the fact that it is rather easy to pick out those p_R and q_R values which should be considered in a given instance.[8]

Discussion

The principal conclusion to be drawn from the results is that the method proposed is sensitive to relatively minor degrees of heterodispersity, *i.e.*, it has a very high resolving power. One clearly can determine the essential features of size distribution curves in practically monodisperse systems.

It may be recalled that nearly monodisperse Dow latices of the type investigated here were used in this laboratory for the purpose of experimentally verifying light scattering functions predicted by the Mie theory.[9]

(4) Interpolation between the p_R and q_R values of the two curves given in Fig. 1, part a, one of the procedures used previously,[3] would lead to a distribution curve almost identical with that given here except that it would reproduce rigidly the type of distribution assumed by eq. 1.[3]

(5) The four curves were obtained by varying p_R and q_R in intervals of 0.2 and picking those four spectra which came closest to a fit with the experimental data.

(6) The half-width W is the numerical difference between the two particle dimensions—expressed in terms of diameters—for which the particle number is 1/2 of the number at the peak of the curve. Thus $W = 2w$, the latter quantity having been used in some of the preceding publications.

(7) The electron microscopic value of D_0 is obtained by disregarding those cells at the lower end of the polygonal frequency distribution in which the number of particles is less than 1% of the total number of particles present in all cells.

(8) See also, for example, Fig. 5 and 6 in ref. 2.

One is now in a position to compare the modal particle diameter obtained by the method described in this paper to the particle diameter to be expected from those earlier experiments which were carried out in monochromatic light by using the Mie data and on assuming ideal monodispersity. To that effect Table I gives the particle diameter D_a, derived from the scattering ratio obtained at the green Hg line assuming ideal monodispersity ($q_R = 0$). Comparison with the modal diameter obtained from the size distribution analysis shows that the % deviations are within the range of uncertainty of the electron microscopic diameters used as a reference in the experiments carried out by Tabibian.[9] It follows from the near coincidence of the D_m and $\bar{D}_n$ values in Table I that the same statements apply also to the number average diameter, $\bar{D}_n$, as compared to the apparent diameter, D_a, obtained in nearly, but not strictly, monodisperse systems from monochromatic scattering experiments.

Acknowledgment. The authors are indebted to Dr. J. H. L. Watson, Director of the Physics Department of the Edsel B. Ford Institute for Medical Research, for his electron microscopic collaboration.

(9) W. Heller and R. Tabibian, *J. Phys. Chem.*, **66**, 2059 (1962), and earlier papers.