resonating acids were found in the chemical literature. It would seem desirable to attempt to measure the association constants for other ion-pairs of the alkaline earths, particularly in view of the fact that the solubility of their hydroxides (in contrast to Ce(OH)$_3$) may allow measurements at high *p*H for oxy-acids having a formal charge of zero.

Summary

1. The distribution of cerous ion between ion exchange resin and solutions of sulfurous, phosphoric and pyrophosphoric acids has been measured.
2. The constants for the reaction between Ce^{+3} and these acids have been calculated.
3. The association constants for CeSO$_3^+$, CePO$_4$ and CeO$_2$O$_7^-$ are 1.1×10^8, 3.4×10^{18} and 1.4×10^{17}, respectively.
4. Bjerrum's theory for ion-pair formation does not predict these association constants.
5. A correlation between the association of oxy-acid anions with H$^+$ and their association with Ce^{+3} has been pointed out.

SAN FRANCISCO 24, CAL. RECEIVED APRIL 11, 1950

[CONTRIBUTION FROM THE UNIVERSITY LABORATORY OF PHYSICAL CHEMISTRY RELATED TO MEDICINE AND PUBLIC HEALTH, HARVARD UNIVERSITY]

Light Scattering Studies of a Polystyrene Latex[1a]

BY WALTER B. DANDLIKER[1b]

The size and shape of the particles in a polystyrene latex (Dow Latex 580-G, Lot 3584) have been studied by various methods in a number of laboratories.[2] The particles have been found to be spheres with a number average diameter of 2590 Å. and have a distribution of size over only an extremely narrow range. Since this material has been used as a means of determining absolute lengths in the electron microscope, it is desirable to have as many independent measurements of particle size as possible. The fact that this latex is nearly monodisperse and that the particles are spherical suggests that additional valuable information can be obtained by light scattering. The exact solution to the problem of light scattering from such spheres is provided by the Mie theory.[3] Several recent reviews[4,5,6] concerning the Mie theory summarize the theoretical and experimental work dealing with light scattering from large spheres, and provide bibliographies to this subject.

In general, the optical properties of a sphere depend upon its relative refractive index m and the value of $\alpha = 2\pi r/\lambda$ where r is the radius of the sphere and λ is the wave length of the light in the surrounding medium. These parameters determine the magnitude, the angular distribution, and the polarization of the scattered intensities which together characterize completely the scattering from an isolated particle. We shall limit our considerations to the horizontal plane containing the incident and scattered beams and shall specify the direction of scattering by ϑ, the angle between the directions of propagation of the incident and scattered rays. The angular distribution can be represented conveniently by the function $P^{-1}(\vartheta)$ which gives reciprocal relative intensities of the vertical component (electric vector vertical) in the scattered light with unpolarized incident light. These reciprocal intensities have been normalized to unity at $\vartheta = 0$. The function $P^{-1}(\vartheta)$ has been plotted against $\sin^2 \vartheta/2$.

Determination of Particle Size from the Angular Position of Minimum Intensity.—Since the positions of minimum intensity in an angular dependence curve are functions of both m and α, the location of these positions ($\vartheta_{\text{Min.}}$) can be used to determine the size of a sphere. This method is similar to one employed by LaMer and Sinclair[7] in studying aerosols and by Johnson and LaMer[8] in measuring the particle size of sulfur hydrosols. These studies have been extended in a series of papers and include measurements carried out in the presence of true absorption.[9] Figure 1 shows ϑ_{Min} (for first order interference) as a function of m for different values of α. The points for $m = 1$ were obtained from the analytical expression given by Debye.[10] The problem of scattering from spheres of small refractive index was earlier solved by Rayleigh.[11] The remaining values were estimated graphically from plots of $P^{-1}(\vartheta)$ using the tabulated values of LaMer and Sinclair[12] for the intensity distribution

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(1) (a) This work was supported by grants from the Rockefeller Foundation, the National Institutes of Health, and from funds of Harvard University. (b) Public Health Service Research Fellow of the National Institutes of Health.

(2) A sample of this latex was kindly supplied by Dr. Robley Williams and Dr. R. C. Backus of the University of Michigan. They have determined (THIS JOURNAL, **71**, 4052 (1949)) the size distribution curve by electron microscopy.

(3) G. Mie, *Ann. der Physik*, **25**, 377 (1908).

(4) H. C. van de Hulst, "Optics of Sperical Particles," Duwaer and Sons, Amsterdam, 1946.

(5) G. Oster, *Chem. Rev.*, **43**, 319 (1948).

(6) D. Sinclair and V. K. LaMer, *ibid.*, **44**, 245 (1949).

(7) V. K. LaMer and D. Sinclair, N. D. R. C., Report 57 (1941) and 1668 (1943); personal communication from Professor LaMer.

(8) I. Johnson and V. K. LaMer, THIS JOURNAL, **69**, 1184 (1947).

(9) A. S. Kenyon and V. K. LaMer, *J. Colloid Sci.*, **4**, 163 (1949).

(10) P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

(11) Lord Rayleigh, *Proc. Roy. Soc. (London)*, **A90**, 219 (1914).

(12) V. K. LaMer and D. Sinclair, "Verification of Mie Theory" O. S. R. D. Report No. 1857 (1943).

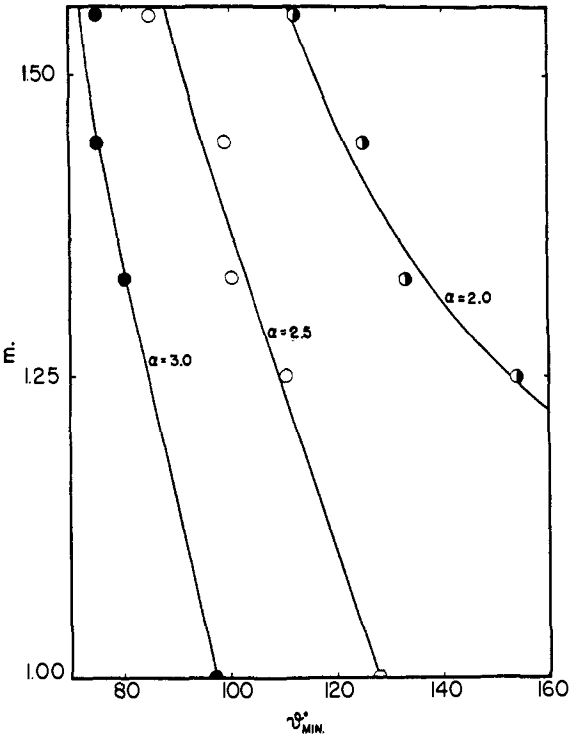

Fig. 1.—Positions of minimum intensity (first order interference) as a function of refractive index and size.

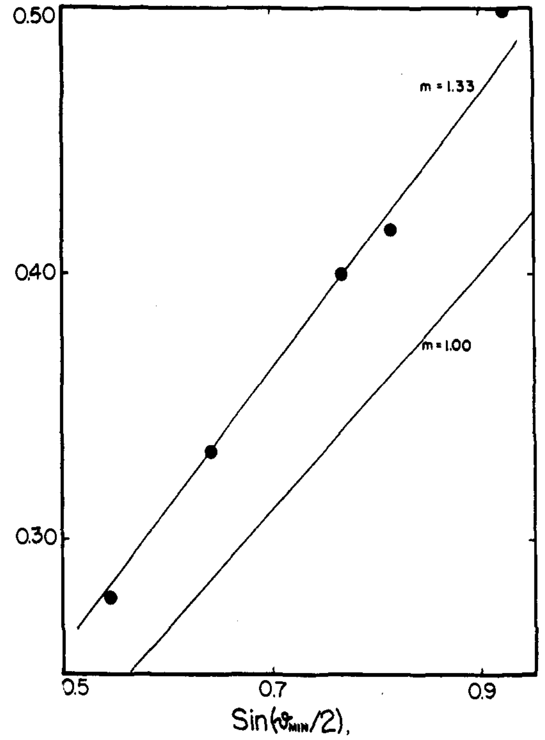

Fig. 2.—Positions of minimum intensity plotted according to Equation 1.

functions from the Mie theory with the exception of the values at $m = 1.25$ which were taken from the tabulations of Blumer.[13] For the limiting case as $m - 1 \rightarrow 0$

$$\sin \vartheta_{\text{Min.}}/2 = k/\alpha \qquad (1)$$

where k is a constant for a given order of interference since the minima always occur at fixed values of $y = 2\alpha \sin \vartheta/2$. The first order minimum occurs at $y = 4.4934$. Equation (1) may be used as an approximation for somewhat higher values of m if the proper value of k can be found. Fig. 2 shows this function (first order) for $m = 1$ and $m = 1.33$ using an average value of k computed from the points to draw the straight line for the higher refractive index.

The foregoing discussion is valid for an isolated particle or a number of identical particles scattering incoherently. However, if we observe the scattering from a system of independent spherical particles with sizes varying over a certain range we may still expect to obtain an intensity minimum if the range of sizes is not too great. If equation (1) were applied to the resulting data some average value of α would result. By considering the limiting case in which $(m - 1) \rightarrow 0$ we can obtain some information about this average and the effect of heterogeneity on the angular dependence curve.

If we let I^0 be the incident intensity, I the scattered intensity per unit volume and b the distance from the scattering volume to the point of observation then we may write the reduced intensity[14] as Ib^2/I^0. The reduced intensity will be denoted by a boldface symbol to denote the component measured in the scattered light as follows: **V** for the vertical component, **H** for the horizontal component and **R** for the sum of both components. In addition each of these symbols will be followed, ordinarily, by two subscripts, the first being the angle ϑ at which the observation is made and the second a lower-case letter v, h or u to indicate the state of polarization of the incident beam, vertically polarized, horizontally polarized or unpolarized, respectively.

We may then write (for the j^{th} species) the reduced intensity of the vertical component in the scattered light using unpolarized incident light as $\mathbf{V}_{\vartheta,\text{u},\text{j}}$. If we have N independent particles of the j^{th} species per unit volume the expression is[6,10]

$$\mathbf{V}_{\vartheta,\text{u},\text{j}} = \frac{N_{\text{j}}\lambda^2\alpha^6_{\text{j}}}{8\pi^2}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \frac{9}{y_{\text{j}}^6}(\sin y_{\text{j}} - y_{\text{j}} \cos y_{\text{j}})^2 \qquad (2)$$

Setting $\frac{\lambda^2}{8\pi^2}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \equiv Q$ and summing over all the species

$$\mathbf{V}_{\vartheta,\text{u}} = Q \sum_{\text{j}} N_{\text{j}}\alpha^6_{\text{j}} \frac{9}{y_{\text{j}}^6}(\sin y_{\text{j}} - y_{\text{j}} \cos y_{\text{j}})^2 \qquad (3)$$

If instead we take a continuous distribution such that the number of particles having values of α between α and $\alpha + \text{d}\alpha$ is $f(\alpha)\text{d}\alpha$ and if we terminate the distribution at two discrete values of

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(13) H. Blumer, *Z. Physik*, **32**, 119 (1925); **38**, 304 (1926).

(14) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

α, *viz.*, α_1 and α_2 then the expression for the intensity is

$$V_{\vartheta,u} = Q\int_{\alpha_1}^{\alpha_2} \alpha^6 \frac{9}{y^6} (\sin y - y\cos y)^2 f(\alpha)\mathrm{d}\alpha \quad (4)$$

In order to simplify the problem further, we consider a rectangular distribution in which

$$f(\alpha)\mathrm{d}\alpha = \frac{N}{\alpha_2 - \alpha_1}\,\mathrm{d}\alpha \quad (5)$$

between the limits of α_1 and α_2 only and equals zero everywhere else. The expression for the intensity then becomes

$$V_{\vartheta,u} = \frac{QN}{\alpha_2 - \alpha_1}\int_{\alpha_1}^{\alpha_2} \alpha^6 \frac{9}{y^6} (\sin y - y\cos y)^2\,\mathrm{d}\alpha \quad (6)$$

Letting $s = 2 \sin \vartheta/2$, substituting $s\alpha = y$, and integrating, we obtain after resubstitution

$$V_{\vartheta,u} = \frac{9QN}{(\alpha_2 - \alpha_1)s^6}\left[\alpha\left\{(\sin 2y)\left(\frac{y}{4} - \frac{5}{8y}\right) + \frac{3}{4}\cos 2y + \frac{y^2}{6} + \frac{1}{2}\right\}\right]_{\alpha_1}^{\alpha_2} \quad (7)$$

It may be noted that the value of $V_{o,u}$ can be found from the expression

$$V_{0,u} = \frac{QN}{\alpha_2 - \alpha_1}\int_{\alpha_1}^{\alpha_2} \alpha^6\,\mathrm{d}\alpha \quad (8)$$

since $P(\vartheta) = 1$ at $\vartheta = 0$. In Fig. 3

$$F(y) = (\sin 2y)\left(\frac{y}{4} - \frac{5}{8y}\right) + \frac{3}{4}\cos 2y + \frac{y^2}{6} + \frac{1}{2} \quad (9)$$

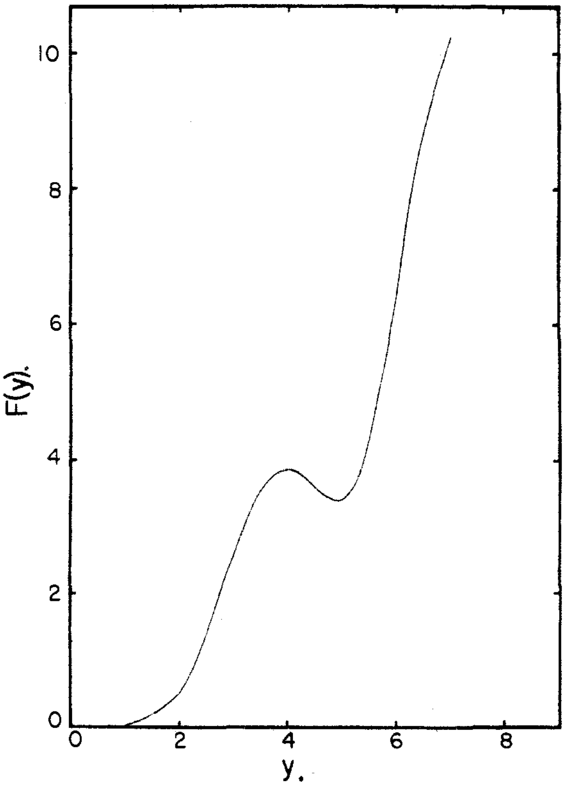

Fig. 3.—$F(y)$ which is related by Equation 10 to the scattered intensities from a heterogeneous system.

is plotted as a function of y so that

$$V_{\vartheta,u} = \frac{9QN}{(\alpha_2 - \alpha_1)s^6}\left[\alpha_2 F(y_2) - \alpha_1 F(y_1)\right] \quad (10)$$

Now in order to find the value of $\vartheta_{\text{Min.}}$ we set $\mathrm{d}V_{\vartheta,u}/\mathrm{d}s = 0$ and obtain

$$\left[\alpha^2\left\{(\sin 2y)\left(\frac{35}{8y^2} - \frac{11}{4}\right) + (\cos 2y)\left(\frac{y}{2} - \frac{23}{4y}\right) - \frac{2y}{3} - \frac{3}{y}\right\}\right]_{\alpha_1}^{\alpha_2} = 0 \quad (11)$$

Similarly we let

$$G(y) = (\sin 2y)\left(\frac{35}{8y^2} - \frac{11}{4}\right) + (\cos 2y)\left(\frac{y}{2} - \frac{23}{4y}\right) - \frac{2y}{3} - \frac{3}{y} \quad (12)$$

and plot this function in Fig. 4. The condition to be satisfied at $\vartheta_{\text{Min.}}$ is that

$$\alpha_2{}^2 G(y_2) - \alpha_1{}^2 G(y_1) = 0 \quad (13)$$

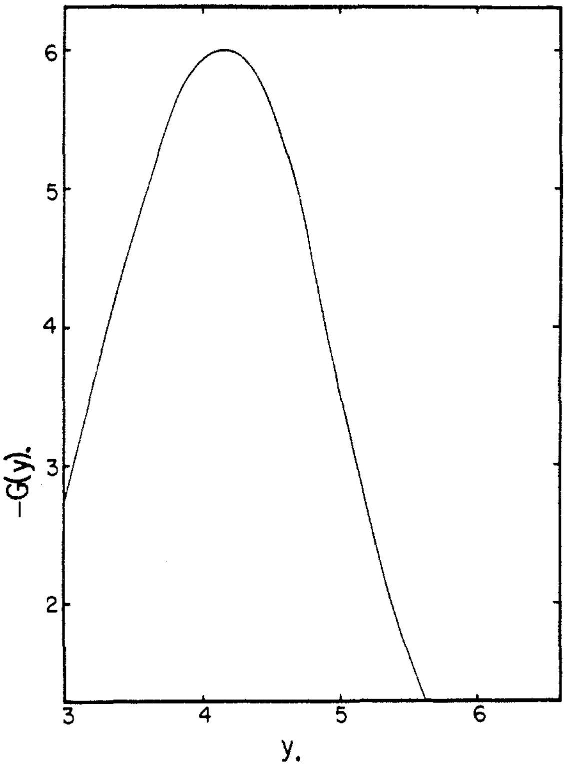

Fig. 4.—$G(y)$ which by Equation 13 specifies the value of $\vartheta_{\text{min.}}$ for a heterogeneous system.

Angular dependence curves calculated from Equations 8, 10, and 13 are given in Fig. 5 for rectangular distributions of different widths. For even the broadest distribution an easily measurable minimum appears and the value of $\vartheta_{\text{Min.}}$ is found to have shifted only slightly. For a homogeneous system of $\alpha = 3$ the minimum intensity is to be found at 97°. For the system having $\alpha_1 = 2.4$ and $\alpha_2 = 3.6$ the minimum appears at 96°. However, the average value of α computed from the weight average particle weight for this distribution is 3.15 and the minimum intensity for $\alpha = 3.15$ would be at 91°. It appears then that the average value of α found by this means, lies between the number average and that found from the weight average particle weight but rather close to the number average. For slightly heterogeneous systems with m greater than unity, it is to be expected that the position of minimum intensity will depend more heavily on the large particles since, in this case, the scattered intensities return to comparatively high values after having passed through a minimum.

This same problem has been discussed by Johnson and LaMer[3] who found that "a 10% impurity of a 2% larger particle can be easily detected." Their method, however, involved the measurement of the red-green intensity ratio and dealt with larger values of both m and α than those discussed here. This would result in the minima of successive orders being closer together and thus being more easily obscured by a few particles of only slightly different size.

Their treatment has been extended by Kerker and LaMer[15] to show quantitatively the effect of heterogeneity on the sharpness of the orders in the Tyndall spectra and on the polarization ratio.

Similar treatments of polydispersity have been given[16] for X-ray scattering from finely divided solids made up of spheres or ellipsoids of revolution scattering incoherently.

It is possible that the above analysis might be useful in connection with certain biological problems where large spherical or nearly spherical particles are encountered. It is interesting to note that Lanni and Campbell[17] have observed the "higher order Tyndall spectra" of LaMer with suspensions of several kinds of bacteria. In the present case of polystyrene latex, the distribution of sizes[2] is so narrow that no appreciable difference from the number average could conceivably be incurred by reason of heterogeneity in determining α from ϑ_{Min}.

Determination of Particle Size from Measurements of Reduced Intensity.—A second means of determining particle weights by light scattering involves the measurement of reduced intensities by comparison with some kind of standard whose reduced intensity is known. Following the notation of Zimm[14] we may write for a solution as c the concentration of solute $\rightarrow 0$

$$\mathbf{R}_{\vartheta,\mathrm{v}} = KcMP\,(\vartheta) \qquad (14)$$

where $\mathbf{R}_{\vartheta,\mathrm{v}}$ is the reduced scattered intensity (in excess of that from the solvent) at the angle ϑ with vertically polarized incident light. M is the molecular weight of the solute and $P(\vartheta)$ is the normalized angular distribution function already mentioned. The factor

$$K = 4\pi^2 n^2 (\partial n/\partial c)^2/\lambda_0^4\,N_0$$

where n is the refractive index of the solvent and $(\partial n/\partial c)$ is the refractive index increment of the solute. λ_0 is the wave length of the incident light *in vacuo* and N_0 is Avogadro's number.

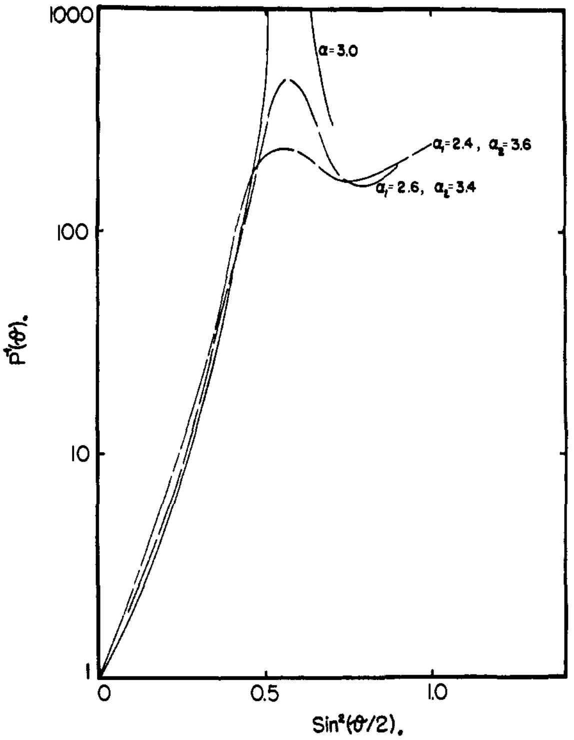

Fig. 5.—Angular dependence curves for a monodisperse system and for heterogeneous systems characterized by rectangular distributions.

Equation (14) holds in general only if the particles are isotropic and if the shift in phase of the incident wave as it traverses a particle is very small. Thus equation (14) will hold for very small isotropic particles (in which case $P(\vartheta) = 1$ for all ϑ) or for large particles with m very near unity. As van de Hulst[4] points out, the condition to be satisfied for equation (14) to be valid in the case of spheres is that $2\alpha(m - 1) \ll 1$. For the polystyrene spheres in question, the above equation may be made applicable by taking account of the phase shift. By a slight modification of the treatment given by Schuster and Nicholson[17a] we find for large refracting particles at zero concentration that

$$\mathbf{R}_{0,\mathrm{v}} = \frac{n^2cM}{\lambda_0{}^4N_0}\left[4\pi^2\left(\frac{\partial n}{\partial c}\right)^2 + \frac{\lambda_0{}^2}{4}\left(\frac{\tau}{c}\right)^2\right] \qquad (15)$$

where τ is the turbidity.

Equally well, we can use the Mie theory to describe the optical behavior of these particles. We shall tentatively assume the latex particles to be isotropic spheres, in which case the theory predicts that the horizontal component (electric

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[15] M. Kerker and V. K. LaMer, THIS JOURNAL, **72**, 3516 (1950).

[16] L. C. Roess and C. G. Shull, *J. Applied Phys.*, **18**, 308 (1947).

[17] F. Lanni and D. H. Campbell, *J. Colloid Sci.*, **3**, 273 (1948).

[17a] A. Schuster and J. W. Nicholson, "Theory of Optics," 3rd Edition, p. 320, Edward Arnold and Company, London (1928). I am very much indebted to Professor Bruno H. Zimm for pointing this out to me.

vector horizontal) will be zero in the scattered light when the electric vector of the incident light is vertical, and observations are confined to the horizontal plane containing the incident beam.[12,18] From Sinclair and LaMer[6] we may write for a volume of 1 cc. containing N independent small particles

$$\mathrm{V}_{\vartheta,\mathrm{u}} = \frac{N\lambda^2\alpha^6}{8\pi^2}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \qquad (16)$$

This is the law for small particles or Rayleigh scattering in which the vertical component is independent of ϑ. Equation (16) can be written in a form analogous to equation (14). The result is, of course, subject to the same limitations that apply to equation (14). In general,[6] for spheres

$$\mathrm{V}_{\vartheta,\mathrm{u}} = \frac{N\lambda^2}{8\pi^2}\,(i_1) \qquad (17)$$

where i_1 gives the angular distribution for the vertical component in the scattered light (unpolarized incident light) and is to be found in the tables of Blumer[13] and of LaMer and Sinclair.[12] In order now to apply the Mie theory we plot in Fig. 6 the quantity $i_{0,1}/\alpha^6$ as a function of α for different m where $i_{0,1}$ is the value of i_1 at $\vartheta = 0$. It will be noted in Fig. 6 that a discrepancy exists between the smooth curve for $m = 1.44$ and the points at $\alpha = 2.4$ and 2.5. It is not known whether the curve should be drawn as shown or should pass through the above points. For the purposes of calculation the smooth curve was used. Equation (2) provides the limit for large spheres with $m = 1$ while equations (16) and (17) show for small particles that $i_{0,1}/\alpha^6 \rightarrow [(m^2 - 1)/(m^2 + 2)]^2$ as $\alpha \rightarrow 0$. A new quantity Φ may be defined by

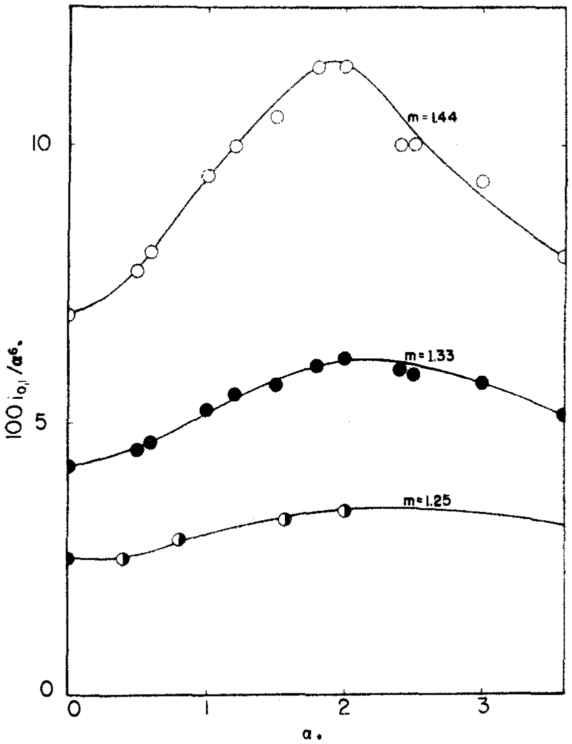

Fig. 6.—The relation between forward scattering and size for different refractive indices.

$$\Phi = \frac{i_{0,1}}{\alpha^6}\Big/\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \qquad (18)$$

This quantity now affords a means of relating the reduced intensity at $\vartheta = 0$ to the particle size. Equation (16) may be revised now to read

$$\frac{2}{\Phi}\left[\frac{\mathrm{V}_{0,\mathrm{u}}}{c}\right]_{c\rightarrow 0} = \frac{9\pi^2 M}{\lambda^4 N_0 d^2}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \qquad (19)$$

where d is the density of the particle. By plotting Φ as a function of m and allowing Φ to approach 1 as $m \rightarrow 1$, we can interpolate to the proper value of m to determine Φ provided we know approximately the value of α in question.

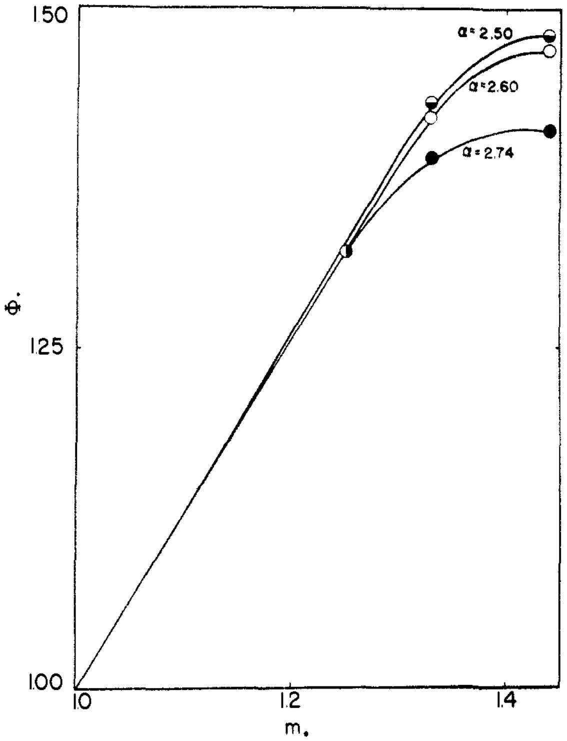

Fig. 7.—The dependence of Φ (see Equation 18) on refractive index and particle size.

Experimental

Apparatus.—The angular dependence measurements reported here were made in a modified Debye apparatus[19] which can measure intensities at all angles between $\vartheta = 20°$ and $144°$. An A-H4 mercury arc serves as a light source and is focused by a condensing lens on a rectangular aperture which in turn is focused into the center of the cell. The angle subtended by the incident beam is about 6° in the horizontal plane. The solution is held in a 12 ml. conical or cylindrical cell which is surrounded by water contained in a large outer rectangular cell. In the case of the cylindrical cell the incident beam is parallel to the axis

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(18) B. H. Zimm, R. S. Stein and P. Doty, *Polymer Bulletin*, **1**, 90 (1945)

(19) P. P. Debye, *J. Applied Phys.*, **17**, 392 (1946).

of the cylinder. A first surface mirror dips into the outer cell and reflects part of the scattered light downward into a 1P21 photomultiplier tube. The mirror and photomultiplier tube move as a unit about the solution cell to allow observation at different angles. The photocurrent is measured directly on a d.c. galvanometer with a sensitivity of 10^{-3} microamperes/mm. (10 cm. scale). The mirror and photomultiplier assembly views an angle of about 5.5° in the horizontal plane. A further description of the instrument will appear in a subsequent paper. Intensity measurements at 90° were made in an instrument previously described[20] and designated by the term MEEZ. In both instruments the blue mercury line was isolated by a Corning filter 5-74.

Light Scattering Measurements.—Angular dependence measurements were made on the polystyrene latex at 5 concentrations from 25 × 10^{-7} g./ml. down to 3.8 × 10^{-7} g./ml. The wave length λ_0 = 4358 Å. unless otherwise noted. The limiting values of $P^{-1}(\vartheta)$ at $c = 0$ were obtained by extrapolation and the results plotted in Fig. 8.

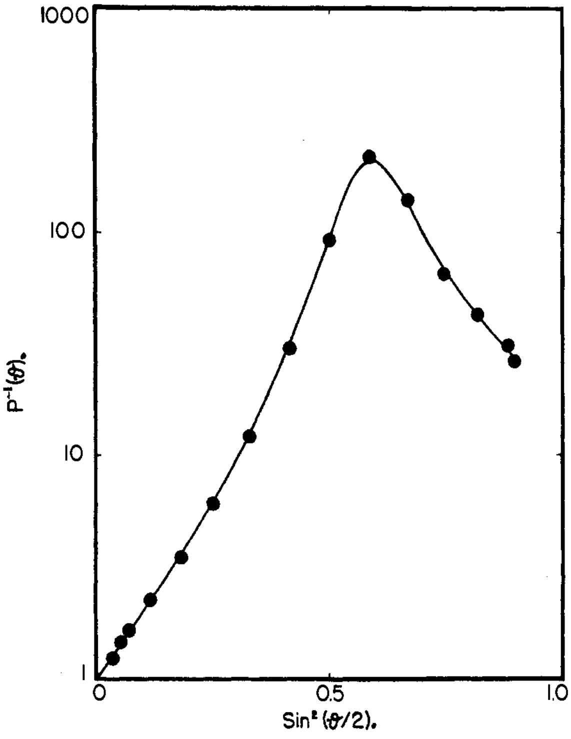

Fig. 8.—The angular dependence curve for polystyrene latex at zero concentration.

Since the experimental points between $\sin^2 \vartheta/2 = 0.12$ and 0.03 fall on a straight line when the reciprocal intensities on a logarithmic scale are plotted against $\sin^2 \vartheta/2$, the extrapolation to $\vartheta = 0$ was made also a straight line. The extrapolated intensity is about 1.2 times as great as the nearest measured intensity. The theoretical curve for $m = 1.33$ and $\alpha = 2.5$ (Fig. 9) resembles the experimental curve rather closely and here it is found also that the portion of the curve below $\sin^2 \vartheta/2 = 0.12$ is very nearly a straight line. Reduced intensities (MEEZ apparatus) were calculated from Carr's measurements[21] on benzene using the value of 49.5 × 10^{-6} cm.$^{-1}$ for the reduced intensity with unpolarized incident light and measuring the total scattered light at 90° (λ_0 = 4358 Å.). Carr's refractive index and volume corrections[21] were applied using the constants previously determined for the MEEZ apparatus.[20]

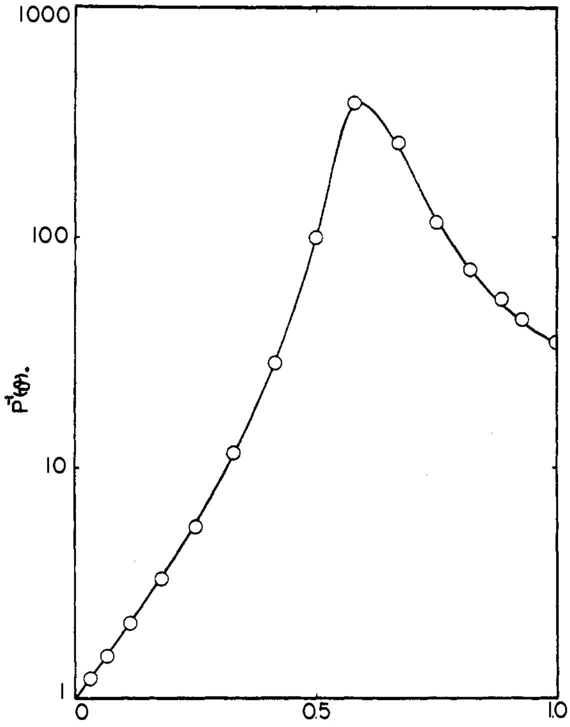

Fig. 9.—Angular distribution of intensities from Mie theory for spheres with m = 1.33 and α = 2.5.

The concentration of latex was determined by dry weight over phosphorus pentoxide at 1 atm. of air. The latex samples were made by dilution of a concentrated latex in freshly distilled water (enclosed all Pyrex still). The depolarization at 90° in unpolarized incident light was measured at a single concentration (6.28 × 10^{-7} g./ml.) and found to be 0.67.

For values of α below ~2.5 this ratio ($H_{90,u}/V_{90,u}$) is a single valued function of α and may be used to estimate the particle size[6] from the values calculated for Mie theory.[12,13] The value of α from this measurement agrees with the results of other methods within the expected error of the interpolation.

The limiting value of $V_{90,u}/c$ at $c = 0$ was found to be 93 and the limiting value of $P^{-1}(90) = 93$ from which the limiting value of $V_{0,u}/c = 8.6 \times 10^3$. The concentration is expressed in g./ml.

As a comparison for these measurements, the Debye polystyrene standard[22] was measured against benzene in the MEEZ apparatus. The excess turbidity was found to be 3.7 × 10^{-3} cm.$^{-1}$. It appears from this measurement that the intensities for polystyrene latex might easily be in error by about 5% and probably high. Evidently, if the Debye polystyrene had been used as a standard taking the value of 3.5 × 10^{-3} cm.$^{-1}$ for the excess turbidity the limiting value of $V_{0,u}/c$ would be about 8.1 × 10^3.

In order to test the assumption that the latex particles are isotropic, the horizontal component in the scattered light was measured in vertically polarized incident light. The horizontal component was on the order of 0.3% of the vertical component. This small depolarization is prob-

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[20] J. T. Edsall, H. Edelhoch, R. Lontie and P. R. Morrison, THIS JOURNAL, **72**, 4641 (1950).

[21] C. I. Carr, Dissertation, University of California, Berkeley, 1949.

[22] This standard was obtained from Professor P. Debye and Dr. A. M. Bueche of Cornell University. The average of several values for the excess turbidity obtained recently in a number of laboratories is about 3.5 × 10^{-3} cm.$^{-1}$ (0.5% solution in toluene; λ_0 = 4358 Å.).

ably not more than that due to secondary scattering in the solution and convergence in the incident beam.

Refractive Index Measurements.—A refractive index measurement ($\lambda_0 = 4358$ Å.) was made in a differential refractometer[23] on a latex containing 0.0016 g./ml. and the value of $(\partial n/\partial c)$ was found to be 0.257 ± 0.005 (c in g./ml.). No significant difference could be found in the refractive index of water and of the clear supernatant fluid produced by centrifugation of a sample of the diluted latex used. Refractive index measurements on the latex are very difficult to carry out because of the great loss of intensity by scattering. From the value of $(\partial n/\partial c)$ we can estimate the refractive index of the polystyrene particles to be 1.64 using the Lorentz–Lorenz equation. If we apply the equation given by Heller,[24] or the equivalent one given by Ewart,[25] we obtain a value of 1.623. If Heller's correction equation[24] is used, a value of 1.613 results. The measured value for bulk polystyrene at the same wave length is 1.614 to 1.615.

Calculation of Particle Size.—The data of Fig. 8 fix the value of $\vartheta_{\text{Min.}}$ at 101°. A closer check of the intensities in this region indicates that the minimum lies between 101° and 102°. The error in alignment of the instrument could be easily 1°. Taking $m = 1.20$ we can evaluate the constant k in equation (1) from Fig. 1. The values of k obtained are 1.98, 2.08, and 2.06. Taking an average value $= 2.04$, we find $\alpha = 2.63$, or $D = 2r = 2720$ Å. The minimum intensity for $\lambda_0 = 4047$ Å. appears at $\vartheta = 94°$. If we assume m to be unchanged over this range of wave length we find $\alpha = 2.80$ or $D = 2680$ Å.

Values of M may be calculated from equation (15) or (19). The value of τ/c was estimated from Fig. 8 and the depolarization $(H_{90,u}/V_{90,u})$ to be 3.1×10^4 at zero concentration. Equation (15) then gives $M = 6.84 \times 10^9$ or $D = 2740$ Å. Here as a special application of Rayleigh's Law of Reciprocity[18] we have replaced $\mathbf{R}_{\vartheta,v}$ by its equivalent $2V_{\vartheta,u}$. To apply equation (19) we choose a value of $\Phi = 1.27$. Since $\lambda_0 = 4358$ Å., n the refractive index of water is taken as 1.3403. The density of the polystyrene particles is known to be 1.052.[2] If m for bulk polystyrene is used in equation (19) then a value of 6.7×10^9 is obtained for M corresponding to $D = 2720$ Å. or $\alpha = 2.63$, indicating that the value of Φ is properly chosen since a second approximation leaves Φ unchanged. The estimates of D from reduced intensity measurements should be more reliable than those evaluated from $\vartheta_{\text{Min.}}$ because of the uncertainties involved in the use of equation (1). If we neglect the variation of Φ over a small range of α then the average diameter resulting from a measurement of reduced intensity and concentration is defined by

$$\bar{D}_w^3 = \frac{\sum_i D_i^6 \nu_i}{\sum_i D_i^3 \nu_i}$$

where ν_i is the number of particles having a diameter D_i. From the distribution curve obtained by electron microscopy[2] we can compute this average to be 2595 Å.

Test for Aggregation in Polystyrene Latex.—In order to test for the presence of aggregates in the latex, a 50-ml. portion containing $\sim 3 \times 10^{-5}$ g./ml. was centrifuged at 4000 times gravity for one hour. A small precipitate could be seen on the bottom of the tube after this time. About 15 ml. of the solution (A) nearest the top of the centrifuge tube was removed and the remaining solution (B) mixed. Within five minutes the extinctions of A and B were determined in a Beckman Quartz Spectrophotometer at 4360 Å. (1-cm. cell). The readings were $A = 0.258$ and $B = 0.323$ indicating that appreciable sedimentation had occurred. B was then diluted to give the same reading at 4360 Å. as A undiluted and readings then taken at 11 wave lengths between 2500 and 6000 Å. No significant difference was found at any wave length and it was concluded that the latex is not aggregated at these concentrations. Of course, rapidly reversible aggregation would not be detected by this method. It is to be noted also that because of the geometry of the Beckman spectrophotometer the extinctions thus measured include a portion of the scattered light in the transmitted intensity, but that for the above comparison this should be immaterial.

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Summary

Light scattering measurements on a polystyrene latex (Dow Latex 580-G, Lot 3584) have been carried out and interpreted on the basis of Mie theory. The sphere diameter by location of minimum intensity in the angular dependence curve is found to be 2720 Å. Reduced intensity measurements indicate a diameter of 2720–2740 Å. The difference between these values and the results of electron microscopy[2] is within the possible experimental error in the measurements reported here.

Fractionation of the latex by differential centrifugation failed to reveal any trace of aggregation or polydispersity.

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[23] The author is indebted to Professor P. M. Doty for the use of this instrument.

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[25] R. H. Ewart, C. P. Roe, P. Debye and J. R. McCartney, *J. Chem. Phys.*, **14**, 687 (1946).