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A Light Scattering Investigation of Cellulose Acetate[1]

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Introduction

In view of the apparent success of the preliminary investigation[3,4,5,6] of the light scattering method[7] of determining molecular weights of polymers, a study of a better characterized series of fractions of cellulose acetate was undertaken. In addition to offering a test of the fundamental theory, a study of cellulose acetate offers an opportunity to examine a case where the angular intensity of light scattered from the solution is not symmetrical about 90°. This dissymmetry (which is easily observed by visual examination) is the direct result of the extension beyond a few hundred Ångströms of the scattering particles.[8] If these molecules were considerably coiled, their largest dimensions would necessarily not exceed about one-twentieth the wave length of light and consequently the angular distribution of intensity would be symmetrical about 90°. However, considerable dissymmetry is present here and its quantitative evaluation leads to two important results: (1) the determination of the correction factor which permits the calculation of molecular weights for the case of Mie (non-symmetrical) scattering; (2) a fairly accurate estimate of the size of the molecule may be made.

Scattering of Light from Solutions of Large Molecules[9]

When light waves pass through a solution, loosely bound electrons are forced into vibration and radiation is emitted in all directions with the frequency unchanged (Tyndall effect). The intensity of this scattered light has been shown to depend on the microscopic heterogeneity of the solution. In the case of high polymer solutions the principal cause of heterogeneity is usually the fluctuations in concentration. The extent of these fluctuations is a function of the work necessary to produce such a local variation in concentration in a volume element, and is obviously related to the free energy of dilution and hence to the osmotic pressure. Debye[7] has adapted the equations of von Smoluchowski[10] and Einstein[11] for the scattering from a solution of small isotropic particles in order to demonstrate this relation. On this basis, or by a somewhat different manner,[3] the following equation may be obtained which relates the turbidity (extinction coefficient in cm.$^{-1}$ due to concentration fluctuations) to the refractive index, n, the concentration c, the refractive index increment, $\partial n/\partial c$, and M_2, the molecular weight of the solute.

$$\frac{32\pi^3 n^2(\partial n/\partial c)^2}{3\lambda^4 N_0}\,\frac{c}{\tau} = H\frac{c}{\tau} = \frac{1}{M_2} + \frac{2B}{RT}c \qquad (1)$$

λ is the wave length of light (monochromatic), N_0 is Avogardro's number and B, which measures

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(1) Presented before the New York Section of the American Chemical Society, June 8, 1945, and included in the 1945 Meeting-in-Print of the Division of Physical and Inorganic Chemistry, American Chemical Society.

(2) Taken in part from a thesis presented in partial fulfillment for the degree of Bachelor of Science, Polytechnic Institute of Brooklyn, June, 1945. Present Address: Department of Chemistry, Princeton University, Princeton, N. J.

(3) P. Doty, B. Zimm and H. Mark, *J. Chem. Phys.*, **12**, 144 (1944).

(4) B. Zimm and P. Doty, *ibid.*, **12**, 203 (1944).

(5) P. Doty, B. Zimm and H. Mark, *ibid.*, **13**, 159 (1945).

(6) W. Heller and H. B. Klevens, *Phys. Rev.*, **67**, 61 (1945).

(7) P. Debye, *J. Applied Phys.*, **15**, 456 (1944). The pioneering work in light scattering that has been sponsored at Cornell University by the Rubber Reserve Company under the direction of Professor Debye has been summarized in reports numbered CR103, CR103A, CR110 and CR296 which have been available. It is understood that further work is described in recent reports but these have not been obtained by the authors.

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

(9) B. Zimm, R. S. Stein and P. Doty, *Polymer Bull.*, **1**, 90 (1945).

(10) M. von Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

(11) A. Einstein, *ibid.*, **33**, 1275 (1910).

the deviation from van't Hoff's law, is the coefficient of the square term in concentration in the expression for osmotic pressure ($\pi = RT\,c/M_2 + Bc^2$). H denotes factors which are constant for a given system.

In the derivation of this equation it was necessary to assume that the scattering particles were small compared to the wave length of light. If, however, a linear dimension of the molecule is a significant fraction of the wave length (>1/20), it can no longer be considered a point source and the scattering from different parts of the same molecule must be considered separately. Thus the light scattered from different parts of the molecule differs in phase due to the difference in path length, and a greater path difference is produced in the backward than in the forward direction. As a result of this interference effect, there will be an all around decrease in scattered intensity with a greater reduction in the backward direction and a consequent dissymmetry in the angular distribution of intensity of the scattered light (radiation envelope).

For first order interference from a polymer solution of homogeneous molecular size and shape, the radiation envelope may be adequately characterized by measuring the ratio of scattered intensity at two angles symmetrical about 90°. The dissymmetry coefficient, *q*, defined as one less than the ratio of forward intensity to backward intensity, can then be evaluated.

This interference pattern may be evaluated by means of an integration over the volume elements of the scattering particle, each element being characterized by the optical path lengths of the associated incident and scattered rays and by the time average density distribution function of the element in the particle. The exact evaluation of this interference effect is difficult when the refractive index of a particle is much different from that of the medium in which it resides. The problem which then arises involves the determination of the effect of the polarization charges on the surface of the particle on the electric field acting upon a particular dipole as a function of the position of the dipole in the particle. A solution of this problem for particles of simple geometric shape (especially spheres) has been worked out by Blumer.[12] P. Debye and P. P. Debye[13] have shown that the solution in which the approximation of no refractive index difference is made is sufficiently accurate for application to polymer solutions. They have obtained simple function solutions for spheres, rods and randomly coiled chains. The latter two shapes correspond to the extremes expected for most polymer molecules and have been applied in this investigation. For a straight rod-shaped molecule, the angular variation of intensity, *I*, is given by[13]

$$I = \frac{1}{x}\int_0^{2x}\frac{\sin x}{x}\,dx - \left(\frac{\sin x}{x}\right)^2 \qquad (2)$$

where the factor ($1 + \cos^2\theta$) has been omitted since it is symmetrical about 90°. $x = \pi L\sigma'/\lambda$ where L = length of molecule, λ = wave length of light in solution and $\sigma' = 2\sin\theta/2$. Similarly, for a randomly coiled molecule (Kuhn[14])

$$I = \frac{2}{v^2}\left[e^{-v} - (1 - v)\right]$$

where

$$v = \frac{2}{3}\left(\frac{\pi R\sigma'}{\lambda}\right)^2 \qquad (3)$$

R^2 is the root mean square separation of the ends of the chain-like molecule. While these equations have been independently confirmed here, it is hoped that a complete treatment will be soon forthcoming from the Debye's.

In the determination of molecular weight by use of equation (1), the measured turbidity will of course be affected by the all around decrease in scattered intensity. The turbidity appearing in (1) refers to the value obtained in the absence of interference. Consequently, for the application of equation (1) the turbidity measured for a solution exhibiting dissymmetry must be augmented by the amount lost due to interference. This correction can be made by use of the dissymmetry coefficient practically independent of the assumption of shape or size of the scattering molecule as demonstrated below, providing the extension of the molecule is not too great.

Measurement of Turbidity and Dissymmetry

Turbidimeter.—A schematic diagram (top) of the turbidimeter[15] constructed for this work is shown in Fig. 1. A vertically mounted mercury arc (AH-4, 100-watt General Electric bulb) serves as a light source (A). The light is rendered monochromatic (5461 Å.) by the filters (B) and parallel by the lens (C) and square diaphragm (D). A glass plate (E) mounted at 45° reflects a small fraction of the incident light on to an opalescent glass plate (F). The square cell (G) containing the polymer solution is immersed in a water-filled chamber (H). A false bottom in this chamber permits temperature control by circulating water from a thermostat. The water in the cell also serves to minimize reflections at interfaces. After passing through the solution, the incident beam is absorbed, through multiple reflection, by the cone (I) at the far end of the chamber. The lens (J) transmits some of the light scattered at 90° into one side of a Zeiss Pulfrich Photometer (K) which is used to compare visually the intensity of this light with that coming from the opalescent plate (F), the reference standard. Provision is made to insert neutral filters (L) into the connecting tube of the photometer in order to limit the in-

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[12] H. Blumer, *Z. Physik*, **32**, 119 (1925); **38**, 304, 920 (1926); **39**, 195 (1926).

[13] P. Debye, lecture given at the High Polymer Seminar, Polytechnic Institute of Brooklyn, November 25, 1944.

[14] W. Kuhn, *Kolloid Z.*, **68**, 2 (1934).

[15] General Gauge and Tool Co., 30 Irving Place, New York, N. Y.

tensity during the calibration. The two beams pass through precision diaphragms of adjustable area, and by means of a prism and lens system, illuminate the two halves of a divided field. The slit areas are adjusted until the two half-fields appear to be equally bright. The relative intensities are then inversely proportional to the respective slit areas, which are indicated on graduated scales on the slit area adjusting dials (M).

Calibration of Turbidimeter.—The calibration was based on a reflectivity measurement of a magnesium carbonate surface. A photometric match was obtained first with the cellulose acetate solution. The solution was then replaced by a magnesium carbonate prism mounted in a glass cell at 45° to the incident beam. In view of the following considerations, it was then possible to correlate the dial readings so obtained with the proportionality constant relating dial readings with absolute turbidity.

Consider a parallel, homogeneous pencil of light of cross-sectional area, A, and intensity, I, striking the prism at an angle, θ, from its surface. The intensity of illumination on the surface of the prism will then be $I \sin \theta$ ergs/cm.^{2} on the subtended area A'. The total reflected energy per unit time will then be $IA'R \sin \theta$ ergs. R is the total diffuse reflecting power of the surface.

The relative reflected intensity, I_r', in any direction at a distance r from the prism surface may then be found with the aid of Lambert's law of diffuse reflection. This relation is

$$I_r' = K \sin \alpha / r^2 \tag{4}$$

The angle between the surface of the prism and the direction r is denoted by α; K is the proportionality constant which may be evaluated by integrating the reflected intensity over the surface, S, of a hypothetical hemisphere surrounding the surface of the prism and equating it to the energy radiated per unit time ($IA'R \sin \theta$).

$$\int_S I_r' \mathrm{d}S = \int_0^{\pi/2} \left(\frac{K \sin \alpha}{r^2}\right) 2\pi r^2 \cos \alpha \mathrm{d}\alpha = \pi K \tag{5}$$

Hence

$$K = \frac{IA'R \sin \theta}{\pi} \tag{6}$$

By substituting this into equation (2) it is seen that

$$I_r' = IA'R \sin \alpha \sin \theta / \pi r^2 \tag{7}$$

Since the apparent field is $A' \sin \alpha$, the reflected intensity per unit area of the apparent field is

$$I_r = IR \sin \theta / \pi r^2 \tag{8}$$

If the magnesium carbonate prism is now replaced with a similar cell containing the solution, the equivalent scattered intensity, I_s, at 90° per unit area of field may be computed. This is

$$I_s = i_0 V' = i_0 h \tag{9}$$

where: i_0 is the scattered intensity at a distance r normal to the incident light from a unit volume of scattering solution; I_s is the total intensity scattered transversely per unit area of observable field at a distance r from the solution; V' is the volume of scattering solution per unit area of observable field; h is the depth of the illuminated solution in the line of view. Consequently, the ratio of the scattered intensities from the solution and the prism is

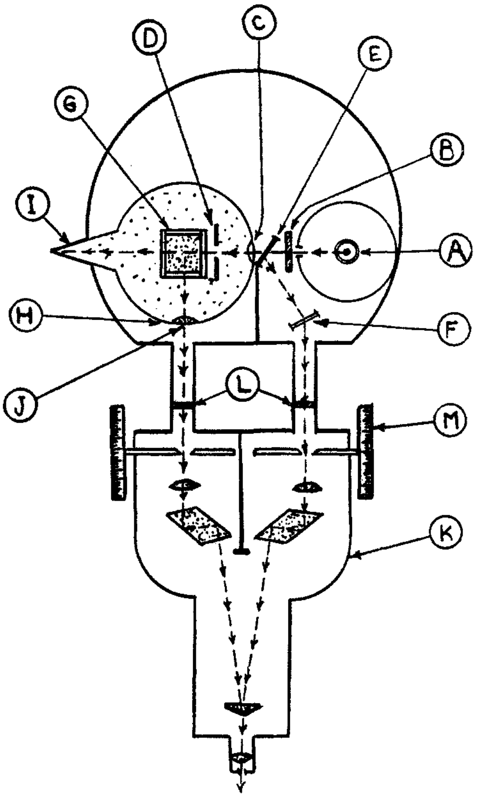

Fig. 1.—The turbidimeter.

$$\frac{I_s}{I_r} = \frac{i_0 h \pi r^2}{IR \sin \theta} \tag{10}$$

Integration of scattered intensity over a sphere surrounding a quantity of solution executing Rayleigh scattering gives as an expression for turbidity

$$\tau = \frac{16}{3} \pi \frac{i_0 r^2}{I} \tag{11}$$

Combining equations (8) and (9) we obtain

$$\frac{I_s}{I_r} = \frac{3h\tau}{16R \sin \theta} \tag{12}$$

which is also equal to the ratio of the dial readings for the solution and the prism. Using 0.97 for the reflectivity of magnesium carbonate, $\theta = 45°$, $h = 1.09$ cm., we obtain for the turbidity of a solution

$$\tau = 3.34 \frac{\text{Dial reading (right) for solution}}{\text{Dial reading (right) for prism}} \tag{13}$$

Solutions measured on a Zeiss Turbidimeter calibrated by a Zeiss opalescent prism in absolute turbidities gave values within 10% of those measured on the turbidimeter calibrated as here described.

Measurement of Dissymmetry.—In general it would be desirable to measure the angular variation of the intensity of the scattered light over the whole range from 0 to 180°. However, inasmuch as the theory indicates that this angular distribution is characterized by only one parameter for particles of homogeneous size in the range we are investigating, and since the influence of very small amounts of colloidal impurities on the dissymmetry is often great enough to limit considerably the accuracy attainable, it was felt that a simple apparatus capable of measuring only a few points on the intensity angle curve would be adequate for the problem at hand. Such an instrument for the direct determination of the dissymmetry was constructed and the essential components are shown in Fig. 2.

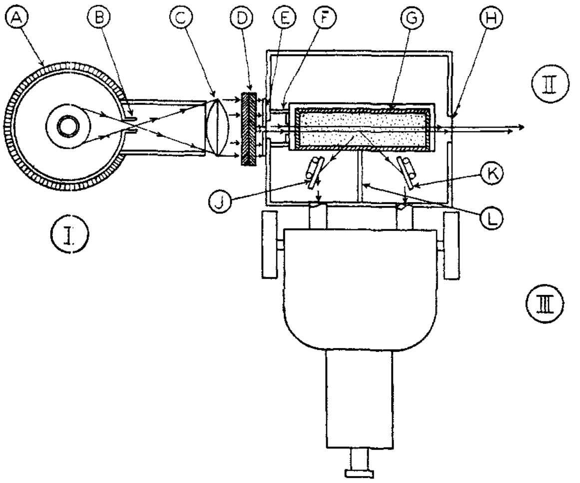

Fig. 2.—Apparatus for measurement of dissymmetry.

A cylindrical water-cooled vertical lamp housing (A) contains a vertically mounted AH-4 mercury arc. A narrow slit (B) in the front of the housing serves as a secondary source. The convex lens (C) renders the light parallel, while a set of Corning color filters (D) isolates the desired mercury line. Two $^1/_8''$ vertical slits (E) and (F) collimate the beam into a narrow rectangular pencil.

The principal component of the dissymmetry apparatus is a metal box (II), 7″ long, 6″ wide and 3″ high, which contains the solution and mirrors. A rectangular glass cell (G) 100 mm. long, 20 mm. wide and 50 mm. high is located in the center of this box by metal guides. The cell is open at the top and is partially filled with a solution of the high polymer. The light beam, upon leaving the collimating slits, passes through the center of this cell and out through the exit hole (H). Light is scattered in all directions from the solution, and two first-surface mirrors (J) and (K) are mounted so as to reflect two symmetrically scattered rays of light out of the box perpendicularly through two circular holes in the front wall. The mirrors are mounted on bases having dowel pins which fit into holes drilled through the bottom of the box. Several sets of these holes are provided so as to permit variation of the mirror angles symmetrically about the 90° axis. A central barrier (L) serves to help prevent stray light from striking the mirrors. The interior of the box is coated with an optically black lacquer.

A Zeiss Pulfrich Photometer (III) (similar to that used with the turbidimeter) is placed so as to receive the light beams passing out through the holes in the front of the box. Its function is to measure the comparative intensity of these two light rays. At balanced fields, the ratio of the intensities of these rays should be inversely proportional to the respective dial readings of the photometer.

The dissymmetry instrument may be tested for symmetry of construction by measuring the dissymmetry of the fluorescent light radiating from a solution of fluorescein placed in the cell. Such a solution should radiate light equally in all directions, and the indicated dissymmetry coefficient should be zero. The effect of stray light may be determined by measuring the dissymmetry of the radiation from successive dilutions of the fluorescein. If stray light is entering the photometer unsymmetrically (as it would probably do if it were present), the observed dissymmetry should become more apparent at lower concentrations. The dissymmetry instrument was tested in this manner, and it was found to give satisfactory measurements in the intensity range over which the scattering measurements were to be made.

Experimental

Preparation of Solutions.—Since the intensity of the scattering from an isolated particle varies approximately with the sixth power of its diameter, and since the backward scattered light from the larger particles is usually destroyed by interference, even a slight concentration of densely packed foreign material of a size that is somewhat greater than the scattering molecules will contribute materially to the observed dissymmetry. Therefore, it is of utmost importance that the solutions be rendered optically clean prior to measurement.

The fractions used in this investigation were prepared by Badgley[16] and were reprecipitated several times in order to remove as much coarse material as possible. After vacuum drying the fractions were dissolved in dried, freshly distilled acetone. In spite of these precautions, the solutions were still found to contain an appreciable amount of optical impurities. These impurities reveal themselves by their Tyndall scattering and observable Brownian movement when the scattering at angles very close to the transmitted beam is visually examined with the aid of a lens. Neither filtration through Corning "Fine" sin-

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[16] W. J. Badgley, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1945. Preliminary publication: *Polymer Bull.*, **1**, 17 (1945).

tered glass filters (15 microns) nor high speed angle centrifugation (6000 r. p. m.) effectively cleaned the solution. For example, a cellulose acetate solution which was found to have a dissymmetry coefficient of 2.5 after the filtering treatment had a coefficient of 0.8 after cleaning by more refined techniques.

After considerable experimentation, fairly satisfactory results were obtained through the use of a pressure-type bacteriological filter[17] having a maximum pore size of 800 millimicrons (Selas #04). All solutions on which dissymmetry measurements were made were filtered in this manner.

Refractive Index Increment Measurements.—The difference in refractive index between solvent and solution is a linear function of concentration. Hence it suffices to measure the difference in refractive index between solvent and solution to any one concentration. The value of $(\partial n/\partial c)$ was found to be 0.116, 0.115, 0.115 and 0.104 for fractions 8B, 18B, 23B and 32B, respectively. These determinations were made with a Zeiss Pulfrich Refractometer.

Turbidity and Dissymmetry Measurements.—The turbidities of these solutions were measured as a function of concentration with the turbidimeter. The turbidity of the solvent was subtracted from each measured turbidity to obtain τ as required for use in equation (1). Values of H (equation 1) were calculated to be $1.14 \times 10^{-6} (\partial n/\partial c)^2$ since $\lambda = 5461$ Å. and $n = 1.359$. The data are plotted in Fig. 3 where it is seen that the points fall fairly well on straight lines of approximately the same slope. The intercepts, molecular weights (assuming small particle scattering) and the slopes are recorded in Table I.

Also included in Table I are the dissymmetry coefficients measured on specially filtered solutions in the dissymmetry instrument. The probable error in measuring q is about ± 0.03. The angles of measurement for the dissymmetry were 30 and 150° in air. The actual angles in solution are found from a simple consideration of the geometry and the effect of refractive index to be 51 and 129°. The effect of concentration on the dissymmetry was measured over the concentration range of 0.25 to 1.0% and found to be independent of concentration within ± 0.02. This constancy of q with respect to concentration indicates that the dissymmetry observed was due to intermolecular interference and that the simple theory relating angular dependence to molecular dimensions should be applicable.

TABLE I

SUMMARY OF LIGHT SCATTERING DATA ON CELLULOSE ACETATE FRACTIONS

Fract.	Intercept $\times 10^6$	Mol. wt. (uncor.)	q	ρ	Mol. wt. (cor. for ρ)
8B	8.50	118,000	0.60	0.017	114,000
23B	10.9	91,700	.60	(.020)	87,700
18B	16.6	60,200	.43	(.037)	55,600
32B	21.2	47,200	.43	.045	43,000
31B	..	.....	.32	...	.....

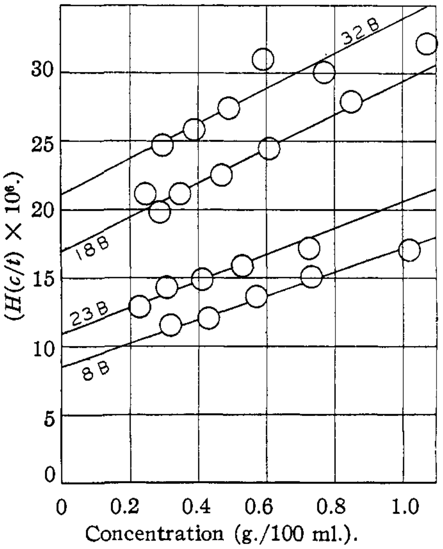

Fig. 3.—Turbidity data for the cellulose acetate fractions.

Depolarization Measurements and Correction.—It is well known that a small contribution to the measured turbidity arises from fluctuations in orientation. Since the turbidity, τ, in equation (1) refers only to fluctuations in concentration, the measured turbidity should be corrected for this extra source of turbidity just as the turbidity due to fluctuations in density was taken into account by subtracting the turbidity of the solvent. The correction for turbidity due to orientation fluctuations is evaluated from depolarization measurements by the use of Cabannes' factor, $(6 - 6\rho)/(6 + 7\rho)$, is the depolarization observed with the incident light unpolarized.

On the basis of the depolarization measurements of cellulose acetate in acetone by Doty and Kaufman[18] the correction was applied with the results shown in the last column in Table I. The values in parentheses were obtained by interpolation; the others by actual measurement.

Angular Dependency of Scattered Light.—In order to determine whether the measured angular dependency agreed with that theoretically predicted, one of the mirrors of the dissymmetry instrument was removed and the position of the other was varied (and *vice versa*), and the ratio of the intensities was measured. In this manner, the ratio of the intensity scattered at any angle to that scattered at 90° may be determined. Several additional corrections must be applied, however, to this measurement. These are

1. The volume of scattering solution in the field of view varies with the angle. This may be approximately corrected by multiplying the measured intensity by sin θ.

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[17] Manufactured by the Selas Company, Philadelphia, Pa.

[18] P. Doty and H. S. Kaufman, *J. Phys. Chem.*, in press.

2. The light that is reflected from a mirror comes from a portion of the solution that is equidistant from the two photometer pick-up tubes, while that which enters the photometer when one of the mirrors is removed (at 90°) comes from a portion of the solution directly in front of one of the pick-up tubes. A correction must be made for the decrease in the intensity of the primary ray resulting from absorption in traversing the distance between these two portions of the solution. The amount of absorption may be determined by removing both mirrors and measuring the ratio of intensities. The correction factor will then approximately equal half of this ratio.

3. The reflectivity of the solution–glass–air interfaces is a function of the angle. This correction[19] is

$$\frac{\dfrac{(1 - r_1^2)(1 - r_2^2)}{1 - r_1^2 r_2^2} + \dfrac{(1 - r_1'^2)(1 - r_2'^2)\cos^2\theta}{1 - r_1'^2 r_2'^2}}{1 + \cos^2\theta}$$

where

$$r = \frac{\sin(\phi_1 - \phi_2)}{\sin(\phi_1 + \phi_2)} \text{ and } r' = \frac{\tan(\phi_1 - \phi_2')}{\tan(\phi_1 + \phi_2)}$$

ϕ_1 and ϕ_2 are the angles of incidence and refraction. The subscripts (1) and (2) on the r's refer to the liquid–glass and glass–air interfaces.

4. The intensities must be normalized in order to account for the variation due to the resolution of polarized components. This is done by dividing by $(1 + \cos^2\theta)$.

The angles are converted from degrees into the corresponding values of σ' ($\sigma' = 2 \sin \theta/2$) in order to facilitate the comparison with the theoretical relationships. These measurements and corrections are summarized in Table II. In Fig. 4 the relative intensities are plotted against σ'. The curve drawn on this graph is the corresponding theoretical plat (see last section). The experimental points fall reasonably close to the curve.

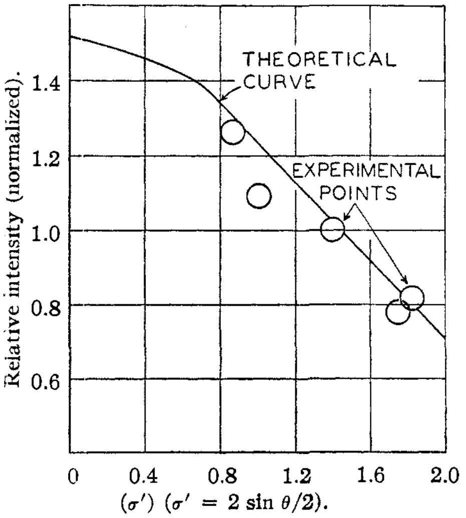

Fig. 4.—Comparison of observed to theoretically predicted dissymmetry.

Table II

Summary of Calculations of Angular Variation of Intensity

θ° (air)	θ° (soln.)	(σ')	$\frac{I_0}{I_{90°}}$	Correction factors: Sin θ	Ab-sorp-tion	Re-flec-tion	$(1 + \cos^2\theta)$	$\frac{I_0 \text{ (cor.)}}{I_{90°}}$
30	51	0.876	2.00	0.777	54/52	1.09	1.395	1.26
45	59	1.00	1.49	0.857	54/52	1.03	1.265	1.09
90	90	1.414	1.04	1.000	54/50	1.00	1.000	1.00
135	121	1.764	1.17	0.857	50/52	1.03	1.265	0.79
150	129	1.812	1.40	0.777	50/52	1.09	1.395	0.82

Molecular Weight Correction for Dissymmetry.—In view of these dissymmetries, it is obvious that cellulose acetate molecules are large as compared with one-twentieth of the wave length of the light. Therefore, the molecular weights presented in Table I are incorrect, and must be multiplied by a correction factor to account for the intramolecular interference which is characterized by the dissymmetry coefficient. This correction factor is equal to the ratio of the intensity of the scattering at 90° in the absence of intramolecular interference (*i. e.*, by equations (2) or (3) where x or v approach zero as a limit) to the observed intensity. The parameters determining the curve for large molecule scattering must be chosen so as to account for the observed dissymmetry coefficient and so that both the large and small molecule scattering laws predict the same intensity at $\theta = 0°$. The molecular weight correction factors were computed as a function of the dissymmetry for the angles, refractive index, and wave length at which the measurements were made by the use of either equation (2) or (3). For particles smaller than half the wave length of light, the relation between intensity and angle is essentially independent of the model chosen; consequently either equation 2 or 3 gives the same curve (within a variation of less than 1%) for a given dissym-

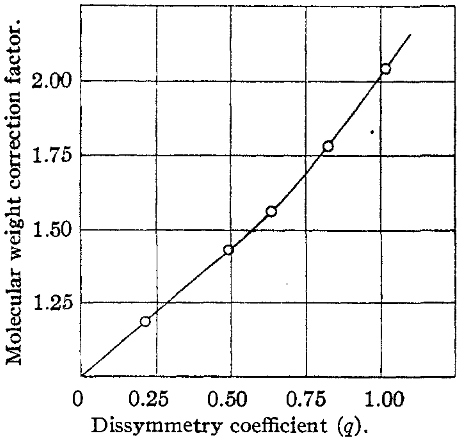

Fig. 5.—Relation between dissymmetry coefficient and molecular weight correction factor.

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(19) P. P. Debye, Thesis, Cornell University, 1944.

metry coefficient. It is convenient to disregard here the factor $(1 + \cos^2 \theta)$, which arises from the combination of the polarized components of the incident light, since, being symmetrical about 90°, it does not affect the dissymmetry. In this manner, Blumer's[12] results for spheres, Debye's[13] equations for rods or coils, or the corresponding equation for X-ray diffraction from spheres gives a family of curves on an intensity $- \sigma'$ plot, one member of which is characterized by a given q value. Having chosen this member, the value of the ratio of the relative intensity at 0° to that at 90° is equal to the correction factor to be applied to the turbidity measured at 90°. The relation between q (measured at 51 and 129°) and the correction factor is shown in Fig. 5. The molecular weights, corrected in this manner, are presented in Table III together with the osmotic pressure and viscosity molecular weights of these fractions as determined by Badgley.[16] The values in parentheses are viscosity values. In this case, however, the viscosity–molecular weight relation was so well calibrated that these viscosity values are considered as reliable as the osmotic pressure values. It is seen that the molecular weights determined by light scattering do not differ by more than 8% from those determined by osmotic pressure and viscosity measurements. This difference is certainly within the probable experimental error.

TABLE III

SUMMARY OF MOLECULAR WEIGHT DATA ON CELLULOSE ACETATE

Fract.	Light scat., mol. wt., (cor. for p)	q	Dissymmetry correction factor	Light scat., mol. wt. (cor.)	Osmotic pressure, mol. wt.
8 B	114,000	0.60	1.52	173,000	(163,000)
23 B	87,700	.60	1.52	135,000	133,000[a]
18 B	55,600	.43	1.38	77,000	(75,000)
32 B	43,000	.43	1.38	60,000	65,000

[a] Unfortunately, due to an error in recording data and the subsequent loss of the fractions, it is not possible to decide with certainty whether this sample was fraction number 23 B with molecular weight 100,000 or fraction number 16 B with molecular weight 133,000. It is believed that it was fraction 16 B that was used instead of 23 B throughout this work.

The slopes of the light scattering curves were also corrected by this factor. It is apparent that, since the factor increases the true turbidities, the slope, $\Delta H(c/\tau)/\Delta c$, must be divided by it. The corrected slopes are presented in Table IV.

TABLE IV

CORRECTION OF $(Hc/\tau) - c$ SLOPES

Fraction no.	Uncor. slope × 10^4	Correction factor	Corrected slope × 10^4
8 B	8.8	1.52	5.8
18 B	13.3	1.38	9.6
23 B	10.1	1.53	6.6
32 B	13.0	1.38	9.4

The average deviation of these slopes from their average value, 7.9×10^{-4}, is approximately 20%.

From these data, it is interesting to calculate the value of the empirical constant, μ, which characterizes the deviation from van't Hoff law behavior for a solute–solvent system. This is defined in the equation given for the osmotic pressure by Huggins[20]

$$\frac{\pi}{c} = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}\left(\frac{1}{2} - \mu\right) c \qquad (14)$$

where V_1 is the molar volume of the solvent and d_2 is the density of the polymer. By comparing this with the power series expansion for osmotic pressure

$$\pi = \frac{RT}{M_2} c + Bc^2$$

it is seen that

$$B = \frac{RT}{V_1 d_2^2}\left(\frac{1}{2} - \mu\right) \qquad (15)$$

Hence, using equation I, μ can be evaluated in terms of the slope of the Hc/τ *versus* c plots, since

$$\frac{\Delta H \frac{c}{\tau}}{\Delta c} = \frac{2B}{RT} = \frac{2}{V_1 d_2^2}\left(\frac{1}{2} - \mu\right) \qquad (16)$$

Using the average value of the slope from Table IV and 1.30 for the density of cellulose acetate, a value of 0.45 ± 0.01 is obtained for μ. For an acetone solution from the osmotic pressure data of Badgley on this series of cellulose acetate fractions a value of 0.430 ± 0.005 was found for μ.

Determination of Size from Dissymmetry

If the solute molecules are smaller in their largest dimension than the wave length of light, the absolute intensity measurement of the transversely scattered light may be used in connection with the dissymmetry coefficient to determine the molecular weight of the solute. This procedure is essentially independent of the choice of molecular model.[21] The dissymmetry coefficient measured for this purpose may also be used to obtain information on the dimensions of the dissolved molecules.

The relative intensities at angles of 51 and 129° for scattering from rods and randomly coiled chains of various sizes were computed for light of a wave length of 5461 Å., in air (4020 Å. in solution) by the use of equations (2) and (3). From these, theoretical dissymmetry coefficients were computed as a function of the root mean square distances between the ends of the molecules of both shapes. These calculations are plotted in Fig. 6.

From the measured dissymmetry coefficients, the root mean square distances between the ends

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(20) M. Huggins, *Ann. N. Y. Acad. Sci.*, **41**, 1 (1942).

(21) Calculations show that the shapes of the intensity-σ' curves for a given dissymmetry coefficient (0–2.0) are practically the same in the region of 0–135° for a sphere, rod or random coil. Consequently, any of these may be used for the interpolation to obtain the value of the intensity at 90°.

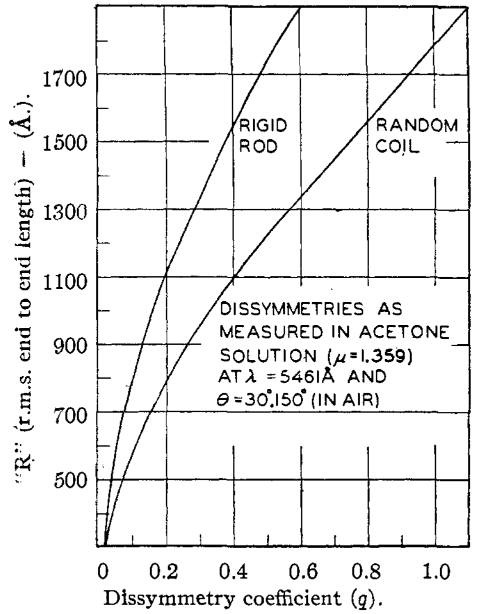

Fig. 6.—Relation between dissymmetry and molecular model dimensions.

of the cellulose acetate molecule in acetone solution were then estimated using these curves. The results are tabulated in Table V together with the lengths calculated from the molecular weights on the assumption that the molecules are completely extended (degree of polymerization times length of monomer unit, 5.1 Å.).

Table V

Dimensions of Cellulose Acetate Molecules

			R.M.S. distance between ends		
			Computed from q		
Fract.	Molecular weight	q	Assuming rigid rod, °A.	Assuming random coil, °A.	Computed from mol. wt., A.°
8 B	163,000	0.60	1900	1340	3100
23 B	135,000	.60	1900	1340	2400
18 B	75,000	.43	1550	1120	1440
32 B	65,000	.43	1550	1120	1250
31 B	52,000	.32	1380	960	1000

It is seen that the measured lengths are considerably less than the lengths computed for completely stretched out molecules for the higher molecular weight range, whereas below about 80,000 molecular weight the values calculated from dissymmetry measurements correspond to the stretched-out lengths within probable experimental error. This indicates that the smaller molecules of cellulose acetate are approximately fully extended in acetone solution, but that the longer ones are bent in gentle waves thereby greatly reducing the rate at which the root mean square separation of the ends increases with molecular weight. This is in agreement with the axial ratio calculations made by Kraemer and Nichols[22] from sedimentation and viscosity measurements and with the depolarization measurements of Doty and Kaufman.[18] More recent calculations by Simha give an axial ratio for 50,000 molecular weight cellulose acetate that is about half that of the completely extended molecule.

The dimensions calculated here cannot be accepted with finality because it was not proven that the solutions were optically clean and free from impurities. It may be that the q values are slightly smaller for this reason; however, in view of the pore size of the filters used and the correlation of q with molecular weight, it is unlikely that the q values are very much in error.

After this investigation was finished a Selas filter (#05) with a maximum pore size of 400 millimicrons was obtained. A one per cent. solution of a commercial grade cellulose acetate of 86,000 weight average molecular weight was filtered through this filter and the filtrate gave a dissymmetry coefficient of 0.56. In view of the larger amounts of impurities in the commercial sample, the q value obtained with the smaller pore size filter is gratifyingly consistent with the data on the fractions presented above.

Although the optical cleanliness of the solutions studied may not have been perfect, it is believed that the correlation of molecular weights and sizes obtained from other types of measurements and the agreement of the measured angular dependency with that theoretically predicted demonstrates the promise of this relatively new method of investigation. It should be noted, however, that in the case of several samples of polystyrene in various solvents (*e. g.*, methyl ethyl ketone) now being investigated in this Laboratory, light scattering measurements indicate molecular weights that are too small compared with osmotic pressure determinations. This is contrary to previous measurements[3] on different polystyrene samples. Consequently, more investigation is probably necessary to establish the range of validity of this method.

Acknowledgment.—The authors are indebted to Dr. B. H. Zimm for his help and advice and to Professors P. Debye and H. Mark for their continued interest in this work. The helpful coöperation of Dr. W. J. Badgley in furnishing the characterized fractions of cellulose acetate is greatly appreciated.

Summary

1. The complications in the light scattering method of molecular weight determination when the molecules are large enough to give a dissymmetrical angular intensity distribution are discussed.

2. An instrument for the absolute measurement of turbidity is described together with the method of calibration.

3. An instrument for the measurement of the

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[22] Chapter by Kraemer and Nichols in "The Ultracentrifuge," Clarendon Press, Oxford, 1940, p. 430.

angular distribution of intensity of scattered light is described.

4. Measurements of turbidity, dissymmetry, refractive index increment and depolarization were made on solutions of four cellulose acetate fractions whose molecular weight had been otherwise determined. The molecular weights calculated from the optical measurements agreed within 8% of those measured by other means.

5. The empirical constant, μ, which characterizes the deviation from van't Hoff law behavior was found to be 0.45 ± 0.01 by light scattering measurements as compared with 0.43 ± 0.005 based on osmotic pressure measurements for the cellulose acetate–acetone system.

6. The angular variation of intensity is found to be in agreement with the theoretical prediction.

7. The comparison of the measured dissymmetry with that predicted theoretically for a rod-shaped or random coil molecule indicates that the cellulose acetate molecule in acetone solution is rather extended up to a molecular weight of about 80,000. At higher molecular weights the molecule may coil back on itself to a degree that increases rapidly with molecular weight.

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X-Ray Investigation of Glycerides. III. Diffraction Analyses of Symmetrical Monoöleyl-disaturated Triglycerides[1,2]

BY L. J. FILER, JR.,[3] S. S. SIDHU, B. F. DAUBERT AND H. E. LONGENECKER

Introduction

Previous publications[4,5] from this Laboratory on X-ray diffraction studies of synthetic glycerides have established the importance of X-ray diffraction methods for obtaining reference data on the compounds provided by synthesis for the later identification of those glycerides which may be isolated from natural sources.

The purpose of this publication is to report X-ray diffraction data for the characterization of a series of synthetic 2-oleyl-1,3-disaturated triglycerides, and the simple triglycerides, tristearin and trielaidin, and also to show how these data may be applied to establish the identity of glycerides obtained from natural fats. The long-spacing X-ray diffraction data obtained in this investigation have made possible a postulation of a molecular configuration for the members of this series of synthetic glycerides.

Experimental

Preparation of Glycerides.—The experimental details for the preparation of the symmetrical monoöleyl-disaturated triglycerides have been published previously.[6] The tristearin and trielaidin were prepared by direct esterification of glycerol with the respective acid chlorides in quinoline–chloroform solution.

The oleyldistearin isolated from the seed fat of *Garcinia Indica* (Kokum butter) by low-temperature solvent crystallization was supplied to us through the courtesy of E. S. Lutton.[7]

X-Ray Diffraction Analyses.—The X-ray diffraction patterns of the glycerides were made by the usual powder method previously described.[4,5] The patterns were repeated with the same specimen and with a pin-hole type of camera using a flat cassette and a specimen-to-film distance of 24 cm.

The low-melting glyceride specimens were maintained in the solid state by surrounding the collimator and specimen mount with a chamber packed with Dry Ice. These compounds were crystallized from solvent, dried *in vacuo* at −30°, and maintained at temperatures below their fusing point prior to and during their exposure.

The radiation employed, with but two exceptions, was filtered CuKα of effective wave length 1.5386 Å. Two specimens were examined with filtered CoKα radiation of effective wave length 1.7866 Å.

Discussion

The isolation of mixed triglycerides from natural sources in a high degree of purity has been reported by many investigators. Although the fatty acid composition and the ratio of saturated to unsaturated fatty acid in these isolated mixed triglycerides have been determined by accepted methods of analysis, the positions of the fatty acids in the molecule of triglyceride have not been fixed with certainty. Positiveness as to the fatty acid configuration of the isolated natural occurring glycerides has been lacking primarily because synthetic compounds of definite and known configurations have not been available for comparison to be made. Since a relatively large number of synthetic glycerides have been prepared recently containing both saturated and unsaturated fatty acids, greater promise of certainty is assured in establishing the configuration of those isolated from natural sources.

The isolation of an oleyldistearin from a number of natural fat sources has been reported recently by Meara.[8] Comparison of the thermal behavior of this natural mixed triglyceride with the thermometric data reported by Daubert and

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[1] A grant by the Buhl Foundation in support of this investigation is gratefully acknowledged.

[2] Taken in part from a paper presented at the 108th Meeting of the American Chemical Society, New York City, Sept. 11–15, 1944.

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[4] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, THIS JOURNAL, **66**, 1333 (1944).

[5] L. J. Filer, Jr., S. S. Sidhu, C. Chen and B. F. Daubert, *ibid.*, **67**, 2085 (1945).

[6] F. L. Jackson, B. F. Daubert, C. G. King and H. E. Longenecker, *ibid.*, **66**, 289 (1944).

[7] Procter and Gamble Co., Ivorydale, Ohio.

[8] M. L. Meara, *J. Chem. Soc.*, 22 (1945).