A portion of this thesis (Parts IV, V, and VI) contains classified information. Hence only Parts I, II, and III have been submitted to the Chemistry Division. The classified material has been deposited in the files of OSRD Contract OEMsr-881 (Room 159, Crellin Laboratory).

This is to certify that Mr. T. S. Gilman has completed the whole of his thesis and has turned over the classified portion of it to be deposited in the files of OSRD Contract OEMsr-881.

Linus Pauling

THE STUDY OF NITROCELLULOSE SOLUTIONS BY LIGHT SCATTERING MEASUREMENTS

Thesis

by

Theodore Silkman Gilman

In Partial Fulfillment of the Requirements

for the Degree of

Master of Science

California Institute of Technology

Pasadena, California

1946

Acknowledgements

The majority of the experiments described in this thesis have been carried out as part of a research project conducted at the California Institute of Technology under contract with the Office of Scientific Research and Development (Contract OEMsr-881), Dr. Linus Pauling, Official Investigator, and Dr. Robert B. Corey, Director of Research.

I am indebted to Professor Pauling for permission to use the results of investigations carried out on this project as thesis material. Through the kindness of Dr. Corey permission was obtained to use the extra copies of the figures from the project investigation reports.

The investigations on which the material presented in this thesis was based have been under the supervision of Professor Richard M. Badger. I am grateful to him for his advice and direction. I also wish to thank Dr. Jurg Waser for many helpful suggestions and criticisms.

All of the supporting osmotic pressure and viscosity data to be presented have been determined by Messrs. Robert M. Blaker and George J. Doyle under the direction of Dr. Richard M. Noyes.

The use of a high speed centrifuge was made possible through the kindness of Dr. Dan H. Campbell.

The design and construction of the optical and electrical parts of the apparatus used in the light scattering studies are to be credited to Professor Badger, Dr. Waser, and Dr. Austin L. Wahrhaftig.

TABLE OF CONTENTS

A STUDY OF NITROCELLULOSE SOLUTIONS BY LIGHT SCATTERING MEASUREMENTS

I. Introduction

In recent years the measurement of the light scattered by dilute solutions of high polymers has been employed for the determination of the molecular weights of these polymers and for the estimation of their molecular weight distributions. It is the purpose of this thesis to present a brief summary of the theory of light scattering, to give the results of the application of this technique to solutions of nitrocellulose, and to compare these results with those obtained in osmometric and viscosimetric studies by other workers in this laboratory.

II. Theory

1. General development

The first theoretical treatment of light scattering was carried out by Lord Rayleigh[1] who derived a formula for the turbidity of a perfect gas using the optical properties of the individual molecules. This approach becomes quite complicated in the case of liquids and real gases because of the interactions which arise from the proximity of the molecules. A different theoretical approach to the problem by von Smoluchowski[2] and Einstein[3] led to a successful treatment of the scattering phenomenon for liquids and solutions. They treated the scattering from a statistical, instead of a molecular point of view. Their derivations form the basis for the discussion in the succeeding paragraphs.

The scattering of light by a solution may be thought of as resulting from statistical fluctuations in the refractive index of the scattering medium. The fluctuations may arise from two effects, one caused by density fluctuations and the other by concentration fluctuations throughout the liquid. If $I\,d\Omega\,dV$ is defined as the amount of light scattered by a volume element dV of solution into a solid angle $d\Omega$ at 90° to the incident beam, the quantity I can be represented by the expression:

$$I = I_1 + I_2$$

in which I_1 represents the scattering due to density fluctuations and I_2 that due to concentration fluctuations. A consideration of the work necessary to produce these fluctuations leads to the following equations:

$$i_1 = \frac{I_1}{I_0} = \frac{\pi^2 R T \beta}{2\lambda^4 N_0}\left(\rho \frac{\partial n^2}{\partial \rho}\right)^2 \times \frac{V}{r^2}, \qquad (1)$$

and

$$i_2 = \frac{I_2}{I_0} = \frac{\pi^2 M_1 c_2 \left(\frac{\partial n^2}{\partial c_2}\right)^2}{2\lambda^4 N_0 \rho \left(-\frac{\partial \ln f_1}{\partial c_2}\right)_{P,T}} \times \frac{V}{r^2}, \qquad (2)$$

in which

i_1 = the ratio of the intensity of the light scattered at 90°, I_1, (as a result of density fluctuations) to the intensity of the unpolarized incident light, I_0,

R = the gas constant (in cm.^{3} - atmospheres per mole-degree),

T = the absolute temperature (298° in all experiments reported here),

β = the isothermal compressibility (in reciprocal atmospheres),

λ = the wave length (in vacuo) of the light used (in cm.),

N_0 = Avogadro's number,

ρ = the density of the scattering medium (in grams per cm.^{3}),

n = the refractive index of the scattering medium,

i_2 = the ratio of the intensity of the light scattered at 90°, I_2, (as a result of concentration fluctuations) to the intensity of the incident light,

M_1 = the molecular weight of the solvent,

c_2 = the weight fraction of the solute (in grams per gram of solution),

f_1 = the fugacity of the solvent,

V = the scattering volume (in cm.^{3}),

and r = the distance (in cm.) at which the scattering is observed.

If the plausible assumption is made that I_1 and I_2 are essentially independent of each other in dilute solutions, I_1 may be replaced by I_p, where $I_p\,d\Omega$ represents the light scattered per unit volume of the pure solvent. The quantity I_2 can thus be determined as the difference between the scattering from the solution and that from the solvent.

It should be emphasized that Equation (2) was derived for the case of a solute which consists of only one molecular species, i.e. for the case in which the weight average and number average molecular weights of the solute are equal. In polymolecular systems the right hand member of the equation is replaced by a sum of terms referring to the respective solute components (see below).

Furthermore Equation (2) was derived for solute particles which are small compared to the wave length of the incident light. Under such conditions the fraction of the incident light, i_θ, which is scattered at an angle θ to the incident beam is given by Rayleigh's law:

$$i_\theta = i\left(1 + \cos^2\theta\right),$$

where i is the fraction of the unpolarized incident light which is scattered at 90° to the incident beam. When the size of the solute particles becomes of the same order of magnitude as the wave length, this angular dependence no longer holds, and the simple form of the scattering equation can no longer be applied.[4]

The simplified assumptions on which the above discussion is based lead to the conclusion that with unpolarized incident light the scattered light should be linearly polarized in a plane perpendicular to the plane formed by the incident beam and the direction of observation. Actually a certain amount of depolarization is always observed. Cabannes[5] has shown that, in certain circumstances at least, the expressions derived above for the total theoretical intensity of light scattered at 90° (i.e. the sum of the intensities of the perpendicular and parallel components) must be multiplied by the factor (known as the Cabannes Factor),

$$\frac{6+6\Delta}{6-7\Delta},$$

in which the depolarization, Δ, is the ratio of the intensities of the parallel and perpendicular components of the light scattered at 90°; the incident unpolarized beam and the direction of observation determine the plane of reference. For this reason the observed values of the total scattering intensity were divided by the proper value of the Cabannes factor in all the experiments described in this thesis in which the depolarization was measured.

Aside from their use in determining the Cabannes factor, depolarization values may provide useful information as to the size and anisotropy of polymeric substances. For a complete classification as to size and anisotropy, however, a further depolarization measurement is necessary.[6] That is the depolarization of the scattered light when the incident light is polarized in a plane perpendicular to the plane formed by the incident beam and the direction of observation. Measurements of this latter quantity were not made, however.

2. Application to the determination of molecular weights

It was Debye[7] who first demonstrated that the relation between the osmotic pressure and the light scattered by solutions makes light scattering measurements an absolute method for molecular weight determination. The quantity $\left(-\frac{\partial \ln f_1}{\partial c_2}\right)_{P,T}$ can be related to any colligative property of a solution. The relationship to osmotic pressure has been selected as most convenient for the study of high polymer solutions. It has been found[8] that the osmotic pressures of dilute high polymer solutions can be expressed to a good approximation by the equation:

$$\Pi = \frac{RT\rho}{M_2} c_2 + K\rho^2 c_2^2 + K'\rho^3 c_2^3 + \cdots , \qquad (3)$$

in which Π is the osmotic pressure in atmospheres, R and T are the same as in Equation (1), M_2 is the molecular weight of the solute (the number average in the case of a polymolecular system), and K is a constant depending on the particular solvent-solute system in question, but not on the solute molecular weight. What evidence there is for the effect of the term containing K' suggests that K' is a constant which may be assumed to be independent of the solute molecular weight for the systems of interest in this work.

The relationship between the osmotic pressure, Π , and the fugacity, f_1 , will now be derived. The fugacity, f_1 , of the solvent in a solution at constant temperature is defined by the equation:

$$\overline{F}_1 = RT \ln f_1 + C \quad ,$$

where $\overline{F}_1$ is the partial molal free energy* of the solvent and C is a constant. Hence

$$\left(\frac{\partial \overline{F}_1}{\partial P}\right)_{T,c_2} = RT\left(\frac{\partial \ln f_1}{\partial P}\right)_{T,c_2} \quad ,$$

where P is the pressure. But since

$$\left(-\frac{\partial \ln f_1}{\partial c_2}\right)_{P,T} = \left(\frac{\partial \ln f_1}{\partial P}\right)_{T,c_2}\left(\frac{\partial P}{\partial c_2}\right)_{T,f_1} ,$$

and

$$\left(\frac{\partial \overline{F}_1}{\partial P}\right)_{T,c_2} = \overline{V}_1 \quad ,$$

where $\overline{V}_1$ is the partial molal volume of the solvent, it follows that

$$\left(-\frac{\partial \ln f_1}{\partial c_2}\right)_{P,T} = \frac{\overline{V}_1}{RT}\left(\frac{\partial P}{\partial c_2}\right)_{T,f_1} .$$

The osmotic pressure of a solution at equilibrium is defined, however, as that pressure, P , which must be exerted on the solution to make the fugacity of the solvent the same in the solution as in its pure state; hence

$$\left(\frac{\partial \Pi}{\partial c_2}\right)_{T} = \left(\frac{\partial P}{\partial c_2}\right)_{T,f_1} .$$

Therefore

$$\left(-\frac{\partial \ln f_1}{\partial c_2}\right)_{P,T} = \frac{\overline{V}_1}{RT}\left(\frac{\partial \Pi}{\partial c_2}\right)_{T} . \qquad (4)$$

---

* G. N. Lewis' nomenclature

When use is made of Equations (3) and (4), when the approximation is made that $\overline{V}_1 = V_1$ ($= M_1/\rho$, where V_1 is the total molal volume of the solvent), and when small changes in ρ with the concentration are neglected, Equation (2) becomes

$$i_2 = \frac{\pi^2 c_2 \left(\frac{\partial n^2}{\partial c_2}\right)^2}{2\lambda^4 N_0 \left(\rho/M_2 + \frac{2K\rho^2}{RT} c_2 + \frac{3K'\rho^3}{RT} c_2^2 + \cdots\right)} \times \frac{V}{r^2},$$

which on rearrangement yields

$$c_2/i_2 = \rho/H\left(1/M_2 + \frac{2K\rho}{RT} c_2 + \frac{3K'\rho^2}{RT} + \cdots\right), \qquad (5)$$

where $H = \frac{\pi^2 \left(\frac{\partial n^2}{\partial c_2}\right)^2}{2\lambda^4 N_0} \times \frac{V}{r^2}$. Hence, if the scattering is measured at several different concentrations and c_2/i_2 is plotted against c_2, extrapolation of the best curve through the points should yield an intercept which is a measure of the molecular weight M_2, and from which M_2 may be calculated provided the value of the quantity $\frac{\partial n^2}{\partial c_2}$ is known.

As has been previously pointed out the above considerations are limited to monomolecular systems in which the number average and weight average molecular weights are equal. In such cases a simple relation exists between the measurements of osmotic pressure and light scattering. If Π/C is plotted against C, the solute concentration in grams per cubic centimeter ($= \rho c_2$), the value of the intercept obtained should yield the same molecular weight as was found from light scattering measurements on the same polymer.

3. The effect of heterogeneity of the solute

When the solute contains a number of different molecular species, the osmotic pressure Equation (3) assumes a new form[9]:

$$\Pi = \sum_i \frac{RT}{M_i}\rho c_i + K\rho^2 c_2^2 + K'\rho^3 c_2^3 + \cdots \quad , \qquad (6)$$

where c_i is the concentration (in grams per gram of solution) of the i^{th} species of molecular weight M_i. $(\sum_i c_i = c_2.)$ When Π/C is plotted against C $(= \rho c_2)$, the intercept is

$$RT \sum_i \frac{c_i/c_2}{M_i} \quad ,$$

but

$$\frac{c_i}{c_2} = \gamma_i = \frac{n_i M_i}{\sum_i n_i M_i} \quad ,$$

in which γ_i is defined and n_i is the number of molecules of molecular weight M_i per gram of solution. Hence

$$\sum_i \frac{c_i/c_2}{M_i} = \sum_i \frac{\gamma_i}{M_i} = \sum_i \frac{n_i}{\sum_i n_i M_i} = \frac{\sum_i n_i}{\sum_i n_i M_i} \, .$$

But the right hand term in the above equations is by definition the reciprocal of the number average molecular weight, $\overline{M}_n$. The intercept is therefore

$$\frac{RT}{\overline{M}_n} \, .$$

This shows that the number average molecular weight is obtained from osmotic pressure data.

Likewise the light scattering Equation (2) must be modified for a polydisperse system[9]:

$$i_2 = H \, M_1/\rho \sum_i \frac{c_i}{\left(- \frac{\partial \ln f_1}{}\right)} \, .$$

Strictly speaking, the quantity $\left(\frac{\partial n^2}{\partial c_2}\right)^2$ contained in H should be included inside the summation as $\left(\frac{\partial n^2}{\partial c_i}\right)^2$. But since the theory is being applied here to a homologous system of molecular apecies, it is reasonable to assume that $\frac{\partial n^2}{\partial c_i}$ is independent of the molecular weights of various species, which would enable it to be factored out of the sum. The validity of this assumption is suggested by the results of some experiments which will be described in a later section. Since Equation (4) is true,

$$\left(-\frac{\partial \ln f_1}{\partial c_i}\right)_{P,T} = \frac{\overline{V}_1}{RT}\left(\frac{\partial \Pi}{\partial c_i}\right)_T ,$$

and thus, with the aid of Equation (6),

$$i_2 = H \sum_i \frac{c_i}{\rho/M_i + \frac{2K\rho^2}{RT} c_2 + \frac{3K'\rho^3}{RT} c_2^2 + \cdots} ,$$

which on rearrangement yields

$$c_2/i_2 = \rho/H \frac{1}{\sum_i \frac{M_i \gamma_i}{1 + \frac{2K\rho}{RT} M_i c_2 + \frac{3K'\rho^2}{RT} M_i c_2^2 + \cdots}} . \qquad (7)$$

This may be expanded in Maclaurin's Series in c_2 to give

$$c_2/i_2 = \rho/H \frac{1}{\sum_i M_i \gamma_i \left(1 - \frac{2K\rho}{RT} M_i c_2 + \frac{M_i \rho^2}{RT}\left(\frac{4K^2}{R^2T^2} M_i - 3K'\right) c_2^2 + \cdots\right)}$$

and by further expansion

$$c_2/i_2 = \rho/H \left\{ \begin{array}{c} \frac{1}{\sum_i M_i \gamma_i} + \frac{2K\rho}{RT} \frac{\sum_i M_i^2 \gamma_i}{\left(\sum_i M_i \gamma_i\right)^2} c_2 \\ - \frac{\rho^2}{\left(\sum_i M_i \gamma_i\right)^2}\left[\frac{4K^2}{R^2T^2}\left(\sum_i M_i^3 \gamma_i - \frac{\left(\sum_i M_i^2 \gamma_i\right)^2}{\sum_i M_i \gamma_i}\right) - \frac{3K'}{RT}\sum_i M_i^2 \gamma_i\right] c_2^2 + \cdots \end{array} \right\} . \qquad (8)$$

But by definition

where $\overline{M}_w$ is the weight average molecular weight. Hence, when c_2/i_2 is plotted against c_2, extrapolation of the curve should yield an intercept, $\frac{\rho}{H\overline{M}_w}$, from which the weight average molecular weight can be calculated.

It was shown above that, for a molecularly homogeneous solute, the molecular weight determined by light scattering measurements is the same as that determined by osmometry, that is $\overline{M}_w = \overline{M}_n$. Ordinarily, however, high polymers contain many different molecular species, in which case

$$\overline{M}_w > \overline{M}_n .$$

4. Molecular weights from viscosity data

(a) General theory

Another property of high polymer solutions which yields information about molecular weights is the viscosity. Since viscosity data have been obtained in this laboratory for all the nitrocelluloses for which light scattering data will be reported in this thesis, a brief summary of the means whereby molecular weights were determined from these viscosities and of the significance of such molecular weights seems appropriate here.

As a basis for the determination of the molecular weight a modification of Staudinger's empirical rule has been used:

$$[\eta] = k\overline{M} , \qquad (9)$$

where $[\eta]$ is called the intrinsic viscosity (defined below), k is a constant depending on the temperature, the solute-solvent system, and the concentration units used, and $\overline{M}$ is an average molecular weight (hereafter called the "viscosity molecular weight"). Originally the expression for Staudinger's rule[10] was

$$\eta_{sp}/C = k\overline{M} ,$$

where η_{sp} is the specific viscosity and C the concentration in any of various units. The specific viscosity is defined by the following equation:

$$\eta_{sp} = \eta/\eta_0 - 1 ,$$

where η is the measured viscosity of the solution and η_0 the measured viscosity of the pure solvent. It was found, however, that η_{sp}/C varied with C and so, in order to make comparison of viscosity data more convenient, and to effect consistency with the simple theory of viscosity, the intrinsic viscosity, $[\eta]$, was brought into use and defined as follows:

$$[\eta] = \underset{C \to 0}{\text{limit}} \left(\eta_{sp}/C \right) = \underset{C \to 0}{\text{limit}} \left(\frac{\ln \eta/\eta_0}{C} \right) ,$$

where C is now the concentration in grams per 100 ml. of solution.

Some further remarks about Staudinger's rule should be made here. In the first place the rule assumes linearity between $[\eta]$ and $\bar{M}$. Actually the relationship is more complicated, and deviations from linearity are not only found experimentally for some systems but are expected on the basis of the more advanced theories about high polymer solutions[11]. The quantity $\bar{M}$ is obviously a weighted average molecular weight, since the heavier solute molecules have a relatively greater effect on the viscosity than the lighter ones. For a randomly kinked molecule the theory predicts

$$\bar{M} = \bar{M}_w{}^{11}.$$

For other chain configurations, however, other averages have been derived. Despite these uncertainties, it has been found profitable in this laboratory to attempt the assignment of molecular weights to various nitrocelluloses on the basis of viscosity data.

(b) Application to nitrocellulose

The calculation of the viscosity molecular weight of a nitrocellulose sample is complicated by the fact that the Staudinger constant k in Equation (9) varies with the nitrogen content of the material[12]. Hence it has been necessary to determine the relationship between k and the nitrogen content. The establishment of this relationship enables the molecular weight to be calculated by merely dividing the intrinsic viscosity by the appropriate value of k. The molecular weight thus obtained is considered to be an approximation to the weight average. It should be pointed out that this calculation rests on the not too well verified assumption that the intrinsic viscosity is proportional to the molecular weight throughout the range of nitrogen contents (between 12 and 14 percent) of the nitrocelluloses which have been studied in connection with light scattering measurements.

5. Interpretation of the slopes of light scattering curves

A consideration of Equation (3) leads to the conclusion that a plot of Π/C against C will be a straight line provided the concentration range is low enough so that the higher order terms, $K'\rho^3 c_2^3 + \cdots$, can be neglected. In general, osmotic studies are made at concentrations at which this provision is true.[11] The slope of this straight line will be a constant, K, for a given solute-solvent system and will be independent of the solute molecular weight.

From Equation (5) it is concluded that, at low concentrations, a plot of c_2/i_2 against c_2 will be a straight line with a slope equal to $\rho/H\left(\frac{2K\rho}{RT}\right)$. Hence for monomolecular systems the slopes of the osmotic and light scattering curves at low concentrations should be in proportion by the factor $\rho/H\left(\frac{2\rho}{RT}\right)$, provided the data are plotted as described above.

For polydisperse systems the osmotic curve will still be a straight line with slope K at low concentrations (Equation (6)), but the light scattering curve will exhibit negative (downward) curvature in the same concentration range owing to the fact that the higher order terms can no longer be neglected (Equation (8)).[4] The extent of this curvature will depend on the degree of dispersion of the molecular weights of the species about the average value.

The initial slope of the curve of Equation (8) is given by the following equation:

$$\underset{c_2 \to 0}{\text{limit}} \; \frac{\partial}{\partial c_2}\left({}^{c_2}/_{i_2} \right) = \rho/H \; \frac{2K\rho}{RT} \frac{\sum_i M_i^2 \gamma_i}{\left(\sum_i M_i \gamma_i\right)^2} . \qquad (10)$$

Since K is the slope (at low concentrations) obtained when Π/C is plotted against C (hereafter referred to as "K_{Os}"), the value of the quantity

$$\frac{\sum_i M_i^2 \gamma_i}{\left(\sum_i M_i \gamma_i\right)^2}$$

may be determined if the initial slope of the scattering curve is known. For this determination it is convenient to define a quantity K_L as follows:

$$\underset{c_2 \to 0}{\text{limit}} \; \frac{\partial}{\partial c_2}\left({}^{c_2}/_{i_2} \right) = \rho/H \; \frac{2K_L\rho}{RT} . \qquad (11)$$

Combining Equations (10) and (11), we have

$$K_L = K_{Os} \frac{\sum_i M_i^2 \gamma_i}{\left(\sum_i M_i \gamma_i\right)^2} ,$$

which on rearrangement becomes

$$K / \quad = 1 + \sum \gamma (M_i - \bar{M}_w)^2 \qquad (12)$$

where, by definition

$$\bar{M}_w = \sum_i M_i \gamma_i \ .$$

Hence by calculating a value for K_L from the initial slope of the light scattering curve and comparing it with the slope of the osmotic pressure curve, K_{0s}, for a given solvent-solute system, useful information on the molecular heterogeneity of the polymeric system being studied may be obtained; the quantity

$$\sum_i \gamma_i \left(\frac{M_i - \bar{M}_w}{\bar{M}_w} \right)^2$$

is the second moment of the molecular weight distribution curve and determines the degree of dispersion of molecular weights about the average value. In the case of a monodisperse system

$$K_L / K_{0s} = 1 \ ,$$

as was shown before.

In practice the determination of $\left(K_L / K_{0s} \right)_{c_2 = 0}$ is difficult, if not impossible. This results from the uncertainty involved in extrapolating the light scattering data to zero concentration; not only are the data themselves increasingly inaccurate as the concentration decreases, but also there may be considerable curvature above and below the experimentally accessible concentration region. The extent of this curvature and the concentration region over which it is exhibited are dependent on the degree of dispersion of molecular weights. This in effect means that, since there is a lower limit to the concentration at which light scattering data may be obtained with accuracy, extrapolation to zero concentration cannot be satisfactorily performed without a knowledge of the molecular weight distribution, which is what this treatment of the data was supposed to determine. A detailed treatment of the limitations to this approach to the determination of molecular weight distributions has recently been published.[13]

III. Description of Apparatus

1. Optical system

A schematic diagram of the optical system of the apparatus used to study light scattering is presented in Figure 1. The light from a General Electric A-H4 100-watt mercury arc lamp, L, was passed through a didymium filter and a pale yellow filter, F, (Corning Nos. 5120 and 3486, respectively) in order to isolate the green line (λ = 5461 A°). A portion of the filtered light was reflected into a compensating phototube, C, which served to eliminate the effect of fluctuations in the intensity of the initial light, and the remainder of the light was reflected upwards by a prism, R, into a bottle, S, containing the scattering medium. The light scattered at 90° was measured with a second phototube, M. A polaroid disc, P, could be inserted between the bottle and the phototube and could be rotated through 90° in order to measure the depolarization. It was found that the light which entered the scattering bottle was slightly polarized by the reflecting prism in a plane perpendicular to the plane formed by the incident and reflected beam. The extent of this polarization was measured, and the observed depolarization of the light scattered by the various solutions studied was corrected using the following equation:

$$\Delta_{corr.} = \frac{2\Delta'}{1+\delta+\Delta'(1-\delta)} ,$$

Figures 1 and 2 are in the classified portion.

where $\Delta_{corr.}$ is the depolarization which would be observed with unpolarized incident light, Δ' is the observed depolarization of the scattered light, and δ is the observed polarization of the incident light by the prism. The value of δ was determined to be 1.25; hence the corrected depolarization values were about 90 percent of the observed values.

Originally the scattering bottles, S, were oil sample bottles of 100 ml. capacity, the bottoms of which were flat and polished in order to minimize distortion of the incident light. The walls were coated with transparent red lacquer except in the region through which the scattered light was observed. Because of the serious effect of dust particles on the scattering power of the liquid in which they are suspended, all of the samples which were studied were forced into the scattering bottles through a Seitz asbestos filter disc and a piece of hardened filter paper. The filtration was effected with compressed air. The filter unit was tapered to fit the ground-glass necks of the bottles and was fitted with an outlet tube so that it was unnecessary to disconnect the filter and bottle at any time during a run. The bottle could be totally or partially emptied through this outlet by inverting the system while pressure was applied to the filter.

Because of the results of some of the earlier experiments, it was decided to obviate pouring off any of the solution during the course of an experiment. Larger scattering bottles (of 150 ml. capacity) were put into use for this purpose. These were made by sealing a 3 1/2 inch length of 35 mm. soft glass tubing onto an oil sample bottle the bottom of which had been blown off. A polished glass disc had been previously fused onto the other end of the tubing with the aid of a low-melting glass cement.[14]

2. Electrical system

A diagram of the electrical circuit is presented in Figure 2. The phototubes were of the electron-multiplier type and were supplied with a constant D. C. potential, 1000 volts, through a vacuum tube voltage regulator. The spurious currents, called "dark currents", which flowed when the phototubes were not exposed to light from the arc could easily be balanced out with the two potentiometers in the lower right hand corner of the diagram. The currents produced when the tubes were illuminated set up potential differences across two potentiometers which were connected to ground. The sliding contacts on the two potentiometers were connected to each other through a galvanometer, and readings were made by adjusting these contacts until a nul reading was obtained with the galvanometer. The step contacts on the main potentiometer were arranged so that the scales of adjoining steps overlapped. This made it possible to avoid changing the step contact setting, when the sliding contact poteniometer was near one end of its scale, every time a small change in the balance of the circuit took place.

3. Scattering standard

The absolute scattering of the solutions studied was not measured directly, but was determined by comparing the intensity of the light scattered from these solutions with that scattered from a standard liquid of known absolute scattering power. By means of this procedure it was possible to eliminate the necessity for the evaluation of the V/r^2 terms in Equations (1) and (2) and in all the subsequent equations in which V/r^2 is contained in the quantity H (Equations (5), (7), etc.).

Carbon disulfide was chosen as a standard because its scattering power is of the same order of magnitude as that of the nitrocellulose solutions studied, and because the absolute value of $\dot{i}$, the fractional intensity of the light scattered at 90°, has been determined experimentally[15]; ($\dot{i} = 120 \times 10^{-6}$ at 22° C. for $\lambda = 4358$ A° and $V/r^2 = 1$). The value of $\dot{i}$ at a different wave length may be calculated by the use of the equation for the scattering at 90° of a pure liquid (Equation (1)), and with the aid of the Lorenz-Lorentz formula:

$$\frac{n^2-1}{n^2+2} \times \frac{1}{\rho} = \text{constant.}$$

The result for $\lambda = 5461$ A° is, for carbon disulfide,

$$\dot{i}\ (\lambda = 5461\ \text{A}^\circ) = 0.329 \times \dot{i}\ (\lambda = 4358\ \text{A}^\circ).$$

Thus the value of $\dot{i}$ is 39.5×10^{-6} for $\lambda = 5461$ A° and for $V/r^2 = 1$. The temperature at which the scattering studies were made was assumed to be 25° C., which is 3° C. higher than the temperature at which the value of $\dot{i}$ was determined. However, the value of $\dot{i}$ is only negligibly changed in going from 22° C. to 25° C.

One scattering standard was prepared by filtering reagent grade carbon disulfide into a scattering bottle with the apparatus described in Section 1 above, and a similar sample was prepared from some C.P. liquid obtained from another source. The precision of the measurements of scattering was about one percent, and the two samples did not differ significantly in scattering power. Filtration of the C.P. specimen several times did not affect its scattering. Therefore it was concluded that a scattering standard of dust-free carbon disulfide could be reproduced at will, and the reagent grade material was adopted for comparison with the nitrocellulose solutions.

After about ten months of use, this standard was compared with a sample of carbon disulfide which had been slowly distilled several times in an all-glass system which had been sealed off under a vacuum. The comparison showed no significant difference between the two liquids.

Parts IV, V, and VI of this thesis contain classified information and have been deposited in the files of OSRD Contract OEMsr-881 (Room 159, Crellin Laboratory).

References Cited

1 Lord Rayleigh, Scientific Papers IV, 397

2 M. von Smoluchowski, Ann. der Physik 25, 205 (1908)

3 A. Einstein, Ann. der Physik 33, 1275 (1910)

4 P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. 13, 159 (1945)

5 J. Cabannes, Ann. de Physique 15, 29 (1921)

6 P. Doty and H. S. Kaufman, J. Phys. Chem. 49, 583 (1945)

7 P. Debye, J. Appl. Phys. 15, 338 (1944)

8 M. L. Huggins, J. Am. Chem. Soc. 64, 1712 (1942)
P. J. Flory, J. Chem. Phys. 10, 51 (1942)

9 B. H. Zimm and P. H. Doty, J. Chem. Phys. 12, 203 (1944)

10 H. Staudinger, "Die hochmolecularen organischen Verbindungen", Berlin, J. Springer, 1932

11 M. L. Huggins, Ind. Eng. Chem. 35, 980 (1943)

12 H. A. Wannow, Kolloid Z. 102, 29 (1943)

13 J. Waser, R. M. Badger, and V. Schomaker, J. Chem. Phys. 14, 43 (1946)

14 G. G. Wright and S. M. Swingle, Science 97, 564 (1943)

15 K. S. Bai, Proc. Ind. Acad. of Sci. 15, 347 (1942)