Some Measurements of Double Refraction of Flow on Carbohydrates

OLLE SNELLMAN

Institute of Physical Chemistry, University of Upsala, Upsala, Sweden

In connection with other investigations of high polymers being carried out at the Institute of Physical Chemistry in Upsala, the double refraction of flow of certain carbohydrates has been studied.

A modification of the so-called Kundt apparatus for the measurement of double refraction of flow was used in these investigations. The construction and use of the apparatus will be described in another connection. The apparatus consists of a fixed outer cylinder and a rotating inner one. The space between the cylinders is filled with the liquid under investigation.

If the rate of rotation of the inner cylinder is lower than a certain limit a definite laminar movement occurs. A definite gradient of velocity is therefore found in the liquid. We can fix three directions: — the direction of flow x_1, the direction of the gradient x_2 and the direction of the light rays x_3 which is perpendicular to $x_1 x_2$. The components of the velocity are $U_1 = G x_2$; $U_2 = 0$; $U_3 = 0$.

Under the influence of flow the liquid behaves as a doubly refractive crystal with one axis in the direction x_3 and the other two in the plane $x_1 x_2$.

We will now go into the attempts which have been made to interpret this phenomenon with special reference to the highly polymeric carbohydrates.

To begin with we will treat the particles as long rigid ellipsoids or cylinders. Under the influence of the flow a certain anisotropic distribution of the particles occurs. It is thus found that particles arrange themselves in such a way that their arrangement is different along the path of the beam of light ($z = x_3$) and in a plane at right angles to this. The axes of distribution x and y, in the plane $x_1 x_2$ are perpendicular to one another, and the x axis lies at an angle (χ) to the x_1 direction.

The distribution function is as follows:

$$\varrho_x = 1 + \frac{\sigma}{2}; \varrho_y = 1 - \frac{\sigma}{2}; \varrho_z = 1 + \frac{\sigma^2}{60}; \sigma = \frac{pG}{2D}; p = \frac{a^2-b^2}{a^2-b^2}; \quad (1)$$

where ϱ_x, ϱ_y, and ϱ_z are the functions of the distribution in the directions x, y, z and a and b the length of the axes of the ellipsoids. G is the gradient of the velocity and D the constant of rotational diffusion.

This distribution function is valid even for long particles. The forces of inertia however impose a limit and these begin to exert an effect when the particles are of the order of sizes of 50,000 Å.

From the optical theory for cases where the field is quasi-stationary a formula can be calculated for the angle between the x-axis and the direction of flow, and, when the orientation is not large, we get the following formula for long cylinders in such dilute solutions that no interaction between them occurs.

$$\lambda = 45° - \chi = \frac{\pi \eta_0 G l^3}{36 k T (\ln \frac{l}{d} - 0.11)} \quad (2)$$

In this formula η_0 is the viscosity of the solvent, l is the length of the particles, d is the diameter of the particles, T is the absolute temperature and k is Boltzmann's constant.

As is seen from the formula, the angle of orientation is not determined by the optical constants (provided that there is no optical activity). It has therefore frequently been assumed without any further thought that this formula had the same field of application as the hydrodynamic theory. In the following pages we shall see that this seems empirically to be the case. However, from a theoretical point of view matters stand rather differently.

According to Snellman and Björnståhl[1] the following formula* is valid for the calculation of χ

$$\begin{aligned}
\text{tg } 2\chi &= \frac{2a_{12}}{a_{11} - a_{22}} \\
a_{12} &= \frac{1}{8\pi} [H - H^1] \iint \sin^3 \Theta \sin 2 \varphi \, d\Theta \, d\varphi \\
a_{11} - a_{22} &= \frac{1}{4\pi} [H - H^1] \iint (-1) \sin^3 \Theta \cos 2 \varphi \, d\Theta \, d\varphi
\end{aligned} \quad (3)$$

In deriving this expression the assumption has been made that the electrical moment $f_j = H_i E_j$ where E_j is the light vector in the direction j. This is the

---

* For definitions of terms see the paper referred to.

first term in a power series in which the subsequent terms can be ignored as we are assuming the field to be quasi-stationary, *i. e.* the size of the particles $\lesssim$ 1500 Å. The subsequent terms may be expected to play a part for larger particles so the optical quantities, will also enter into formula (3). The various parts of the particle do not excite the same phase of the light-wave and such a calculation leads to very complicated functions.

It is not possible to give a general solution to the problem owing to the extremely complicated expression which results when the dimensions of the particle are greater than the wave-length of light in all directions. There is a possibility for particles which have only one dimension longer than the wave-length of light. We have discussed this in another connection [2]. It is found here also that equation (2) should be valid. The magnitude of the double refraction is thus a function of the cylinderradius of the particles.

THE KUHN-HERMANS THEORY

Kuhn [3] and later Hermans [4] have proposed a statistical theory for high-polymeric compounds which takes into account their greater or less degree of coiling. The theory contains many crude approximations and can only be considered as a first attempt to tackle the special conditions which may be supposed to prevail among high polymers. In this connection Kuhn has only treated a two-dimensional case.

The actual statistical treatment for the coiled molecule has been principally developed by Kuhn. The first assumption, that the molecule is not straight but more or less curled up owing to the greater or less degree of free rotation, appears to be confirmed by the investigations which have been carried out concerning the rotation of the groups in simpler molecules.

In order to avoid the question of interference with this free rotation Kuhn has divided the thread-like molecules into sections (fibre-elements). The direction of each fibre-element is chosen so that it can be treated as being independent of all others fibre-elements. A statistical calculation is made as to the probability of there being a given distance between the end-points of the whole molecular chain. In the calculations it has been found desirable to treat this distribution of end-points as a diffusion equilibrium.

It cannot be denied that there are certain difficulties inherent in the actual treatment of the orientation which only takes account of the distribution of the end-points of the molecules. The impulse to execute Brownian movement, and thus to sway in the direction of the gradient of flow must be attributed to the whole fibre-molecule. All the fibre-elements must be affected and be connected with one another in this orientational effect.

In this connection it is strange that in double refraction of flow the molecules are acted on as units while in magnetic or electrical double refraction this appears not to be so. From the experiments which the present author did with the latter types of double refraction it appears that, in very dilute solutions such double refraction as can be attributed with certainty to free molecules is very slight and below the limit of observation. Those phenomena of double refraction which sometimes appear among highly polymeric compounds can usually be attributable to aggregated molecules where, as a result of this stabilisation of the long threads, such double refraction appears.

An interpretation of these conditions would certainly be possible on the assumption that, during orientation in a magnetic or electrical field, the individual elements try to move independently of one another. The forces by which a fibre-element is linked to other elements which do not respond oppose the orientation of that element. These forces are so strong that little or no orientation occurs. The kinematic orientation of double refraction of flow, on the other hand, is determined by movement of the neighbourhood.

A certain difficulty exists in arriving at a satisfactory treatment of the optical side of the problem in accordance with the theories developed by Kuhn and Hermans. The whole molecule should not be regarded as contributing to the polarisation of the individual residue but it may be tentatively supposed that the immediate environment, with its axial character, contributes to this polarisation. On account of the dependence of double refraction on the properties of the solvent it cannot either be assumed that the individual elements are optically free particles. As a first approximation it may perhaps be assumed that the element which is polarised by the light wave coincides in length with a fibre-element, and treat this as an elongated cylindrical resonator. If this cylinder has a sufficiently great length the end effects can be ignored. Such an assumption is perhaps the best that can be made at present. In the future, when much more experimental material is available it will beccome apparent what corrections must be made.

Calculations based on these premises can only be made when the molecule has, on the average, rotational symmetry about the line joining its end-points. It must also be postulated that the molecules are coiled to so slight an extent that the various fibre-elements do not interact optically as this makes the calculations extremely complicated. The assumptions which have been made here should be valid for nitrocellulose where the residues are comparatively large and the chain is loosely coiled. The fibre-element must not be so large that the field cannot be treated as quasi-stationary.

We also make the assumption that, in such an element, the residues affect one another and that the fibre-element therefore consists of several coupled

resonators. In the limiting case, for a large number of coupled resonators the fibre-element may be treated as a material having the optical principal dielectric constants ε and ε'.

It is now possible to calculate the relative principal polarisabilities h and h' for the general case where the light vector is not parallel with the optical axes. We further assume that the material is anisotropic and that the optical and geometrical axes of the element coincide. We can then write:

$$h = \frac{(\mu_r{}^2 - 1)}{4\pi + (\mu_r^2 - 1)\,P} \; ; h' = \frac{(\mu'_r{}^2 - 1)}{4\pi + (\mu''_r{}^2 - 1)\,P'} \; ; \qquad (4)$$

where μ_r and μ_r' are the complex relative optical principal dielectric constants and P and P' are functions of the dimensions of the element.

The use of Hermans' methods of calculation leads to the final formula given below.

For small deviations of the extinction angle from $45°$ to the direction of flow the amount of the deviation is given by the expression:

$$\lambda = \frac{\eta_0 \; G \; l_g{}^3 \; Z^2}{3 \; k \; T} \frac{s^3}{p^2} \qquad (5)$$

where η_0 is the viscosity of the solvent

$\qquad G$ is the gradient of velocity

$\qquad T$ is the absolute temperature

$\qquad k$ is Boltzmann's constant

$\qquad l_g$ is the length of the component residue

$\qquad Z$ is the degree of polymerisation

$\qquad s$ is a factor dependent om the relation between the mean length of the element and the length of the residue

$\qquad p$ is the number of residues in an element.

For the difference in the refractive index between the axes which lie in the plane normal to the axis of symmetry of the cylinder we get the following expression:

$$n_x - n_y = \frac{8\pi}{15} \; G \; \eta_0 \; \frac{v \; (h - h')^R}{n_0 \; k \; T} \; l_g{}^3 \frac{s^3}{p^2} \; Z^2 \; c' \qquad (6)$$

$\quad c'$ is the number of chain-molecules dissolved per unit volume

$\quad v$ is the volume of the fibre-element

$\quad n_0$ is the refractive index of the solvent

or when $c' = \dfrac{Nc}{Z10^3}$

where N is Avogadro's number and c is the number of component residues per litre

$$n_x - n_y = \frac{8\pi}{15} \, G \, \eta_0 \, \frac{Nv \, (h - h')^R}{n_0 \, k \, T} \, l_g^3 \, \frac{s^3}{p^2} \, Zc \qquad (7)$$

If the lengths of the elements are several times as great as their diameters $[h - h']$ is independent of the length and therefore it is a constant for a homologous series of polymers in one and the same solvent. For an anisotropic non-absorbing polymer one may therefore write:

$$[h' - h']^R = \frac{n_0{}^2}{4\pi} \cdot \frac{m^2 - 3 \, m'^2 + \dfrac{m^2 \, m'^2}{n_0{}^2} + n_0^2}{n_0{}^2 + m'^2} \qquad (8)$$

where m and m' are the refractive indices of the fibre-element in different directions.

If we now vary the refractive index of the solvent we find that for $m < m'$ the value of $[h - h']^R$ is always positive while for $m < m'$ the value of $[h - h']^R$ is negative between

$$m_0{}^2 = \frac{m^2 - 3 \, m'^2}{2} \pm {}^1\!/_2 \, \sqrt{(m^2 - 3 \, m'^2) - 4 \, m'^2 \, m^2} \; .$$

POLYDISPERSITY

All the calculations which have been made are applicable to monodisperse solutions. Polydispersity upsets the results of the measurements very considerably. Calculations of length from double refraction of flow using formula (2) gives a mean value for length in which the longer molecules have the greatest weight. We have taken weighted means as the values for the degree of polymerisation and the length.

In such investigations one may generally expect to get higher values for length from experiments with double refraction of flow than from data obtained with the ultracentrifuge so long as other factors do not come in. This is due to polydispersity.

The Kuhn-Hermans theory also gives a mean value which is strongly influenced by polydispersity. Our experimentally derived data as well as the theoretical deduction are based on the assumption that the solution is monodisperse.

Hermans has shown that for degrees of polymerisation from equ. 5 one gets $\dfrac{\overline{Z}^4}{\overline{Z}^2}$ where as from the actual double refraction one gets thus $\dfrac{\overline{Z}^2}{\overline{Z}}$ in the latter case there is less dependence on polydispersity.

VISCOSE

Two different preparations of viscose in strong sodium hydroxide (2 N) were investigated. The solutions were very dilute. In these investigations it was observed that the solutions only consisted of free particles at the point where their viscosities were minimal. Both before and after this point aggregated particles appeared in the solution. Investigation of the magnetic double refraction revealed the same phenomenon. Before and after the point of minimum viscosity there was strong magnetic double refraction which immediately became saturated. It was also possible to observe long relaxation times when the field had been removed. On the other hand we found no measurable double refraction at the point of minimal viscosity. The time during which it was possible to carry out measurements of double refraction of flow without being interfered with by aggregated particles in the solution was about one day. In table 1 the degrees of polymerisation are calculated both from measurements of double refraction of flow and from molecular weight determinations carried out by Gralén.

Table 1. Viscose. The degree of polymerisation from double refraction of flow and from the ultracentrifuge.

l	Degree of polymerisation	Degree of polymerisation determined ultracentrifugally
2200 Å	113000	113000
1200 Å	62000	62000

This result appears to indicate that the molecules are very loosely coiled. This may perhaps be expected to be the case when the molecules are highly charged.
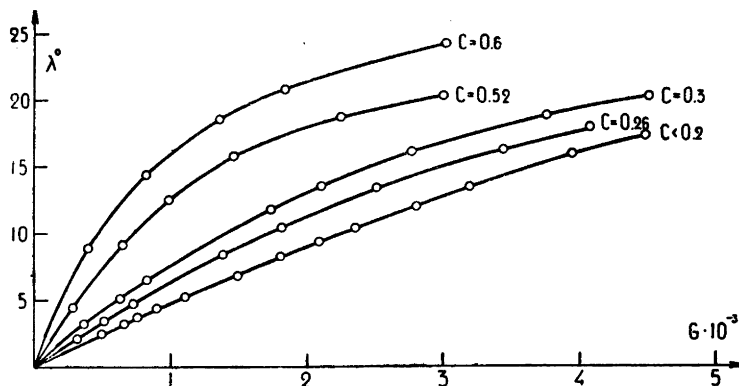
Fig. 1. The dependence of the angle of extinction on the gradient at different concentrations (g/100 ml) for a highly polymeric nitrocellulose (solvent butyl acetate).

NITROCELLULOSE

The preparation of nitrocellulose was dried over silica gel before weighing. The solutions were alloved to stand for 24 hours before the measurement were made so that the nitrocellulose might become evenly dispersed. Berl and Lange [6] have found that a solution of nitrocellulose in acetone shows anomalies of viscosity at first. These are caused by incompletely dissolved nitrocellulose. Most of the measurements reported here were carried out on solutions of nitrocellulose in butyl acetate at 20° C.

Gralén [5] carried out molecular weight determinations and viscosity measurements on some of the preparations and Jullander [7] carried them out on the others. These are described in their papers.
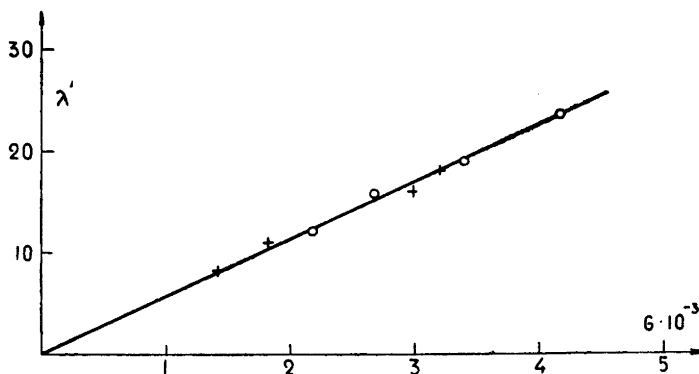

Fig. 2. The dependence of the angel of extinction on the gradient at two different concentrations for a less highly polymeric nitrocellulose (solvent cyclohexanone).
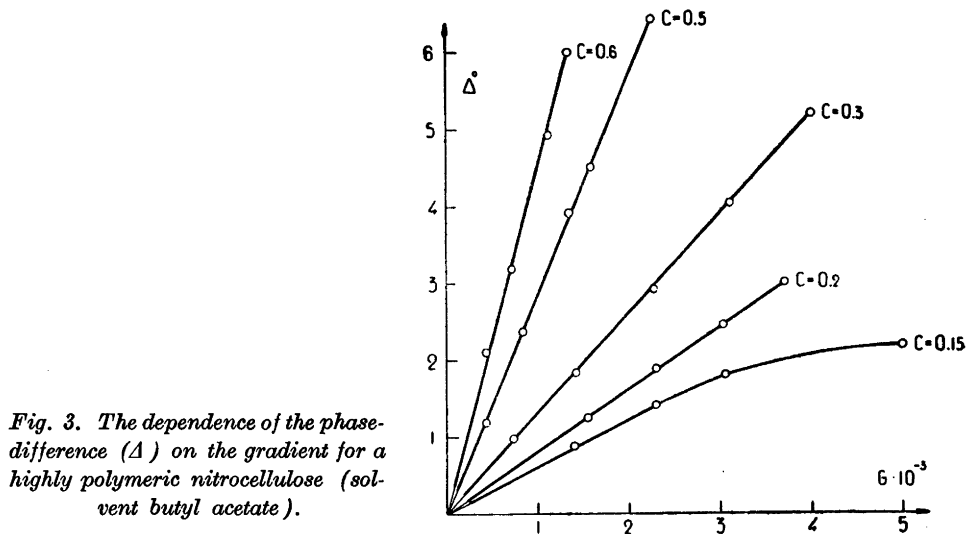
Fig. 3. The dependence of the phase-
difference (Δ) on the gradient for a
highly polymeric nitrocellulose (sol-
vent butyl acetate).

Figures 1, 2 and 3 are given as examples of the dependence of the angle of extinction (λ) and phase-difference (Δ) on the gradient (G) at different concentrations.

At the lower concentrations the angle of extinction varies linearly with the gradient, at least to begin with. This agrees with the theories of double-refraction of flow. When there is a high degree of polydispersity other conditions
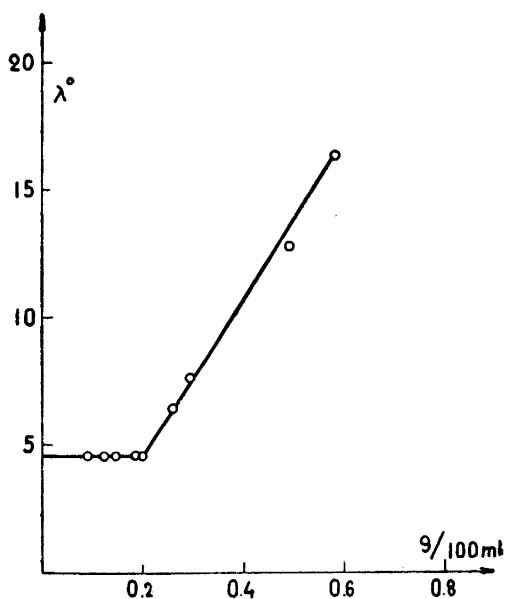

Fig. 4. The dependence of the angle of
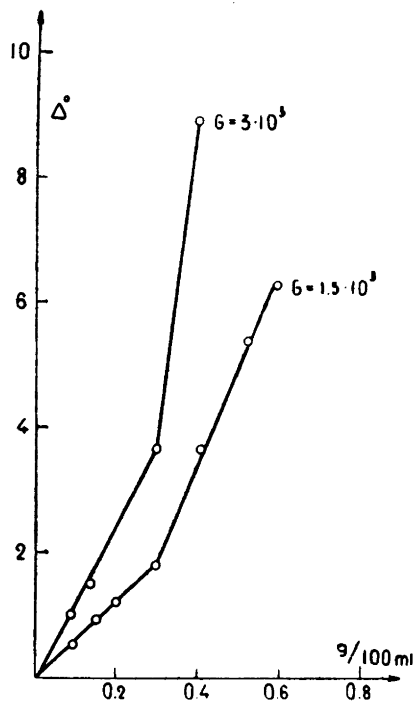extinction on the concentration when the
gradient is constant.

Fig. 5. The dependence of the phase-diffe-
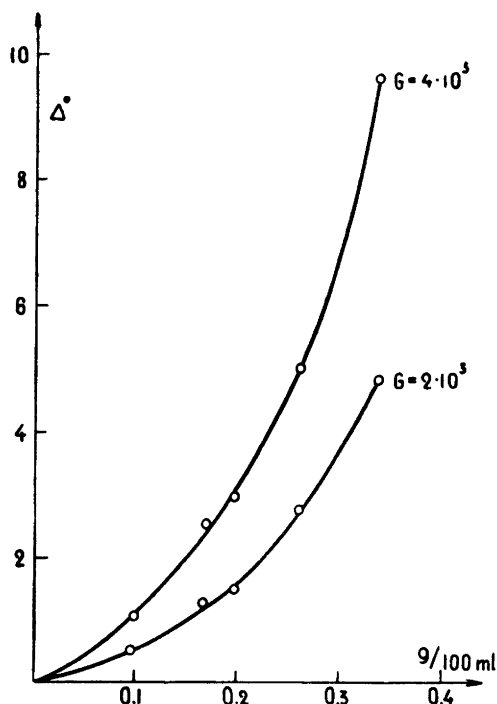rence on the concentration when the gradient
is constant.

Fig. 6. The dependence of tye phase-diffe-
rence on the concentration when the gradient
is constant (great polydispersity).

may be expected to obtain. The double refraction should also stand in a linear relation to the concentration.

The dependence of the angle of extinction and the double refraction on the concentration at various gradients are shown for two preparations (figs. 4 and 5). These may serve as typical examples. In almost all cases the relationship to the concentration changes markedly at a certain concentration. Figure 6 shows that, in certain exceptional cases, another appearence is found. This is probably caused by greater polydispersity.

In table 2 data are given for the degree of polymerisation, calculated from data obtained by means of the ultracentrifuge, and for the lengths of the molecules determined both by the dissymmetry factor (f/f_0) and by the measurements of double refraction of flow and viscosity. The length is calculated from the measurements of double refraction of flow by means of formula (2).

The length determined by the double refraction method is usually greater than that derived from f/f_0. If the length is calculated directly from the

Table 2. Nitrocellulose. The lengths of the molecules at different degrees of polymerisation.

Degree of polymerisation (ultracentrifuge)	Length in Å (from f/f_0)	Length in Å (double refract. of flow)
2000	5300	6100
1700	6300	5700
1200	4600	4000
1010	4100	4700
1000	3700	4500
1000	2800	3800
1000	2800	3100
997	2900	3000
854	2600	2500
820	3700	3400
528	1700	2100
320	1200	1800
71	450	550

molecules weight the result obtained is always greater than that obtained by the other methods except in the case of very low molecular weights where the results of all methos are the same.

The applicability of the Kuhn-Hermans theory has been tested in respect of some preparations of nitrocellulose. The data are given in tables 3 and 4. For this purpose s^3/p^2 has been calculated from previously known data by the use of formula (5) in order to see whether this value remained constant. The same calculation was made in respect of formula p^3/s^2 $(h - h')$ v which should also remain constant for the same solvent. There is no obvious alteration in the values though there is a certain scatter, probably due to polydispersity.

Table 3. Nitrocellulose. The value of the factor s^3/p^2 in the theory of flexible molecules.

Degree of polymerisation	s^3/p^2
1700	26.0
1200	20.3
1010	30.2
1000	35.5
1000	20.3
1000	22.9
820	25.5
560	21.7
512	25.6
350	32.4
320	16.9

3

Table 4. Nitrocellulose. The value of the constant factor of the double refraction in the theory of flexible molecules.

Degree of polymerisation	$s^3/p^2 (h - h')^R v$
1000	300×10^{-24}
854	338 »
512	273 »
350	286 »
320	240 »

POLYURONIC ACIDS

In collaboration with Säverborn [8] the author has investigated the double refraction of flow of some highly polymeric polyuronic acids. The determinations of molecular weight and other information concerning this work are described in Säverborn's paper [9]. The pectins themselves do not show any double refraction as may easily be understood on theoretical grounds. However hydrolysed or nitrated pectins give results which are in agreement. The degrees of polymerisation calculated in this way agree with those obtained from determinations of the molecular weights of pectins. With gum arabic direct determinations can be made. There are no anomalies here.

Table 5. Polyuronic acids. The lengths of the molecules from molecular weight and from double refraction of flow.

Molecular weight	Length in Å	Length in Å (double refract. of flow)
Apple pectin 99000	2850	2600
Citrus pectin 210000	7000	3800
Gum arabic 285000	945	1000

The descrepancy in the measurements on citrus pectin was probably due to some peculiarity in the preparation used. Later determinations of the molecular weight gave results of only about half this size, which agree with the results of the measurements of the double refraction of flow.

It is the side-chains of gum arabic which make its molecular weight so large. Its double refraction is but small which also indicates that this is the case. The theory dealing with rigid rods ought to be applicable here.
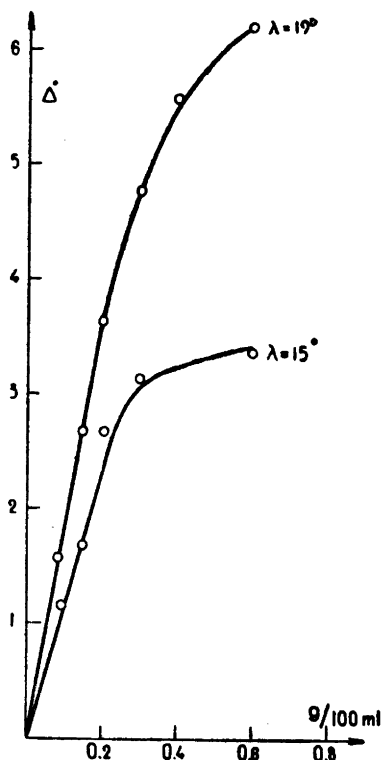
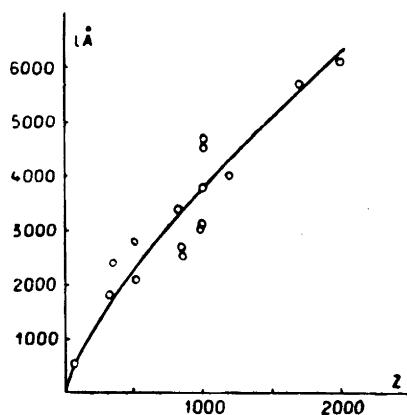Fig. 7. *The dependence of the phase-difference on the concentration when the angle of extinction is constant.*

Fig. 8. *The dependence of the length on the degree of polymerisation for the nitrocelluloses here investigated.*

DISCUSSION OF THE RESULTS OF THE MEASUREMENTS

It is scarcely possible to enter on a discussion of details before the problem of the production of more or less monodisperse polymers has been satisfactority solved. Polydisperse solutions give shifting values which are hard to compare with those expected on theoretical grounds. External circumstances are responsible for the fact that this work has been carried out entirely with polydisperse solutions.

Table 2 gives an indication of the significance of polydispersity. Comparison at the lengths of substances having a degree of polymerisation of 1000 shows that they vary from 3000 to 4700 Å.

As is seen from the material, calculations of length from the double-refraction of flow by formula (2) gives lengths which, for nitrocellulose are
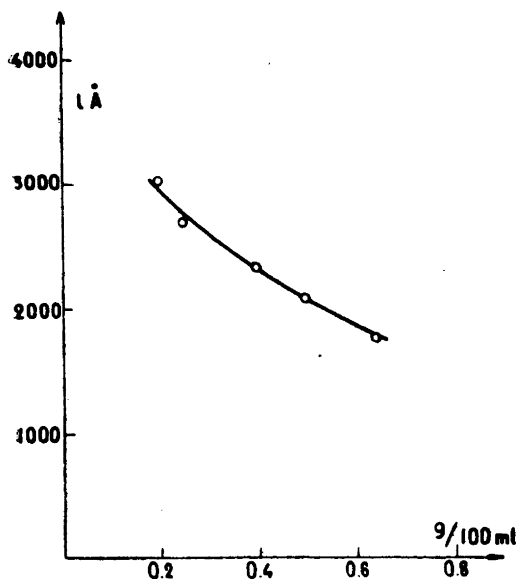
OLLE SNELLMAN

Fig. 9. The dependence of the critical concentration on the length.

somewhat larger than those calculated from f/f_0. Similarly, if the degree of polymerisation is calculated from the double-refraction of flow it is found to be less than that calculated from the date obtained with the ultracentrifuge at high degrees of polymerisation.

The critical concentration where λ and $\varDelta$ become dependent on concentration has been determined. The relation between the degree of polymerisation and this point is seen in fig. 9. It appears empirically has though $\log c$ were proportional to l (fig. 10).
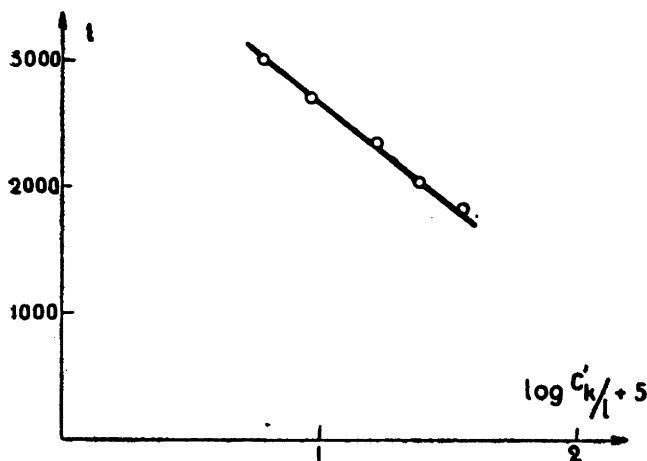

Fig. 10. The logarithmic relationship between the critical concentration and the length.

The results calculated from the Kuhn-Hermans theory show a relatively great degree of constancy. As we did not compare substances of the same degree of polydispersity, but substances which were derived from material treated in different ways, our results may be considered satisfactory. Our values for s^3/p^2 are higher than those calculated by Hermans on the basis of other measurements. However we used figures for the degree of polymerisation derived from data obtained with the ultracentrifuge while he did not.

The difficulty in comparing the different theories on the basis of the present data lies in the fact that here $Z^2 = K \dfrac{l^3}{ln\ l/d - 0.11}$ as a rough aproximation. It is possible that other classes of substances might give more decisive evidence as to the applicability of the Kuhn-Hermans theory.

We have also tried to check the theory by investigating the constancy of $\dfrac{\Delta}{c\lambda}$ which may be derived from the formulas (table 5). Other premises however lead to similar formulae. The viscosity is not included in this expression. It may therefore be expected to be independent of the viscosity over a long period. This appears from table 6 to be the case.

Table 6. The factor independent of the viscosity for a nitrocellulose at different velocity gradients.

G	$\Delta/c\lambda$		
	$C = 0.5510^{-2}$	$C = 0.2710^{-2}$	$C = 0.09310^{-2}$ g/ml
10^3	3.70	3.65	3.61
3.10^3	3.72	3.68	3.61
6.10^3	3.61	3.64	3.62

It must be pointed out that the theory is not valid for greatly coiled chain-molecules, and also that when the component residues have a small diameter in comparison with those of the solvent the optical quantity $h - h'$ has a different significance from that which it has in the theory used here.

Amongst other evidence we have Gralén's numerous observations in the determination of their molecular weights, to show that the derivatives of cellulose are very loosely coiled. The differences between the values for the lengths calculated on the basis of data from the ultra-centrifuge, directly from the molecular weight or from the dissymmetry factor (the differences between the last two are obvious) are thought by Gralén to be due to internal movements

in the chain (Brownian movement) which shorten it. This lends support to the Kuhn-Hermans theory. The fact that the nitrocelluloses are so slightly coiled is thought by Huggins [10] to be due to the existence of hydrogen bonds between the — O and — OH groups in adjacent glucose residues.

SUMMARY

Measurements of the double-refraction of flow have been carried out on several carbohydrates. The values obtained have been compared with those expected according to the different theories. Certain of the theoretical assumptions underlying these theories have been discussed. No experimental evidence could be established in favour of either of the theories on account of the polydispersity of the material under investigation.

REFERENCES

 1. Snellman, O., and Björnståhl, Y. *Koll. Beih.* **52** (1941) 403.
 2. Snellman, O. *Arkiv Kemi, Mineral. Geol.* **24B** (1946) no. 2.
 3. Kuhn, W., and Kuhn, H. *Helv. Chim. Acta* **26** (1943) 1391.
 4. Hermans, J. J. *Physica* **10** (1943) 777; *Kolloid Z.* **106** (1944) 22.
 5. Gralén, N. Diss. Upsala (1944).
 6. Berl, E., and Lange, B. *Cellulosechemie* **7** (1926) 145.
 7. Jullander, I. *Arkiv Kemi, Mineral. Geol.* **21A** (1945) no. 8.
 8. Snellman, O., and Säverborn, S. *Kolloid-Beihefte* **52** (1941) 467.
 9. Säverborn, S. Diss. Upsala (1945).
10. Huggins, M. *J. Applied Phys.* **10** (1939) 700.