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TRANSACTIONS

12—THE STRUCTURE OF CELLULOSIC RAYONS. Part II. THE VISCOSITY OF SOLUTIONS OF CELLULOSE ACETATE

By FRANK HOWLETT, ERIC MINSHALL,
and ALEX. R. URQUHART.
(British Cotton Industry Research Association)

I. INTRODUCTION AND SUMMARY

The present paper is devoted to an enquiry into some of the factors influencing the viscosity of solutions of cellulose acetate. The chief object of the work is to find the best method of using viscosity data to obtain a measure of the mean chain length of the acetate molecules in solution. It is appreciated that any method relying upon viscosity data is unlikely to provide values that are accurate in an absolute sense, but the method is so easy experimentally that it seemed desirable to investigate the conditions under which it can be used to provide values that will be accurate relative to a chosen standard.

One characteristic of solutions of long-chain compounds is that their viscosity increases very rapidly as the concentration of solute is raised. Many relations have been proposed to represent this dependence of viscosity upon concentration. It is not intended to discuss these equations here, for they have been adequately considered and inter-related elsewhere [1, 2, 3, 4, 5, 6]. It has been suggested, however, that the equation due to Baker[7] is valid over a greater concentration range than the others. The relation utilised by Staudinger[8], and extensively considered by him and others, in which the function η_{sp}/c is linearly related to c for low concentrations of solute, has been the subject of much controversy independent of its application to the determination of molecular weights. Bungenberg de Jong[9] showed that the relation between the logarithm of η_{sp}/e and c was linear up to high concentrations, and later Staudinger[10] advocated the use of this relation over concentration ranges where the plot of η_{sp}/c against c is not a straight line. Staudinger also found from experiments on materials with molecules of widely different chain lengths that extrapolation to zero concentration gave identical values of η_{sp}/c whether the extrapolation were made on the direct or on the logarithmic plot.

Relations between the viscosity and temperature of pure liquids have been derived theoretically by Andrade[11], Sheppard[12], and others[11]; these are of the form $\eta = Ae^{B/T}$ where A and B are constants, and T is the absolute temperature. They have been successfully applied to many pure liquids. An equation of identical form has been derived for solutions by Karrer[13], and found to be valid for solutions of cellulose esters[13, 14, 15, 16]. In an earlier publication Berl and Umstätter[17] had suggested that the viscosity of cellulose ester solutions was inversely proportional to the square of the temperature in degrees Centigrade, but this relation does not appear to have been further used. Lawrence, in a recent discussion[18], drew attention to the fact that increase of temperature should *increase* the viscosity due to the solute by increasing its kinetic motion. Burgers[19] has stated that

the dependence of viscosity on temperature will vary with the molecular weight of the solute, solutes of low molecular weight causing a decrease of specific viscosity with increase of temperature, and solutes of high molecular weight an increase of viscosity. Actually, a decrease of specific viscosity almost invariably accompanies an increase of temperature, although Staudinger[8,10] working with dilute solutions of highly polymerised polystyrene reported that the value of η_{sp}/c extrapolated to zero concentration was independent of temperature over the range 20-60°C.; later, a direct dependence on temperature seemed to be found[20]. More recently, Mark[21], from theoretical considerations predicted, and with a small amount of experimental work on rubber and polystyrene confirmed, that the specific viscosity of solutions in good solvents decreases with increasing temperature whereas in poor solvents the specific viscosity increases.

In his earlier work, Staudinger suggested that the value of η_{sp}/c extrapolated to zero concentration was the same for solutions in different solvents, but later recognised [20, 22, 23, 24], by the provision of different K_m values in his equation (see below) for cellulose and cellulose derivatives in various solvents, that this quantity did in fact vary from one solvent to another. The initial decrease in viscosity that occurs when small amounts of water are added to solutions of cellulose esters in organic solvents has often been mentioned[25, 26, 27], but Staudinger[10] was able to add up to 50 per cent. of benzene or 25 per cent. of certain other organic liquids to a solution of cellulose nitrate in butyl acetate without causing any alteration in η_r or η_{sp}/c. Furthermore, the addition of from 2 to 10 per cent. of water to acetone solutions of cellulose nitrate did not cause a change in η_r.

Another factor likely to alter the viscosity is a variation in the number of ester or ether groups attached to the cellulose chain. It was shown by Staudinger[23] that in a solvent in which both acetates dissolved the viscosity of a secondary cellulose acetate was always greater than that of the corresponding triacetate of the same chain-length. It was also found[24] that the limiting values of η_{sp}/c for three methyl- or ethyl- celluloses of the same chain length increased with the amount of combined methoxyl or ethoxyl.

Reference has already been made to Staudinger's use of the function η_{sp}/c. His main work in this field has of course been the correlation of the viscosity of solutions of long-chain compounds, by means of this function, with the molecular weight or chain length of the compound. He began[8] by studying the viscosities of long-chain paraffins, acids, esters, and alcohols of known chain-length, and proposed the empirical equation $\lim_{c\to 0} \eta_{sp}/c = K_m \times M$ to represent his results, K_m being a constant for a given series of polymers, and M the molecular weight; $\lim_{c\to 0} \eta_{sp}/c$ is now generally referred to as the "intrinsic viscosity," and denoted by $[\eta]$. He then prepared polystyrenes, polyvinyl acetates, and polyoxymethylenes and examined them cryoscopically; the equation connecting intrinsic viscosity and molecular weight was again found to be valid up to the limiting molecular weight determinable cryoscopically—about 10,000. Determinations of the osmotic pressures of solutions of these polymers, of rubbers, and of celluloses were then made to confirm the equation for these materials of still higher molecular weight. It is important to note, however, that most high polymers used in work of this kind have molecules covering a range of molecular weights, and that osmotic pressure methods give a *number-average* molecular weight, whilst the viscosity method gives a *weight-average* molecular weight[28], and hence osmotic pressure methods should not be used to obtain the value of K_m unless the material has been well fractionated, so that it is practically homogeneous with respect to chain-length.

Staudinger's work stimulated theoretical treatments of the problem, and these have definitely pointed to a relation between the viscosity of

dilute solutions of a long-chain substance and its molecular weight. (The equation due to Flory[29] relating the viscosity of molten polymers to the square root of the molecular weight is not considered pertinent here). For example, Burgers[30] derived an expression similar to the Staudinger equation on the assumption that the molecules are very long, are so far apart that they do not hinder one another's motion, and have negligible Brownian movement. Huggins[31] has also deduced Staudinger's equation for very long, randomly-kinked molecules in dilute solution, using a model in which the molecule is taken as a series of spheres connected by rigid rods.

The Staudinger equation has not been universally accepted. Thus Dobry[32] and Buchner and Samwel[33] contend that only osmotic pressure methods are reliable, and that the results obtained from them do not agree with the viscosity equation. Eisenschitz and Rabinowitsch[34] conclude that neither osmotic pressure nor viscosimetric methods are of value since, at the concentrations normally used, the dissolved particles do not move independently. Hess and Sakurada[35], after a survey of the position, also conclude that the Staudinger method of molecular weight determination cannot be applied to cellulose derivatives.

On the other hand, Obogi and Broda[36] have compared osmotic pressure and viscosimetric methods and state that the Staudinger relation holds as an approximate rule up to a molecular weight of 60,000. Schulz[37], from work on polystyrene, polyisobutylene, and cellulose nitrate, concludes that the viscosity method of determining molecular weight is not invalidated by heterogeneity provided this is not too great. An interesting proof of the validity of the Staudinger equation has been given by Kraemer and van Natta[38], and by Baker, Fuller and Heiss[39], as a result of their work on ω-hydroxydecanoic acid self-polyesters. The chain lengths of these were determined by direct titration of the carboxyl groups, and a comparison with the intrinsic viscosities showed that the Staudinger equation was valid down to a molecular weight of 5,000, below which K_m gradually increased. Association of the polymers in solution was stated to be negligible. Similar drifts in K_m, becoming constant in the chain-length range of natural products have been found by Staudinger[23,40] for polyvinyl acetate, polystyrene, and cellulose acetate.

Kraemer has determined molecular weights of high polymers with the ultracentrifuge, and has compared the values so obtained with the intrinsic viscosities of the substances; this work represents the most comprehensive correlation so far made between viscosity and molecular weight determined by a method to which no exception can be taken. Various technical and fractionated cellulose acetates were examined, and the intrinsic viscosity was found to be a linear function of molecular weight over a wide range of values (50,000—250,000)[28, 41, 42]. Similar results were obtained for cellulose, cellulose nitrate, and ethylcellulose, and the conclusion was drawn that the intrinsic viscosity is determined essentially by the chain length, and is relatively slightly affected by solvation or aggregation of the molecules, or by minor changes of chemical composition. A comprehensive summary of the literature on this subject has recently been presented by Lauffer,[43] who concludes that "a linear relationship between intrinsic viscosity and molecular weight exists for each homologous or polymeric series," although the relation may not always be one of direct proportionality.

The work now to be described was initiated with two main objects. In the first place, it was desired to investigate the methods available for determining the intrinsic viscosity $[\eta]$ from the experimental viscosity data, in order that an accurate value might be obtained with the utmost economy of effort. In the paper just referred to Lauffer[43] mentions three methods of determining $[\eta]$.

(1) η_{sp} is plotted as a function of c, and the tangent to the curve at $c = 0$ is drawn. The slope of this tangent is

$$[\eta] = \operatorname{Lim}_{c \to 0} \eta_{sp}/c$$

(2) Log η_r is plotted against c, giving an approximately linear relation over a fair concentration range, and $(\log \eta_r)/c$ is evaluated. Natural logarithms are used, and when $\eta_{sp} = \eta_r - 1$ is very small, then

$$\frac{\log \eta_r}{c} \simeq \frac{\eta_r - 1}{c} = [\eta].$$

(3) A power series $\eta_{sp} = Ac + Bc^2 + Cc^3 \ldots$ is fitted to the data, and

$$[\eta] = \operatorname{Lim}_{c \to 0} \eta_{sp}/c = A$$

These methods are laborious, and demand a reasonably large number of viscosity determinations at different concentrations to give an accurate value of $[\eta]$; the same objection applies to Staudinger's method of plotting η_{sp}/c against c, and extrapolating to zero concentration. Two additional methods have now been examined in some detail; these are

(1) $\eta_r^{\frac{1}{3}}$ is plotted against c, giving an excellent straight line over a wide concentration range, and the intrinsic viscosity evaluated as

$$[\eta] = 8 \frac{\mathrm{d}\,\eta_r^{\frac{1}{3}}}{\mathrm{d}c}$$

(2) Log η_{sp}/c is plotted against c, this also giving an excellent straight line over a wide concentration range, and is extrapolated to obtain the intercept on the axis of zero concentration. The intrinsic viscosity is thus obtained as $[\eta] = \text{antilog} \left\{ \operatorname{Lim}_{c \to 0} \log (\eta_{sp}/c) \right\}$

In both these methods the linear relations are so good that accurate values of $[\eta]$ can be obtained from viscosity determinations at three concentrations only. As a result of the examination of these methods the conclusion has been reached that the method of calculating $[\eta]$ from the slope of the $\eta_r^{\frac{1}{3}}$ plot is preferable to that using the zero intercept on the log (η_{sp}/c) diagram, in that it provides more regular results with fewer anomalies. The relation between the constants of these two equations is described in an Appendix to this paper.

The second main object of the work to be described was to derive a set of values of K_m which could be used subsequently for the determination of the chain lengths of a variety of cellulosic derivatives differing in chemical composition. For this work, the effects of temperature, solvent, and acetic acid yield were studied and also some aspects of the oxidation of cellulose acetate. The values of K_m are given in Section IV of the paper, together with some chain lengths calculated with their aid. It is desirable to emphasize here that no claim is made that these chain lengths are accurate in an absolute sense; what has been done is to accept one value as standard (using what appeared the most probable value for this standard), and to calculate the other values relative to this one. It is hoped that as the result of work now proceeding in these laboratories it may be possible in the not too distant future to determine the chain lengths of some of the materials examined by an absolute method, and so obtain chain length values that will be accurate in an absolute as well as a relative sense.

II. EXPERIMENTAL METHODS

(a) Preparation of Acetylated and Hydrolysed Samples

The cellulosic materials used for the experimental work were commercial samples of viscose and secondary acetate rayons which had been freed from all oil and soap, and the same materials acetylated or de-acetylated by methods which produce negligible degradation and ensure a random distribution of the different side groups; these methods have been described in Part I of this series.[44] The determination of the acetic acid yield of the materials used has also been separately described.[45]

(b) The Determination of Viscosity and Density

Samples of the material were dried in vacuo over phosphorus pentoxide, weighed, and transferred to glass-stoppered tubes. The requisite amount of solvent was added from a burette, and the tube and contents were shaken on a mechanical shaker for 17 hours. The viscometers used were made to the specifications of the British Standards Institution and were of the Ostwald type, those in the lower viscosity ranges being pipette-filled. For the very low viscosity range, an Ostwald type viscometer was specially designed with a time of flow for acetone of about 200 seconds. The filled viscometers were fixed vertically in a thermostat maintained constant to 0·05°C., the temperature being checked by a thermometer calibrated by the National Physical Laboratory. A suitable cover over the viscometer ensured that no vapour of the solvent escaped while the viscosity was being determined, and the time of flow of each solution was determined five times with the aid of a stop-watch calibrated at intervals with an electric stop-clock. The viscometers were all calibrated with air-free distilled water as ultimate reference liquid, the value of 1·005 centipoises for the viscosity of water at 20°C., as advocated by Bingham,[46] being taken as standard. Except where otherwise stated the viscosities were determined at 20°C.

The viscometers were so designed that no kinetic energy correction was needed, and since no pressure other than that of the column of liquid itself was used the viscosity was calculated by means of the equation

$$\eta = K\rho t$$

where η is the viscosity of the liquid in centipoises,
ρ is the density of the liquid relative to that of water at 4°C.,
t is the time of flow in seconds,
and K is the constant of the particular viscometer used.
Other symbols used are :
η_r the relative viscosity $= \eta/\eta_0$, where η is the viscosity of the solution and η_0 that of the solvent.
η_{sp} the specific viscosity $= \eta_r - 1$
$\lim_{c\to 0} \eta_{sp}/c$ is the intrinsic viscosity $[\eta]$, c being the concentration of the solute in grams per litre of added solvent.

The densities of the solvents were determined at 20°C. with pyknometers that had been calibrated with air-free distilled water. The densities of the solutions were not determined as they did not differ sufficiently from those of the solvents to alter the results significantly.

III. EXPERIMENTAL RESULTS AND DISCUSSION

(a) The Viscosity-Concentration Relation

The viscosities at 20°C. of acetone solutions of the secondary cellulose acetate rayon Seraceta were determined over the concentration range 0 to 44 grams per litre. The results are presented in two sections in Table I, the first section giving a general survey over the concentration range, the second a more detailed examination of the region of low concentrations. The two series of determinations were made at different times with different batches of acetone, which probably accounts for the slight difference in the viscosities of the solvent. The results are given in the Table to more places of decimals than the accuracy of the viscometry warrants ; this has been done in order that accuracy should not be lost in their mathematical manipulation. The data were used to test the Baker equation, $\eta_r = (1+pc)^n$, for different values of n by plotting $\eta_r^{1/n}$ against c for integral values of n between 1 and 10. For values of n from 1 to 6 the curves were concave upwards, and when n was 9 or 10 they were convex upwards. The curve for $n=7$ was very slightly concave upwards, whilst that for $n=8$ was a vrey good straight line with perhaps a slight tendency to become convex upwards at the highest concentrations. This is shown by the data of

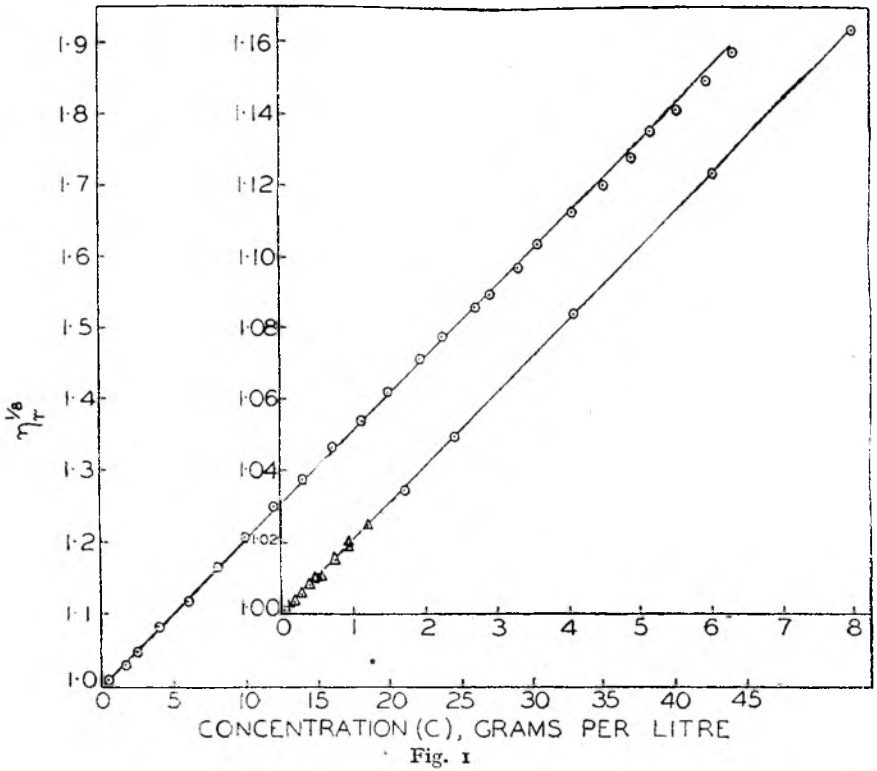

1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
$\eta_r^{1/8}$
1·16
1·14
1·12
1·10
1·08
1·06
1·04
1·02
1·00
0 1 2 3 4 5 6 7 8
0 5 10 15 20 25 30 35 40 45
CONCENTRATION (C), GRAMS PER LITRE

Fig. 1

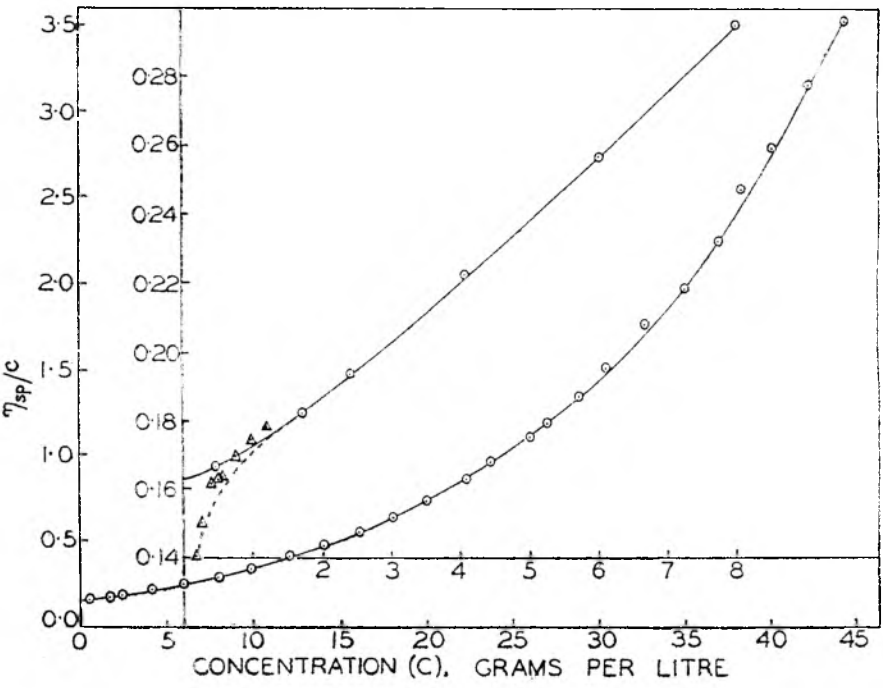

3·5
3·0
2·5
2·0
1·5
1·0
0·5
0·0
η_{sp}/c
0·28
0·26
0·24
0·22
0·20
0·18
0·16
0·14
2 3 4 5 6 7 8
0 5 10 15 20 25 30 35 40 45
CONCENTRATION (C), GRAMS PER LITRE

Fig. 2

Table II, which gives values of $(\eta_r^{1/n}-1)/c$ for different values of c and n. As c increases this function will increase or decrease according as the curve is concave or convex upwards, whereas if the graph is a straight line the function will have a constant value. The greatest degree of constancy is attained when $n=8$, and in the subsequent work the Baker equation is therefore used in the form $\eta_r^{\frac{1}{8}}=1+pc$.

The results presented in Table I are variously plotted in Figs. 1, 2 and 3, and on these the following comments may be made:

(1) The plot of the one-eighth power of the relative viscosity against the concentration is a good straight line, (Fig. 1) and the enlarged diagram of the low concentration region shows that the linear relation applies down to the lowest concentration examined. The equation $\eta_r^{\frac{1}{8}}=1+pc$ therefore satisfactorily represents the data over the concentration range 0 to 40 grams per litre.

(2) In Fig. 2 η_{sp}/c is plotted against the concentration. Staudinger originally suggested that this quantity tends to a constant value at low concentrations. Fig. 2 provides no evidence of such a tendency; indeed the enlarged diagram of the low-concentration region suggests that there is a point of inflexion below which the value of η_{sp}/c decreases rapidly as the concentration is further lowered.

Table I

Viscosities of Acetone Solutions of Seraceta at 20° C.

Concentration (gram/litre)	η centipoises	η_r	$\eta_r^{\frac{1}{8}}$	η_{sp}/c	$\text{Log}_{10}(\eta_{sp}/c)$
0·000	0·326	1.0000	1.0000	—	—
0·498	0·353	1·0828	1·0100	0·1663	$\bar{1}$·2208
1·718	0·428	1·3129	1·0346	0·1821	$\bar{1}$·2604
2·414	0·479	1·4693	1·0493	0·1944	$\bar{1}$·2887
4·082	0·622	1·9080	1·0841	0·2224	$\bar{1}$·3472
6·010	0·830	2·5460	1·1239	0·2572	$\bar{1}$·4103
8·004	1·096	3·3620	1·1637	0·2951	$\bar{1}$·4700
9·960	1·444	4·4294	1·2045	0·3443	$\bar{1}$·5370
12·104	1·931	5·9233	1·2490	0·4068	$\bar{1}$·6093
14·016	2·471	7·5798	1·2881	0·4694	$\bar{1}$·6716
16·070	3·222	9·8834	1·3316	0·5528	$\bar{1}$·7426
18·046	4·030	12·362	1·3693	0·6296	$\bar{1}$·7991
20·008	5·097	15·635	1·4101	0·7315	$\bar{1}$·8642
22·254	6·564	20·135	1·4554	0·8598	$\bar{1}$·9344
23·734	7·759	23·801	1·4862	0·9607	$\bar{1}$·9826
26·022	9·703	29·764	1·5283	1·1054	0·0435
26·990	10·78	33·068	1·5485	1·1881	0·0749
28·850	12·98	39·816	1·5849	1·3454	0·1289
30·425	15·38	47·178	1·6189	1·5178	0·1812
32·765	19·16	58·773	1·6635	1·7633	0·2463
35·030	22·78	69·877	1·7004	1·9662	0·2936
37·000	27·38	83·988	1·7399	2·2429	0·3508
38·265	32·07	98·374	1·7746	2·5447	0·4056
40·125	36·83	112·98	1·8056	2·7908	0·4457
42·350	43·96	134·85	1·8460	3·1606	0·4998
44·275	51·39	157·64	1·8824	3·5379	0·5487
0·000	0·322	1·0000	1·0000	—	—
0·176	0·330	1·0248	1·0031	0·1409	$\bar{1}$·1489
0·290	0·336	1·0435	1·0053	0·1500	$\bar{1}$·1761
0·403	0·343	1·0652	1·0079	0·1618	$\bar{1}$·2089
0·496	0·348	1·0807	1·0098	0·1627	$\bar{1}$·2114
0·513	0·349	1·0839	1·0101	0·1636	$\bar{1}$·2136
0·752	0·363	1·1273	1·0151	0·1693	$\bar{1}$·2286
0·954	0·374	1·1615	1·0189	0·1693	$\bar{1}$·2286
0·960	0·376	1·1677	1·0196	0·1747	$\bar{1}$·2423
1·203	0·391	1·2143	1·0246	0·1781	$\bar{1}$·2508

Table II

Values of $(\eta_r^{1/n}-1)/c$ for Different Values of c and n

c	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=10$
0·498	·166	·0815	·0540	·0404	·0321	·0267	·0228	·0201	·0179	·0161
1·718	·182	·0849	·0553	·0410	·0326	·0270	·0231	·0201	·0179	·0161
2·414	·194	·0879	·0567	·0418	·0331	·0274	·0234	·0204	·0181	·0162
4·082	·222	·0934	·0589	·0429	·0338	·0277	·0237	·0206	·0182	·0163
6·010	·257	·0991	·0591	·0438	·0342	·0280	·0238	·0206	·0182	·0163
8·004	·295	·1041	·0622	·0442	·0343	·0280	·0236	·0204	·0180	·0161
9·960	·344	·1109	·0649	·0452	·0348	·0283	·0238	·0205	·0180	·0161
12·104	·407	·1185	·0670	·0463	·0354	·0286	·0239	·0206	·0181	·0164
16·070	·553	·1335	·0713	·0481	·0362	·0289	·0236	·0206	·0180	·0160
20·008	·732	·1477	·0750	·0494	·0366	·0290	·0240	·0205	·0179	·0158
23·734	·961	·1635	·0791	·0509	·0373	·0293	·0241	·0205	·0178	·0157
26·990	1·190	·1760	·0819	·0519	·0375	·0293	·0240	·0203	·0176	·0155
30·425	1·518	·1930	·0859	·0533	·0380	·0296	·0241	·0203	·0176	·0154
35·030	1·966	·2100	·0890	·0540	·0382	·0301	·0238	·0200	·0172	·0151
40·125	2·792	·2401	·0956	·0563	·0392	·0299	·0240	·0201	·0172	·0152
44·275	3·537	·2611	·0994	·0574	·0395	·0299	·0239	·0199	·0170	·0149

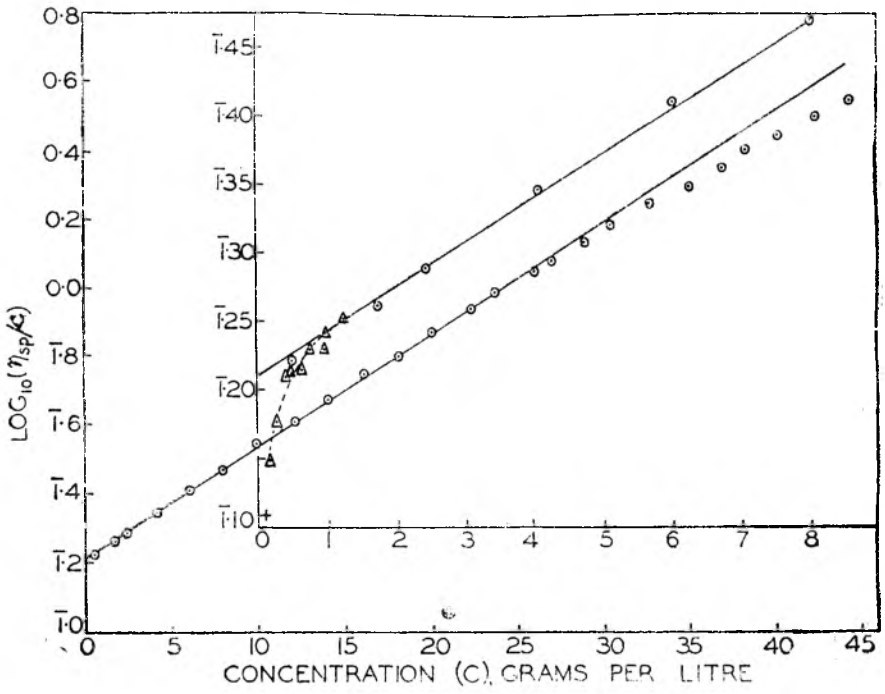


Fig. 3

(3) In Fig. 3 $\log_{10}(\eta_{sp}/c)$ is plotted against the concentration. The plot is linear over the concentration range 1 to 25 grams per litre, but as in Fig. 2 there appears to be a tendency for the viscosity function to decrease rapidly at the lowest values of the concentration. [The use of $\log(\eta_{sp}/c)$ has been advocated by Staudinger[10] in preference to η_{sp}/c for systems for which the latter is unsatisfactory].

(4) As mentioned above, there is a suggestion (Figs. 2 and 3) that at very low concentrations the η_{sp}/c and log (η_{sp}/c) curves may turn downwards making the former sigmoid and the latter non-linear. At such low concentrations the experimental error in preparing small volumes of solution is relatively large, and 500 c.c. of a 0·01 per cent. solution were made up and the viscosity measured to check the point. The time of flow of this solution was 205·2 secs. compared with 202·6 secs. for acetone, and the results obtained were :

$$\begin{aligned} c &= 0{\cdot}0998 \text{ gram per litre.} \\ \eta_r &= 1{\cdot}0128 \\ \eta_r^{\frac{1}{2}} &= 1{\cdot}0016 \\ \eta_{sp}/c &= 0{\cdot}1283 \\ \log_{10} \eta_{sp}/c &= \bar{1}{\cdot}1081 \end{aligned}$$

These values of η_{sp}/c and $\log_{10}(\eta_{sp}/c)$ lie so far below the curves in Figs. 2 and 3 that they have not been inserted; yet the value of $\eta_r^{\frac{1}{2}}$ falls reasonably on the straight line of Fig. 1 (plotted as a cross on Fig. 1). It seems possible, therefore, that the apparent bending of the η_{sp}/c and log (η_{sp}/c) curves in the low concentration region may be real, but its more detailed study would require facilities for very accurate viscometry, and the question was not pursued further.

(5) The curve of Fig. 2 was produced to cut the η_{sp}/c axis, the lower points at very low concentrations being neglected. The intercept on this axis gives $[\eta]$ directly as $\underset{c\to 0}{\text{Lim}}\ \eta_{sp}/c$. Similarly the straight line portion of Fig. 3 was produced to cut the $\log_{10}(\eta_{sp}/c)$ axis, the intercept being $\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)$, the antilog of which is also $[\eta]$. Finally from Fig. 1 $[\eta]$ can be obtained by multiplying the slope of the line by eight, so that three estimates of its value are available :

$$[\eta] = 8\frac{d(\eta_r^{\frac{1}{2}})}{dc} = 0{\cdot}1640$$

$$[\eta] = \underset{c\to 0}{\text{Lim.}}\ \eta_{sp}/c = 0{\cdot}1630$$

$$[\eta] = \text{antilog}\ \left\{\underset{c\to 0}{\text{Lim}}\ (\log\ \eta_{sp}/c)\right\} = \text{antilog}\ \bar{1}{\cdot}211$$

$$= 0{\cdot}1626$$

These values are within the limits of error identical, and there is no obvious reason why any one of them should be preferred to any other. Linear extrapolation is so greatly to be preferred, however, that in the later work the determination of $[\eta]$ as $\underset{c\to 0}{\text{Lim}}\ \eta_{sp}/c$ was not further considered, attention being confined to the two linear methods. This obviously made it possible very greatly to reduce the number of viscosity determinations.

(b) The Effect of Temperature

To examine in a general way the effect of temperature on the viscosity of solutions of cellulose acetate, pyridine was chosen as solvent in preference to acetone so that viscosities could be measured over a wider range of temperature. The results of determinations of the viscosities of solutions of Seraceta in pyridine over the temperature range 20—70°C. are given in Table III. Fig. 4 shows the plot of $\eta_r^{\frac{1}{2}}$ against c, and Fig. 5 that of log (η_{sp}/c) against c. Both methods of plotting give a series of reasonably good straight lines, those of Fig. 4 showing a decrease of slope with increase of temperature, and those of Fig. 5 a decrease of intercept on the axis of zero concentration together with a slight decrease of slope. Estimates of the intrinsic viscosity $[\eta]$ were obtained on the basis of these linear relations; the figures are given in Table IV.

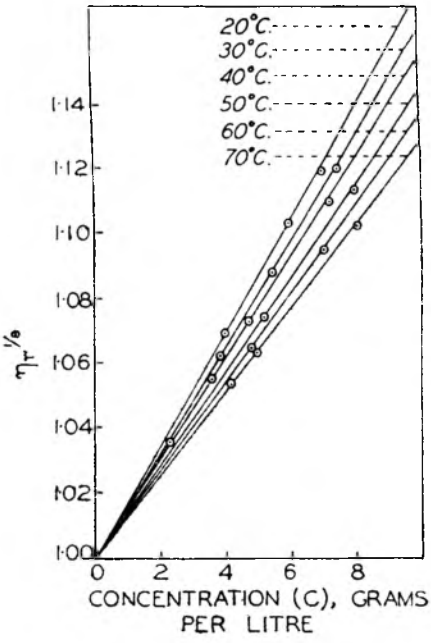


Fig. 4

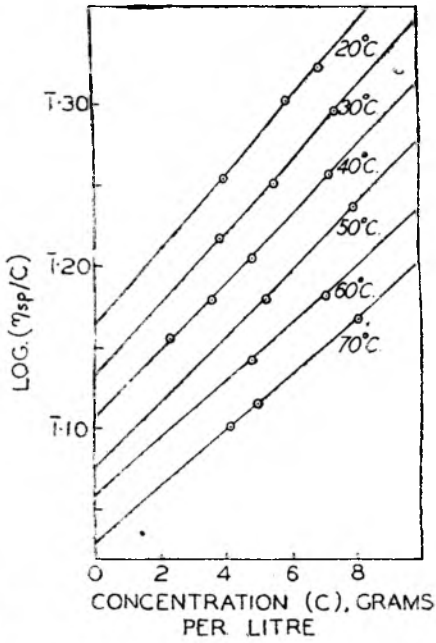


Fig. 5

Table III
Viscosities of Pyridine Solutions of Seraceta, 20-70°C.

Temperature, °C.	Concentration* (*c*) (grams/litre)	η_r	$\eta_r^{\frac{1}{8}}$	$\text{Log}_{10}(\eta_{sp}/c)$
20	3·943	1·7085	1·0693	$\bar{1}$·2545
,,	5·928	2·1903	1·1030	$\bar{1}$·3027
,,	6·923	2·4562	1·1189	$\bar{1}$·3229
30	3·800	1·6262	1·0627	$\bar{1}$·2169
,,	5·431	1·9692	1·0884	$\bar{1}$·2515
,,	7·447	2·4759	1·1200	$\bar{1}$·2971
40	2·270	1·3254	1·0358	$\bar{1}$·1564
,,	3·539	1·5358	1·0551	$\bar{1}$·1801
,,	4·732	1·7592	1·0732	$\bar{1}$·2053
,,	7·201	2·3015	1·1098	$\bar{1}$·2571
50	5·140	1·7791	1·0747	$\bar{1}$·1806
,,	7·930	2·3700	1·1139	$\bar{1}$·2374
60	4·762	1·6625	1·0656	$\bar{1}$·1434
,,	7·000	2·0673	1·0950	$\bar{1}$·1832
70	4·124	1·5201	1·0537	$\bar{1}$·1008
,,	4·969	1·6491	1·0645	$\bar{1}$·1160
,,	8·023	2·1833	1·1025	$\bar{1}$·1688

* Concentrations were determined at room temperature.

Table IV
Intrinsic Viscosities of Pyridine Solutions of Seraceta, 20-70°C.

Temperature °C. :—	20	30	40	50	60	70
$[\eta] = 8d\eta_r^{\frac{1}{8}}/dc$	0·139	0·130	0·124	0·116	0·109	0·103
$[\eta]$ = antilog $\{\underset{c\to 0}{\text{Lim}}\ (\log \eta_{sp}/c)\}$	0·146	0·136	0·128	0·119	0·114	0·107

Unlike the results given in section (a), the values obtained by the two methods differ appreciably, but the figures themselves provide no evidence to justify the choice of one set in preference to the other.

Owing to the different concentrations at which the viscosities were measured, the data of Table III cannot be used directly to demonstrate the

effect of temperature on the viscosity of solutions of cellulose acetate in pyridine. The linear relation between $\eta_r^{\frac{1}{2}}$ and c has therefore been used to calculate the relative viscosities at concentrations of 1, 2, 4, 6 and 8 grams per litre; these values are plotted in Fig. 6.

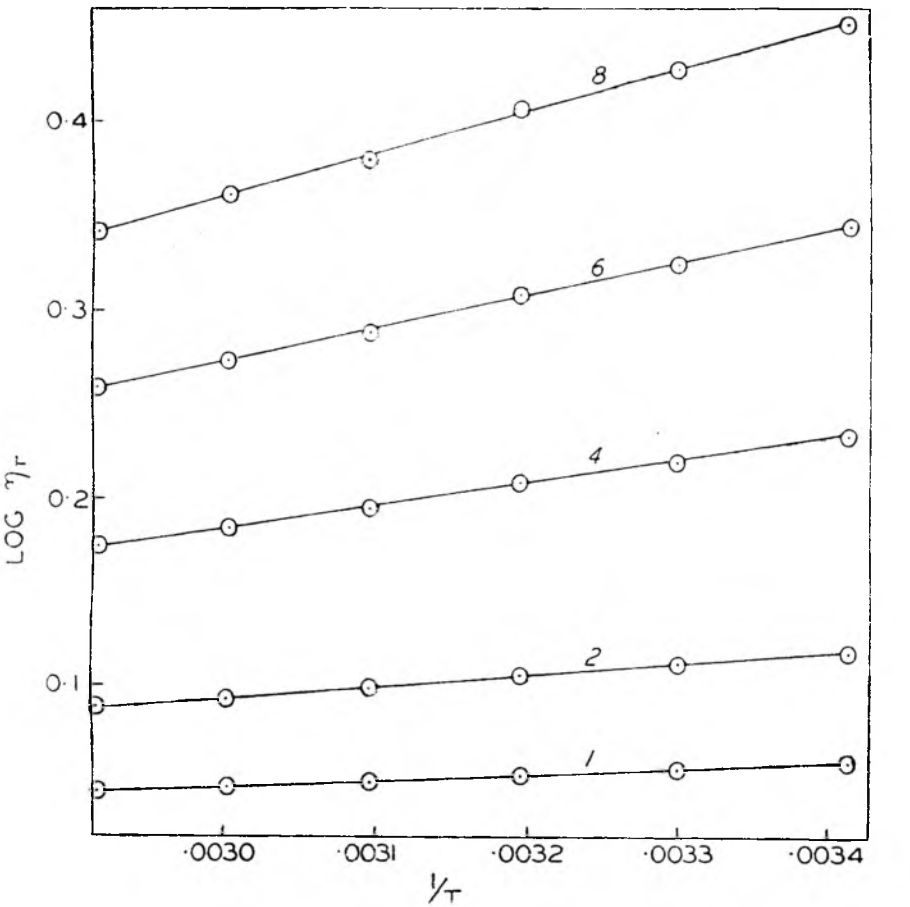


Fig. 6. The concentration in grams per litre is indicated against each line.

It has already been mentioned that Andrade[11] and Sheppard[12] have proposed an equation of the form $\eta = Ae^{B/T}$ to represent the relation between the temperature and the viscosity of a pure liquid, and that Karrer[13] has derived an equation of identical form for solutions. If both these relations apply, then it follows that the *relative* viscosity of a solution should also conform to the same relation and hence that the plot of log η_r against $1/T$ should be a straight line. Fig. 6 shows that an excellent straight line is obtained for each solution, indicating a large degree of conformity with the above relation over the temperature range examined.

The viscosities of acetone solutions of Seraceta, of a sample of Seraceta oxidised by sodium hypochlorite in neutral solution, and of fractions of different molecular chain length derived from these by methods to be described in a later paper of this series, have been determined at 20, 25, 30 and 35°C., three concentrations of solution being examined for each material at each temperature. The results obtained with Seraceta and the fractions prepared from it are given in Table V. In Fig. 7 $\eta_r^{\frac{1}{2}}$ is plotted against concentration, giving a series of straight lines that decrease in slope with increasing temperature. (In order to avoid confusion the data for the original Seraceta are not plotted on this Figure). The lines for fraction 6

are less satisfactory than the others; the lines shown are the best straight lines that can be drawn through the three given points and they pass above the points at the lowest concentration, through those at the intermediate concentration, and below those at the highest concentration, suggesting that these points really lie on a curve that is slightly concave upwards. If this is so then the values of $[\eta]$ obtained by using the best straight lines through all the points will be too high, and better values would be obtained by using the data for the lowest concentrations only.

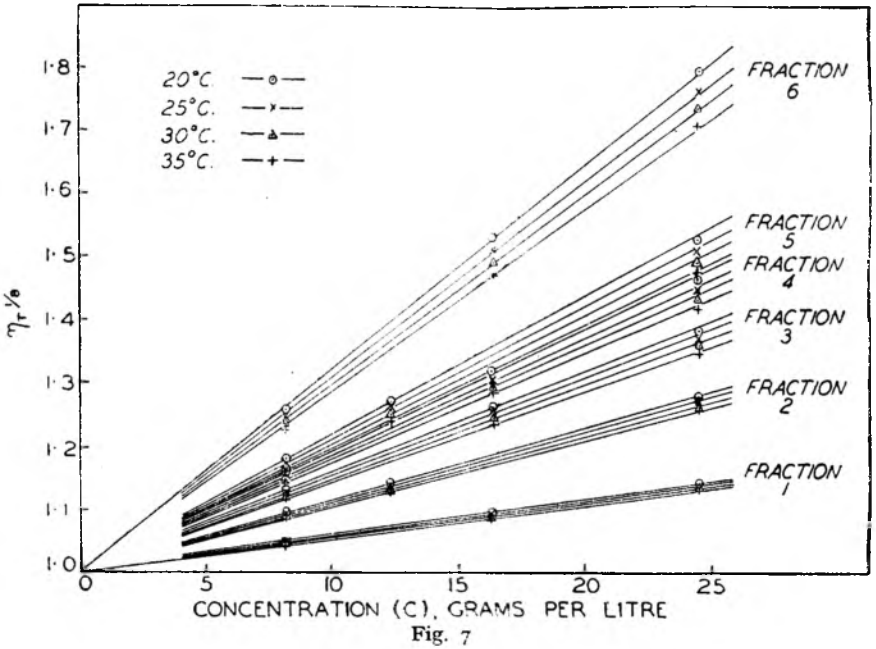


Fig. 7

Table V

Viscosities of Acetone Solutions of Seraceta and its Fractions at Different Temperatures

Sample and concentration (grams/litre)		Values of η; centipoises			
		20° C.	25° C.	30° C.	35° C.
Solvent	0·000	0·322	0·306	0·292	0·280
Original Seraceta...	8·155	1·101	1·002	0·9194	0·8424
	16·31	3·260	2·892	2·562	2·274
	24·46	8·287	7·158	6·238	5·439
Fraction 1... ...	8·155	0·4680	0·4421	0·4193	0·3968
	16·31	0·6723	0·6270	0·5868	0·5488
	24·46	0·9566	0·8788	0·8119	0·7698
Fraction 2... ...	8·155	0·6775	0·6259	0·5839	0·5459
	12·23	0·9473	0·8700	0·8034	0·7405
	24·46	2·337	2·101	1·888	1·789
Fraction 3... ...	8·155	0·8718	0·8021	0·7415	0·6855
	16·31	2·067	1·882	1·703	1·524
	24·46	4·312	3·822	3·404	3·035
Fraction 4... ...	8·155	1·068	0·9768	0·8969	0·8239
	16·31	2·954	2·611	2·310	2·082
	24·46	6·829	5·968	5·230	4·614
Fraction 5... ...	8·155	1·226	1·112	1·016	0·9315
	12·23	2·188	1·959	1·750	1·573
	24·46	9·530	8·226	7·150	6·279
Fraction 6... ...	8·155	2·030	1·795	1·605	1·442
	16·31	9·690	8·279	7·137	6·170
	24·46	34·97	28·90	24·31	20·40

Fig. 8 is a plot of log (η_{sp}/c) against c for the same data, those for the original Seraceta being again omitted ; a series of straight lines is obtained, and as with the pyridine solutions both the slopes of these lines and their intercepts on the axis of zero concentration decrease with increasing temperature.

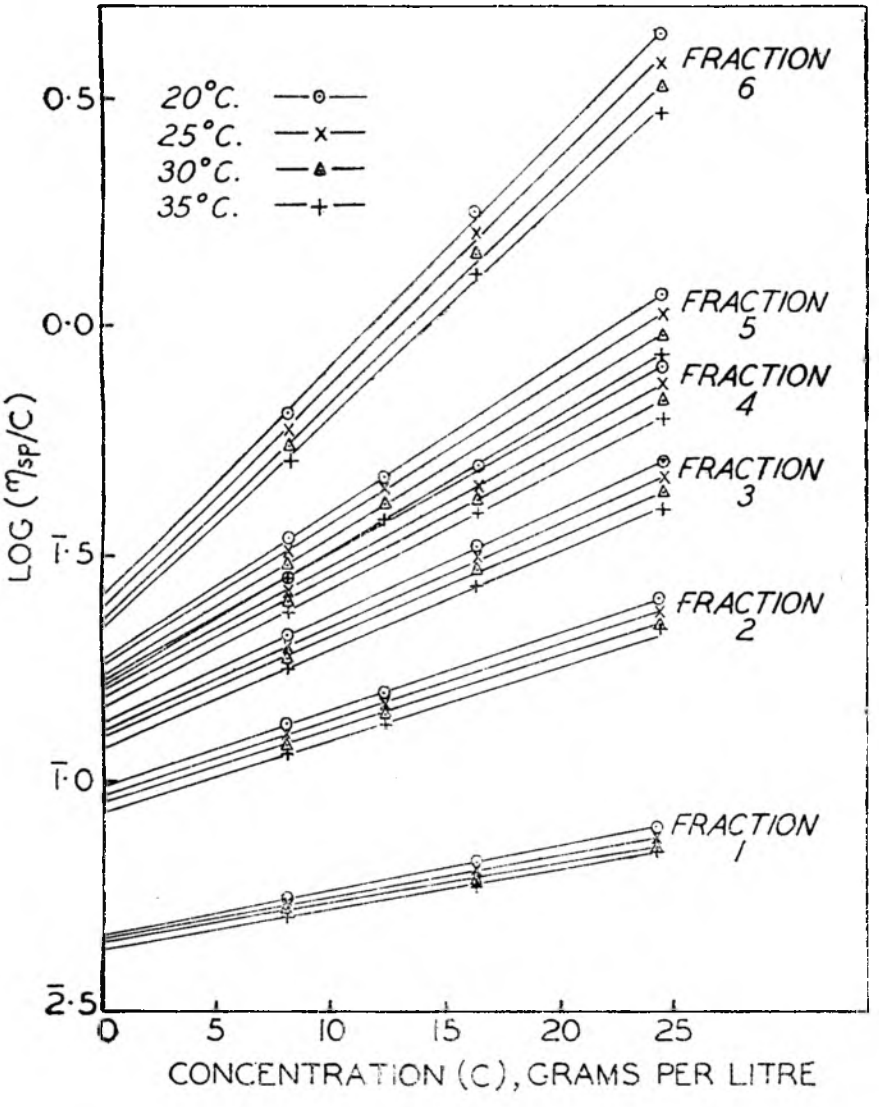


Fig. 8

Values of $[\eta]$ obtained by the two methods of plotting are given in Table VI. The two methods lead to appreciably different results but again there is no internal evidence justifying the choice of one method in preference to the other. It should be noted, however, that the data for the original Seraceta at 20°C. constitute an independent set of determinations which ought to give the same result as the data of Table I ; the values of $[\eta]$ obtained are

$[\eta] = 8d\eta_r^{\frac{1}{2}}/dc = 0{\cdot}1640$ and $0{\cdot}1638$

$[\eta] = \text{antilog}\{\underset{c\to 0}{\text{Lim}} \log(\eta_{sp}/c)\} = 0{\cdot}1626$ and $0{\cdot}1618$

Table VI

Intrinsic Viscosities of Acetone Solutions of Seraceta and its Fractions, 20-35°C.

$(a) = 8d\eta_r^{\frac{1}{8}}/dc$ $(b) = \text{antilog}\left\{\underset{c\to 0}{\text{Lim.}}(\eta_{sp}/c)\right\}$

Temperature, °C.	20		25		30		35	
Sample	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Original Seraceta ...	·164	·162	·158	·156	·152	·149	·146	·142
Fraction 1 ...	·047	·046	·046	·046	·045	·045	·044	·043
Fraction 2 ...	·094	·098	·091	·094	·088	·091	·085	·084
Fraction 3 ...	·128	·136	·124	·131	·120	·126	·115	·119
Fraction 4 ...	·156	·168	·145	·160	·145	·155	·140	·147
Fraction 5 ...	·176	·188	·170	·179	·163	·172	·157	·163
Fraction 6 ...	·258	·255	·248	·240	·238	·227	·229	·216

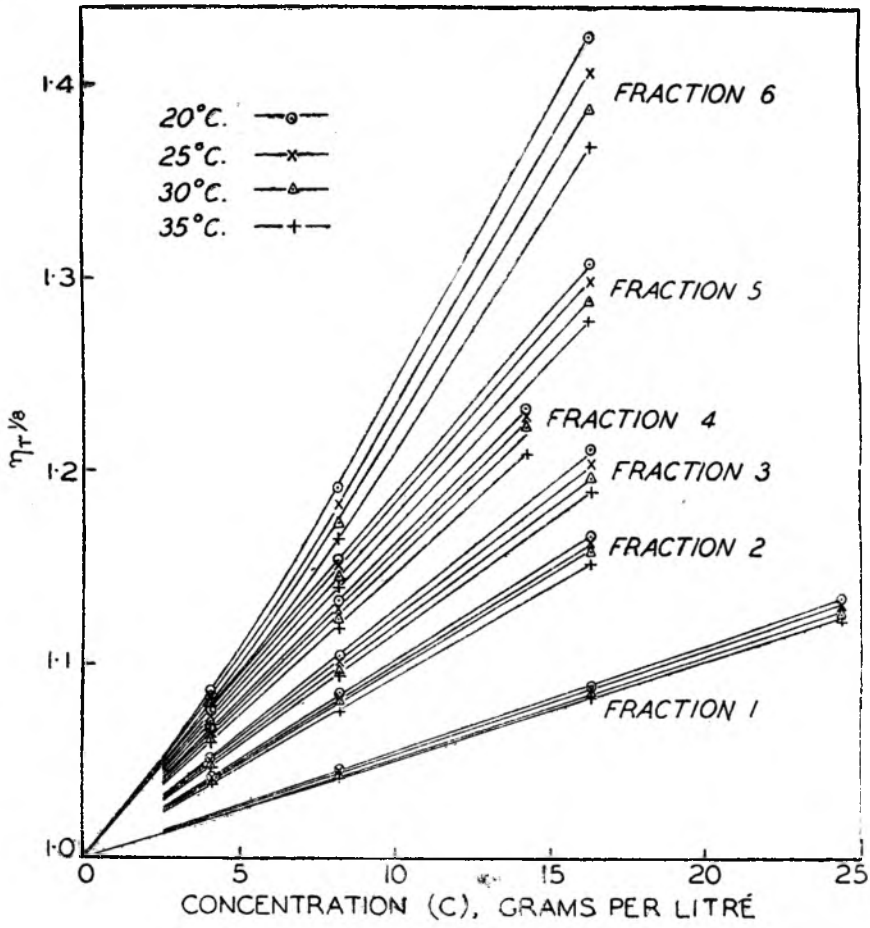


Fig. 9

The agreement between the results of the two series of determinations is excellent whichever method of determining $[\eta]$ is adopted, such difference as there may be favouring the use of $\eta_r^{\frac{1}{8}}$ rather than $\log(\eta_{sp}/c)$. This agreement is an indication of the excellence of the linear relations, the first values being obtained from viscosities at many concentrations, the second at three only.

The results obtained with the sample of oxidised Seraceta and the fractions prepared from it are given in Table VII. Fig. 9 is a plot of $\eta_r^{\frac{1}{4}}$ against c for the six fractions, the lines for the material from which they were prepared being again omitted to avoid confusion. The lines for fractions 1—5 are straight, but the data for fraction 6 can only be represented by a curve that is distinctly concave upwards. The other plot, of log (η_{sp}/c) against c, is shown in Fig. 10; here all the fractions give straight lines, but those for fraction 6 are again anomalous, their slopes being so much greater than those for fraction 5 that the lines cross those of fraction 5 to give *lower* intercepts on the axis of zero concentration.

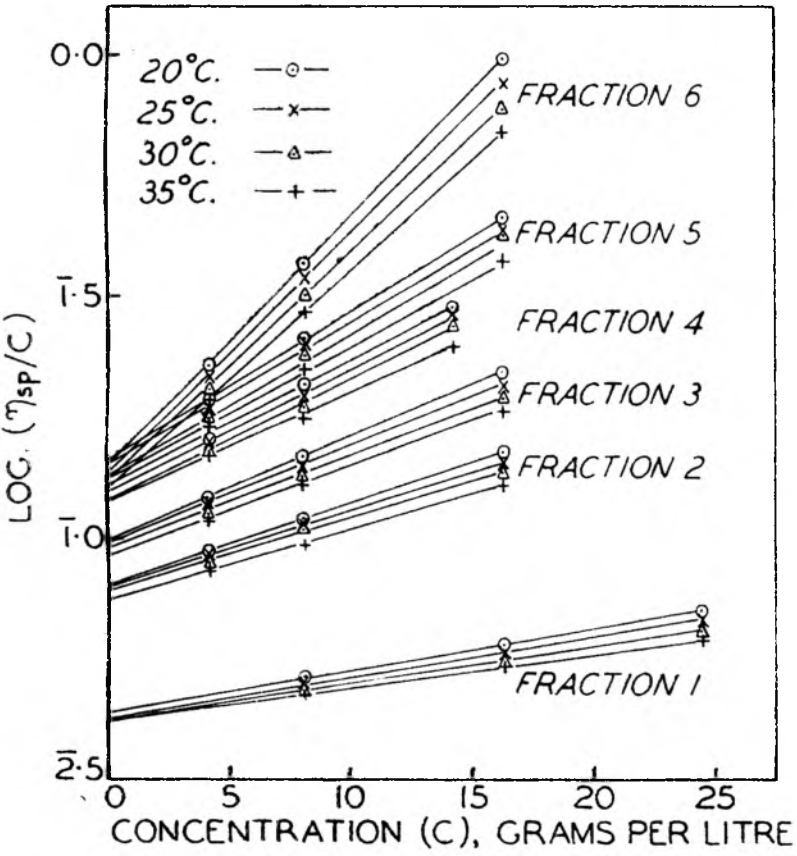


Fig. 10

The values of $[\eta]$ obtained from these two plots are given in Table VIII. It will be noticed from Fig. 9 that the curves for fraction 6 must in the region of low concentrations be almost identical with the straight lines joining the origin to the points at the lowest concentration; the slopes of the latter have therefore been used to determine $[\eta]$. The data for the oxidised Seraceta from which the fractions were extracted also lie on curves (see Fig. 13) that are concave upwards, and the same method has therefore been used to determine the values of $[\eta]$ for it. In the other method (that using Fig. 10) the linearity of the lines compels the adoption of the normal method of extrapolation, and hence the result is obtained that the intrinsic viscosity of fraction 6 is less than that of fraction 5.

Table VII

Viscosities of Acetone Solutions of Oxidised Seraceta and its Fractions at Different Temperatures

Sample and concentration (grams/litre)		Values of η; centipoises			
		20° C.	25° C.	30° C.	35° C.
Solvent	0·000	0·322	0·306	0·292	0·280
Oxidised Seraceta ...	8·155	0·7314	0·6744	0·6253	0·5820
	16·31	1·655	1·496	1·352	1·228
	24·46	3·426	3·035	2·687	2·408
Fraction 1	8·155	0·4571	0·4302	0·4083	0·3910
	16·31	0·6375	0·5984	0·5607	0·5348
	24·46	0·8812	0·8145	0·7553	0·7037
Fraction 2	4·078	0·4448	0·4213	0·3991	0·3774
	8·155	0·6089	0·5702	0·5453	0·4995
	16·31	1·116	1·023	0·9519	0·8700
Fraction 3	4·078	0·4812	0·4537	0·4276	0·4042
	8·155	0·7103	0·6600	0·6146	0·5731
	16·31	1·492	1·347	1·226	1·119
Fraction 4	4·078	0·5360	0·5051	0·4751	0·4491
	8·155	0·8746	0·8024	0·7403	0·6853
	14·27	1·710	1·587	1·456	1·274
Fraction 5	4·078	0·5763	0·5381	0·5036	0·4751
	8·155	1·011	0·9456	0·8666	0·7973
	16·31	2·769	2·477	2·214	1·995
Fraction 6	4·078	0·6220	0·5766	0·5342	0·5001
	8·155	1·306	1·174	1·051	0·9477
	16·31	5·479	4·692	3·986	3·430

Table VIII

Intrinsic Viscosities of Acetone Solutions of Oxidised Seraceta and its Fractions, 20-35 °C.

$(a) = 8\mathrm{d}\eta_r^{\frac{1}{8}}/\mathrm{d}c$; $(b) = \text{antilog}\left(\underset{c\to 0}{\text{Lim}}\ \log\ (\eta_{sp}/c)\right)$

Temperature, °C.	20		25		30		35	
Sample	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Oxidised Seraceta	·106	·099	·102	·095	·098	·091	·094	·087
Fraction 1	·044	·044	·043	·043	·042	·042	·041	·042
Fraction 2	·082	·080	·080	·080	·079	·078	·074	·074
Fraction 3	·102	·099	·099	·098	·096	·095	·092	·091
Fraction 4	·130	·128	·127	·124	·123	·120	·117	·119
Fraction 5	·150	·145	·146	·142	·141	·133	·136	·132
Fraction 6	·168	·141	·162	·136	·154	·130	·148	·126

This implies, of course, that the mean molecular chain length of fraction 6 is less than that of fraction 5, a result that is certainly in error, for the viscosities of solutions of fraction 6 are greater than those of fraction 5 even at the low concentrations at which both lines show a tendency to curve downwards. The data obtained by the other method of determining $[\eta]$ show no such anomaly, and the absence of the anomaly is not due to the fact that the slope in the low concentration region only was used in the calculation, for if all the data had been used the value of $[\eta]$ obtained from the slope of the best straight line through all the points would have been still greater than quoted in Table VIII. Here for the first time,

therefore, is definite evidence from the figures themselves that the determination of $[\eta]$ from the $\eta_r^{\frac{1}{2}}$ plot may be preferable to that using log (η_{sp}/c).

It should be mentioned that the data provided in Tables V and VII all give straight lines when the logarithm of the viscosity of any of the solutions is plotted against the reciprocal of the absolute temperature; the temperature range covered is, however, small, and hence the data plotted in Fig. 6 provide more reliable evidence of the linearity of this relation. It is of interest to note that over the range of chain lengths covered by these fractions there is no tendency for the temperature effect to change direction with increasing molecular weight, as was suggested by Burgers.[19]

(c) The Effect of Heterogeneity

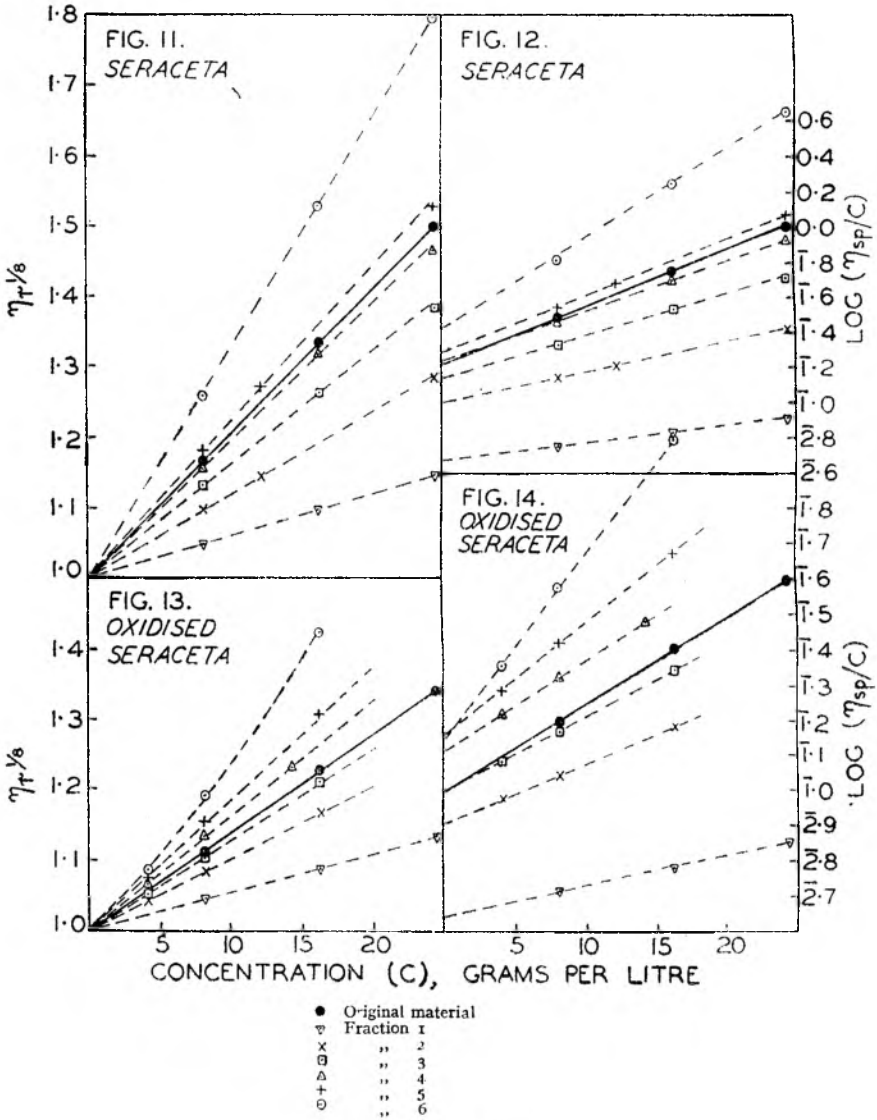
Although data for the original Seraceta and oxidised Seraceta are included in Tables V and VII it proved impossible to include these data in Figs. 7-10 without confusing the whole picture. Figs. 11-14 have therefore been prepared to permit a comparison of the results obtained from the original materials with those from the various fractions into which they were subdivided, attention being confined to one temperature only. Fig. 11 shows $\eta_r^{\frac{1}{2}}$ plotted against concentration for Seraceta and its fractions at 20°C. The line for the original Seraceta falls naturally into place among those for the various fractions, its slope indicating a value of $[\eta]$ between those for fractions 4 and 5 (Table VI). On Fig. 12 log (η_{sp}/c) is plotted against c, and there it will be noticed that the line for the original Seraceta cuts across those for the fractions, with a slope abnormally large for its position in the series. As a result of this the value of $[\eta]$ obtained by extrapolation lies between those of fractions 3 and 4 (Table VI), though all the points on the line lie between the corresponding points for fractions 4 and 5. A similar effect is observed in Figs. 13 and 14, where the data for the oxidised Seraceta are similarly plotted. It will be noted that the line obtained by plotting $\eta_r^{\frac{1}{2}}$ against c for the oxidised Seraceta is, like that for fraction 6, concave upwards (Fig. 13). The slope near the origin is a little greater than that for fraction 3, and hence gives a slightly greater value of $[\eta]$ (Table VIII), but on the log (η_{sp}/c) plot (Fig. 14) the slope of the line for the oxidised Seraceta is sufficiently great to bring down the value of $[\eta]$ to one identical with that of fraction 3 (Table VIII), in spite of the fact that at all concentrations examined the viscosities of the material as a whole are greater than those of fraction 3 prepared from it.

Table IX

Intrinsic Viscosities of Seraceta and Oxidised Seraceta, 20-35°C.

		20° C.	25° C.	30° C.	35° C.
Seraceta					
$[\eta] = 8d\eta_r^{\frac{1}{2}}/dc$	Observed	·164	·158	·152	·146
	Calculated from values for fractions...	·155	·149	·144	·138
$[\eta] = \text{antilog } \underset{c\to 0}{\text{Lim}} \log(\eta_{sp}/c)$	Observed	·162	·156	·149	·142
	Calculated from values for fractions...	·160	·152	·149	·138
Oxidised Seraceta					
$[\eta] = 8d\eta_r^{\frac{1}{2}}/dc$	Observed	·106	·102	·098	·094
	Calculated from values for fractions...	·105	·102	·099	·094
$[\eta] = \text{antilog } \underset{c\to 0}{\text{Lim}} \log(\eta_{sp}/c)$	Observed	·099	·095	·091	·087
	Calculated from values for fractions..	·099	·097	·093	·091

The essential difference between the original material and its fractions is one of heterogeneity of molecular chain length, the material being a very intimate mixture of the various fractions. The fractions themselves will not of course be homogeneous with respect to chain length, but at least they are much more homogeneous than the material from which they were prepared. It would appear, therefore, that heterogeneity has no effect on



Figs. 11-14

the $\eta_{ir}^{\frac{1}{8}}$ plot, but on the log (η_{sp}/c) plot confers on the line a slope appreciably greater than that of a more homogeneous material of the same intrinsic viscosity.

According to the Staudinger equation the intrinsic viscosity is linearly related to the molecular weight by means of a constant that is independent

of the molecular weight. If this assumption is justified then it follows that since the molecular weight is a strictly additive property the intrinsic viscosity should be also; that is, the intrinsic viscosity of the original material should be calculable from those of its various fractions by taking a mean, weighted according to the proportions in which the fractions are present. Values obtained in this way are given in Table IX. The agreement between observed and calculated values is reasonably good throughout, though considerably less good for the values obtained for Seraceta by the use of the plot of $\eta_r^{\frac{1}{8}}$ than for any of the others. No explanation of this is at present available. It will be noted that excellent agreement is obtained by the use of the log (η_{sp}/c) plot, in spite of the fact that some of the individual results involved in the comparison are, as has been mentioned above, distinctly anomalous. Taken as a whole the figures support Staudinger's contention that there is a unique relation between $[\eta]$ and molecular weight, at any rate over the range of molecular weight covered by these materials.

(d) The Effect of Solvent

Staudinger has shown[20, 22, 23] that different values of $[\eta]$ are obtained for a given cellulose derivative according to the solvent used; only a few solvents were examined by him, however, and a further examination of the magnitude of this effect was considered desirable.

The viscosities of solutions in various solvents of Seraceta and a triacetate prepared from it by non-degradative acetylation[44] were determined at 20°C. The results of these determinations are presented in Tables X and XI. As before, straight lines varying in slope are obtained when $\eta_r^{\frac{1}{8}}$ is plotted against c, and a plot of log (η_{sp}/c) against c gives a series of lines varying both in slope and in the intercept on the axis of zero concentration, the variation in slope being sufficient to cause crossing of some of the lines.

Table X

Viscosities of Seraceta in Various Solvents at 20°C.

Solvent and concentration (grams/litre)	η centi-poises	η_r	$\eta_r^{\frac{1}{8}}$	$\log_{10}(\eta_{sp}/c)$	$8d\eta_r^{\frac{1}{8}}/dc$	Antilog Lim log (η_{sp}/c) $c\to 0$
Acetone (From Table I)					·164	·163
Dioxane ... 0·000	1·280	1·000	1·000	—	·173	·189
Dioxane ... 11·43	7·685	6·004	1·251	$\bar{1}$·6413		
Dioxane ... 16·54	14·81	11·57	1·358	$\bar{1}$·8055		
Dioxane ... 26·68	47·04	36·75	1·569	0·1271		
Pyridine ... 0·000	0·9727	1·000	1·000	—	·139	·146
Pyridine ... 3·943	1·662	1·709	1·069	$\bar{1}$·2546		
Pyridine ... 5·928	2·130	2·190	1·103	$\bar{1}$·3026		
Pyridine ... 6·923	2·389	2·456	1·119	$\bar{1}$·3229		
m-Cresol ... 0·000	17·37	1·000	1·000	—	·166	·173
m-Cresol ... 2·169	24·83	1·430	1·046	$\bar{1}$·2967		
m-Cresol ... 3·940	32·45	1·868	1·081	$\bar{1}$·3431		
m-Cresol ... 6·232	45·03	2·592	1·126	$\bar{1}$·4074		
Methylene chloride (70 parts) ethyl alcohol (30 parts) by volume 0·000	0·5116	1·000	1·000	—	·144	·150
Methylene chloride (70 parts) ethyl alcohol (30 parts) by volume 4·385	0·9397	1·837	1·079	$\bar{1}$·2807		
Methylene chloride (70 parts) ethyl alcohol (30 parts) by volume 5·277	1·070	2·092	1·097	$\bar{1}$·3156		
Methylene chloride (70 parts) ethyl alcohol (30 parts) by volume 8·061	1·491	2·914	1·143	$\bar{1}$·3756		
Methylene chloride (70 parts) ethyl alcohol (30 parts) by volume 10·49	2·011	3·931	1·187	$\bar{1}$·4462		

Table XI
Viscosities of Seraceta Triacetate in Various Solvents at 20°C.

Solvent and concentration (grams/litre)		η centi-poises	η_r	$\eta_r^{\frac{1}{8}}$	$\log_{10}(\eta_{sp}/c)$	$8d\,\eta_r^{\frac{1}{8}}/dc$	Antilog $\{\text{Lim}_{c\to 0} \log(\eta_{sp}/c)\}$
Chloroform	0·000	0·5738	1·0000	1·0000	—	·089	·092
	7·139	1·063	1·8526	1·0801	$\bar{1}$·0771		
	9·262	1·257	2·1907	1·1030	$\bar{1}$·1091		
	11·05	1·445	2·5183	1·1224	$\bar{1}$·1380		
	14·55	1·879	3·2747	1·1598	$\bar{1}$·1941		
m-Cresol ...	0·000	17·37	1·0000	1·0000	—	·114	·126
	3·631	26·46	1·5233	1·0540	$\bar{1}$·1587		
	7·678	39·89	2·2965	1·1095	$\bar{1}$·2275		
	11·42	55·89	3·2176	1·1573	$\bar{1}$·2882		
Methylene chloride (70 parts), ethyl alcohol (30 parts) by volume	0·000	0·5121	1·0000	1·0000	—	·110	·113
	2·516	0·6750	1·3181	1·0351	$\bar{1}$·1019		
	4·985	0·8688	1·6965	1·0683	$\bar{1}$·1453		
	11·36	1·595	3·1146	1·1526	$\bar{1}$·2698		

The values of $[\eta]$ obtained with these solvents and with acetone show that there is quite a large variation of $[\eta]$ according to the solvent used. Measurements were also made on a sample of viscose rayon that had been acetylated non-degradatively to the triacetate; *m*-cresol and chloroform were used as solvents, and the results presented in Table XII show that here also the intrinsic viscosity varies with the solvent.

Table XII
Viscosities of Acetylated Viscose Rayon in *m*-Cresol and Chloroform at 20°C.

Solvent and concentration (grams/litre)		η_r	$\eta_r^{\frac{1}{8}}$	$\log_{10}(\eta_{sp}/c)$	$8d\,\eta_r^{\frac{1}{8}}/dc$	Antilog $\{\text{Lim}_{c\to 0} \log(\eta_{sp}/c)\}$
m-Cresol ...	4·278	1·856	1·0804	$\bar{1}$·3012	·148	·161
	5·701	2·231	1·1055	$\bar{1}$·3343		
	7·938	2·917	1·1432	$\bar{1}$·3829		
Chloroform	6·262	2·050	1·0939	$\bar{1}$·2245	·118	·127
	7·877	2·407	1·1161	$\bar{1}$·2519		
	11·69	3·490	1·1691	$\bar{1}$·3284		

This variation is also shown by the data of Table XVI, which gives the intrinsic viscosities of a series of cellulose acetates having acetic acid yields between those of secondary cellulose acetate and cellulose triacetate; the detailed results obtained with these materials are given in the succeeding section.

Solvents composed of two liquids in varying proportions have also been used; the results given in Table XIII show that the intrinsic viscosities of Seraceta in mixtures of acetone and water do not vary with the amount of water present (within the range of composition examined), though they are appreciably lower than the values obtained for solutions in pure acetone (0·1640 and 0·1626). In addition, it can be shown graphically that the relative viscosities are also independent of solvent composition. These results are similar to Staudinger's observations on acetone-water solutions of cellulose nitrate.[10] The values of $[\eta]$ obtained from the log (η_{sp}/c) plot are more irregular than those from the $\eta_r^{\frac{1}{8}}$ plot, but it appears to be random irregularity, without any definite trend. It may be noted that although the relative and intrinsic viscosities are independent of the water content of the solvent the absolute viscosities of both solvent and solution were found to increase continuously as the water content of the solvent is increased.

Table XIII
Viscosities of Seraceta in Acetone-Water Mixtures at 20°C.

Per cent. acetone by volume	c	η_r	$\eta_r^{\frac{1}{2}}$	$\log_{10}(\eta_{sp}/c)$	$8d\eta_r^{\frac{1}{2}}/dc$	Antilog $\{\text{Lim}_{c\to 0} \log(\eta_{sp}/c)\}$
97·5	3·985	1·8051	1·0766	$\bar{1}$·3055	·155	·152
	7·723	3·0441	1·1493	$\bar{1}$·4227		
	11·53	5·0147	1·2233	$\bar{1}$·5418		
95·0	4·039	1·8490	1·0799	$\bar{1}$·3226	·156	·164
	5·985	2·4362	1·1177	$\bar{1}$·3802		
	7·769	3·0570	1·1499	$\bar{1}$·4229		
	11·58	4·9597	1·2216	$\bar{1}$·5340		
90·0	4·155	1·8603	1·0807	$\bar{1}$·3161	·153	·159
	8·155	3·1945	1·1562	$\bar{1}$·4299		
	11·81	4·9753	1·2221	$\bar{1}$·5271		
85·0	4·061	1·8523	1·0801	$\bar{1}$·3220	·154	·164
	7·776	3·0336	1·1488	$\bar{1}$·4175		
	11·54	4·7920	1·2164	$\bar{1}$·5167		
80·0	3·915	1·8004	1·0763	$\bar{1}$·3106	·153	·162
	5·585	2·2649	1·1076	$\bar{1}$·3550		
	9·162	3·5578	1·1719	$\bar{1}$·4459		
	11·07	4·5261	1·2077	$\bar{1}$·5031		

Results of viscosity determinations on solutions of Seraceta and its triacetate in mixtures of methylene chloride and ethyl alcohol are given in Table XIV. Again it is found that the relative and intrinsic viscosities of the solutions do not vary with the composition of the solvent within the range studied, though the absolute viscosities of the solvents and the solutions increase with increasing alcohol content.

Table XIV
Viscosities of Seraceta and Seraceta Triacetate in Methylene Chloride-Ethyl Alcohol Mixtures at 20°C.

Ratio of methylene chloride to alcohol by volume	c	η_r	$\eta_r^{\frac{1}{2}}$	$\log_{10}(\eta/_{sp}c)$	$8d\eta_r^{\frac{1}{2}}/dc$	Antilog $\{\text{Lim}_{c\to 0} \log(\eta_{sp}/c)\}$
Seraceta						
65 : 35	3·723	1·6862	1·0675	$\bar{1}$·2656	·143	·148
	7·386	2·6896	1·1316	$\bar{1}$·3594		
	11·31	4·2483	1·1982	$\bar{1}$·4582		
70 : 30	4·385	1·8370	1·0790	$\bar{1}$·2808	·144	·150
	5·277	2·0926	1·0967	$\bar{1}$·3161		
	8·061	2·9148	1·1431	$\bar{1}$·3757		
	10·49	3·9333	1·1867	$\bar{1}$·4466		
75 : 25	4·439	1·8465	1·0797	$\bar{1}$·2803	·142	·148
	7·832	2·7795	1·1363	$\bar{1}$·3677		
	11·24	4·1772	1·1957	$\bar{1}$·4513		
Seraceta triacetate						
65 : 35	3·847	1·5276	1·0544	$\bar{1}$·1372	·109	·118
	7·700	2·2172	1·1047	$\bar{1}$·1989		
	11·49	3·1172	1·1527	$\bar{1}$·2654		
70 : 30	2·516	1·3185	1·0352	$\bar{1}$·1024	·110	·113
	4·985	1·6963	1·0683	$\bar{1}$·1451		
	11·36	3·1148	1·1526	$\bar{1}$·2699		
75 : 25	4·170	1·5591	1·0571	$\bar{1}$·1274	·110	·111
	6·247	1·9567	1·0875	$\bar{1}$·1851		
	9·986	2·7717	1·1359	$\bar{1}$·2490		

Table XV. Viscosities in Various Solvents of Cellulose Acetates of Different Acetic Acid Yields at 20 °C.

Acetone			Pyridine			Chloroform			Methylene chloride (70 parts), ethyl alcohol (30 parts), by volume		
Acetic acid yield per cent.	Concentration, grams/litre	η_r	Acetic acid yield per cent.	Concentration, grams/litre	η_r	Acetic acid yield per cent.	Concentration, grams/litre	η_r	Acetic acid yield per cent.	Concentration, grams/litre	η_r
54·1	4·040	1·837	46·0	3·631	1·654	57·0	8·470	2·539	53·8	4·385	1·837
,,	7·932	3·207	,,	4·285	1·793	,,	11·44	3·621	,,	5·277	2·092
,,	11·51	5·124	,,	4·877	1·926	,,	16·15	5·888	,,	8·061	2·915
—	—	—	,,	5·832	2·126	,,	18·77	7·816	,,	10·49	3·931
—	—	—	,,	6·670	2·395	—	—	—	—	—	—
57·0	5·095	2·138	47·0	3·469	1·572	57·3	4·201	1·584	54·1	3·980	1·801
,,	10·535	4·410	,,	3·708	1·635	,,	8·188	2·391	,,	7·754	2·929
,,	13·68	6·419	,,	4·955	1·900	,,	10·88	3·078	,,	11·39	4·403
—	—	—	,,	6·763	2·345	,,	15·11	4·745	—	—	—
—	—	—	—	—	—	,,	18·27	6·259	—	—	—
57·3	4·254	1·877	52·3	3·800	1·671	58·3	8·061	2·390	57·5	4·246	1·726
,,	7·231	2·773	,,	5·608	2·101	,,	9·232	2·713	,,	7·800	2·614
,,	9·018	3·468	,,	7·745	2·706	,,	11·09	3·452	,,	11·67	4·003
,,	11·80	4·906	—	—	—	,,	12·17	3·724	—	—	—
—	—	—	—	—	—	,,	14·84	5·032	—	—	—
57·5	4·977	2·042	53·8	3·216	1·545	58·6	5·023	1·702	59·4	4·239	1·611
,,	5·362	2·158	,,	5·077	1·973	,,	10·32	2·845	,,	8·054	2·336
,,	6·863	2·596	,,	5·754	2·101	59·4	3·424	1·402	,,	11·92	3·362
,,	8·100	3·042	,,	7·463	2·606	,,	7·700	2·017	—	—	—
,,	11·15	4·528	—	—	—	,,	14·88	3·576	—	—	—
58·3	3·816	1·764	57·5	3·854	1·643	60·8	8·054	1·970	60·8	4·101	1·563
,,	6·092	2·355	,,	4·740	1·804	,,	22·29	5·285	,,	6·378	1·948
,,	10·51	4·034	,,	6·016	2·076	,,	23·23	5·740	,,	7·814	2·215
—	—	—	,,	7·663	2·524	—	—	—	,,	11·68	3·115
58·6	5·635	2·239	58·3	3·524	1·557	62·5	7·139	1·856	—	—	—
,,	6·387	2·479	,,	5·077	1·879	,,	9·262	2·191	—	—	—
,,	15·025	6·889	,,	7·132	1·367	,,	11·05	2·519	—	—	—
,,	—	—	—	—	—	,,	14·55	3·276	—	—	—

(e) The Effect of Acetic Acid Yield

The results given in the previous section have already shown that Seraceta and the triacetate obtained from it by non-degradative acetylation have quite different intrinsic viscosities even when these are determined in the same solvent. The only difference between the two materials after they have been dissolved in the solvent is that of acetic acid yield, and it was therefore considered desirable to investigate the effect of this variable in greater detail. Samples with acetic acid yield varying from 46 to 62·5 were therefore prepared from Seraceta by the methods of non-degradative acetylation and de-acetylation previously described, and their viscosities in several solvents were determined. These viscosities are given in Table XV, and intrinsic viscosities determined by the methods previously used are given in Table XVI. Owing to the wide range of their acetic acid yields, the samples exhibited considerable differences in solubility and it was impossible to determine the viscosities of all the samples in one solvent, but the different series overlap sufficiently to show that the intrinsic viscosity decreases as the acetic acid yield increases. This trend is most pronounced when the solvent is a mixture of methylene chloride and ethyl alcohol, and relatively small when acetone is used.

Table XVI

Intrinsic Viscosities of Cellulose Acetates of Different Acetic Acid Yields, at 20°C.

$(a) = 8\mathrm{d}\eta_r{}^{\frac{1}{2}}/\mathrm{d}c$; $(b) = \text{antilog}\ \{\underset{c\to 0}{\text{Lim}} \log(\eta_{sp}/c)\}$

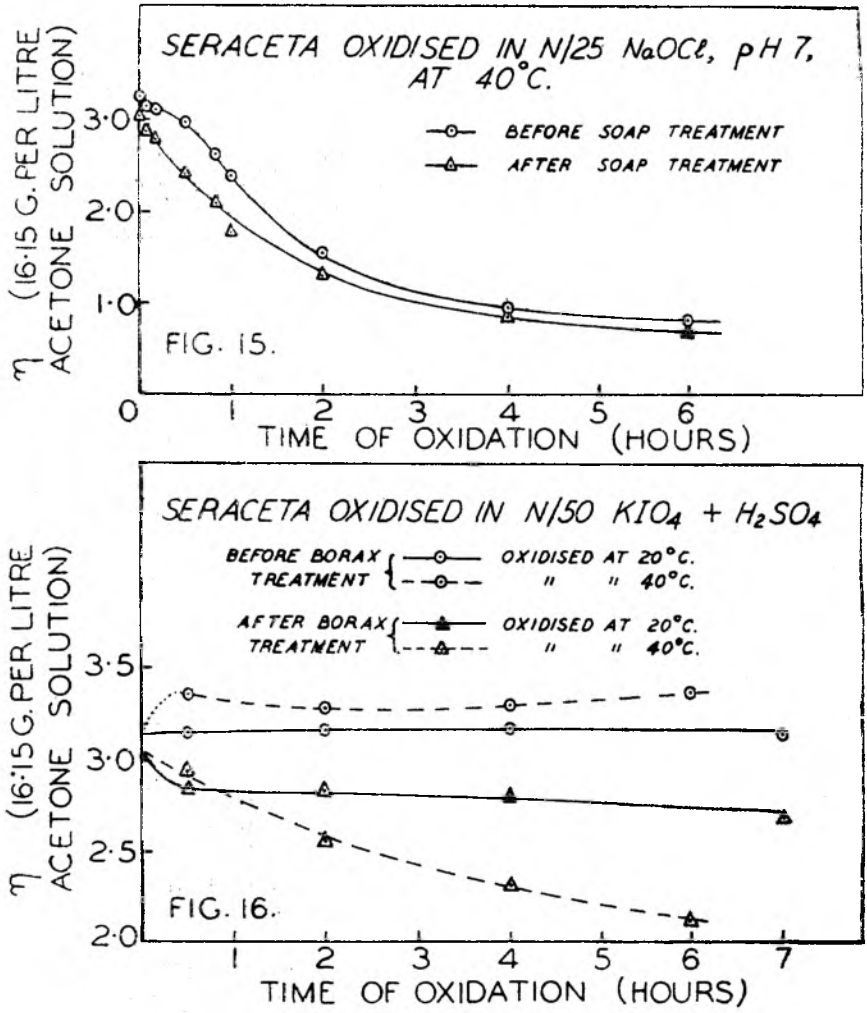
Solvent	Acetone		Pyridine		Chloroform		Methylene chloride 70 parts, ethyl alcohol 30 parts by volume	
Acetic acid yield, per cent.	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
46·0	—	—	·140	·155	—	—	—	—
47·0	—	—	·135	·138	—	—	—	—
52·3	·159	·157	·138	·143	—	—	—	—
53·8	·164	·163	·138	·147	—	—	·144	·150
54·1	·157	·155	—	—	—	—	·148	·163
57·0	·155	·159	—	—	·122	·107	—	—
57·3	·151	·157	—	—	·113	·111	—	—
57·5	·149	·152	·129	·139	—	—	·131	·135
58·3	·149	·161	·129	·131	·118	·102	—	—
58·6	·149	·156	—	—	·109	·111	—	—
59·4	—	—	—	—	·104	·104	·112	·120
60·8	—	—	—	—	·086	·090	·108	·119
62·5	—	—	—	—	·089	·092	·110	·113

(f) The Effect of Oxidation

In Table VIII are given the intrinsic viscosities of a sample of oxidised Seraceta and fractions prepared from it, and the effect of the oxidation may be assessed by comparing the figures there given with those for unoxidised Seraceta presented in Table VI. It will be seen that the main effect is a large decrease of the intrinsic viscosity of the unfractionated material (from 0·164 to 0·106), an even larger decrease of the intrinsic viscosity of the highest fraction (from 0·258 to 0·168), and scarcely any alteration of the value for the lowest fraction (0·047 to 0·044).

The oxidised sample referred to above had been prepared by treating Seraceta for two hours at 40°C. in N/25 sodium hypochlorite solution buffered at *p*H7, treatment at *p*H7 being necessary to prevent hydrolysis and to secure a fair degree of oxidation in a reasonable time because cellulose acetate is highly resistant to oxidation. It has been shown,[47] however,

that the oxidation of cellulose in non-alkaline media causes some of the bonds adjacent to the points of attack to be so alkali-sensitive that they are broken, with consequent shortening of the molecular chains, on treatment with very dilute alkali. This behaviour has been ascribed[48] to oxidation occurring at two adjacent hydroxyl groups, and it was obviously of interest to enquire if cellulose acetate rayon behaved similarly, since with most of the hydroxyl groups esterified it seemed unlikely that the distribution of those remaining would permit the frequent occurrence of two such groups



Figs. 15 and 16

on adjacent carbon atoms of the chain-molecules. A difficulty arises here in that the dilute alkaline solutions ordinarily used to demonstrate the existence of these alkali-sensitive bonds rapidly de-acetylate acetate rayon. In the first experiments made in this connection the samples were boiled in 0·7 per cent. soap solution for 1½ hours, but almost immediately a treatment for 1½ hours in M/20 borax at 97°C. was substituted, and has been used since. Even this treatment is by no means ideal, for it probably does cause a small amount of superficial de-acetylation, but it is good enough for the immediate purpose.

Fig. 15 shows the viscosities in acetone solution at 20°C. of samples of Seraceta oxidised in N/25 sodium hypochlorite, *p*H7, at 40°C. for times up to six hours, before and after the soap treatment described. There is a definite reduction of viscosity following the soap treatment, and to enhance this potassium periodate in sulphuric acid was tried as the oxidising agent, Davidson[49] having shown that on cellulose this reagent is considerably more effective than neutral hypochlorite in producing the type of oxidation under consideration. The continuous curves of Fig. 16 show the effect of oxidation at 20°C. in N/50 potassium periodate acidified with sulphuric acid; the viscosity before the borax treatment is practically unchanged by the oxidation, whilst that after the treatment shows a steady though small fall. The experiment was repeated with the temperature of oxidation increased to 40°C., and the discontinuous curves of Fig. 16 show the results obtained. The fall of viscosity following the borax treatment is much more pronounced, but the viscosities of the oxidised samples before the treatment are *greater* than that of the unoxidised material. (These experiments are the first in which a rise of viscosity following oxidation was noticed). A still more

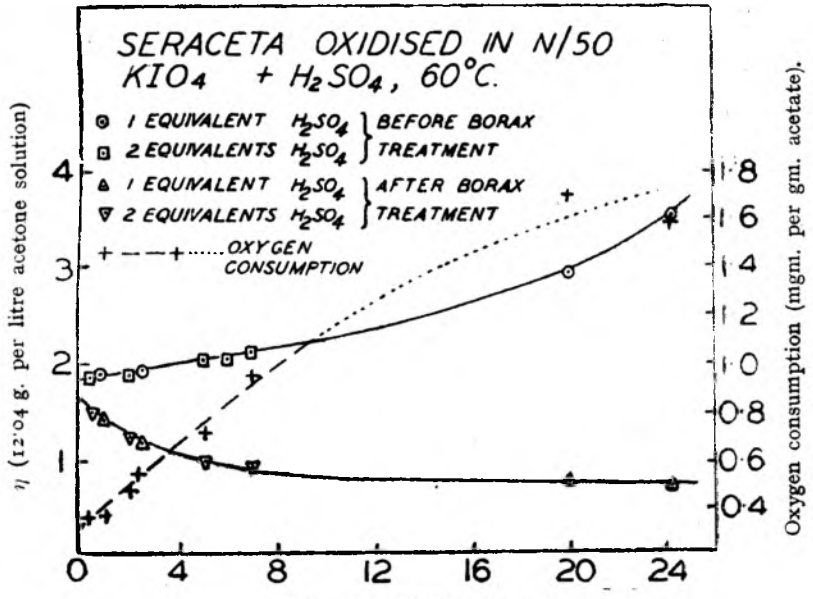


Fig. 17

vigorous oxidation was next tried, the temperature being increased to 60°C., and the time to 24 hours, with the results shown in Fig. 17. The rise of viscosity is here very pronounced, the viscosity of the sample oxidised for 24 hours being nearly double that of the original material, though after the borax treatment the same sample has a viscosity only half that of unoxidised Seraceta. (It is of course possible that the specific character of the oxidation is not retained at the rather high temperatures employed here).

In the above experiments no evidence was obtained that periodate oxidation might cease after a certain point, as might have been expected if the occurrence of two hydroxyl groups on adjacent carbon atoms of the chain was infrequent. (It had already been found that these solutions had no appreciable oxidising action on cellulose triacetate, so that possible oxidation of the acetyl groups could be neglected). It was at first considered that the failure to reach an end-point might be due to a general slowing

down of the reaction caused by at least some of the chains being accessible to the reagent only with difficulty, and attempts were made to oxidise the material while it was in a highly swollen condition. Since the swelling of cellulose acetate is to a large extent reversible this meant oxidising in the presence of a swelling agent, and the attempts were unsuccessful because no swelling agent that was itself unaffected by periodic acid was found. To overcome this difficulty attempts were made to oxidise Seraceta dissolved in aqueous pyridine by N/12 periodic acid at 25°C. and N/50 periodic acid

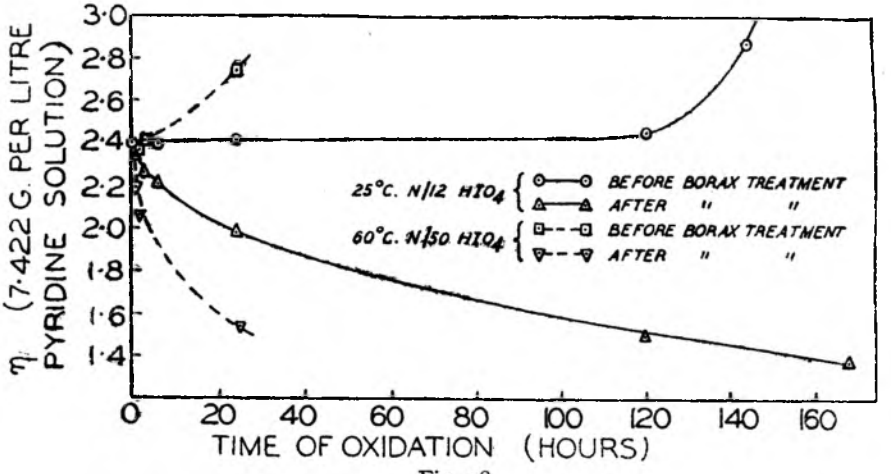
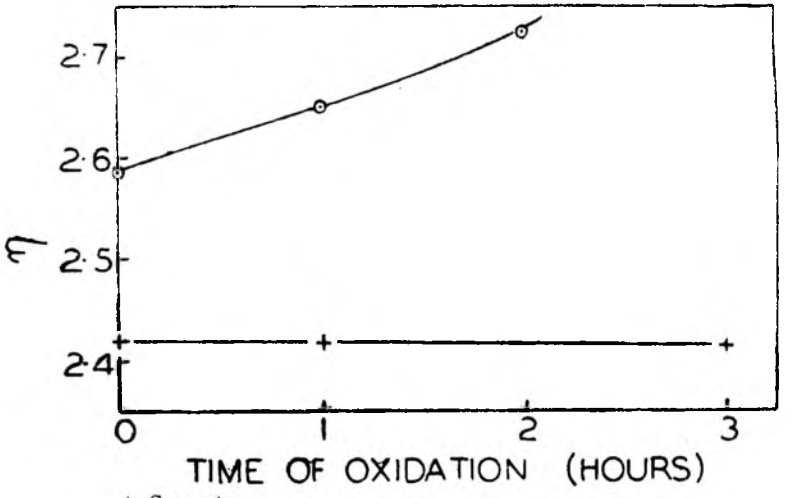


Fig. 18



(Viscosity measured on pyridine solutions, 7·422 gm. per litre.)

Fig. 19

at 60°C., but the substance had no oxidising action in these solutions. Comparable experiments with periodic acid in aqueous solution were run at the same time to obtain data for the corresponding heterogeneous oxidation. The results of these are shown in Fig. 18; they are similar to those previously obtained with periodate, showing a rise of viscosity before the alkaline treatment, and a fall of viscosity after it.

Another method was tried to elucidate the effect of the number of hydroxyl groups. A sample of Seraceta was hydrolysed to an acetic acid yield of 46 per cent. by the method of homogeneous non-degradative

de-acetylation previously referred to; the hydrolysed material, like the original, was soluble in pyridine. Both were oxidised in N/50 aqueous periodic acid at 60°C. for periods up to 24 hours. Of the oxidised samples only those treated for periods not greater than 2 hours were soluble in pyridine, and none of the borax-treated samples would dissolve. The results of viscosity determinations on those samples that would dissolve are given in Fig. 19. Though severely limited in scope, they show that the increase of viscosity is much more pronounced for the hydrolysed than for the unhydrolysed material.

The frequency of occurrence of two adjacent hydroxyl groups can be calculated on the assumption that these groups are randomly distributed among the possible points of attachment. There are three such points per glucose unit, but only when one of the three possible pairs of points are occupied will the hydroxyl groups be on neighbouring atoms of the chain. The probability of finding two hydroxyl groups in juxtaposition is therefore essentially the probability of filling a *specified* two out of three positions. If the number of hydroxyl groups available per glucose unit is n then this probability is $(n/3)^2$. The number n is related to the acetic acid yield A per cent. by the relation

$$n = \frac{3000 - 48A}{1000 - 7A}$$

and for a secondary acetate of acetic acid yield 53·8, n has the value 0·67. The probability of the occurrence of hydroxyl on two neighbouring atoms of the molecular chain is therefore $(0{\cdot}67/3)^2$, or 0·05. This corresponds to a frequency of occurrence of about once in every twenty glucose units. This is a good deal more frequent than had been thought likely at first, and no other explanation is needed to account for the failure to reach an "end-point" in the oxidation process, the mean chain length of the most highly oxidised sample being of the order of at least 100 glucose units after treatment with borax solution.

The increases of viscosity caused by oxidation are most probably due to association through the —CHO groups formed during the oxidation. At any rate association through —COOH groups seems unlikely, for the increase of viscosity was also found in dioxane solution, and there is some evidence[50] that bonds between —COOH groups are broken down in the presence of dioxane. It is clear that in using viscosity data to determine the molecular weight of oxidised samples, the possibility that association may occur must not be neglected, otherwise entirely erroneous results might be obtained.

IV. THE EVALUATION OF THE INTRINSIC VISCOSITY AND THE DETERMINATION OF CHAIN LENGTH

The previous sections have shown the effects of some of the factors that influence the viscosity of solutions of cellulose acetates. These effects have been summarised by the evaluation of the intrinsic viscosity, two methods having been used to determine this quantity. Although these methods were based on the linear relationships between $\eta_r^{\frac{1}{3}}$ and c on the one hand and log η_{sp}/c and c on the other, the graphs themselves were not used to determine $[\eta]$, algebraic methods being preferred in order to eliminate personal bias in the placing of the lines. There are two obvious methods of determining $[\eta] = 8\mathrm{d}\,\eta_r^{\frac{1}{3}}/\mathrm{d}c$ apart from orientating the best straight line among the points by eye. The first is to determine the mean values of $\eta_r^{\frac{1}{3}}$ and c as $\overline{\eta_r^{\frac{1}{3}}}$ and $\bar{c}$, and to set $(\overline{\eta_r^{\frac{1}{3}}} - 1)/\bar{c} = \mathrm{d}\,\eta_r^{\frac{1}{3}}/\mathrm{d}c$; the second is to evaluate $(\eta_r^{\frac{1}{3}} - 1)/c$ for each of the experimental points, and to take the mean value of this function as $\mathrm{d}\eta_r^{\frac{1}{3}}/\mathrm{d}c$. In general the experimental points are so close to the best straight line among them that it makes very little difference which method is adopted, but the latter has been preferred since the former tends to give greater weight to the observations at higher

concentrations, where the linearity of the relationship is more in doubt. The principle adopted in determining $\lim_{c \to 0} \log (\eta_{sp}/c)$ was to use the method of zero sum to substitute two points for the experimental points however many in number, and to determine algebraically the intercept on the axis of zero concentration of the straight line through these points. Actually, it is of course unnecessary to determine the coordinates of the substitute points, the following formulae being applicable according to the number of experimental points available ($\bar{y}$ denotes $\lim_{c \to 0} \log (\eta_{sp}/c)$ and $y_1, y_2 \ldots y_n$ the experimental values of $\log \eta_{sp}/c$ at concentrations $c_1, c_2, \ldots c_n$).

(*a*) Two experimental points

$$\bar{y} = \frac{c_2 y_1 - c_1 y_2}{c_2 - c_1}$$

(*b*) Three experimental points

$$\bar{y} = \tfrac{1}{3}\left[\frac{2c_3 + c_2}{c_3 - c_1} y_1 + y_2 - \frac{2c_1 + c_2}{c_3 - c_1} y_3\right]$$

(*c*) Four experimental points

$$\bar{y} = \tfrac{1}{2}\left[\frac{(c_3+c_4)(y_1+y_2) - (c_1+c_2)(y_3+y_4)}{(c_3+c_4) - (c_1+c_2)}\right]$$

(*d*) Five experimental points

$$\bar{y} = \tfrac{1}{5}\left[\frac{c_3+2c_4+2c_5}{(c_4+c_5)-(c_1+c_2)}(y_1+y_2) + y_3 - \frac{2c_1+2c_2+c_3}{(c_4+c_5)-(c_1+c_2)}(y_4+y_5)\right]$$

The values of $[\eta]$ given in previous tables were obtained by these methods except (*a*) where it has been indicated that the lines are curved, and (*b*) in three instances where an experimental point was so far from the straight line defined by the other observations as to be obviously erroneous.

As indicated in the Introduction, there is a large amount of evidence that the intrinsic viscosity $[\eta]$ is linearly related to the molecular weight and hence the molecular chain length of the dissolved substance. In this work it is more convenient to use the chain length expressed in glucose units, because this eliminates the effect of variations in the acetic acid yield of the materials used, which of course cause alteration of molecular weight even when the chain length remains constant. The Staudinger equation is therefore used in the form

$$[\eta] = K_m l$$

where $[\eta]$ is the intrinsic viscosity, l is the chain length in glucose units, and K_m is the factor relating the one to the other. Whilst there is little doubt about the correctness of this equation (the possibility that a constant term[43] has been omitted need not be considered since there is no means of testing it so far as these data are concerned), there is quite a large amount of doubt about the correct numerical value of K_m for any given material under specified conditions. For this reason, and since none of the materials examined in this work has as yet had its chain length determined by a method to which no exception can be taken, the authors have preferred to choose from the various values given in the literature one that they considered reasonably probable, to use that value to determine the chain length of the material, and from that chain length to calculate other values of K_m corresponding to the other conditions under which the same material, or other material of identical chain length, was examined. These values of K_m were then used to determine the chain lengths of other materials of different chain length and since these were usually also examined under several conditions a fair amount of cross-checking could be done. In this way a system of self-consistent values is obtained which may, however, be in error in an absolute sense; it is hoped that work in progress will eventually lead to a rigorous check of the values now suggested.

Examination of the results obtained reduced the number of possible reference points for this scheme to two, involving the use of the intrinsic viscosity of either (*a*) cellulose triacetate in chloroform or (*b*) secondary cellulose acetate in acetone. The former has the advantage that the substance used is of more definite composition, so that differences due to variations of acetic acid yield could not introduce error. On the other hand, its use would involve the acceptance of the value of K_m proposed by Staudinger[23, 24] for this system ($5{\cdot}3 \times 10^{-4}$) which is based on molecular weights determined osmotically. This would give a number-average molecular weight for the heterogeneous material examined, which would not be comparable with the weight-average molecular weight that is related to the viscosity, and hence would be unsuitable for comparing the chain length of a material with those of fractions prepared from it. (The weight-average molecular weight could, however, be calculated from the number-average if the distribution of chain lengths about the mean were known.) Secondary cellulose acetate is admittedly a less definite material, but its solutions in acetone have been given more detailed study than any of the other systems so that its intrinsic viscosity is known with greater accuracy, and it has the advantage that a value of K_m can be obtained on the basis of molecular weights determined by means of the ultracentrifuge. This second system has therefore been chosen, and a value of K_m of $4{\cdot}3 \times 10^{-4}$ has been calculated from Kraemer's[42] work on cellulose acetates of chain lengths varying between 190 and 950. (This value is less than half that obtained for this system by using as reference point Staudinger's value of $5{\cdot}3 \times 10^{-4}$ for cellulose triacetate in chloroform, and consequently the chain lengths here calculated are rather more than twice those obtained by using the Staudinger figure. This difference emphasizes the necessity of regarding the calculated chain lengths as relative only until the values for some of the materials can be determined by a more rigorous method.) By applying the value $4{\cdot}3 \times 10^{-4}$ to the intrinsic viscosities 0·1640 and 0·1626 calculated from $\eta_{ir}^{\frac{1}{2}}$ and log (η_{sp}/c), respectively, the corresponding values of the chain length of Seraceta were found (from the formula $l=[\eta]/K_m$) to be 381 and 378. These chain lengths were then used to determine the values of K_m for Seraceta in other solvents, with the results given in Table XVII. (In this and subsequent Tables the values of K_m are given to two places of decimals in order to indicate any general trends; there is of course no implication that they can be used to determine chain lengths to a comparable degree of accuracy).

Table XVII

Values of K_m for Seraceta in Various Solvents

(*a*) Calculated from $[\eta] = 8\mathrm{d}\,\eta_{ir}^{\frac{1}{2}}/\mathrm{d}c$; (*b*) Calculated from $[\eta] = \text{antilog}\,\{\underset{c\to 0}{\text{Lim}}\,\log(\eta_{sp}/c)\}$

(All K_m values have been multiplied by 10^4)

Solvent	(*a*)	(*b*)
Acetone 100 Water 0	4·3	4·3
,, 97·5 ,, 2·5	4·05	4·01
,, 95·0 ,, 5·0	4·08	4·34
,, 90·0 ,, 10·0	4·01	4·22
,, 85·0 ,, 15·0	4·03	4·34
,, 80·0 ,, 20·0	4·00	4·27
Methylene chloride 65, Ethyl alcohol 35	3·74	3·95
,, ,, 70, ,, ,, 30	3·78	3·97
,, ,, 75, ,, ,, 25	3·72	3·92
Dioxane	4·53	5·01
Pyridine	3·65	3·87
m-Cresol	4·34	4·56

Table XVIII

Values of K_m in Various Solvents, for Samples of Different Acetic Acid Yields Derived from Seraceta

(*a*) Calculated from $[\eta] = 8\mathrm{d}\eta_r^{\frac{1}{2}}/\mathrm{d}c$, assuming $l = 381$.

(*b*) Calculated from $[\eta] = \text{antilog}\left\{\underset{c\to 0}{\text{Lim}} \log(\eta_{sp}/c)\right\}$, assuming $l = 378$.

(All K_m values have been multiplied by 10^4)

Acetic acid yield, per cent.	Acetone		Pyridine		Chloroform		Methylene chloride 65 parts, Ethyl alcohol 35 parts, by volume		Methylene chloride 70 parts, Ethyl alcohol 30 parts, by volume		Methylene chloride 75 parts, Ethyl alcohol 25 parts, by volume		*m*-Cresol	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
46·0	—	—	3·66	4·07	—	—	—	—	—	—	—	—	—	—
47·0	—	—	3·53	3·66	—	—	—	—	—	—	—	—	—	—
52·3	4·17	4·14	3·63	3·78	—	—	—	—	—	—	—	—	—	—
53·8	4·3	4·3	3·62	3·90	—	—	3·74	3·95	3·77	3·97	3·72	3·92	4·34	4·56
54·1	4·13	4·09	—	—	—	—	—	—	3·88	4·32	—	—	—	—
57·0	4·06	4·22	—	—	3·17	2·83	—	—	—	—	—	—	—	—
57·3	3·95	4·15	—	—	2·95	2·94	—	—	—	—	—	—	—	—
57·5	3·91	4·03	3·39	3·67	—	—	—	—	3·44	3·57	—	—	—	—
58·3	3·91	4·27	3·37	3·47	3·09	2·70	—	—	—	—	—	—	—	—
58·6	3·90	4·12	—	—	2·85	2·93	—	—	—	—	—	—	—	—
59·4	—	—	—	—	2·73	2·74	—	—	2·94	3·18	—	—	—	—
60·8	—	—	—	—	2·26	2·39	—	—	2·82	3·14	—	—	—	—
62·5	—	—	—	—	2·33	2·43	2·87	3·12	2·87	2·99	2·89	2·93	3·00	3·32

Similarly, K_m values can be calculated for cellulose triacetate and other acetates of different acetic acid yield, it having been shown that the acetylation and de-acetylation processes used in preparing these materials from Seraceta have not caused any change of chain length; these values are given in Table XVIII.

All viscosity measurements subsequent to those in the initial general survey were made at 20°C., and consequently the K_m values corresponding to other temperatures are of no direct interest so far as the ultimate purpose of this work is concerned. However, a useful test of the self-consistency of the results can be made by determining the K_m values for samples of Seraceta at 20, 25, 30 and 35°C., and using these values to determine the chain lengths of the Seraceta fractions, of the sample of oxidised Seraceta, and of its fractions; the chain lengths so determined should of course be independent of temperature. The K_m values referred to are given in Table XIX and the calculated chain lengths obtained by using them in Table XX. The chain lengths are in fact constant within the limits of error of chain length determination, though it is apparent that the degree of constancy is appreciably greater when they are calculated from $[\eta]$ determined on the basis of the $\eta_r^{\frac{1}{2}}$ plot than when log (η_{sp}/c) is used.

Table XIX

Values of K_m for Seraceta at 20, 25, 30 and 35°C.

(All K_m values have been multiplied by 10^4).

Temperature, °C.	20	25	30	35
K_m determined from $[\eta]=8d\eta_r^{\frac{1}{2}}/dc$, assuming $l=381$	4·30	4·14	3·99	3·83
K_m determined from $[\eta]=$antilog $\{\text{Lim}_{c\to 0} \log (\eta_{sp}/c)\}$, assuming $l=378$...	4·28	4·12	3·94	3·74

Table XX

Chain Lengths of Seraceta, Oxidised Seraceta, and their Fractions, calculated from Viscosity Determinations at 20, 25, 30 and 35°C.

Sample		Chain length determined from $[\eta]=8d\eta_r^{\frac{1}{2}}/dc$ at:				Chain length determined from $[\eta]=$antilog $\{\text{Lim}_{c\to 0} \log (\eta_{sp}/c)\}$ at:			
		20°C.	25°C.	30°C.	35°C.	20°C.	25°C.	30°C.	35°C.
Seraceta fractions ...	1	110	111	112	114	108	111	113	115
	2	219	219	220	222	230	228	231	225
	3	298	300	300	300	317	317	318	317
	4	362	362	363	364	395	389	392	393
	5	409	410	409	410	439	436	435	435
	6	601	599	597	597	595	583	577	576
Oxidised Seraceta		247	246	246	245	231	230	231	233
Oxidised Seraceta fractions	1	102	103	104	107	102	104	108	112
	2	190	193	197	194	186	193	199	197
	3	238	240	240	241	231	237	240	243
	4	302	307	308	306	298	301	304	319
	5	349	353	353	354	339	344	338	354
	6	392	390	385	385	330	331	330	336

The sum of the squares of the deviations from the group means is 33 for the chain lengths of Seraceta derived from $\eta_r^{\frac{1}{2}}$ and 329 for the chain lengths derived from log (η_{sp}/c); similarly for the sample of oxidised Seraceta and its fractions the corresponding values are 119 and 688.

Another check can be made by calculating the chain lengths of the viscose triacetate for which the intrinsic viscosities in chloroform and *m*-cresol are given in Table XII. The calculations have been made with

the aid of the appropriate K_m values taken from Table XVIII, and the results are given in Table XXI. All the values are reasonably consistent, but the difference between the two values obtained from log (η_{sp}/c) is appreciably greater than that between the values obtained from $\eta_r^{\frac{1}{8}}$.

Table XXI
Chain Length of Acetylated Viscose

Solvent	$[\eta] = 8d\,\eta_r^{\frac{1}{8}}/dc$	$K_m \times 10^4$	Chain length	$[\eta] = \text{Antilog}\left\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\right\}$	$K_m \times 10^4$	Chain length
m-Cresol ...	·148	3·00	493	·161	3·32	485
Chloroform ...	·118	2·33	506	·127	2·43	523

Sufficient evidence has now been obtained to justify a decision on the preferred method of calculating the intrinsic viscosity $[\eta]$, from the experimental viscosity data; this evidence may be summarized as follows:—

(1) The plot of $\eta_r^{\frac{1}{8}}$ against c is usually linear down to the lowest concentrations examined; the plot of log (η_{sp}/c) against c *may* be non-linear at low concentrations, all the experimental points at such concentrations being on one side of the straight line defined by the data at higher concentrations. On the other hand the $\eta_r^{\frac{1}{8}}$ plot is occasionally curved (e.g., Fig. 9) at the concentrations normally used, where the log (η_{sp}/c) plot is completely linear.

(2) Although the plot of $\eta_r^{\frac{1}{8}}$ against c for fraction 6 of the sample of oxidised Seraceta is non-linear (Fig. 9), its use provides a more reasonable value of the intrinsic viscosity than the straight line of the log (η_{sp}/c) plot, which indicates that the intrinsic viscosity of fraction 6 is less than that of fraction 5 (Table VIII).

(3) The difference between the values of the intrinsic viscosity of Seraceta determined (*a*) from viscosity measurements on the material itself, and (*b*) by calculation from the intrinsic viscosities of its fractions is appreciably less when $[\eta]$ is determined from log (η_{sp}/c) than when $\eta_r^{\frac{1}{8}}$ is used. On the other hand for the sample of oxidised Seraceta the use of $\eta_r^{\frac{1}{8}}$ gives values at least as concordant as does the use of log (η_{sp}/c).

(4) The data of Table XIII show that the intrinsic viscosity of Seraceta in mixtures of acetone and water does not vary with variations of water content between 2·5 and 20 per cent., but the random variation is greater when $[\eta]$ is determined from log (η_{sp}/c) than when $\eta_r^{\frac{1}{8}}$ is used.

(5) The irregularity in the chain lengths recorded in Table XX is considerably greater when they are calculated from antilog $\left\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\right\}$ than when they are calculated from $8d\,\eta_r^{\frac{1}{8}}/dc$.

(6) The difference between the two determinations of the chain length of the acetylated viscose (Table XXI) is smaller if $8d\,\eta_r^{\frac{1}{8}}/dc$ is used in preference to antilog $\left\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\right\}$.

The balance of the above evidence is unquestionably in favour of the determination of $[\eta]$ as $8d\eta_r^{\frac{1}{8}}/dc$ rather than antilog $\left\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\right\}$ and an *a priori* examination of the methods themselves, altogether apart from the results they provide, leads to the same conclusion. The determination of $[\eta]$ as antilog $\left\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\right\}$ is essentially an extrapolation, and the value of $[\eta]$ obtained is very sensitive to the way the line is orientated among the experimental points. On the other hand the determination of $[\eta]$ as $8d\,\eta_r^{\frac{1}{8}}/dc$ is an interpolation, so that the possible variation in $[\eta]$ determined from a given set of data is strictly limited. Moreover, the use of the latter method provides an additional point on the graph ($c=0$, $\eta_r^{\frac{1}{8}}=1$), positioned with absolute accuracy.

This method will therefore be used in later papers of this series for determining the intrinsic viscosity $[\eta]$ and hence the chain length. Values

of K_m appropriate to this method of calculation are given in Table XXII for the various materials and solvents used. These have been rounded off for actual use in calculating chain lengths.

Table XXII
Values of K_m for Cellulose Acetates in Various Solvents at 20° C.
(All K_m values have been multiplied by 10^4)

Acetic acid yield, per cent.	Acetone	Acetone-water (2·5-20% water)	Pyridine	Methylene chloride/Ethyl alcohol			Dioxane	*m*-Cresol	Chloroform
				65/35	70/30	75/25			
46·0	—	—	3·6	—	—	—	—	—	—
47·0	—	—	3·6	—	—	—	—	—	—
52·3	4·3	—	3·6	—	—	—	—	—	—
53·8	4·3	4·0	3·6	3·7	3·7	3·7	4·5	4·3	—
54·1	4·1	—	—	—	3·7	—	—	—	—
57·0	4·1	—	—	—	—	—	—	—	3·1
57·3	4·0	—	—	—	—	—	—	—	3·1
57·5	3·9	—	3·4	—	3·4	—	—	—	—
58·3	3·9	—	3·4	—	—	—	—	—	3·1
58·6	3·9	—	—	—	—	—	—	—	2·8
59·4	—	—	—	—	2·9	—	—	—	2·7
60·8	—	—	—	—	2·9	—	—	—	2·3
62·5	—	—	—	2·9	2·9	2·9	—	3·0	2·3

The self-consistency of these values is to some extent indicated by the data for chain lengths given in Table XXIII for various cellulosic materials. This Table shows the chain lengths of a series of cellulose acetates determined from (*a*) the viscosities of solutions of the acetates in acetone and (*b*) the viscosities of solutions in chloroform of triacetates prepared from these acetates by non-degradative acetylation (with the exception of one sample, which, with an acetic yield of 56·2 per cent., was soluble in both acetone and chloroform). The K_m values for acetone and chloroform are those given in Table XXII; these of course correspond to a chain length of 381 for Seraceta. The chain lengths derived from measurements of viscosities in the different solvents are reasonably concordant, the greatest discrepancy being about 5 per cent. They therefore encourage the hope that the methods adopted and the K_m values derived may be used to determine with some accuracy the relative chain lengths of different cellulosic materials and of fractions prepared from them, whatever correction may have to be applied later to obtain results of greater absolute accuracy.

Table XXIII
Chain Lengths of Cellulose Acetates

Solvent:—	Acetone				Chloroform			
Sample	$[\eta]$	Acetic acid yield per cent.	K_m	Chain length	$[\eta]$	Acetic acid yield per cent.	K_m	Chain length
Seraceta	·1640	53·8	4·3	381	·0888	62·5	2·3	381
Celanese	·178	52·6	4·3	415	·092	62·5	2·3	396
Lansil	·156	52·7	4·3	364	·083	62·5	2·3	356
Rhodiaceta	·168	53·4	4·3	391	·091	61·7	2·3	391
Hercules, Acetate ...	·166	53·0	4·3	385	—	—	—	—
Hercules PM3, Acetate	·151	51·3	4·3	351	—	—	—	—
Hercules, High-acetyl acetate	·169	56·2	4·1	412	·132	56·2	3·2	412
Eastman, Acetate ...	·154	51·2	4·3	359	—	—	—	—

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APPENDIX*

ON THE RELATION BETWEEN THE $\eta_r^{\frac{1}{3}}$ AND LOG (η_{sp}/c) PLOTS

(i) Determination of $[\eta]$ from the $\eta_r^{\frac{1}{3}}$ Plot.

In this paper two methods have been used for determining $[\eta] = \lim_{c \to 0} \eta_{sp}/c$, one based on the linear relation between $\eta_r^{\frac{1}{3}}$ and c, the other on the linear relation between log (η_{sp}/c) and c. These relations are expressible algebraically as follows :—

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(1) $\eta_r = (1+pc)^8$

(2) $\log_{10}(\eta_{sp}/c) = a'c + b'$

$\log_e(\eta_{sp}/c) = ac + b$, where $a = 2{\cdot}3026\,a'$ and $b = 2{\cdot}3026\,b'$

$\eta_{sp}/c = e^{ac+b}$

and $[\eta] = \lim_{c\to 0} \eta_{sp}/c = e^b$

But $\eta_{sp} = \eta_r - 1$

where $\eta_r = (1+pc)^8$

$\therefore\ \eta_{sp} = (1+pc)^8 - 1$

$\therefore \lim_{c\to 0} \eta_{sp}/c = \lim_{c\to 0} \left(\frac{(1+pc)^8 - 1}{c}\right)$

Putting $c = 0$, this is of the form 0/0. Hence differentiate numerator and denominator and take limits:

$$\frac{d}{dc}\left[(1+pc)^8 - 1\right] = 8p\,(1+pc)^7$$

$$\therefore \lim_{c\to 0} \eta_{sp}/c = \lim_{c\to 0} \frac{8p\,(1+pc)^7}{1} = 8p$$

i.e., $[\eta] = 8p$, where p is the slope of the $\eta_r^{\frac{1}{8}}$ plot.

From these two values of $[\eta]$ it is clear that $e^b = 8p$.

(ii) Correlation of the two Equations.

The equation $\eta_{sp}/c = e^{ac+b}$

can be written in the form $\eta_r = 1 + ce^{ac+b}$,

and since the experimental data are also expressible by the relation

$$\eta_r = (1+pc)^8$$

we have the identity $(1+pc)^8 = 1 + ce^{ac+b}$

i.e., $(1+pc)^8 = 1 + e^b ce^{ac}$

If this equation is an identity the coefficients of c^n on each side of the equation must be equal. But the left-hand side has no terms of power greater than 8 in c, whilst the right-hand side has; the equation cannot therefore be a true identity. If, however, ac is small the terms $\frac{(ac)^9}{\lfloor 9}$ etc., can be neglected, in which case the equation may be regarded as an identity.

In these circumstances we have

$$(1+pc)^8 = 1 + e^b c\left[1 + ac + \frac{(ac)^2}{\lfloor 2} + \frac{(ac)^3}{\lfloor 3} + \frac{(ac)^4}{\lfloor 4} + \ldots + \frac{(ac)^8}{\lfloor 8}\right]$$

Comparing coefficients of c, we have

$8p = e^b$, identical with the result given in (i) above. Substituting in the above equation, we have

$$(1+pc)^8 = 1 + 8pc\left[1 + ac + \frac{(ac)^2}{\lfloor 2} + \frac{(ac)^3}{\lfloor 3} + \ldots + \frac{(ac)^8}{\lfloor 8}\right]$$

Comparing coefficients of c^2, $a = 3{\cdot}50p$

,, ,, c^3, $a = 3{\cdot}74p$

,, ,, c^4, $a = 3{\cdot}74p$

,, ,, c^5, $a = 3{\cdot}60p$

,, ,, c^6, $a = 3{\cdot}55p$

,, ,, c^7, $a = 2{\cdot}99p$

,, ,, c^8, $a = 2{\cdot}51p$

The lack of agreement between the various values of a is of course due to the fact that the equation is not a true identity, but there is reasonable agreement up to coefficients of c^5, the values being

$$a = 3{\cdot}50p,\ 3{\cdot}74p,\ 3{\cdot}74p,\ \text{and}\ 3{\cdot}60p.$$

giving a mean value of $a = 3{\cdot}64p$.

(iii) The Relation of the Constants.

From the exact equation $[\eta] = e^b = 8p$ and the approximate one $a = 3{\cdot}64p$ we have $[\eta] = e^b = 8p = 8a/3{\cdot}64 = 8 \times 2{\cdot}3026a'/3{\cdot}64$, i.e., $[\eta] = 5{\cdot}1\,a'$

It would appear, therefore, that there is a unique relation between the zero intercept (b' = antilog $[\eta]$) and the slope (a') of the log (η_{sp}/c) plot, so that $[\eta]$ should be calculable from either.

The extent to which this deduction is in agreement with observation will be evident from Fig. 20, in which $[\eta]$ = antilog $\{\underset{c\to 0}{\text{Lim}} \log (\eta_{sp}/c)\}$ is plotted against a', the slope of the log (η_{sp}/c) line. The straight line on this diagram is that representing the relation deduced above, $[\eta]=5.1a'$, whilst the points are those for practically all the systems mentioned in the paper. The scatter of the points is fairly large, but this is not surprising in view of the fact that a slight difference in the orientation of the line on the log (η_{sp}/c) plot produces a large change in $[\eta]$. The only set of data that is widely displaced is that for fraction 6 of the oxidised Seraceta, and here agreement is not expected since the data do not yield straight lines when $\eta_r^{\frac{1}{2}}$ is plotted against c. The experimental points refer to many widely different systems—secondary cellulose acetates of several kinds, other acetates of acetic acid yield varying from 46 to 62·5, dissolved in pure and mixed solvents differing widely in constitution, at several temperatures—and the figure may therefore be regarded as confirmation of the deduction that for systems which give linear relations between c and both $\eta_r^{\frac{1}{2}}$ and log (η_{sp}/c) the slope and the zero intercept of the log (η_{sp}/c) plot do not vary independently, but are related by the equation given above.

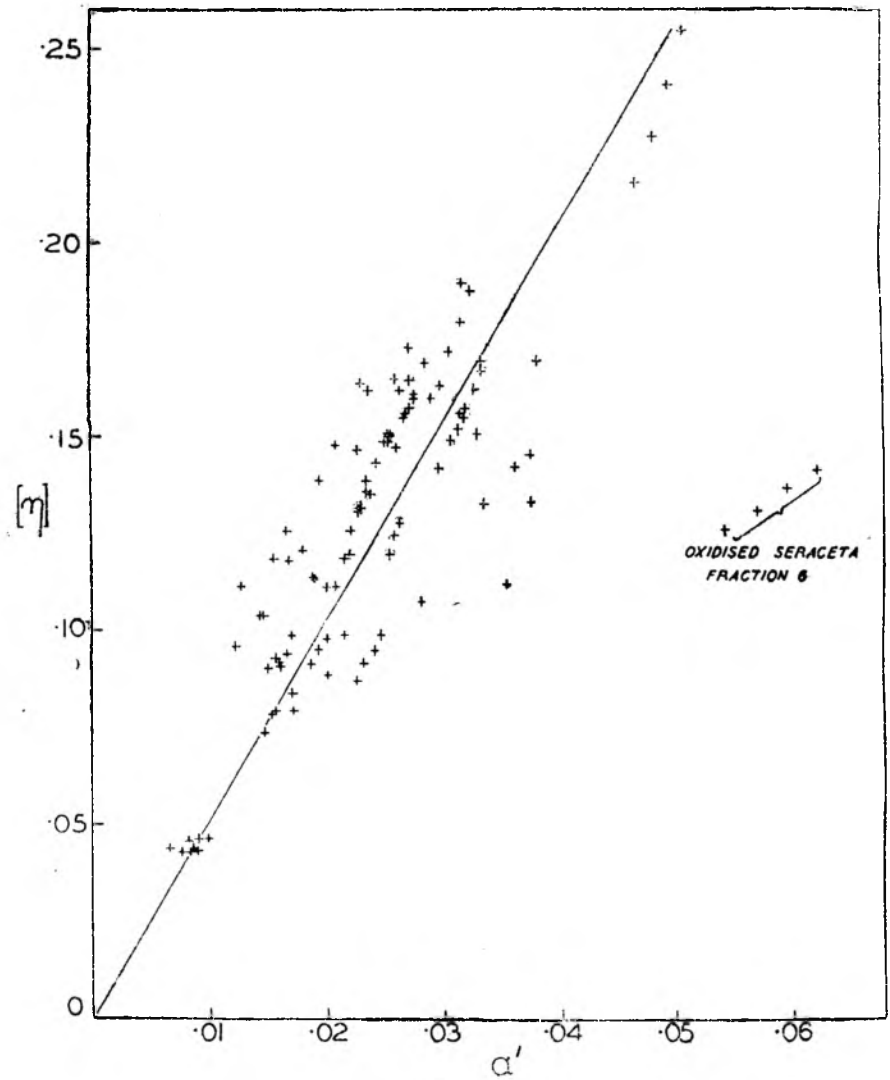

Fig. 20