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Gradient Dependence of Viscosity of Cellulose Tricarbanilate in Tetrahydrofuran

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Summary

The dependence of viscosity of cellulose tricarbanilate in tetrahydrofuran on the velocity gradient $D < 2500\ s^{-1}$ for molecular weights up to 1.2×10^6 was determined, and an empirical equation for the determination of the limiting viscosity number for zero velocity gradient was derived. Errors involved in the viscosity determination from a single concentration using an approximate formula were also ascertained.

Introduction

For a basic investigation of the fractionation of cellulose by its transformation into cellulose tricarbanilate followed by the determination of GPC curve and of viscosities of all GPC fractions (KÖSSLER et al. 1980), an expression had to be found for the calculation of molecular weights from viscometric measurements at a higher velocity gradient.

Experimental

All experiments were carried out with cellulose tricarbanilate (CTC) Rauma RR (sulphite celluloses from conifer wood containing 99% of α-cellulose). Seven fractions of $M_v = 7.3\times10^3$ to 1.2×10^6 obtained by elution fractionation on a column with temperature gradient from an acetone solution were used (cf. DAŇHELKA et al. 1976). The viscosities were measured with viscometers of the Ubbelohde type with five measuring cells (SCHURZ, IMMERGUT 1952) in a modification with U-shaped capillaries; the heights of the centres of measuring cell over the outlet of the capillary were h = 40, 74, 108, 142 and 175 mm. The average velocity gradients for tetrahydrofuran (THF), $D = 580, 1068, 1562, 2046$ and $2524\ s^{-1}$, were determined from the dimensions of the viscometer and flow times t, using the formula $D = 4V/\pi r^3 t$, where V is the volume of the measuring flask and r is the radius of the capillary.

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Results

Using the flow times t of CTC solutions in THF at a concentration 1.89×10^{-3} g/ml and the flow times of THF at 25°C, η_{sp}/c were determined and the respective gradients D were calculated for all the five measuring cells of the viscometer. Simultaneous extrapolation of η_{sp}/c both to zero concentration c=0 and zero gradient D=0 or zero shear S=0 (i.e. h=0) was used according to KRATOCHVÍL, MUNK 1960; SCHURZ 1963 (Fig.1). The small range of the velocity gradient for CTC solutions in THF (D = 236 to 2561 s^{-1}) allowed a linear scale to be used for η_{sp}/c, instead of the more usual logarithmic scale.

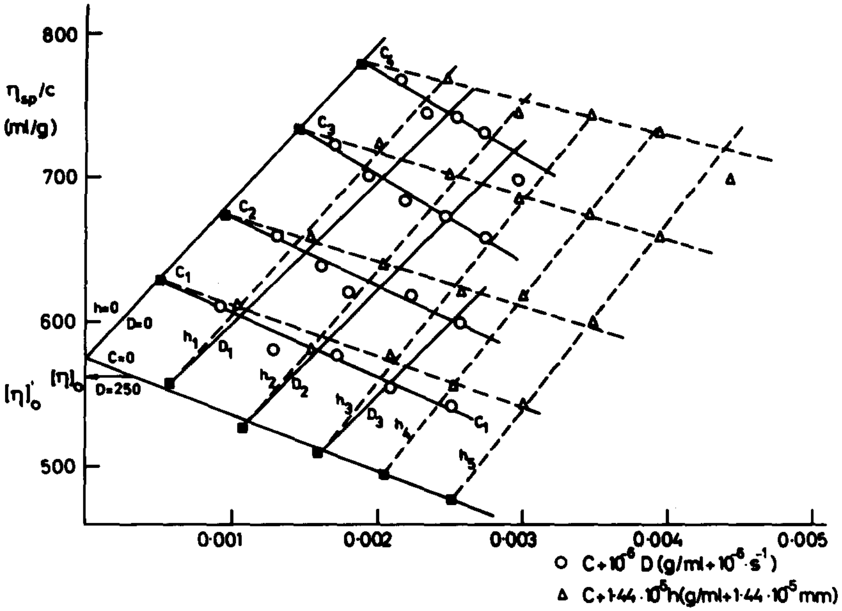

Fig.1 Extrapolation of η_{sp}/c to c=0 and D=0
○ η_{sp}/c for c + 10^{-6}D, △ η_{sp}/c for c + 1.44×10^{-5}h;
■ extrapolated values, concentration in g/ml:
$c_1 = 0.473 \times 10^{-3}$, $c_2 = 0.945 \times 10^{-3}$, $c_3 = 1.42 \times 10^{-3}$, $c_4 = 1.89 \times 10^{-3}$, heights of measuring cells in mm:
$h_1 = 40$, $h_2 = 74$, $h_3 = 108$, $h_4 = 142$, $h_5 = 175$.

In the extrapolation to S=0 (i.e. h=0), η_{sp}/c was plotted against $(c + K_1h)$ by employing a procedure used in the construction of the Zimm diagram. In the other procedure used for extrapolation, viz., to D=0, the points η_{sp}/c were plotted against $(c + K_2D)$; K_1, K_2 are constants, K_2 being selected so as to make the scales on the x-acis coincide in both extrapolations, i.e. so that it would hold for the gradient of THF that $K_2D = K_1h$. Curves were drawn through values obtained for the same concentrations, and points of the chosen D (including the value extrapolated for D=0) were determined on these curves. The further procedure was similar to that employed in the first extrapolation.

TABLE 1

The dependence of constants B and K_D on molecular weight M_w

$M_w \mathrm{x}10^{-5}$	$[\eta]_o$ (ml/g)	$\mathrm{Bx}10^{-5}$ (s)	K_D
3.3	233	4.0	0.26
4.6	207	4.2	0.44
6.1	384	4.4	0.47
9.1	541	4.9	0.36
9.5	560	5.5	0.34
9.9	581	6.1	0.40

TABLE 2

The dependence of the Huggins constant K_D for gradients D of the fraction with $[\eta]_o$ = 560 ml/g

D (s^{-1})	K_D
0	0.34
580	0.32
1068	0.36
1562	0.35

It is reported in the literature that the dependence of the limiting viscosity number $[\eta]_D$ on the velocity gradient D is an S-shaped curve (KINSINGER 1971). For a sufficiently narrow range of D, (D = 100 to 1000), the curve may be replaced with a straight line satisfying the expression $[\eta]_D = [\eta]'_0 (1 - BD)$, and a linear extrapolation to D=0 may be made (WIND, HERMANS 1951; IMMERGUT et al. 1953; CLAESSON, LOHMANDER 1961, and others). In this way the "limiting viscosity number $[\eta]'_0$" for "zero gradient" may be determined. The value of $[\eta]'_0$ thus obtained is somewhat higher than that which would be obtained by the extrapolation of values for D approaching zero. For purposes indicated in the introduction, we started from the finding that in the range D = 100 to 400 s^{-1} no dependence of $[\eta]_0$ on the gradient could be observed up to the molecular weight $3x10^6$, or no such dependence could be determined from the scattered experimental data (DAŇHELKA et al. 1976). For this reason the mean value from the range D=0 to D=250 s^{-1} was chosen for the molecular weight determination using the Kuhn-Mark relation $[\eta]_0 = K.M^a$, or in other words, it was assumed that $[\eta]_0 = [\eta]_{250}$ (Fig.1). The values used in the molecular weight calculations were $K = 5.3x10^{-3}$ and a = 0.84 (DAŇHELKA et al. 1976).

The dependence of $[\eta]_{sp}/c$ both on the concentration c and on the velocity gradient D may in the first approximation be described by the equation

$$(\eta_{sp}/c)_D = [\eta]_0[1-B.(D-250)] + [\eta]^2_D.K_D.c \qquad (1)$$

where B, K_D are constants (K_D is the Huggins constant for the gradient D).

In the range of molecular weights used (cf.Table 1), B depends on molecular weight. In order to express this dependence on $[\eta]_0$, an approximate extrapolation to $[\eta]_{250} = 0$ (Fig.2a) was made, and it was found that experimental points are satisfied by the empirical equation

$$\log(B - 3.6x10^{-5}) = 1.9 \log [\eta]_0 - 9.966 \qquad (2)$$

(Fig.2b), i.e.

$$B = 3.6x10^{-5} + 1.08x10^{-10}[\eta]_0^{1.9} \qquad (3)$$

The difference between the measured $[\eta]_D$ and $[\eta]_0$ corrected for the velocity gradient at D = 2500 s^{-1} and $M = 1.2x10^6$ was 17%. The arithmetic mean of the Huggins constant $K_D = 0.38$ (Table 1) is in agreement with the arithmetic means measured earlier, K = 0.36 (DAŇHELKA et al. 1976) and K = 0.43 (KÖSSLER et al. 1980).

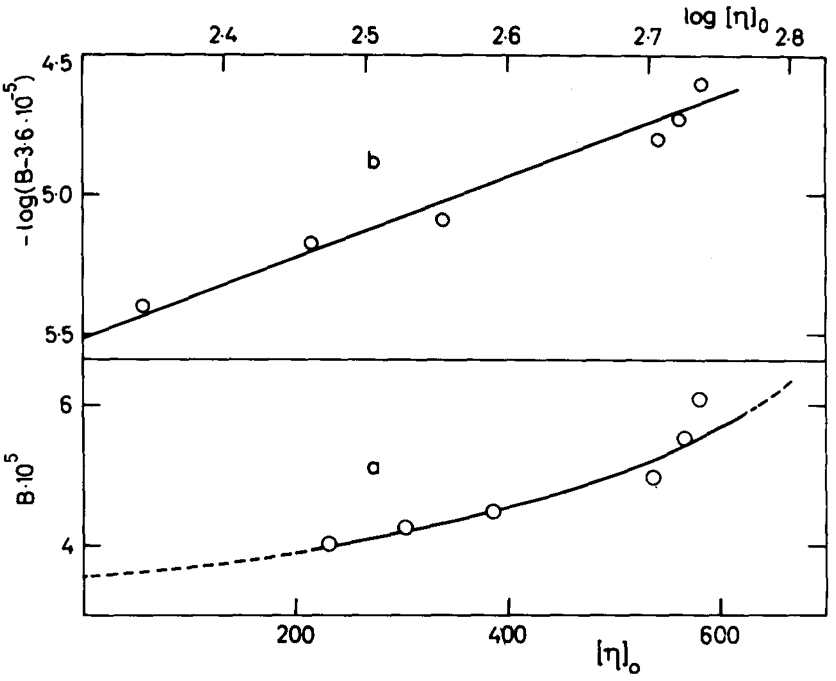

Fig.2 The dependence of constant B of Eq.(1) on the limiting viscosity number $[\eta]_0$

Procedure employed in the determination of $\bar{M}_v$

(1) Using the known geometric dimensions of the viscometer (r - radius of the capillary, V - volume of the measuring cell, h - distance of the cell centre from the orifice of the capillary) and the flow time of THF t_o, $D = 4V/\pi r^3 t_o$ for THF is determined.

(2) The flow times of CTC solutions in THF at various concentrations are used to determine $[\eta]_D$.

$[\eta]_D$ may be determined from a single measurement using an approximate formula $\eta_{sp} - \ln \eta_{rel} = c^2[\eta]_D^2/2$ (SOLOMON, CIUTA 1968). The magnitude of the error depends on molecular weight, as shown by Table 3.

TABLE 3

Error in the determination of the limiting viscosity number $[\eta]_D$ from a single measurement

$[\eta]_D$ extrapolated:	860	825	487	431	363	354
$[\eta]_D$ according to formula:	924	861	505	441	372	357
deviation in %:	7.4	4.4	3.7	2.3	2.5	0.8

(3) From Eq.(3), the first approximation to the parameter B is determined by using the measured $[\eta]_D$ instead of $[\eta]_o$. The error for D = 2500 and M = = 1.2×10^6 for $\bar{M}_v$ was < 2%.

(4) $[\eta]_o$ is calculated from the equation

$$[\eta]_o = [\eta]_D/[1-B(D-250)]$$

using the calculated B and the velocity gradient D for THF.

(5) If necessary, the corrected B can be calculated from Eq.(3) and according to point 4 the corrected $[\eta]_o$ can be determined.

(6) $\bar{M}_v$ is determined from

$$\bar{M}_v = 512.[\eta]_o^{1.19}$$

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