

A Structure Rheological Study of Cellulose Trinitrate in Ethyl Acetate

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SUMMARY

A structure rheological analysis was undertaken with cellulose trinitrates dissolved in ethyl acetate. Empirical scaling laws with molecular mass and concentration were found for the zero shear viscosity η_0 and the critical shear rate $\dot{\gamma}_c$ at the onset of shear thinning. Values for the apparent chain element A' were calculated from the concentration dependent network strand M_e and extrapolated to zero concentration. They were compared with dilute solution data. From the concentration dependence of the mass of network strand M_e a network with hindered penetration was inferred.

ZUSAMMENFASSUNG

An Cellulosetrinitraten in Ethylacetat wird eine strukturrheologische Analyse vorgenommen. Empirische Zusammenhänge mit der Molekülmasse und der Konzentration werden für die Null-Viskosität η_0 und für das kritische Geschwindigkeitsgefälle $\dot{\gamma}_c$ beim Einsetzen der Strukturviskosität gefunden. Aus der konzentrationsabhängigen Netzwerkstrang-Masse wird das scheinbare Kettenelement A' ermittelt und auf $c = 0$ extrapoliert. Dieser Wert wird mit Daten aus verdünnten Lösungen verglichen. Aus der Konzentrationsabhängigkeit von M_e wird auf ein Netzwerk mit behinderter Durchdringung geschlossen.

INTRODUCTION

In several previous papers by one of the authors various investigations on cellulose trinitrates dissolved in ethyl acetate have been described.^{1,2} As these investigations included flow curves at different concentrations and molecular masses in the low and medium shear rate range, a structure rheological evaluation appeared advisable, and is presented in this paper, based on the concept of the equivalent entanglement network model, as put forward by one of the authors.³

SAMPLES USED

The samples have been described in previous papers. Degree of substitution (DS) was 2.9. This gives a molecular mass of the basic unit of $m_0 = 292$, its length (l_0) being 5.15 Å. The degree of polymerization P has been calculated from intrinsic viscosity according to⁴ (with $M = P \cdot m_0$):

$$\left. \begin{aligned} [\eta]_{\text{acetone}} &= 0.82 \cdot P \\ [\eta]_{\text{ethylacetate}} &= 1.06 \cdot P \end{aligned} \right\} \text{for } P < 1000$$
$$\left. \begin{aligned} [\eta]_{\text{acetone}} &= 4.46 \cdot P^{0.76} \\ [\eta]_{\text{ethylacetate}} &= 5.70 \cdot P^{0.76} \end{aligned} \right\} \text{for } P > 1000$$

The ratio between $[\eta]_{EA}$ and $[\eta]_{Ac}$ is constant and equals 1.28. That means, that the exponent in the viscosity equation must be equal in both solvents according to the relation:

$$\frac{[\eta]_{EA}}{[\eta]_{Ac}} = \frac{K_{EA}}{K_{Ac}} \cdot M^{a_{EA} - a_{Ac}}$$

Flow curves in ethyl acetate have been obtained for different P and c values; they have been presented in a former paper.² From these flow curves, the zero shear viscosity η_0 and the critical shear rate $\dot{\gamma}_c$, which indicate the onset of shear thinning, could be readily obtained and were used for the subsequent analysis.

FLOW CURVES AND SCALING LAWS

Both η_0 and $\dot{\gamma}_c$ are related to molecular mass and concentration by means of scaling laws:

* To whom correspondence should be addressed.
Dedicated to Prof. Dr. Otto Kratky on the occasion of his 90th birthday.

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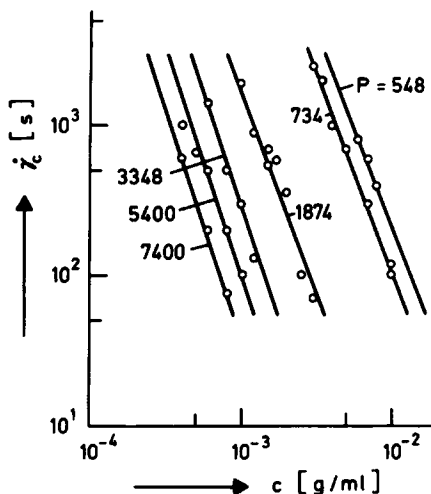


Figure 1 Critical shear rate $\log \dot{\gamma}_c$ as a function of $\log c$ for different P values.

$$\eta_0 = k_1 M^a \quad \eta_0 = k'_1 c^\alpha$$

$$\dot{\gamma}_c = k_3 M^{-c} \quad \dot{\gamma}_c = k'_3 c^{-\gamma}$$

A short note on these matters has recently been published.⁵ First we shall discuss the scaling of the critical shear rate $\dot{\gamma}_c$ with P and c . In Figure 1, we have plotted $\log \dot{\gamma}_c$ versus $\log c$ for different values of P . From these plots, we have constructed a plot of $\log \dot{\gamma}_c$ versus $\log P$ for different concentrations (Fig. 2). The exponents lie between -2.75 and -3.5 for the scaling with P (Fig. 2), and between -2.5 and -3.1 for the scaling with c (Fig. 1). The individual lines of Figure 2 can be combined to one mas-

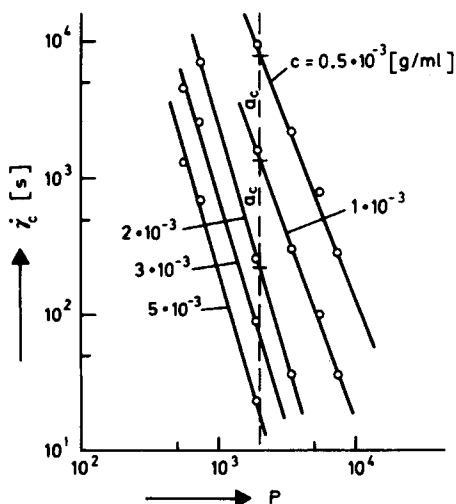


Figure 2 Critical shear rate $\log \dot{\gamma}_c$ as a function of $\log P$ for different c values.

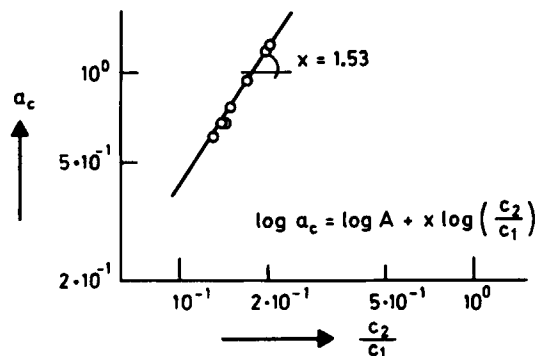


Figure 3 Shift factor $\log a_c$ as a function of the concentration ratio $\log c_2/c_1$.

ter curve by means of a shift factor a_c , which is proportional to $(c_2/c_1)^{1.5}$, as shown in Figure 3. Therefore, we can write

$$\log \dot{\gamma}_{c,2} = \log \dot{\gamma}_{c,1} - \log a_c \quad c_2 > c_1$$

$$a_c = k (c_2/c_1)^{1.5}$$

Probably this concentration dependence of the shift factor will itself slightly depend on the molecular mass, but our experiments are too few for a generalization. If we assume that the reciprocal of $\dot{\gamma}_c$ is equal or very close to the largest (terminal) relaxation time θ' of the polymer

$$\theta' = \frac{1}{\dot{\gamma}_c}$$

we obtain θ' values between 0.2 and 10^{-4} s, and this appears quite reasonable.

THE KNICK-DIAGRAM

The scaling of $\log \eta_0$ with $\log P$ (with c as parameter) yields the well known Knick-diagram (Bueche), where the "Knick"³ (intersection point of the network-branch line and the particle solution branch line) gives P_c respectively the molecular mass $M_e = M_c/2$ indicating the onset of entanglements. Thus M_e represents the mass between two entanglements (network strands) and determines, together with the degree of coiling of the macromolecule, the respective distance, the entanglement spacing. In Figure 4 such Knick-diagrams are shown. The theoretical expectations are not fulfilled, since the exponents of both branches deviate from the ideal values of 3.5 for $M > M_c$ and 1 for $M < M_c$ (Table I). However, the Knick (intersection) is clearly discernible. It depends on concentration according to

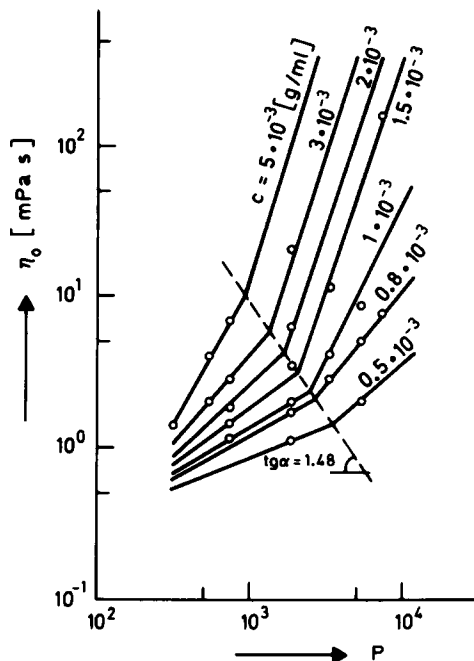


Figure 4 Zero shear viscosity $\log \eta_0$ as a function of $\log P$ for different c values (Knick-diagram).

$$M_e \cdot c^x = \text{constant}$$

where $x = 0.6$ (Figure 5). The Knick-diagram has been constructed from a plot of $\log \eta_0$ versus $\log c$ with P as parameter (Figure 6). As usual, in this diagram a transition from a particle-solution branch to a network solution branch is not discernible. In Figure 7 we have plotted $\log P$ versus $\log c$ for constant η_0 . We observe straight lines with a break point (Knick), which lie on a 45° -line.

THE STATISTICAL CHAIN ELEMENT

The mass of network strand M_e can be used to calculate an apparent statistical chain element A' . This

Table I P_c and Slopes of the Knick-Diagram as a Function of c

c (g/10 ⁻³ mL)	P_c	Slope $\text{tg} \alpha$	
		$P < P_c$	$P > P_c$
0.5	3500	0.40	0.90
0.8	2650	0.58	1.2
1	2500	0.61	2.0
1.5	2080	0.75	2.9
2	1700	0.97	2.9
3	1320	1.4	3.1
5	940	1.8	3.3

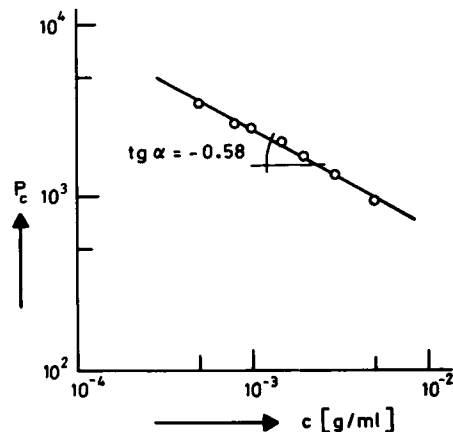


Figure 5 $\log P_c$ as a function of $\log c$.

is an equivalent figure and indicates both the coiling of the macromolecule and the interpenetration during the formation of the entanglement network.⁴ Unfortunately, we cannot separate both effects; but we can extrapolate the apparent statistical chain elements to zero concentration to obtain the true chain element A of the isolated molecule in the respective solvent. This can be compared with data from other measurements (e.g. light scattering, viscosity). Of course A also corresponds to the real state in the solvent used and not to the unperturbed state corresponding to a θ -solvent. The formula used is:

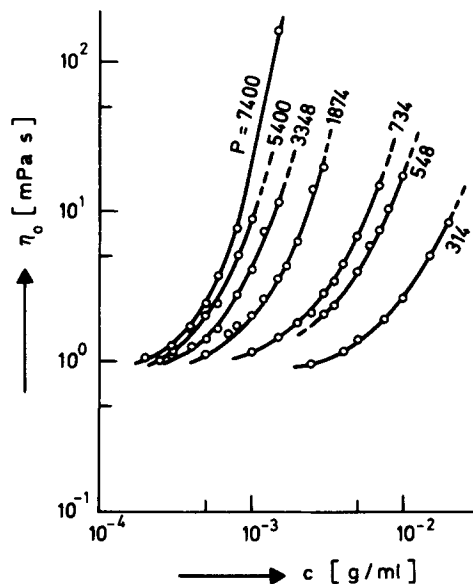


Figure 6 Zero shear viscosity $\log \eta_0$ vs. $\log c$ for different P values.

$$A' = \sqrt[3]{\frac{36}{(\pi N_L)^2} \cdot \frac{m_0}{l_0}} \cdot \sqrt[3]{\frac{1}{M_e \cdot c^2}}$$

We have calculated the A' values for different concentrations and extrapolated them to zero concentration (Fig. 8). We obtain $A = 320 \text{ \AA}$. This shows that the molecule is rather extended in the solvent ethyl acetate, even more so than in acetone, for which A -values around 200 \AA have been published. This agrees with the fact, that $[\eta]$ in ethyl acetate is higher than in acetone. Direct measurements of A in ethyl acetate are not available, so a direct comparison is not possible. However, the results fit into the picture of cellulose trinitrate as a rather extended molecule consisting of freely draining coils. The apparent chain element A' is defined for a network solution. It represents an equivalent figure, namely the chain element we would obtain if we replace the entangled network solution at hand by a particle solution consisting of molecules of mass M_e at the critical concentration c^* where the chains just begin to overlap.

PENETRATION HINDRANCE

When coiled macromolecules form an entanglement network after surpassing the critical concentration c^* (with $[\eta] \cdot c^* = 1$), the molecular segments must either penetrate each other or the molecular coil must be compressed. Both effects will lead to a decrease of the apparent statistical chain element A' . In general, we will encounter neither free penetration nor absence of penetration (mere compression of the coils), but a somewhat hindered penetration. The best way to express this penetration hindrance

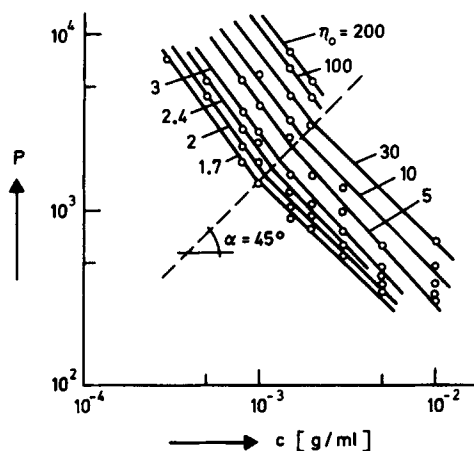


Figure 7 Log P vs. log c for constant values of η_0 .

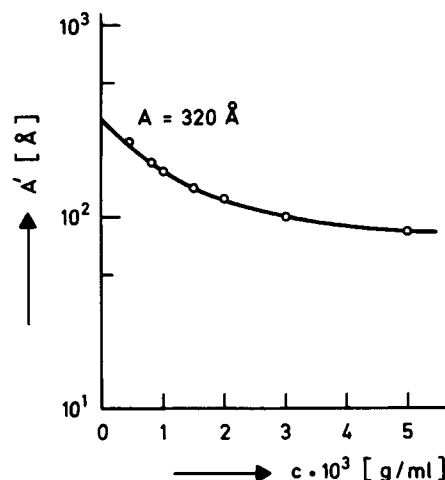


Figure 8 Apparent chain element log A' vs. c and extrapolation to $c = 0$.

is the entanglement fraction β , which is the ratio between the number of entanglements possible for free penetration and that actually formed.⁶ It can be measured as the ratio of a shear modulus at rest G_0 , calculated from M_e , to that directly measured in start-up experiments. The idea is that in direct measurements the actual state of solution is obtained, while M_e is approached from measurements at concentrations lower than c^* , from the realm of particle solutions, so that M_e represents the point where the molecular chains overlap for the first time and where penetration hindrance will not play a role.

Suitable measurements of G_0 are not available, so we must resort to other means. We have seen, that M_e is concentration dependent according to $M_e \cdot c^x = \text{constant}$ resp. $M_e = k \cdot c^{-x}$. This finding can be explained by a concentration dependence of the number of entanglements per unit volume ν :

$$\nu = \frac{cN_L}{M_e} = k \cdot c^n$$

where $n = 1 + x$. When $x = 0.6$, we obtain $n = 1.6$. That means, that M_e increases with concentration less than expected for free penetration ($x = 1$, $n = 2$), but more than for $n = 1$; $x = 0$, which means that M_e is independent of c and we have no penetration at all. Therefore, we conclude that in ethyl acetate, cellulose trinitrate will form an entanglement network with hindered penetration.

This behavior is also reflected in the dependence of A' on c . We can derive:

$$A' = K \cdot c^{(x-2)/3}$$

If we plot $\log A'$ versus $\log c$, we obtain a straight line with slope -0.47 , in agreement with the above formula.

Unfortunately, this formula is not suitable for extrapolation to zero concentration, as A' would approach infinity. It only describes the behavior of the network, if the concentration is enhanced, but does not hold in the particle solution realm. Therefore, in order to obtain A for $c = 0$ we must rely on our empirical extrapolation method, which is certainly not without ambiguities, but has proved to give reasonable results, and can be checked against independent measurements of A .

MOLECULAR DIMENSIONS OF CELLULOSE TRINITRATE IN SOLUTION

The structure rheological evaluation yields a chain element for cellulose trinitrate (CTN) in ethyl acetate of 320 \AA . This figure is rather high and indicates a considerable expansion. Unfortunately, little is known about molecular dimensions of CTN in solution, and no direct measurements are available on its unperturbed dimensions. For CTN in acetone and butyl acetate A -values of 200 \AA and 220 \AA have been published.⁷ This is in agreement with data from structure rheological measurements of A in butyl acetate,⁶ which also yielded a value of 220 \AA . Little is known about the unperturbed dimensions. In older papers⁸ it was reported, that a 1:1 mixture of butyl acetate and ethanol is a θ -solvent for CTN at 25°C , and from this solvent an A_θ of 160 \AA was measured. However, since these solutions (which had a second virial coefficient of zero) probably contained a considerable supermolecular gel fraction, this figure is probably too high. In another paper,⁹ a rather risky extrapolation yielded an A_0 value of 20 \AA . We can use these A_0 values to calculate the characteristic ratio C_∞ according to $C_\infty = A_0/l_0$. The condition of sufficiently high molecular mass is fulfilled at $P > 1,000$; there A becomes independent of P . If we take the extrapolated value of $A_0 = 20$, we can calculate the expansion factor:

$$\alpha^2 = \frac{\overline{h^2}}{h_0^2} = \frac{A}{A_0}$$

We obtain $\alpha = 3.2, 3.3$, and 4.0 for acetone, butyl acetate, and ethyl acetate, respectively. In the Poly-

mer Handbook,⁷ we find $h_0^2/M = 0.720\text{--}0.810 \text{ \AA}$. This can be used to calculate A_0 according to

$$A_0 = \frac{\overline{h_0^2}}{M} = \frac{m_0}{l_0}$$

We obtain $A_0 = 33\text{--}38 \text{ \AA}$, a value in the neighborhood of the extrapolated figure mentioned above. For ethyl acetate, the expansion factor $\alpha = 4$ is rather high and suggests a very expanded freely draining coil. Our results agree with the model of CTN as a very extended and stiff macromolecule, while the question of its unperturbed dimension is still open.

From the $\dot{\gamma}_c$ values, we can calculate the largest (terminal) relaxation time θ' under the assumption that $\theta' = 1/\dot{\gamma}_c$. The values for θ' lie in the range of 0.2 to 20 ms and scale with c with an exponent of -2.5 to -3.1 for $2 \times 10^5 < M < 2, 2 \times 10^6$. The scaling of $\dot{\gamma}_c$ with P varies with concentration, and the exponent is between -2.5 and -3.5 for c between 0.5 g/mL and $5.0 \times 10^{-3} \text{ g/mL}$. This is in qualitative agreement with a generalized formulation of the terminal relaxation time θ' as

$$\theta' = K \cdot RT \frac{\eta_0 M^\alpha}{c}$$

This formula explains the scaling laws found in a qualitative way. For a detailed analysis however more experimental data are needed.

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