# Shear Rate Dependence of the Viscosity of Cellulose Nitrate Solutions in the Dilute Concentration Regime Revisited

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## Synopsis

A detailed rheological study of cellulose nitrate in ethylacetate had been carried out in the dilute concentration (c) regime, covering a degree of polymerization (DP) range between $300 < DP_\eta < 7000$ and shear rates ($\dot{\gamma}$) between $100$ s$^{-1}$ $< \dot{\gamma} < 2000$ s$^{-1}$. The results show a strong dependence of the transition Newtonian to non-Newtonian behavior on the three variables $\dot{\gamma}$, DP, and c, similar to that found recently on solutions of synthetic polymers. Emphasis has been put on the critical concentrations corresponding to the standard shear rate $1000$ s$^{-1}$ to correspond to the standard conditions ($\dot{\gamma} \cong 1000$ s$^{-1}$; $0.3 < [\eta] \cdot c < 0.6$; $DS = 2.90 \pm 0.02$) proposed for the determination of the intrinsic viscosity $[\eta]$ of cellulose nitrates. It is shown that solutions with concentrations adjusted according to the above given conditions still exhibit Newtonian behavior, up to the highest range of DP. It follows, therefore, that applying the standard conditions, an extrapolation to $\dot{\gamma} = 0$ as has been proposed often for the intrinsic viscosity determination of cellulose nitrate is not advisable and results in considerable error. Considering the relationship between $[\eta]$ and DP, the present results indicate that the decrease of the exponent (a) from $a = 1.0$ to $a = 0.76$, taking place above a $DP \cong 1000$, is not a consequence of the applied shear rate but rather of the molecular properties of the solutes themselves.

## INTRODUCTION

Polymer solutions are known to show generally a non-Newtonian behavior, that is, the viscosity does not remain constant as in the case of Newtonian liquids, but decreases with increasing shear rate. As a consequence, the exact definition of the intrinsic viscosity $[\eta]$ is given by

$$[\eta] = \left(\eta_{\mathrm{sp}}/c\right)_{\substack{c=0 \\ \dot{\gamma}=0}} \tag{1}$$

Determination of $[\eta]$ as defined by eq. (1) is, however, somewhat problematic because measurements at $\dot{\gamma} = 0$ demand the use of special equipment. In cases where this is not available, extrapolation to $\dot{\gamma} = 0$ from data obtained at different shear rates had often been suggested, similarly with the extrapolation to the concentration $c = 0$. For purposes of practical molecular weight determinations it had been suggested to work at a defined shear rate with respect to the solvents used.[1] This can be achieved easily by the use of capillary viscometers with standardized dimensions.

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Concerning viscometric measurements on unsubstituted cellulose or cellulose derivatives such as nitrate, the application of one concentration only in connection with the use of the equation of Schulz-Blaschke,

$$[\eta]_{stdr} = \frac{\eta_{sp}/c}{1 + k_\eta \cdot \eta_{sp}} \qquad (2)$$

had been suggested. A further standardization was also introduced by adjusting the concentration of the solution in such a way that the product $[\eta] \cdot c$, that is, the specific viscosity, renders between 0.3 and 0.6.[2] By this, a constant range of shear rate with respect to the solutions is achieved.

During the last decade, more detailed rheologic investigations on solutions of synthetic polymers have allowed deeper insight into their rheologic behavior, especially in its dependence on the variables shear rate, concentration, and molecular weight. Since in the field of cellulose and its derivatives such definitive knowledge is still lacking, a detailed rheologic study on cellulose nitrate solutions has been started in our laboratories. Respective results concerning the high diluted regime and a range of shear rates up to $\dot{\gamma}$ = 2000 s$^{-1}$ are displayed in the present paper, and their significance with respect to the viscometric determination of DP is discussed.

## EXPERIMENTAL

The samples were obtained from purified cotton cellulose by acid-catalyzed hydrolysis[3] and subsequent nitration which is known to render a homogeneous degree of substitution DS = 2.90 $\pm$ 0.02.[4]

The intrinsic viscosity determinations[2] and their conversion to degree of polymerization[5] had been carried out according to two previous studies.

Freshly distilled ethylacetate p.a. was used as solvent. Each sample was measured at 4–6 different concentrations, preparing at least three different batches of each concentration.

The instrument was a rotational viscometer (Haake RV 2) equipped with a speed programmer, using a coaxial cylinder sensor system (Haake NV) as measuring system. The measuring temperature was 20.0 $\pm$ 0.1°C, in accordance with that applied in the elaboration of the $[\eta]$-DP relationship.[5] The range of shear rates applied in the context of the present paper covers the standardized shear rates used in the conventional intrinsic viscosity determinations.

## RESULTS

A total of 8 samples covering a range of DP between 300 and 8000 had been studied. Figure 1(a)–(c) exhibit the viscosity curves obtained on three representative samples in the low, medium, and high range of DP, respectively.

In Figure 1(a)–(c), the viscosity curves of cellulose nitrate solutions reveal the same characteristic features as have been found recently for polymers like polystyrene or polyacrylamide.[6-8] They consist of a strong dependence of the transition Newtonian to non-Newtonian regime on the three variable parameters: molecular weight (here expressed as degree of polymerization), concentra-
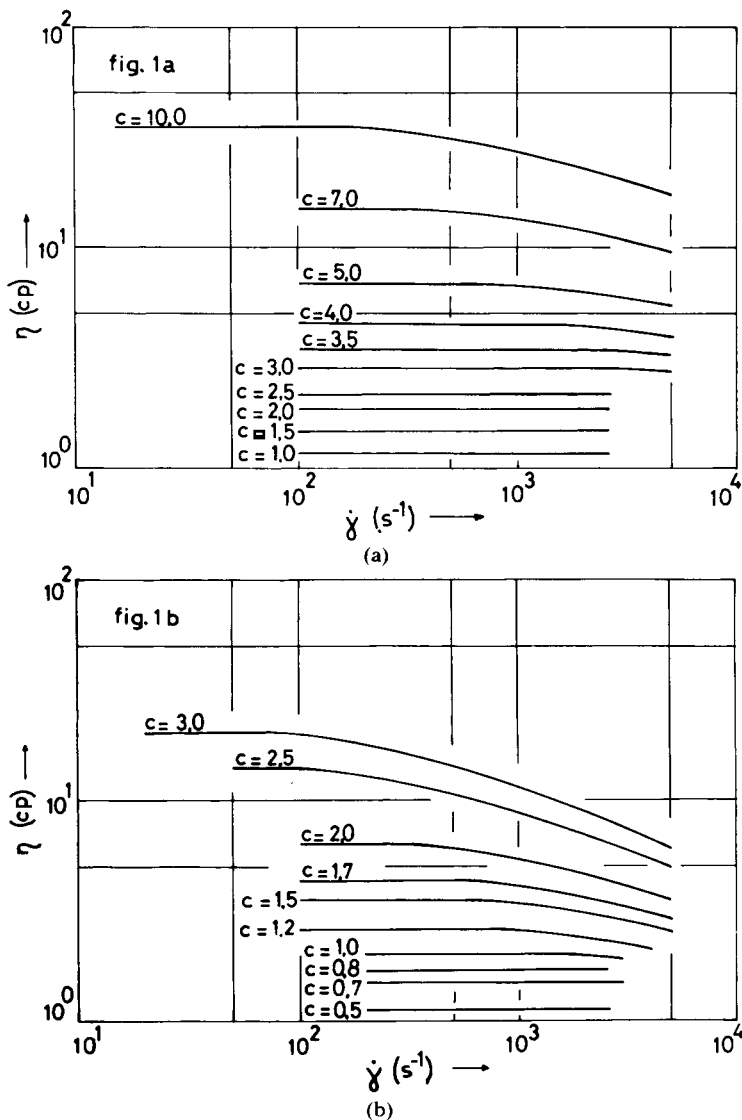
Fig. 1.   Viscosity curves at different concentrations [$c$ given in (g/mL) $\times$ $10^3$]. (a) $DP_\eta$ = 734; (b) $DP_\eta$ = 1874; (c) $DP_\eta$ = 5400.

tion, and shear rate. The higher the DP, the lower the critical concentration $c^*$ (the concentration where transition Newtonian to non-Newtonian behavior occurs) at a given shear rate, and the critical shear rate $\dot{\gamma}^*$ at a given concentration. In the case of cellulose nitrate, however, the critical concentrations are very much lower than those observed for flexible synthetic polymers of comparable degrees of polymerization (or molecular weights) and shear rates.

In cases where the critical concentration difference between two subsequent investigated concentrations was too large for a strict estimation of $c^*$, this was also derived from the inflection point in the log $\eta_{sp(\dot{\gamma}=1000 \text{ s}^{-1})}$ vs. log $c$, or
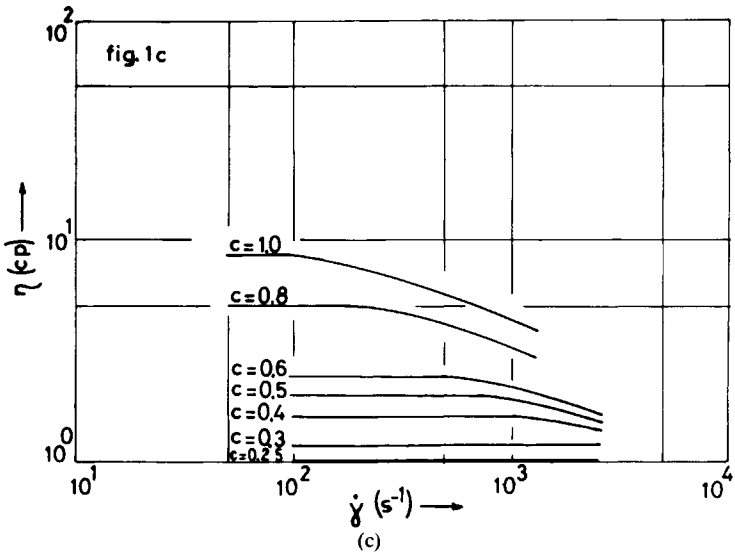
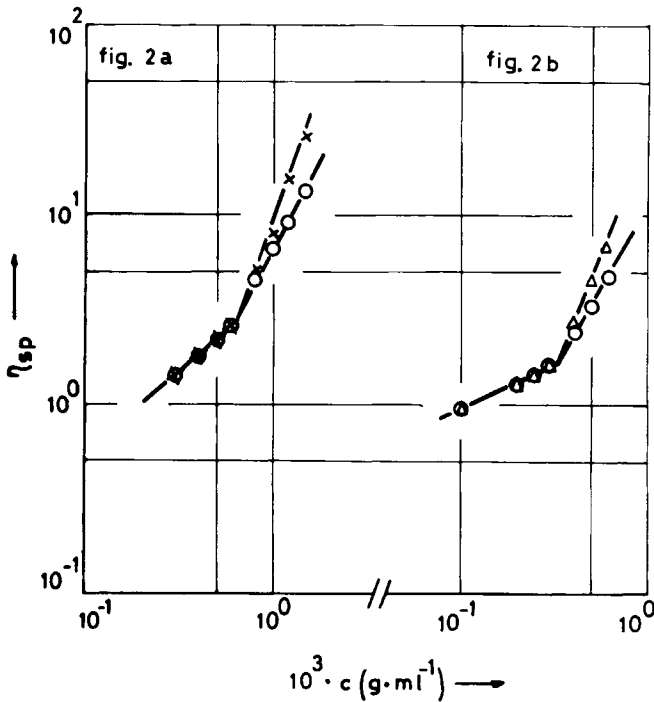Fig. 1. (Continued from the previous page.)



Fig. 2. Specific viscosity ($x$, $\Delta$ + $\eta_{sp(newt)}$; 0: $\eta_{sp(\dot{\gamma}=1000 s^{-1})}$) vs. concentration. (a) $o$, $x DP_\eta$ = 3348; (b) $c$, $\Delta DP_\eta$ = 7400.

log $\eta_{sp(newt)}$ vs. log $c$, plot [Fig. 2(a)–(b)]. Up to the inflection point, $\eta_{sp(\dot{\gamma}=1000 s^{-1})}$ as a function of $c$ behaves identically as $\eta_{sp(newt)}$ because at $\dot{\gamma} = 1000$ s$^{-1}$ the respective concentrations still obey the Newtonian regime. From the inflection point on, however, the slope of both straight lines differs

TABLE I
Comparison of Standardized Concentrations ($c_{[\eta]}$) and Critical Concentrations ($c^*$)
of Cellulose Nitrate Solutions, in Dependence on the DP

| DP[a] | $[\eta]_{stdr}$ (Ethylacetate) (mL/g) | $[\eta]_{stdr}$ (Acetone) (mL/g) | $c_{[\eta]} \times 10^{3\,b}$ (Ethylacetate) (g/mL) | $c_{[\eta]} \times 10^{3\,b}$ (Acetone) (g/mL) | $c^{*\,c}$ at $\dot\gamma = 1000$ s$^{-1}$ (Ethylacetate) (g/mL) | $c^{*\,d}$ (Ethylacetate) (g/mL) ` |
|---|---|---|---|---|---|---|
| 314 | 330 | 258 | 0.91–1.82 | 1.2–2.5 | $\gg 20$ | |
| 479 | 503 | 393 | 0.59–1.19 | 0.7–1.5 | $\gg 13$ | |
| 548 | 576 | 450 | 0.52–1.04 | 0.6–1.3 | 5.0–5.6 | |
| 734 | 764 | 597 | 0.39–0.78 | 0.5–1.0 | 3.5–4.0 | |
| 1874 | 1755 | 1370 | 0.17–0.34 | 0.3–0.45 | 1.0–1.2 | 1.1 |
| 3348 | 2725 | 2129 | 0.11–0.22 | 0.15–0.28 | 0.6–0.8 | 0.61 |
| 5410 | 3924 | 3066 | 0.08–0.15 | 0.10–0.20 | 0.38–0.40 | |
| 7400 | 5030 | 3900 | 0.06–0.12 | 0.08–0.15 | 0.30–0.38 | 0.36 |
| 13000 | 8300 | 6500 | 0.04–0.08 | 0.05–0.10 | 0.13[e] | |

[a] Derived from the corresponding $[\eta]_{stdr}$ in acetone according to $[\eta]_{stdr} = 0.82 \times DP$ for $[\eta]_{stdr} < 800$ mL/g and $[\eta]_{stdr} = 4.46 \times DP^{0.76}$ for $[\eta]_{stdr} > 800$ mL/g.
[b] Standardized according to $0.3 < [\eta] \cdot c < 0.6$.
[c] Derived from viscosity curves.
[d] Derived from $\eta_{sp(newt)}$ vs. $c$ plot ($\log_{10}$–$\log_{10}$).
[e] Derived by extrapolation $[\eta]_{stdr} = 8300$ mL/g to the corresponding $c^*$ (Fig. 3).

because from this concentration on the viscosity at $\dot\gamma = 1000$ s$^{-1}$ enters the non-Newtonian regime. The coincidence of the inflection points of both representations allows practical determination of $c^*$ simply from the $\eta_{sp(newt)}$ vs. $c$ plot. The elaboration of a "master curve" by plotting $\eta_{sp(newt)}$ as a function of $c[\eta]$,[8] concerning the viscosity data of all samples, will be discussed in another paper in the context of additional results obtained at larger concentrations and shear rates.[10]

A compilation of the critical concentrations for a shear rate of $\dot\gamma \simeq 1000$ s$^{-1}$, which has been proposed and applied for viscometric measurements on cellulose nitrates, is given in Table I. The standardized concentrations ($c_{[\eta]}$) utilizing the standardization according to $0.3 < [\eta] \cdot c < 0.6$ are also included. The congruence between the specific viscosities derived from the viscosity curves and those obtained on much more diluted solutions in the capillary viscometer had been proven by means of the $\eta_{sp}$ vs. $c$ plot to be satisfactory.

Table I shows that the concentrations $c_{[\eta]}$ are lower than the respective critical concentrations $c^*$ by at least a factor of 3. This means that the standardized concentrations deliver solution with a Newtonian character up to the high DP range. Since between $[\eta]_{stdr}$ in ethylacetate and $[\eta]_{stdr}$ in acetone there is a constant ratio of 1.28 independent from the DP,[2] the concentration to be used for measurements in acetone must be about 30% greater than those in ethylacetate. According to the values of $c^*$ and those of the respective $c_{[\eta]}$ exhibited in Table I, this does not affect the Newtonian behavior.

In Figure 3, the critical concentrations exhibited in Table I are plotted as a function of $[\eta]_{stdr}$. It renders a straightline which permits estimation of the $c^*$ values for $[\eta]_{strd}^{EA} > 6000$ up to the highest possible one of $[\eta]_{stdr} \simeq 8300$ mL/g (derived from $[\eta]_{stdr} = 6500$ mL/g in acetone[9] by use of the above mentioned intrinsic viscosity ratio). According to the extrapolation in Figure 3 and
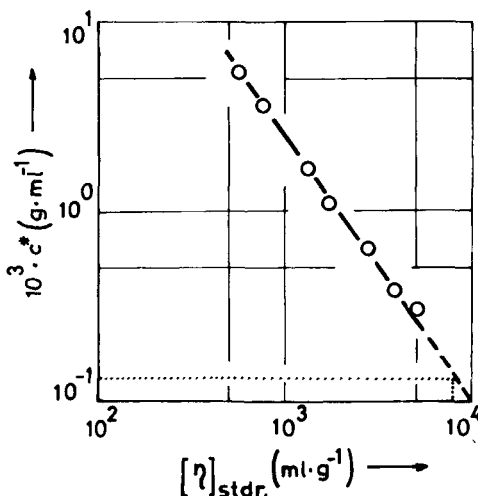
Fig. 3.    Critical concentration at $\dot{\gamma} = 1000 \text{ s}^{-1}$ as a function of standardized intrinsic viscosity ($[\eta]_{\text{stdr}}$) in ethylacetate. (....extrapolation $[\eta]_{\text{stdr}} = 8300$ to $c^*$).

column 4 of Table I, it can be assumed that $c_{[\eta]} < c^*$ also holds for $[\eta]_{\text{stdr}}^{\text{EA}} > 5000 \text{ mL/g}$.

## DISCUSSION

The present results reveal for dilute solutions of the semirigid cellulose nitrate the same rheological features as are exhibited by solutions of flexible synthetic polymers. This coincidence may favor the concept that the transition of the Newtonian to a non-Newtonian regime is principally a consequence of the appearance of an entanglement between the molecules above a certain critical concentration, the "loosening" of which under the action of the shear force originates the non-Newtonian behavior.[6]

In the present context, the rheologic behavior at a shear rate of about $\dot{\gamma} \simeq 1000 \text{ s}^{-1}$ was of special interest because shear rates up to $\dot{\gamma} = 1000 \text{ s}^{-1}$ are usually applied in the determination of $[\eta]_{\text{stdr}}$. Table I shows clearly that at the proposed standard conditions, the viscosity remains in the Newtonian regime up to the highest degrees of polymerization.

This finding is of importance not only in regard to the exactness and comparability of practical viscometric molecular weight determinations, but also in regard to the discussion of conformational and hydrodynamic solution properties in the context of relevant respective theories. Various linear extrapolation methods of viscosity data, determined at different shear rates, to $\dot{\gamma} = 0$ had been proposed[11-13] and applied in order to facilitate the obtainment of $[\eta]_{\dot{\gamma}=0}$. For example, *in the case of cellulose nitrate* $[\eta]_{\text{stdr}}$ *when larger than* 800 mL/g *were converted according to Refs. 13 and 14 to, as we know now not true, intrinsic viscosities* $[\eta]_{\dot{\gamma}=0}$.[15] The present results show, however, that concerning semirigid polymers like cellulose nitrate, linear extrapolation methods are incorrect and their application results, therefore, in considerable error.

That the untrue representation of $[\eta]_{\dot{\gamma}=0}$ (derived from the $[\eta]_{\text{stdr}} > 800$ mL/g) as a function of DP according to

$$\log[\eta] = \log K + \mathbf{a} \cdot \log \text{DP} \tag{3}$$

delivered a single straight line[15] seemed to corroborate the hypothesis that the decrease of **a** from **a** = 1 to **a** = 0.76, observed at DP > 1000 when $[\eta]$ is given as $[\eta]_{stdr}$,[5] would be caused by disregarding $[\eta]_{\dot\gamma=0}$. In Ref. 5, the decrease of **a** was achieved by taking into account more than 60 representative $[\eta]$-DP value pairs from the literature and adjusting the respective intrinsic viscosities to the above mentioned standard conditions. The data from the literature, which differed widely before standardization, afterward fell on a well-defined curve characterized by a decreasing **a** in the range of DP > 1000. The values derived in reference 5 for the parameters $K$ and **a** in the ranges DP < 1000 and DP > 1000, respectively (see also footnote of Table I), were confirmed by recent intrinsic viscosity and light scattering measurements on freshly prepared cellulose nitrates, determining $[\eta]$ at the standardized conditions in regard to DS, $\dot\gamma$, and the product $[\eta] \cdot c$.[16] The coincidence of $[\eta]_{stdr}$ with $[\eta]_{newt}$ exhibited in the present investigation permit the conclusion that the decrease of the exponent **a** is real and can be interpreted as being a consequence of the molecular properties themselves. Since the radius of gyration does not seem to show an abrupt change at the respective DP,[16,17] one may assume that the decrease of **a** is caused by changes in the stiffness or in the draining behavior of the molecules rather than by their conformational properties. In this context it may be of interest that the same effect of a decrease in **a** above DP $\simeq$ 1000 can be observed also on solutions of cellulose tricarbanilate in acetone and 1,4-dioxane,[18,19] although it has not been discussed by the respective authors. DP range constant ratios between the intrinsic viscosities of cellulose nitrate in different solvents,[2] as well as between those of cellulose nitrate and unsubstituted cellulose[20] (standardized shear rate of copper ethylenediamine solutions $\dot\gamma$ < 500 s$^{-1}$; concentration adjustment same as for the nitrates), show the independence of **a** from solvent whether cellulose is derived or not. This allows the conclusion that the decrease of **a** is a consequence of the proper "back bone" of the cellulose molecule, but not of the introduction of substituents.

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