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Evaluation of the accessibility of celluloses by the intrinsic viscosity ratio $[\eta]^{\text{cell.nitr.}}_{\text{acetone}} / [\eta]^{\text{unsubst.cell.}}_{\text{CuEn}}$

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Summary

Standarization of the nitration procedure as well as of the conditions of viscosimetric measurements on cellulose nitrates and unsubstituted celluloses leads to a constant Intrinsic Viscosity Ratio $[\eta]^{\text{Cell.nitr.}}_{\text{Acetone}}/[\eta]^{\text{Unsubst.cell.}}_{\text{CuEn}} = 1.95\pm0.05$, independently from the range of DP. Since nitration under the standarized conditions occurs without degradation and delivers a reproducible constant degree of substitution of DS = 2.90±0.02, intrinsic viscosity ratios lower than 1.90 indicate a diminished accessibility of the respective cellulose. Determination of the intrinsic viscosity ratio reveals, therefore, the possibility to evaluate the accessibility of a cellulose sample.

Introduction

The accessibility of cellulose is a determinating factor not only in its technological processing but also in its basic and applied research. Nevertheless, the methods proposed for its evaluation are still insatisfactory because they refer to not well defined fundamentals what often may give rise to conflicting results.

In what follows it will be shown that the Intrinsic Viscosity Ratio (abreviated here IVR), i.e. the ratio between $[\eta]$ of cellulose nitrate in a given solvent (here acetone) and $[\eta]$ of the corresponding unsubstituted cellulose in CuEn (ethylenediamine-copper II-complex) represents a well defined criteria to characterize the accessibility of a cellulose sample.

As it had been pointed out recently, when $1.40<\text{IVR}<<1.95\pm0.05$, the IVR can be used to determine the degree of substitution DS (expressed by the nitrogen content) of cellulose nitrate (1). The method is based on the facts that the intrinsic viscosity of a cellulose derivative depends strongly on the DS, existing in the case of cellulose nitrate in the range 2.5<DS<2.9 a well established quantitative relationship between DS and $[\eta]$ (2) (the $[\eta]$-DS-relationship was not derived for nitrates having a DS<2.5 (%N<12.8) because of the impossibility to prepare the derivative without risking degradation and/or inhomogeneous distribution of the substituent), and that the IVR $[\eta]_{\text{Ac}}/[\eta]_{\text{CuEn}}$ is independent from the degree of polymerization for identical degrees of substitution of the nitrates (3). Using adequate standarized nitration conditions (2) which warrent a polymer analogous nitration (i.e. without any degradation) as well as a homogeneous degree of substitution of DS = 2.90±0.02, the IVR shows, within the limits of error, a value of 1.95±0.05 (3). IVR values lower than 1.90, appearing in spite of the use of standarized nitration conditions, indicate then consequently a lower degree of substitution caused by a diminished accessibility of the respective cellulosic material for the nitration mixture. It is thus obvious that the IVR delivers not only information about the degree of substitution of the derivative, but also about the accessibility of the unsubstituted cellulose sample. This conclusion is corroborated in the next chapter by means of recent data obtained on cellulose samples representative for adequate and hindered accessibilities.

Experimental Data

Fig. 1 exhibits for 2.5<DS<2.9 the relationship between IVR and DS.

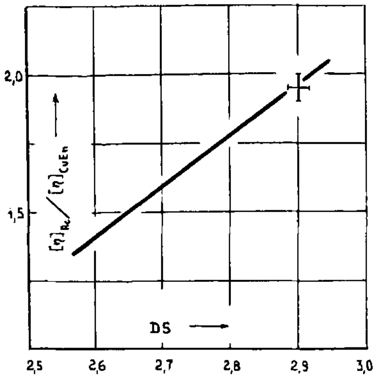

Fig. 1: Intrinsic Viscosity Ratio $[\eta]_{Ac}/[\eta]_{CuEn}$ as a function of the degree of substitution DS of the nitrate.
(+: limits of error)

In Table 1 are compiled nearly 30 IVR-data obtained on samples of quite different origins. It is to see that at DP>>800, an IVR of 1.95±0.05 is generally occurring. The only exceptions are the samples which had not been dewaxed before nitration, what caused a reduced accessibility of them. Concerning the range of DP<<800, however, where most samples had been obtained by a rigorous acid catalyzed hydrolysis, the IVR shows a notable decrease which is the more pronounced the lower is the DP, e.g. the more prolongated is the hydrolytic reaction. The suspicion that this deviation from the normal IVR may be a consequence of variations of the $[\eta]$-DP-relationship parameters corresponding to the unsubstituted cellulose in CuEn can be discarded because of the occurrence of "normal" IVR-ratios according to the pretreatment of the respective samples. For cellulose nitrate the exponent a = 1 of the Staudinger-Mark-Howink-eq. be valid in the range of DP<<1000 had been confirmed recently (4).

TABLE 1: Intrinsic viscosity ratio and degrees of substitution for cellulose nitrates of different pretreatments and different degrees of polymerization.

N°	Material	DP_η	$[\eta]^{\text{Nitr.}}_{\text{Ac.}}/[\eta]_{\text{CuEn}}$	DS of the Nitrate
1	Cotton cellulose taken from closed cotton balls dewaxed and purified (a)	12800	1.970	2.93
2	Cotton cellulose taken from already opened cotton balls dewaxed and purified (a)	9170	1.970	2.93
3	Cotton cellulose, commercial mechanically purified, not dewaxed	9300	1.82	2.86
4	Linters cellulose,commercial dewaxed and purified (a)	9000	1.950	2.91
5	Cotton cellulose,commercial mechanically purified, not dewaxed and purified with NaOH	7700	1.76	2.83
6	Linters, degraded (b)	6400	1.970	2.92
7	Cotton cellulose gently degraded	6100	1.950	2.91
8	Linters, degraded (b)	4800	1.95	2.91
9	Cotton cellulose, degraded (b)	3150	1.95	2.90
10	Cotton cellulose, degraded (c)	3120	1.92	2.89
11	Linters, degraded (b)	2270	1.92	2.88
12	Linters, degraded (b)	1860	1.970	2.91
13	Cotton cellulose, degraded (b)	1670	1.93	2.89
14	Cotton cellulose, degraded (b)	1370	1.970	2.91
15	Spruce pulp	1300	1.95	2.90
16	Linters, degraded (b)	1260	1.92	2.88
17	Beech pulp	1000	1.94	2.89
18	Cotton cellulose, degraded (b)	988	1.980	2.91
19	Cotton cellulose, degraded (b)	790	1.95	2.90
20	Pulp, degraded (b)	750	1.82	2.83
21	Cotton cellulose, strongly degraded (c)	650	1.83	2.83
22	Pulp, degraded (b)	610	1.73	2.78
23	Cotton cellulose, strongly degraded (c)	514	1.75	2.79
24	Cotton cellulose, degraded (b), preswollen before nitration	500	1.98	2.91
25	Technol.treated cellulose, oxyd. degraded	480	1.94	2.89
26	Cotton cellulose, strongly degraded (c)	365	1.65	2.73

TABLE 1 (continued)

N°	Material	DP_η	$[\eta]^{Nitr.}_{Ac.}/[\eta]_{CuEn}$	DS of the Nitrate
27	Cotton cellulose, degraded preswollen before nitration	300	1.95	2.89
28	Linters cellulose, degraded strongly (c)	295	1.47	2.63
29	Cotton cellulose, degraded strongly (c)	231	1.46	2.63

(a) dewaxing by consecutive extraction with acetone and bencene, purification by boiling 1% NaOH in N_2-atmosphere.

(b) degradation medium: 0.5 M $KHSO_4$, 40°C

(c) degradation medium: 0.5 M $KHSO_4$ or 1 N HCl, 60°C.

It can be concluded, therefore, that also at DP<<800 the observed lowering in the IVR is a consequence of a diminished accessibility.

Discussion

It is obvious that in the range $1.40<[\eta]_{Ac}/[\eta]_{CuEn} < 1.95$, the IVR reflects truly the accessibility of cellulose provided standarized preparative and measurement conditions are applied. The IVR can be considered, therefore, as a well defined parameter to characterize the accessibility of celluloses like cotton, linters and pulps which contrary to lignified cellulose dissolve quantitatively in a molecular disperse order. The presence of hemicelluloses, however, will shift the IVR to higher values because a great portion of them dissolve during nitration, affecting thus the intrinsic viscosity of the unsubstituted material by decreasing it, but no more the intrinsic viscosity of the nitrate. An adequate correction of one of the two intrinsic viscosities, $[\eta]_{Ac}$ or $[\eta]_{CuEn}$, taking into account the proportion of the non cellulosic material dissolved during nitration, will bring back the IVR to the normal range, making it possible by this way an evaluation of the accessibility of the respective celluloses.

Discussing the features involved in the accessibility, one may consider firstly conformational ones and their consequences on the formation of intra- and intermolecular hydrogene bridges and the lateral packing of the molecules. A more pronounced contribution to the accessibility will bring about the morphologic "rough" structure responsible in turn for the "inner surfaces". A critical reduction or altogether disappearance of these "inner surfaces" as a consequence of inadequate and/or too hard drying conditions may lead to a pronounced inaccessibility and finally to a cornification of the respective samples. Unfortunately neither the present nor another method distinguishes between the distinct features. Neither is the aim of the present paper to find out the proper reasons of the reduced accessibility of some of the samples shown in Table 1. Nevertheless, since the drying method applied on all of them was a standarized one, one may argue that the lower accessibility exhibited by the rigorously degraded samples may be a consequence of changes in the proper conformational and/or supermolecular fine structure produced by the action of the acidic medium and the temperature rather than only of a drastic reduction of the inner surfaces occurred in the drying step.

Standarized Methodological Details

- Unsubstituted Cellulose in CuEn: Preparation of CuEn according to (5), conditions of $[\eta]$-measurements: t = 20°C, shear rate solvent = 500 sec^{-1}. Adjustment of the applied concentrations to $0.3<[\eta]c<0.6$. Elaboration of $[\eta]$ according to Schulz-Blaschke with $k_\eta = 0.29$. Conversion of the intrinsic viscosities in degrees of polymerization DP_η by means of the equ. (1) and (2) according to whether $[\eta]$ is lower or higher respectively than $[\eta] \simeq 400\ ml.g^{-1}$ (3).

$$[\eta] ml.g^{-1} = 0.42xDP \quad (1)$$

$$[\eta] ml.g^{-1} = 2.29xDP^{0.76} \quad (2)$$

All samples conditioned to 65% humidity before weighting.

- Nitrates: Nitration mixture and conditions according to (2), involving a nitration time and temperature of 16 hrs and 0°C respectively, and a cellulose concentration in the nitration mixture 1% weight/vol. Viscosimetric measurements: t = 20°C, shear rate of solvent = 1200 sec^{-1}, adjustment of the concentrations as above indicated. Elaboration of $[\eta]$ according to Schulz-Blaschke using values of k_η between 0.25 and 0.4 according to the range of $[\eta]$ (6). Conversion of the intrinsic viscosities in degrees of polymerization by means of the eqn. (3) and (4) respectively according to whether $[\eta]$ is lower or higher than $[\eta] = 800\ ml.g^{-1}$ (3).

$$[\eta] ml.g^{-1} = 0.82xDP \quad (3)$$

$$[\eta] ml.g^{-1} = 4.46xDP^{0.76} \quad (4)$$

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