Gelatine sizing of paper and its impact on the degradation of cellulose during aging: a study using size-exclusion chromatography

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Appendix 5-1. Viscometry method for the analysis of dilute solutions of cellulose in Cadoxen

A5-1.1 Experimental

A5-1.1.1 The dissolution method

A5-1.1.1.1 Cadoxen solvent preparation

Cadoxen is an aqueous solution of cadmium tri-ethylenediamine dihydroxide \([\text{Cd(En)}_3](\text{OH})_2\) (En = \(\text{H}_2\text{N(CH}_2\text{)}_2\text{NH}_2\)).

Cadoxen was prepared according to the procedure described by Donetzhuber [1]. Ethylenediamine was purified by re-distillation, and the fraction of boiling point (b.p.) 116-117°C was collected. A solution of about 6.5 \(M\) was made by mixing 466.5 mL of this purified ethylenediamine with 1080 mL of water in a 2L-erlenmeyer flask. The solution was kept overnight at 4°C.

The flask was then placed in an ice-sodium chloride bath and chilled to a temperature between −8°C and −16°C under constant stirring. 135 g of cadmium oxide was then added slowly over a period of 3 hours. The mixture was stirred for one additional hour and placed at 4°C for 24 to 48 hours to allow the settling of the excess precipitate of cadmium hydroxide.

The clear solution was separated from the precipitate by centrifugation at 3000 rpm for 20 minutes. An aqueous solution of sodium hydroxide (2.26 \(M\)) made by dissolving 21 g of NaOH in 232.5 mL of water was mixed with 90.3 mL of purified ethylenediamine. This solution was cooled to 4°C and mixed with the cold cadmium oxide/ethylenediamine prepared previously to make up the Cadoxen stock solution. The Cadoxen stock was left overnight at room temperature before use.

A solution of Cadoxen 50% was prepared by diluting the Cadoxen stock in water in a 1:1 ratio to be used as the viscosity effluent. The water used for all solutions was milli-Q 18.2 MΩ cm (RiOs Ellx, Millipore).

A5-1.1.1.2 Sample pre-treatment

The paper was immersed in a solution of sodium borohydrdride 0.5 \(M\) in ethanol with a 1/0.1 (wt/v) ratio for 16 hours. NaBH₄ reduces the carbonyl residues present on the

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1 The experiments detailed here were carried out at the Canadian Conservation Institute (CCI), Ottawa, Canada.
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cellulose chain to hydroxyl groups. This reduction is a preventive treatment in order to
decrease the solvent-induced degradation during dissolution [2].

The solution was decanted and the paper thoroughly rinsed several times in water until
the pH of the rinse water was neutral. The paper was air dried for at least three days at
room temperature and its moisture content was determined according to the standard
TAPPI T 412 om-94 [3].

A5-1.1.1.3 Dissolution

The procedure was done following the method by Doty and Spurlin [4] later modified by
Burgess [5]. Paper is cut in pieces 2 mm × 2 mm, weighted, and placed in a 20 mL
Erlenmeyer flask. Twenty millilitres of Cadoxen stock solution was added.

The amount of paper needed in order to fall in the kinetic viscosity range specified by the
viscometer supplier is usually between 60 and 300 mg, depending on the molar mass of
cellulose (state of degradation) and on the presence of other fibrous and non-fibrous
compounds in the paper.

The suspension of paper in Cadoxen was left dissolving under magnetic stirring for 90
minutes at room temperature. Then 20 mL of water was added to obtain the sample stock
solution. This solution was centrifuged for 15 minutes at 3000 rpm, and the supernatant
used for the dilutions. With pure cellulose Whatman No.1 paper, dissolution is complete,
and no residue is observed.

A5-1.1.1.4 Sample solutions

Three solutions of cellulose at different concentration are required for the viscometry
measurement in order to extrapolate the value of the intrinsic viscosity ([η]). Two more
solutions in addition to the stock solution are prepared by diluting the sample stock
solution with Cadoxen 50% in 1:1 and 2:1 ratios.

A5-1.1.2 Viscosity measurements

Seven millilitres of the solution to be analysed was poured into the capillary viscometer
Routine 100 (Cannon-Fenske) (Figure A5-1 1) from the tubular branch end (1) using a
pro-pipette. The viscometer was placed in a water bath at 30±0.1°C to equilibrate for a
few minutes. The liquid was then suctioned up with a suction bulb in (2) to slightly above
(A) mark. The efflux time of the liquid, which is the time taken for the solution to flow
from (A) to (B) was then measured.

The measurement began with the solvent Cadoxen 50%, followed by the solutions of
cellulose, starting with the more diluted. For each solution the measurement was repeated
until three consecutive efflux times agreed within 0.1 seconds maximum difference. The viscometer was then drained, rinsed twice with 3.5 mL of the cellulose solution to be analysed, and drained again well before charging with the 7 mL aliquot of the next solution. Three viscosity repeat measurements were carried out for each sample, and the efflux time values averaged. After one series of dilutions, the viscometer was well rinsed with Cadoxen 50% before rinsing with the next cellulose solution.

**Figure A5-1.1.** capillary glass viscometer Routine 100 (Cannon-Fenske).

### A5-1.2 Calculation of the intrinsic viscosity and $DP_v$

The viscosity of a polymer solution depends not only on the size and shape of the molecular chains but also on its concentration, as well as on the temperature, pressure and solvent.

The viscosity average molar mass ($M_v$) of cellulose is calculated by measuring the intrinsic viscosity of cellulose in dilute solutions, typically of the order of 1% by mass [6]. From $M_v$, the value of the viscosity-average degree of polymerisation ($DP_v$), which is the ratio of $M_v$ of cellulose by the molecular mass of an anhydroglucose unit (162 g mol$^{-1}$) is calculated.

$$DP_v = \frac{M_v}{162}$$

For cellulose, $M_v$ is obtained from the Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K' M_v^a$$

Where $K'$ and $a$ are constants for a given polymer-solvent system, temperature and molar mass range. For cellulose in Cadoxen at 30°C, the equation is [1]:

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\[
[\eta] = 3.85 \times 10^{-4} \, M_v^{0.76}
\]

Converting \( M_v \) to \( DP_v \), the equation becomes:
\[
[\eta] = 1.84 \times 10^{-2} \, DP_v^{9.76}
\]

Then, \( DP_v = \left( \frac{[\eta]}{1.84 \times 10^{-2}} \right)^{1.316} \)

In order to obtain the value of \([\eta]\), the specific viscosity \( (\eta_{sp}) \) of each diluted solution of cellulose has to be calculated. In practice the viscosity is not measured directly. Instead, as explained in section A5-1.1.2, the time of flow for the polymer solutions and pure solvent in a capillary viscometer, the so-called efflux time is measured. We have:
\[
\eta_{sp} = \frac{t_{cell} - t_{solv}}{t_{solv}}
\]

\( t_{cell} \) is the average efflux time of the solution of cellulose (seconds).

\( t_{solv} \) is the average efflux time of the Cadoxen 50\% (seconds).

The reduced viscosity \( (\eta_{spc}) \) in dL g\(^{-1}\) for each dilution is calculated by:
\[
\eta_{spc} = \frac{\eta_{sp}}{c}
\]

Where \( c \) is the concentration of cellulose in solution (g dL\(^{-1}\)) calculated using the dry mass of the paper \( (m_{dry}) \), which is defined by:
\[
m_{dry} = m \left( 1 - \frac{MC}{100} \right)
\]

Where \( m_{dry} \) is the dry mass of paper (g),

\( m \) is the mass of sample weighted (g),

\( MC \) is the moisture content (\%).

The concentration of the stock sample solution is then:
\[
c_{stock} = 2.5 \times m_{dry}
\]

The concentration of each diluted solution is then calculated, and the curve \( \eta_{spc} = f(c) \) is plotted. We have:
\[
[\eta] = \lim_{c \to 0} \eta_{spc}
\]

Thus, the value of the intrinsic viscosity \([\eta]\) is given by the intercept of the linear regression curve \( \eta_{spc} = f(c) \). The correlation coefficient R is determined. In the present measurements, a value of \([\eta]\) was accepted only when \( R^2 \) exceeded 0.998. The viscosity measurement for the sample was otherwise repeated.
**Chemicals and materials**

Sodium chloride (NaCl), ethanol and sodium hydroxide were obtained from Fisher Scientific (Springfield, NJ, USA). Sodium borohydride (NaBH₄) and ethylenediamine (En) were purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA).

**Instruments**

The capillary glass viscometer Routine 100 was obtained from Cannon-Fenske, now Cannon Instrument Cie (State College, PA, USA).

**References**
