Characterization of cadoxene solutions of some cellulose esters by ultraviolet spectroscopy

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Ultraviolet absorption spectra for cadoxene solutions of benzoyl-, 2-furoyl-, 2-furoylacetyl-, 3-(2-furyl)acryloyl-, 3,5-dinitrobenzoylcellulose, methyl 2,3,4,6-tetra-O-(2-furoyl)- α -D-glucopyranoside, and octa-O-(2-furoyl)cellobiose have been measured. The obtained spectral data were satisfactorily used in the determination of the degree of substitution of the substrates. The chemical changes during the process of dissolution of cellulose esters in cadoxene have been studied.

Были сняты ультрафиолетовые спектры поглощения бензоил-, 2-фуроил-, 2-фуроилацетил-, 3-(2-фурил)акрилоил- и 3,5-динитробензоилцеллюлозы, а также метил-2,3,4,6-тетра-О-(2-фуроил)-α-D-глюкопиранозида и окта-О-(2-фуроил)целлобиозы при использовании кадоксена как растворителя. Спектральные данные были успешно использованы для определения степени замещения. Исследовано химическое воздействие кадоксена на ацильные производные целлюлозы во время их растворения.

The use of u.v. spectroscopy in the characterization of cellulose materials is limited by the availability of suitable solvents. This lack has been partially overcome by the development of a method which, taking advantage of the *Kubelka—Munk* relations on the light absorption and scattering by solid substances, makes it possible to study solid samples [1]. The method has been widely used in the evaluation of the discoloration of cellulose and recently *Polčin* and *Rapson* [2, 3] widened still the application of the method by using it in the ultraviolet and visible region for studying the discoloration of lignin.

Introduction of cadoxene (cadmium tris-1,2-diaminoethane hydroxide) and the discovery of its solvation properties opened new possibilities for the use of u.v. spectroscopy in the studies on cellulose materials. Cadoxene shows no absorption in the region above 235 nm and, besides good solvation properties, it has little degrading effect upon cellulose. Owing to these properties cadoxene has been used in studies on pulp, cellulose and its derivatives by u.v. spectroscopy. In addition, using cadoxene solutions u.v. spectroscopy has been applied in studying various aspects of lignin—cellulose system [4—11] and in the determination of clarifiers and dyes in cellulose [12—15].

In order to determine the degree of polymerization (DP) of cellulose *Blair* and *Cromie* [16, 17] have investigated the u.v. spectra of cellulose derivatives with the

modified aldehydo end group. The relation between the absorption coefficient at the characteristic wavelength and the DP of cellulose phenylhydrazones, phenylosazones, semicarbazones, thiosemicarbazones and oximes was studied. Cellulose phenylosazones with a different DP showed a maximum absorption at 390 nm and the intensity of the absorption depended upon the number of end groups, which could be used for the end group assay. Since in the presence of oxygen the phenylosazones are oxidized the determination had to be carried out in nitrogen. No linear dependence between the DP and the spectral data could be found for other cellulose derivatives.

So far, cadoxene solutions of cellulose esters have not been investigated by spectroscopy. In the present work attention has been focussed on the chemical interaction of cadoxene with cellulose esters. Spectral properties of cadoxene solutions of the corresponding carboxylic acids and their mixtures with cellulose as well as cellulose esters have been studied with the objective to find a relation between the found data and the degree of substitution (DS) of the cellulose derivatives under investigation.

Experimental

Benzoyl cellulose [18], 2-furoylcellulose, 2-furoylacetylcellulose, methyl 2,3,4,6-tetra--O-(2-furoyl)- α -D-glucopyranoside, octa-O-(2-furoyl)cellobiose [19-21], 3-(2-furoyl)acryloylcellulose [22] were prepared as described. 3,5-Dinitrobenzoylchloride [23] was converted to 3,5-dinitrobenzoylpyridinium hydrochloride and this was used for the preparation of 3,5-dinitrobenzoylcellulose (DS 0.186) in the same manner as described for the preparation of 2-furoylcellulose [19]. Cadoxene (5.80% Cd) was prepared according to [7].

Ultraviolet absorption spectra were measured with Spektronom 203 (MOM, Budapest) instrument using 1 cm cells. The sample was dissolved in cadoxene, diluted with an equal amount of water and further dilutions were made by addition of a cadoxene—water mixture (1:1). Blank measurements were done against a cadoxene—water (1:1) mixture. When monitoring the spectral purity of cadoxene itself the measurements were done against distilled water. All measurements were carried out with the same batch of cadoxene.

Infrared absorption spectra were measured in KBr pellets (3 mg/g) with a double-beam UR-10 spectrophotometer (Zeiss, Jena).

The effect of cadoxene upon cellulose esters

The respective ester was dissolved in cadoxene at room temperature and left to stand for the time indicated in Table 2. The solution was cooled in an ethanol—dry ice mixture and 5% hydrochloric acid was added with stirring to neutralize 1,2-diaminoethane. The product was filtered, washed with water and hot ethanol and, after drying, used for spectral measurements. The thus obtained data served for DS calculations.

Results and discussion

The spectral data found for the cellulose esters studied are listed in Table 1. The spectra of cadoxene solutions of the corresponding acids showed that benzoic acid absorbed in a region not suitable for the intended studies. 2-Furoic, 3-(2-furyl)acrylic, and 3,5-dinitrobenzoic acids displayed the same spectral characteristics (λ_{max} and a_w) as the corresponding esters. The found data remained constant during the period of two days. The identity of the spectra of the acids and esters (the band intensities being dependent on the amount of the acyl groups) follows from Fig. 1. The above-mentioned results indicated that the spectral data found for cadoxene solutions of cellulose esters might be used for the calculation of DS.

The validity of the Lambert—Beer's law for our substrates was ascertained by running spectra of mixtures of cellulose containing known amount of the respective acid. For all acids studied a linear dependence has been found between the actual amount of the added acid and that calculated according to the Lambert—Beer's law, taking into account the absorbancy at λ_{max} of the mixtures and the weight absorption coefficient of the corresponding acid (Fig. 2).

Assuming that the cadoxene solutions of the esters have the same spectral properties as the cellulose—acid mixtures, the spectral data found for the acids were further used for the calculations of DS of the esters. The spectra of esters with



Fig. 1. Ultraviolet absorption spectra of: a)
2-furoic acid; b) 2-furoylcellulose (DS 2.22);
c) cellobiose; d) cellulose; e) 3-(2-furyl)acrylic
acid; f) 3-(2-furyl)acryloylcellulose (DS 1.35);
g) 3,5-dinitrobenzoic acid; h) 3,5-dinitrobenzoylcellulose (DS 0.186).



Fig. 2. The amount of the acids added to cellulose vs. that found by calculation from the spectral data. ○ 2-Furoic acid; □ 3-(2-furyl)acrylic acid;

 \triangle 3,5-dinitrobenzoic acid.

the known DS were measured and, using the weight absorption coefficient of the corresponding acid at the characteristic wavelength, the DS was calculated as follows. When the number of moles of the acid in the ester $X = A/a_w M_{acid}$, and the number of moles of cellulose

$$Y = \frac{c - \frac{A}{a_{w}} \left(\frac{M_{\text{acid}} - 17.008}{M_{\text{acid}}}\right)}{M_{\text{cell.}}},$$

then the degree of substitution

$$DS = \frac{X}{Y} = \frac{A \ M_{cell.}}{c \ a_{w} \ M_{acid} - A(M_{acid} - 17.008)} ,$$

where A is the absorbancy of the ester of a molecular weight $M_{cell.}$ at the concentration $c [g dm^{-3}]$, a_w is the weight absorption coefficient of the corresponding acid at $\lambda_{max} [dm^3 g^{-1} cm^{-1}]$, and M_{acid} is the molecular weight of the respective acid. For mixed cellulose esters and model saccharide derivatives the molecular weight without the acyl residue is used in these calculations.

From the data in Table 1 a very good agreement can be seen between the DS calculated according to the above equation and that found from the weight increments. This holds for 2-furoyl-, 2-furoylacetyl-, and 3,5dinitrobenzoylcellulose well for methyl 2,3,4,6-tetra-O-(2as as -furoyl)- α -D-glucopyranoside and octa-O-(2-furoyl)cellobiose. When studying the DP of cellulose phenylosazones Cromie and Blair [17] used cellobiose phenylosazone as a model compound and found it not suitable owing to its low absorbancy and also because cellulose itself absorbed in the region of the absorbancy of the phenylosazone. In our case the cellobiose weight absorbancy coefficient (Fig. 1) is virtually negligible when compared with the a_{w} of octa-O-(2-furoyl)cellobiose and, thus, the method is well suitable for the DS determination.

Anomalous behaviour was found for cadoxene solutions of 3-(2-furyl)acryloyl-cellulose and the method proved to be not suitable for the DS determinations in the whole range of DS. Good areement between the calculated DS and those found from the weight increments were obtained in the range of low DS (~0.04) whereas in the range of higher DS the calculated values were somewhat lower. Therefore this ester was further examined. The spectrum of a cadoxene solution of 3-(2-furyl)acrylic acid remaining stable during two days indicated that the acid was stable in this solution. The corresponding cellulose ester (DS 0.04) readily dissolved in cadoxene and no difficulties were encountered during the DS determination: a sample of this ester with DS 0.4 was also well soluble, the found DS value, however, was lower than that determined in an independent way. Esters

| Material | DS based on weight increment | λ _{max} nm | cg dm ⁻³ ·10 ² | A | $dm^3g^{-1}cm^{-1}$ | <i>M</i> acid | DS calculated from the spectral data |
|---|------------------------------------|------------------------|--------------------------------------|----------------------------------|---------------------|------------------|--|
| | 0.70 | | 2.670 1.525 | 0.293 0.498 | | | 0.67 0.72 |
| | 0.85 | | 2.000 1.568 | 0.741 0.623 | | | 0.80 0.88 |
| 2-Furoylcellulose | 2.22 | 245 | 0.734 0.426 | 0.485 0.275 | 98.32 | 112.08 | 2.25 2.14 |
| | 1.06 | | 3.016 1.800 | 1.352 0.785 | | | 1.07 1.02 |
| 2-Furoyl _(DS1.06) acetyl _(DS1.91) - cellulose | 1.06 | 245 | 2.575 | 0.830 | 98.32 | 112.08 | 0.98* |
| Octa-O-(2-furoyl)cellobiose | 8.00 ^v | 245 | 0.610 | 0.487 | 98.32 | 112.08 | 7.93** |
| Methyl 2,3,4,6-tetra-O-(2-furoyl)- -a-D-glucopyranoside 3,5-Dinitrobenzoylcellulose | 4.00 ^y 0.186 0.04 | 245 335 | 1.390 1.500 6.150 4.860 | 1.052 0.295 0.260 0.233 | 98.32 92.49 | 112.08 212.12 | 3.84*** 0.201 0.038 0.043 |
| 3-(2-Furyl)acryloylcellulose | 0.42 0.68 1.35 | 295 | 1.420 1.220 1.350 3.150 | 0.398 0.370 0.420 0.812 | 145.50 | 138.11 | 0.27 0.30 0.31 0.24 |
| · | 1.62 | | 0.938 0.948 | 0.691 0.705 | | | 1.07 , 1.08 |

Table 1. Spectral data and DS of cellulose esters and model carbohydrate derivatives

y) Theoretical values; * $M_{cell.}$ 242.21; ** $M_{cell.}$ 342.30; *** $M_{cell.}$ 194.19.

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of still higher DS dissolved less readily, e.g. time required for complete dissolution of samples with DS 0.68 and 1.35 was 21 and 70 hrs, respectively, and the DS calculated according to the spectral data were considerably lower. The spectrum of solution of 3-(2-furyl)acryloylcellulose was therefore taken again 24, 72, and 96 hrs after dissolution and a decrease of the band intensity from the original value 21.78 dm³ g⁻¹ cm⁻¹ to 20.10, 18.40, and 17.40 dm³ g⁻¹ cm⁻¹, respectively, was observed together with the appearance of a shoulder at ~ 285 nm. Since precautions against the presence of oxygen were not taken in those experiments its effect upon the cadoxene solution of 3-(2-furyl)acryloylcellulose (DS 0.68) was studied in such a way that air was passed through this solution for one, two, and three hours. Under these conditions the band intensity at 295 nm decreased and a new band was observed at 275 nm the intensity of which increased rapidly reaching the value 52 dm³ g⁻¹ cm⁻¹ after 3 hrs. The appearance of the shoulder at 285 nm and of the new band at 275 nm indicated shortening of the conjugated system of the 3-(2-furyl)acryloyl residues by breaking the double bond in the side chain. This could occur due to cross-linking of the 3-(2-furyl)acryloyl residues, similarly to what was observed by u.v. irradiation of 3-(2-furyl)acryloylpoly(vinyl alcohol) [24]. Moreover, grafting copolymerization and oxidation by air oxygen could also occur. The decreased solubility in cadoxene may, possibly, be explained by the course of these reactions.

The studies on 2-furoylacetylcellulose show that the described method makes it possible to determine acyl residues having an absorption at wavelength above 235 nm when other, not interfering, acyl groups are present.

The method for the DS determination of cellulose esters by u.v. spectrometry was elaborated assuming that the behaviour of the solutions of the esters, as far as the spectrometry is concerned, is comparable to that of mixtures of cellulose with the corresponding acid. From this point of view it seemed interesting to ascertain the general principle of the dissolution of cellulose esters in cadoxene. Chemical pulp, the starting material for the preparation of the esters, dissolved rapidly and was completely soluble in cadoxene; its spectrum is shown in Fig. 1. The esters dissolved much more slowly. It is known that the formation of a cellulose-cadoxene complex, with which the process of the dissolution of cellulose in cadoxene is associated, requires free hydroxyl groups at C-2 and C-3 of the D-glucose units [25]. We have investigated the effect of cadoxene on 2-furoylcellulose (DS 1.06) and 3,5-dinitrobenzoylcellulose (DS 0.186) during 60 and 80 min, respectively. After the acyl derivatives were treated with cadoxene for the time indicated, cadoxene was decomposed with dilute hydrochloric acid, the separated product was isolated, redissolved in cadoxene and the DS was calculated from the spectral data obtained on such a regenerated sample. It follows from the found decrease of the DS (Table 2) that cadoxene has a strong deacylating effect upon cellulose esters.

Table 2

| | 200 10 10 1 | | | |
|--|-------------|-------|--------------------------|-------|
| Material | Time min | Α | с g dm ⁻³ | DS |
| | 5 | 0.497 | 1.283×10^{-2} | 0.885 |
| | 10 | 0.848 | 2.530×10^{-2} | 0.693 |
| | 15 | 0.940 | 3.601×10^{-2} | 0.520 |
| 2-Furoylcellulose (DS 1.06) | 20 | 0.364 | 1.639×10^{-2} | 0.410 |
| 2 - | 30 | 0.508 | 3.299×10^{-2} | 0.226 |
| | 60 | 0.523 | 7.748 × 10 ⁻² | 0.106 |
| | 3 | 0.416 | 5.8 $\times 10^{-4}$ | 0.063 |
| | 10 | 0.277 | 5.4 $\times 10^{-4}$ | 0.044 |
| 3,5-Dinitrobenzoylcellulose (DS 0.186) | 20 | 0.162 | 6.3 $\times 10^{-4}$ | 0.021 |
| <i>H</i> 00 | 40 | 0.105 | 11.5×10^{-4} | 0.007 |
| | 80 | 0.028 | 14.5×10^{-4} | 0.001 |

Deacylation of cellulose esters affected by cadoxene

The dissolution of cellulose esters in cadoxene results in deacylation and subsequent formation of a cadoxene—cellulose complex. The esters are virtually completely deacylated and during the spectral measurements the resulting cadoxene solution behaves as a mixture of cellulose with the respective acid. The fact that the esters only slowly dissolve in cadoxene, although the main portion of the acyl residues is liberated relatively rapidly, remains unexplained.

Deacylation of cellulose esters by cadoxene occurs under conditions milder than are those applied when the DS is being determined by saponification with aqueous sodium hydroxide. Under the latter conditions unwanted decomposition often accompanies the process of deacylation, as a result of the excess of the alkali applied, this being an important drawback when less stable cellulose esters, such as those of the furan family, are the substrates. The DS found for 2-furoylcellulose determined by saponification with aqueous sodium hydroxide was above the theoretically possible value [26]. Therefore, our DS values for 2-furoylcellulose are based upon either the weight increments or the content of the double bonds. Another advantage in the determination of DS by spectroscopy lies in the fact that the separation of the acids from the heterogeneous mixture with cellulose fibres, normally required when the determination is done with aqueous alkali, is not necessary.

Infrared spectra served as a useful complementary information in the present study showing the presence or absence of the bands characteristic of the respective functional groups. The sample of 2-furoylcellulose (DS 1.06) showed bands corresponding [19, 20] to the 2-furoyl residues, 3-(2-furyl)acryloylcellulose



Fig. 3. Infrared absorption spectra of: a) 3,5-dinitrobenzoylcellulose (DS 0.186); b) 3,5-dinitrobenzoylcellulose recovered from its cadoxene solution (DS 0.001).

(DS 1.35) showed the same bands as found for samples of 3-(2-furyl)-acryloylpoly(vinyl alcohol) [24], 3,5-dinitrobenzoylcellulose (DS 0.186; Fig. 3) showed bands at 3105 (C—H), 1750 (C=O), 1648 (C=C), 1557 (NO₂), and at 1352 cm⁻¹ (NO₂).

The spectra of the material recovered from the cadoxene solutions of cellulose esters showed no bands characteristic of the acyl residues which further supports the deacylation effect of cadoxene upon acyl derivatives of cellulose.

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