Polymer Bulletin 28, 697–702 (1992)

Polymer Bulletin

On the polarity and donor-acceptor-properties of polysaccharides

I. Investigations on the acceptor properties of cellulose acetates by means of the solvatochromic technique

S. Spange, T. Heinze, and D. Klemm*

Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University Jena, Humboldtstrasse 10, O-6900 Jena, Federal Republic of Germany

SUMMARY

Acidic parameters according to the GUTMANN's acceptor numbers (AN) of cellulose acetates and unmodified cellulose have been determined by means of the negatively solvatochromic probe dye Fe(phen)$_2$(CN)$_2$. Unmodified cellulose possesses a relatively high acceptor strength due to cooperative hydrogen bonds while increasing acetate contents in the polymer chain lower the acceptor strength. The dependence of AN on the acetate content can be used to estimate the degree of substitution (DS). Pecularities in the substitution interval (DS = 0 to DS = 1.5)are discussed.

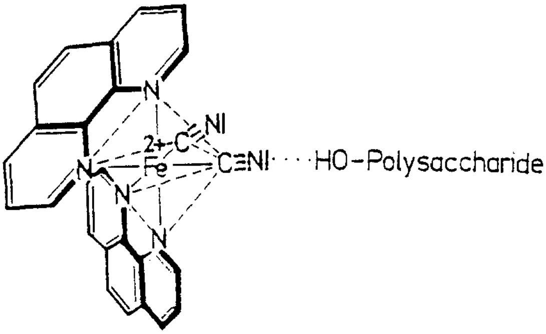
INTRODUCTION

Recently, simple coordination models describing the mechanism of dissolving of unmodified cellulose have taken into account donor-acceptor interactions considering hydrogen bonds /1,2/. Unfortunately, the determination of primary donor numbers as well as of primary acceptor numbers of solid surfaces, polymer films or plugs is not possible by calorimetric and spectroscopic techniques, respectively. The required techniques are exclusively defined for homogeneous solutions /3/. Thus, acceptor and donor parameters of various polysaccharides failed /1/.

However, the application of correlation analysis /4/ allows the determination of secondary acceptor number by means of the solvatochromic iron complex: cis-dicyano-bis /1, 10/ phenanthroline ferric II [Fe(phen)$_2$(CN)$_2$] /5-8/. The visible absorption band of Fe(phen)$_2$(CN)$_2$ is attributed to a intramolecular metal-ligand charge-transfer transition $3d$-π^* (MLCT)/9, 10/. Both, increasing polarity of the surrounding media and enhanced acceptor attack upon the cyano groups of the complex cause bathochromic shifts of the long wave UV-VIS maxima as demonstrated in scheme 1:

---

*Corresponding author



The outstanding negative solvatochromic behaviour of $Fe(phen)_2(CN)_2$ complex offers special applications in analytical chemistry /7, 11/.

The acceptor numbers of GUTMANN /3, 8/ correlate well with the absorption of $Fe(phen)_2(CN)_2$ as reported by several authors /3-8/ (eq. 1).

$$AN = 0.01298\,\tilde{\nu}_{max}(MLCT)\ [cm^{-1}] - 195.8,\ r = 0.993 \quad (1)$$

This paper is to demonstrate the application of $Fe(phen)_2(CN)_2$ for the determination of both acceptor properties and polarity of cellulose acetates and cellulose.

EXPERIMENTAL

Samples

Cellulose beech sulfit pulp (Heweten) sheets were ground before use. Bead cellulose (Leipziger Arzneimittelwerk, O-7050 Leipzig) in water suspension was dehydrated by a stepwise solvent exchange (water-ethanol-acetone-dichloromethane).
Cellulose acetates, with a degree of substitution (DS) = 2.8 and 2.5, resp. were commercial products (Eilenburger Chemiewerke, O-7280 Eilenburg). Cellulose acetate with a DS = 0.8 was kindly provided by Dr. Hoheisel, Kalle AG Wiesbaden.
Other cellulose acetates (DS = 2.0, 1.8) were synthesized by hydrolysis of a commercial cellulose acetate with DS = 2.9 in glacial acetic acid/hydrochloric acid mixture within 30 and 35 h, resp.. The DS values were determined by the alkali saponification method /12/.

Preparation of the dye - probes

The adsorption of $Fe(phen)_2(CN)_2$ onto cellulose and cellulose acetates, resp. was carried out in 1,2-dichloroethane or dichloromethane, resp.(blue solution). The $Fe(phen)_2(CN)_2$ cellulose plugs (red...violett) were dried carefully in vacuum and measured as a ground powder by means of the reflectance technique or as transparent films using a SPECORD M40 spectrometer (CARL ZEISS Jena).

RESULTS AND DISCUSSION

Some representative UV spectra of $Fe(phen)_2(CN)_2$ being both chemically adsorbed onto cellulose derivatives and included into transparent films, resp. , are shown in Fig. 1.

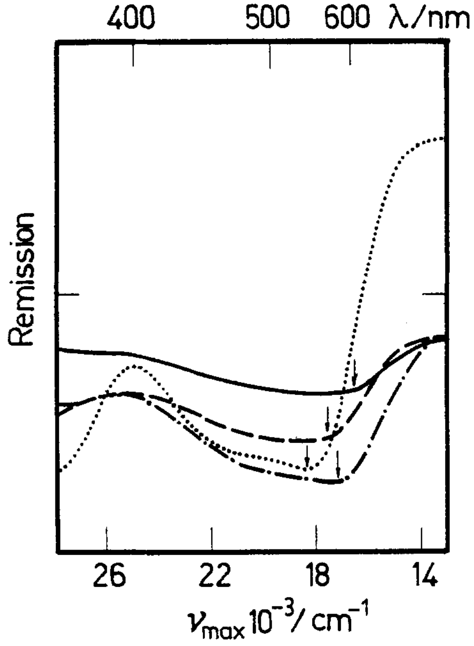


Figure 1 Qualitative UV-VIS reflectance spectra of $Fe(phen)_2(CN)_2$ adsorbed at cellulose acetates. The arrows indicate the relevant maxima to determine the acceptor number .... cellulose, ---- DS=2.0, -.-.- DS=2.5, ——— 2.8

It is obvious, that increasing acetate content in various cellulose acetates shifts the visible MLCT absorption to higher wave length (lower energy) due to the disturbance of the polysaccharide OH...NC-$Fe(phen)_2CN$ coordination by neighbouring acetate groups.
A similar behaviour was observed for grafted silica derivatives where enhanced conversion of neighbouring silanols

drastically changes the adequate $Fe(phen)_2(CN)_2$ absorption /7, 11/. The dependence of the MLCT absorption of $Fe(phen)_2(CN)_2$ on the degree of acetate substitution (DS) is shown in Fig. 2.

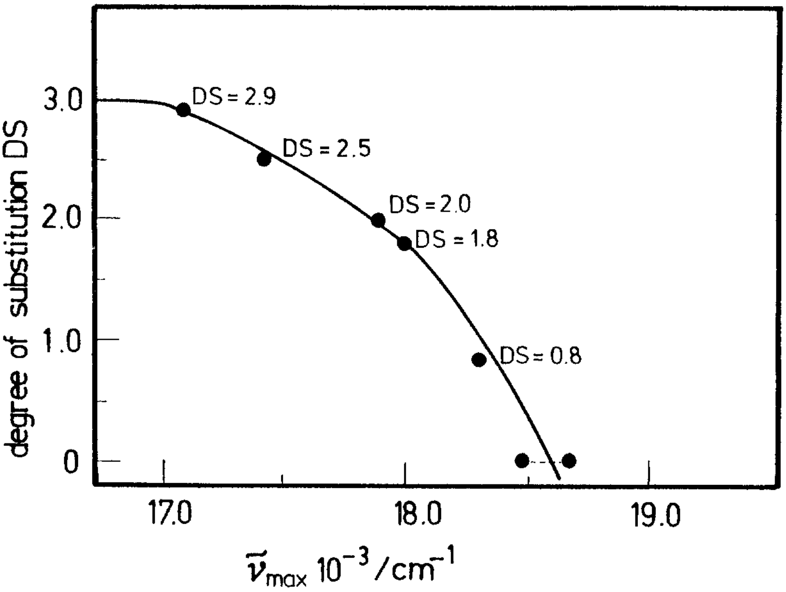


Figure 2 Dependence of the degree of substitution of several cellulose acetates on the respective MLCT absorption of $Fe(phen)_2(CN)_2$

The plots allow the quantitative determination of the DS, mainly in the interval from DS = 3 to DS = 1.5. The validity of these plots points at a statistical contribution of the acetate groups. Disadvantageously, low content of acetate or any other groups causes the polymer chain to become formally a block copolymer.
This case the observed absorption of $Fe(phen)_2(CN)_2$ is attributed to media influences of both cellulose and cellulose acetate blocks. Thus, broad absorptions due to superimposing of chemically differntly bonded $Fe(phen)_2(CN)_2$ are observed. Almost the same behaviour is found for mixtures (blends) of pure cellulose and cellulose acetate (DS 3) as well as for blends of polyvinylacetate and polyacrylic acid /13/.

However, in the interval 3 > DS > 1.5 the iron complex $Fe(phen)_2(CN)_2$ is favoured in a region which is mainly relevant for technical applications.
The classification of cellulose derivatives relating to the acceptor scale of GUTMANN in comparison to model compounds is shown in Figure 3.

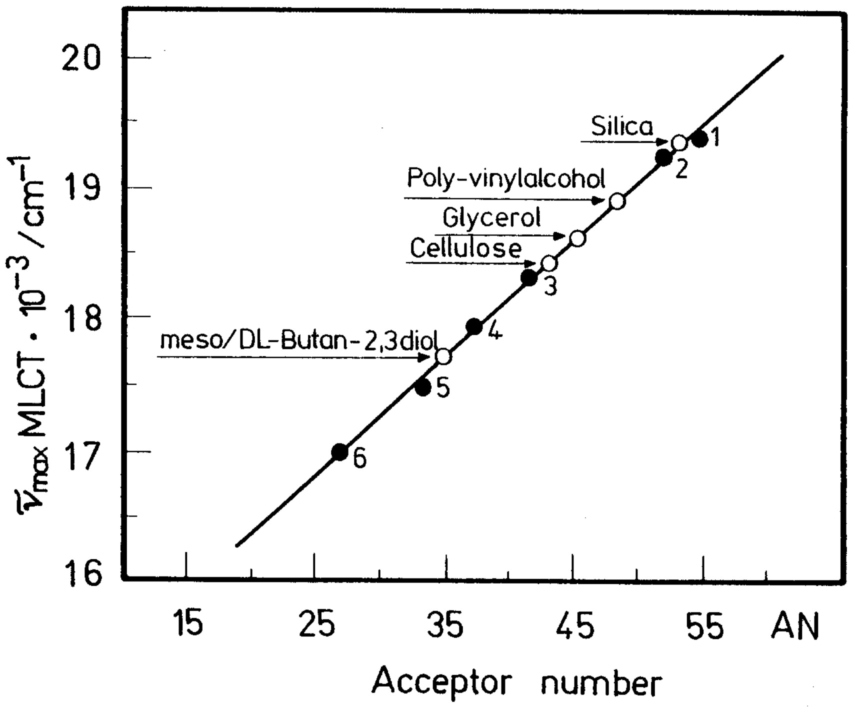


Figure 3 Graphical search for cellulose acceptor properties among alcohols and inorganic solids (1=water, 2= 2,2,2-trifluorethanol, 3=methanol, 4=ethanol, 5=propan-2-ol, 6=tert.butanol)

The acceptor strength of unmodified cellulose approaches that of model compounds such as ethane-1,2-diol or glycerol /5/, whereas the acceptor strength of cellulose acetate (DS · 3.0, AN = 25.2) is close to tert. butanol (AN = 27.5). Surprisingly, unmodified cellulose possesses acceptor properties, which are stronger than expected in comparison to similar alcohols like 2,3-butandiols. A comparison of cellulose with other solids and acidic compounds of similar acceptor number is shown in Table 1.

Solvent combinations being applicable for dissolving of unmodified cellulose particularly possess similar acceptor properties /1,2/. This indicates that donor - acceptor effects are well suited to explain the interactions of the substituents of cellulose with both each other and surrounding solvents.

Table 1 Comparison of secondary AN of cellulose with compounds of similar acceptor properties obtained by means of the probe dye $Fe(phen)_2(CN)_2$

Compound	AN	Condition	Reference
aerosil[a]	49.1	from $C_2H_4Cl_2$, dried at 423 K	/7/
cellulose[b]	44.4	from CH_2Cl_2, via solvent exchange	this work
cellulose[c]	46.5	from $C_2H_4Cl_2$, without drying	this work
alumina-C[d]	47.5	from $C_2H_4Cl_2$, after drying	/11/
3-methylphenol	43.4	in $C_2H_4Cl_2$, 10 cg/g solvent	/5/
N-Methyl-pyridinium	45.1	in $C_2H_4Cl_2$, $B(C_6H_5)_4^-$	/14/

[a] from DEGUSSA, BET = 278 $m^2\ g^{-1}$

[b] never dried bead cellulose

[c] beech sulfit pulp ("Heweten")

[d] from DEGUSSA, BET = 170 m^2 g

REFERENCES

/1/ S.M. Hudson, J.A. Cuculo, J. Macromol. Sci., Rev. Makromol. Chem. C 18, (1) (1980) 1-82
/2/ W. Berger, M. Keck, Do Van Sang, B. Philipp, Z. Phys. Chem. (Leipzig) 266, (1985) 436
/3/ V. Gutmann, Electrochim. Acta, 21 (1976) 661
/4/ Chr. Reichardt, "Solvents and Solvent Effects in Organic Chemistry" sec. Ed. VCH Verlagsgesellschaft Weinheim 1988
/5/ S. Spange, H. Meißner, H. Hotzel, G. Heublein, Z. Chem. 21, (1984) 258
/6/ S. Spange, M. Lauterbach, A.K. Gyra, Chr. Reichardt, Liebigs. Ann. 1991, 323
/7/ S. Spange, P. Hortschansky, A. Ulbricht, G. Heublein, Z. Chem. 27, (1987) 207
/8/ R.W. Soukup, R. Schmid, J. Chem. Educ. 62, (1985) 459
/9/ A. Al-Alousy, J. Burgess, Inorg. Chim. Acta 169, (1990) 167
/10/ J. Burgess, Spectrochimica Acta, Part A 26, (1970) 1369
/11/ S. Spange, P. Hortschansky, G. Heublein, Acta Polymerica 40, (1989) 602
/12/ Y.-I. Shimizu, J. Hayaski, Cellulose Chem. Technol. 23, (1989) 661
/13/ S. Spange, B. Heublein, M. Markloff, G. Heublein, Z. Chem. 28 (1988) 438
/14/ S. Spange, G. Heublein, Z. Chem. 29 (1989) 143

Accepted April 14, 1992 C