Polymer Bulletin 5, 399–406 (1981)

Polymer Bulletin

^{13}C- and ^{23}Na-NMR Investigations on Alkali Cellulose

J. Kunze[1], A. Ebert[2], B. Schröter[3], K. Frigge[1] and B. Philipp[1]

[1] Akademie der Wissenschaften der DDR, Institut für Polymerenchemie, Kantstrasse 55,
1530 Teltow, German Democratic Republic

[2] Technische Hochschule „Carl Schorlemmer" Merseburg, Sektion Physik, 4200 Merseburg,
German Democratic Republic

[3] Friedrich-Schiller-Universität Jena, Sektion Physik, 6900 Jena, Max-Wien-Platz 1,
German Democratic Republic

Presented at the 22nd Microsymposium, "Characterization of Structure and Dynamics of Macromolecular Systems by NMR Methods", Prague, CSSR, July 20–23, 1981

Summary

Solid state ^{23}Na- and ^{13}C-NMR spectra of alkali cellulose are presented as a function of NaOH-concentration of the steeping lye, steeping temperature and amount of adhering lye (press factor). Results are discussed with regard to "chemical binding" of NaOH to the cellulose chain in the system cellulose/NaOH/H_2O.

Introduction

The interaction of cellulose with aqueous solutions of NaOH has been known for a long time and is one of the most important technical reactions of cellulose. Depending on NaOH-concentration and temperature, alkali celluloses (soda celluloses) of different lattice modifications are formed. In spite of a large number of experimental investigations on this topic, mechanism of formation and structure of alkali celluloses are not completely known. Further progress in this field depends largely on progress in analytical methods for investigating this highly swollen system of cellulose, NaOH and water. In solving analogous problems, ^{13}C- and ^{23}Na-NMR measurements in liquids and solids have proved to be efficient analytical tools. This article is concerned with some results on alkali cellulose obtained with these NMR-methods.

Experimental

Bleached and scoured cotton linters ($DP_{Cu} \approx 1600$) were treated with aqueous NaOH-solution in the range of concentration from 3 to 45 weight % at a temperature of 298 K. Subsequently, the adhering lye was removed to a varying extent by pressing. The alkali cellulose obtained was sealed in a polyethylene foil for further investigation.

^{23}Na-NMR spectra were obtained with an instrument SXP 4-100 (Bruker) by using the PFT-technique and a resonance frequency of 23.8076 MHz (90° pulses, pulse duration ca. 6 μs).

The ^{13}C/CP/DD/MASS/NMR spectra were recorded with a pulse spectrometer operating at 15.087 MHz. The spectra were obtained by use of a single coil. The sample was rotated around

0170-0839/81/0005/0399/$01.60

an axis at 54.7° ± 0.1° with respect to the static field. The spinning rate was ca. 2 kHz.

^{13}C-NMR spectra of the system cellobiose/NaOH/D_2O were obtained with a Bruker-spectrometer HX-90 operating at 22.635 MHz.

Results of ^{23}Na-NMR spectroscopy of alkali cellulose

Due to a spin number of 3/2 sodium-23 has an electric quadrupole moment $e \times Q$. If an asymmetric charge distribution in the coordination sphere of the Na^+-ion provokes a gradient in the electric field $e \times q$, this gradient interacts with the sodium nucleus. This interaction is characterized by the quadrupole coupling constant: $\chi = (eQeq)/h$.

The linewidth of the ^{23}Na-line in liquids is given according to the equation 1 (extreme motional narrowing) /3/:

$$\Delta\nu_{\frac{1}{2}} = (2\pi/5)\ (e^2qQ/h)^2\ \tau_c \qquad (1)$$

where τ_c is the correlation time of the quadrupole interaction.

The chemical shift of the ^{23}Na-line is determined by the donicity of the environment of the sodium nucleus. Increasing donor strength results in a line shift to lower field strength. In the system cellulose/NaOH/water two states of the Na^+-ion may be assumed: the state of an Na^+-ion closely associated to the cellulose and the state of an Na^+-ion in the volume phase of the lye. These two states lead to a different linewidth. If a fast exchange between the two binding states of Na^+ can occour, a single line with an average width according to equation 2 is obtained:

$$(\Delta\nu_{\frac{1}{2}})_{exp} = (\Delta\nu_{\frac{1}{2}})_{I}\ X_I + (\Delta\nu_{\frac{1}{2}})_{II}\ X_{II} \qquad (2)$$

where X are the mole fractions; I, II are the binding states.

In Figure 1 the ^{23}Na-NMR spectra of alkali cellulose samples are shown. These were prepared by steeping with 18 weight % NaOH-solution and pressing to a different degree, resulting in a different loading of the sample with the steeping lye. Generally, the linewidth increases from "a" to "g" when the relative amount of the lye decreases in the same order. These results can be interpreted by equation 2, as here the second term of this equation can be neglected due to the large excess of the adhering lye. In samples "e", "f", "g" (Fig.1) the adhering amount of steeping lye is very small. The spectrum is determined by the Na-ions associated with the cellulose and showing only a low mobility. Additionally, a trend to line splitting can be observed. This may be interpreted as an immobilization of the Na^+-ions and an inhibition of the exchange between the two binding states. Additionally, some kind of anisotropy of relaxation within the solid phase may be assumed.

With increasing NaOH-concentration in the steeping lye an increase in linewidth has been observed (Fig. 2). Also, a more distinct line splitting as compared to Figure 1 has been found. These results indicate an increasing amount of Na^+-ions firmly bound to the cellulose at higher concentrations of NaOH in the steeping lye. Also, with decreasing steeping temperature, a broadening and a more distinct splitting of the line result (Fig. 3). This may be due to a decrease in the rate of exchange between "associated" and "free" Na^+-ions.

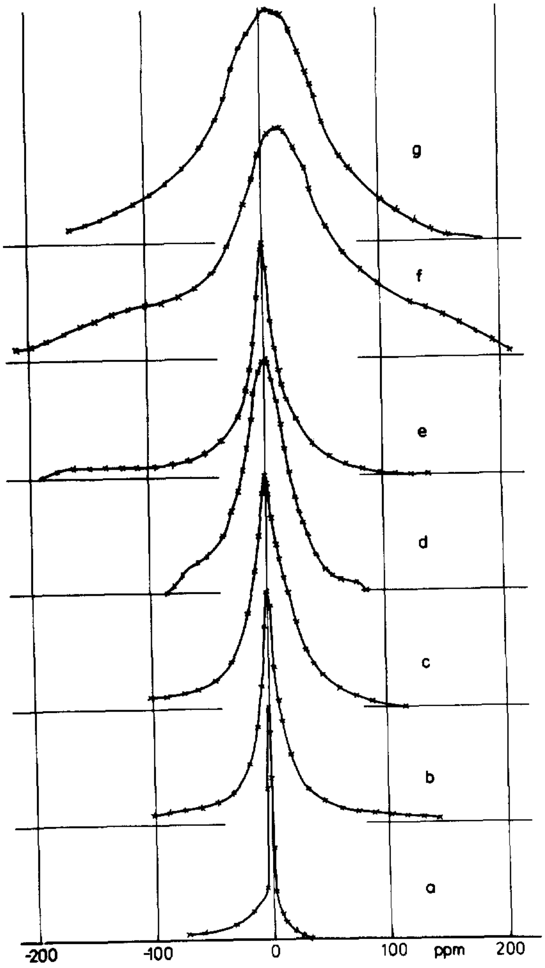

Figure 1.
Relationship between the ^{23}Na-NMR spectrum and the amount of solution taken up by cellulose. δvalues (ppm) relative to an aqueous solution of NaCl = 0; concentration of NaOH: 18 weight %

a - 311.1 g lye
b - 248.4 g lye
c - 216.0 g lye
d - 213.1 g lye
e - 195.9 g lye
f - 107.5 g lye
g - 80.8 g lye

(relative to 100g cellulose)

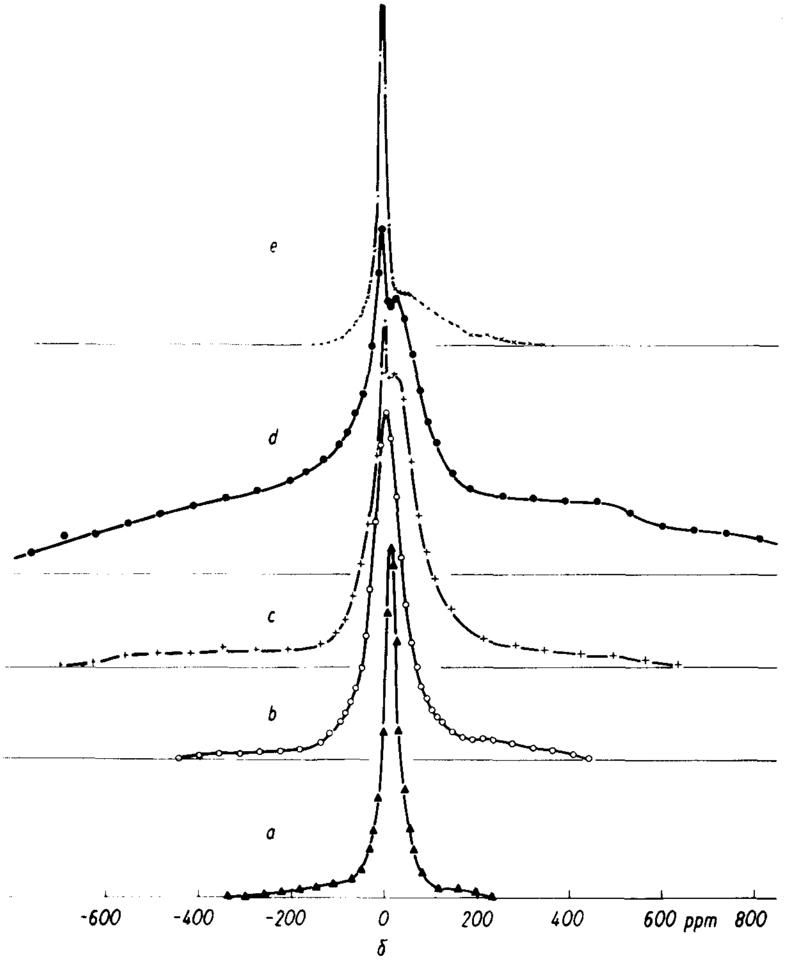

Figure 2. ^{23}Na-NMR spectra of alkali cellulose prepared by various concentrations of alkali. δ values (ppm) relative to an aqueous solution of NaCl = 0. Concentrations of sodium and amount of solution taken up by cellulose:

a - 7 weight % (53.5 g lye)
b - 18 " " (131.8 g ")
c - 33 " " (185.1 g ")
d - 35 " " (181.8 g ")
e - 40 " " (222.8 g ")

(relative to 100 g cellulose)

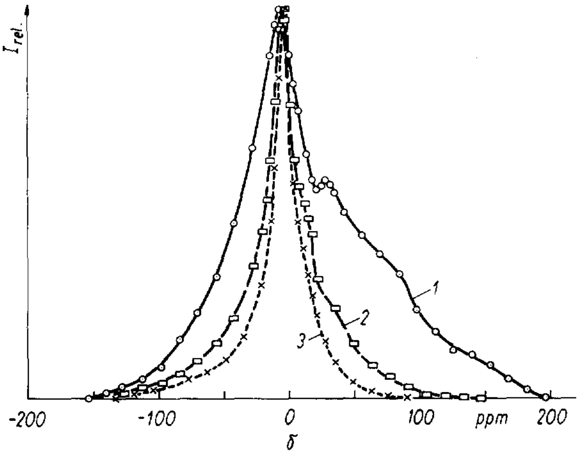

Figure 3. Effect of temperature on the ^{23}Na-NMR spectrum.
Concentration of NaOH: 30 weight %.
Amount of solution taken up by cellulose:
231.6 g lye/100 g cellulose.
Temperature: 1 - 252 K; 2 - 303 K; 3 - 343 K

Results of ^{13}C-NMR spectroscopy with Alkali Cellulose

High-resolution ^{13}C-solid state-NMR may provide information on the interaction of the Na^+-ion or the NaOH ion pair with the different C-atoms of the anhydroglucose unit. In the case of a selective interaction of NaOH with the OH-groups of the anhydroglucose unit, chemical shift and change in linewidth may be different for each line to be associated with appropriate C-atom.

According to ATALLA /1/, already with chemically unmodified cellulose, chemical shifts and in some cases a line splitting was observed as a function of lattice type and state of order of the cellulose sample. Obviously, changes in chain conformation and chain packing exert a rather strong influence on the electronic environment of the different C-atoms. According to our results shown in Figure 4, the ^{13}C-NMR spectrum of cellulose remains unchanged up to a steeping lye concentration of 9 weight %. As shown in Figure 6 /2/ in the same range of concentration no lattice conversion is indicated in the X-ray diffractograms. With steeping lye concentrations above 9 weight % the different lines of the spectrum are shifted and changed in width to a different extent. Changes in susceptibility due to the varying lye concentration can be excluded according to tests with an internal standard. With the sample treated with a steeping lye concentration of 12 weight %, a mixture of cellulose I and soda cellulose I is indicated by the NMR spectrum as well as by the X-ray

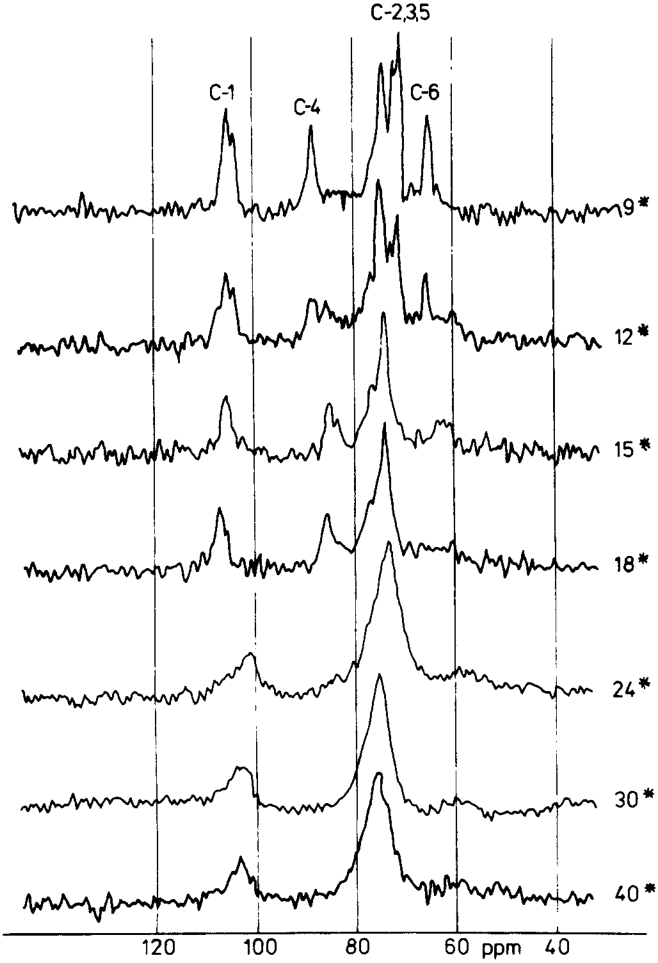

Figure 4. ^{13}C/CP/DD/MASS/NMR spectra of alkali cellulose prepared by various concentration of alkali (chemical shifts in ppm relative to TMS = 0) * indicates the concentration of NaOH (weight %)

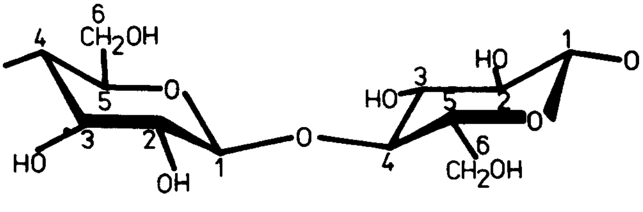

Figure 5. The structure of cellulose

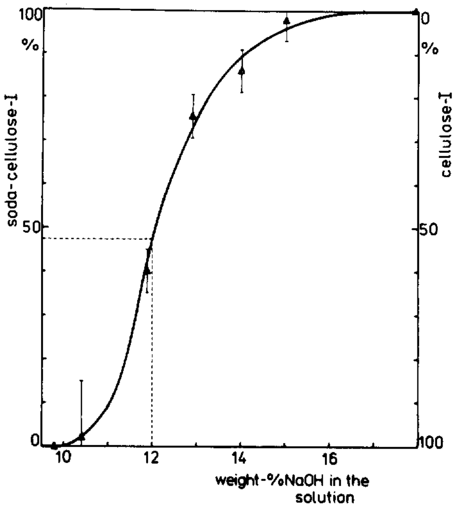

Figure 6.
Lattice conversion as indicated by the X-ray diffractograms /2/ after treatment of cotton linters with aqueous NaOH solutions of different concentrations

diffractogram. A second transition process is observed in the NMR spectrum within the concentration range between 18 and 24 weight %.

Results of ^{13}C-NMR spectroscopy in the cellobiose/NaOH/D$_2$O system

In contrast to the results obtained with alkali cellulose already a low NaOH-concentration of 5 weight % caused a significant change in the ^{13}C-NMR spectrum of the cellobiose in D$_2$O. At a NaOH-concentration higher than 9 weight % the concentration dependence of the ^{13}C-NMR spectrum of the cellobiose solution was rather similar to that found with alkali cellulose (cf. Fig.7).

Conclusions

According to the results presented here, ^{23}Na-NMR and ^{13}C-high-resolution solid-state NMR are efficient methods for a further elucidation of alkali cellulose structures and may be promising also for structural investigations of similar highly swollen polysaccharide systems. By the application of ^{23}Na-NMR data on the state of association of Na$^+$ or NaOH resp. and on the structure of the cellulose moiety are obtained, which are essential for a better understanding of lattice transformations in the mercerization process and of the chemical reactivity of alkali cellulose as an intermediate in the viscose process and in cellulose etherification.

By ^{13}C-NMR, details of interactions between NaOH and the different C-atoms, resp. the different OH-groups of the

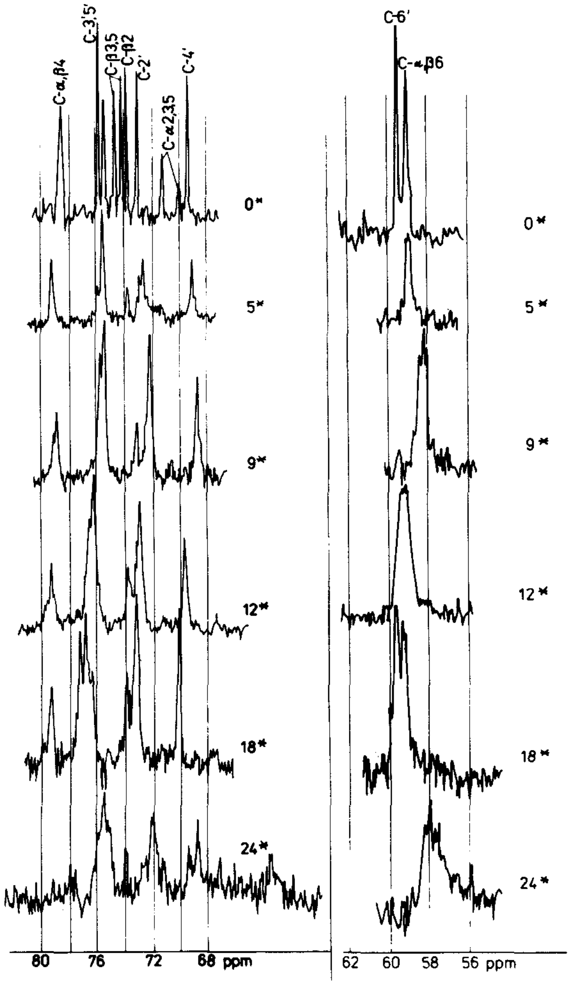

Figure 7.
^{13}C-NMR lines of cellobiose dissolved in caustic soda/heavy water solutions
* indicates the concentration of NaOH (weight %) (chemical shifts in ppm relative to TMS = 0)

anhydroglucose unit can be revealed as well as conformational changes due to this interaction. Concerning the effect of NaOH-concentration, NMR data are consistent with WAXS-diagrams. According to the results of ^{13}C-NMR spectroscopy, an impeding influence of the supermolecular order of cellulose on alkali cellulose formation is evident at an NaOH-concentration < 9 weight %, while above this concentration ^{13}C-NMR spectra of the heterogeneous system "cellulose/NaOH/water" and of the homogeneous system "cellobiose/NaOH/D_2O" show rather similar changes with NaOH-concentration.

References

/1/ ATALLA, R.H. et al.: J. Amer. Chem. Soc. 102, 3249(1980)
/2/ FINK, H.-P. et al.: Acta Polymerica in press
/3/ LASZLO, P.: Angew. Chem. 90, 271 (1978)

Received July 16, 1981, revised August 14, 1981, accepted September 7, 1981