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Adsorption of Polysaccharides on a Calcite Using Spin Labelled Polymers

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Summary

The experimental results given in this paper concern the preparation of spin labelled amylose and amylopectins. These polymers are then used to investigate the adsorption on a calcite dispersed in water. From analysis of the electron spin resonance spectrum, the fractions of monomers involved in trains (p) are deduced ; the dependence of p on the molecular weight of the amylopectins and the molecular structure of the polymers are discussed.

INTRODUCTION

The mechanism of the adsorption of water soluble polymers at a solid interface is still under discussion. The conformation of the polymer in the adsorbed layer has been extensively developed ; it can be suggested from the dependence of the maximum polymer weight Qs adsorbed as a function of its molecular weight : $Qs = KM^c$ in which K and c are two constants (PERKEL and ULLMANN, 1961) ; c equals zero when polymer segments lie on the surface, c equals 1/2 when they form loops and trains in Θ solvent and c = 1 when they are attached on the surface only by one chain end.

EXPERIMENTAL

The amylose is a commercial sample from AVEBE ; it is characterized by 70 % of β-amylolysis. The amylopectin is produced by Société Française des Produits du Maïs ; it is pure at 98 %. The samples are defatted with a solution of $DMSO/CHCl_3$(50/50 V/V), dissolved in DMSO then reprecipitated in methanol before use to increase the solubility in water.
The polysaccharides are eventually partially hydrolyzed in HCl and recovered in methanol after neutralization. All the samples are characterized by their intrinsic viscosity $[\eta]$ ($ml.g^{-1}$) determined in NaOH 1 M.
The viscosity measurements are performed in an automatic Fica viscosimeter using an Ubbelohde capillary (inner diameter : 0.46mm) at 25°C ± 0.05. The isotherms of adsorption are all from Langmuir type and drawn after determination of the equilibrium polymer concentration C in the supernatant by optical rotation measurements at 300 nm.
The rotary power α is determined with a spectropol 1b from Fica in a quartz cell of 5 cm thickness.
The ESR spectra are obtained with a Varian E-104 spectrometer using quartz tube with 1 mm diameter with a temperature controll at 20°C.
The calcite is produced by OMYA (France) ; the average diameter of particles is 3µm ; the total area is 1.8 m^2/g of solid.
The isotherms are established on 100 g/l solid dispersion ; the sediment is recovered by filtration, washed rapidly with water and redispersed in water for ESR determination.

RESULTS AND DISCUSSION

A) Preparation of the spin labelled polysaccharides.

The nitroxyde radical was prepared following OGAWA and Mc CONNEL (1967) ; it is a 4-(2-iodoacetamido)-2,2,6,6-tetramethyl-piperidonoxyl. The substitution on the polysaccharides was performed in DMSO as solvent using sodium hydride to prepare the methylsulfonyl carbanion which is the reactive form (BJORNDAL et al, 1970) (Table I). The yield of the nitroxyde on the polymer is around 50 % compared to the predicted content from stoechiometry of the reaction. The nitroxyde content on the polymer was determined using ESR or UV spectroscopies in DMSO and calibration curves established with the free nitroxyde in DMSO ; the agreement is very good when it is assumed that the extinction coefficient ε^{262} is the same for the nitroxyde free and substituted on the polymer.

TABLE I

Polysaccharides (monomoles)	Anion (moles)	Nitroxyde * (moles)	Degree of labelling
Amylopectin 1.54×10^{-3}	1.25×10^{-4}	1.47×10^{-4}	1 per 28 monomers
Amylopectin 3.08×10^{-3}	1.56×10^{-4}	1.57×10^{-4}	1 per 40 monomers
Amylose 3.08×10^{-3}	3.12×10^{-4}	3.13×10^{-4}	1 per 20 monomers

* Nitroxyde is dissolved in 2 ml DMSO. Total volume of reaction = 12 ml.

The ESR spectrum of the labelled amylose is given in Figure 1 ; at 20°C, the third line is enlarged due to reduced mobility on the polymer ; spectrum A will be used as reference for the "free nitroxyde" in adsorption experiments ; the spectrum B obtained in glycerol/H_2O mixture (75/25) at -65°C will be considered as the bound form

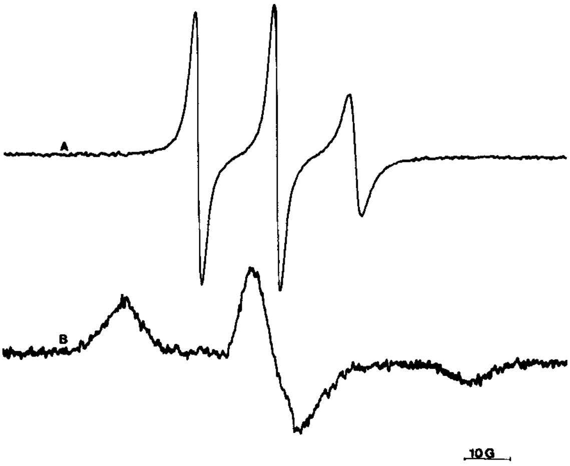

FIGURE 1 : Spectra of labelled amylose (1 $g.l^{-1}$) ; A = in water at 20°C (gain $10 \times 10^2 \times 2.5$) ; B = in glycerol/$H_2O$ mixture (75/25) at -65°C (gain $10 \times 10^2 \times 8$).

B) Adsorption of polysaccharides on calcite.

Unlabelled polymers have been used for isotherms establishment. Their characteristics are given in Table II. From the plateau of the Langmuir isotherms the maximum weight of polymer adsorbed per gram of solid (Qs) are deduced ; considering an area of $25\ A^2$ per monomeric unit, the weight of polymer necessary to recover the solid Q_{max} is 1.9 mg/g ; from this value a degree of coverage Θ is calculated. The ratio between Q_{max} and Qs can be assumed as the maximum value of p, the fraction of monomeric unit in the trains. With amylose, Qs is independent of the molecular weight in favour with a flat attachment ; p is large. In opposite with amylopectin Qs varies with the molecular weight (Figure 2) ; the values extrapolated to $[\eta] \rightarrow 0$ give Q_{max} and then Qs increases. A relation $Qs = K1 + K2\ M^b$ as proposed by PERKEL and ULLMANN (1961) seems to reflect the behaviour of the amylopectins ; it means that low molecular weight are directly bound to the interface and that loops are formed when it increases corresponding to a decrease of p. Labelled polymers prepared from the initial polysaccharides and for which no important decrease in $[\eta]$ was observed after substitution, were used to confirm these results. First, the isotherms were drawn with the labelled polymers (Figure 3) ; a small variation is observed by comparison with the initial polymers ; it may be due to a slight depolymerization. An experimental ESR spectrum obtained on sediment is given in Figure 4 ; it is interprated from recalculated spectra obtained by combination of the two limit forms corresponding to the free nitroxyde (included in loops) and "bound" nitroxyde (immobilized in trains) (Figure 1).

From the figure 1, it is pointed out at the first line (H1) of (A) is unaffected by the bound fraction of nitroxyde ; the second line (H2) is the more affected, so the ratio H2/H1 is directly related to p ; from the calculated spectra, the ratio H2/H1 is determined as a function of the "bound" form yield ; the experimental value of the H2/H1 ratio gives directly the values of p using this calibration curve. Table II

Polysaccharides	Amylopectin					Amylose	
	I	II	III	IV	V	I	II
Time of hydrolysis by HCl (mn)	0	15	30	60	120	0	30
$[\eta]$ ml.g^{-1}	125	109	87	48	26	117	66
Qs mg/g	13 (10)	8	5	3.5 (3.5)	2.6	4 (3.5)	4
Θ	6.7	4.1	2.5	1.8	1.3	2.1	2.1
p from ESR				0.93	-	0.80	-
p from isotherm	0.19	-		0.47		0.47	

( ) Qs obtained with labelled polymer.

The values obtained from ESR determination are larger due to the fact that monomer in the loops near the surface may have a reduced mobility ; the choice of the nitroxyde "bound" spectrum is also questionnable : the nitroxydes in the trains are perhaps not as immobile as at -65°C in water-glycerol mixture ; if the reference spectrum is taken at a higher temperature, the values of p obtained decrease. The same conclusions have been developed previously by ROBB and CLARK et al (1976) and HOMMEL et al (1978).

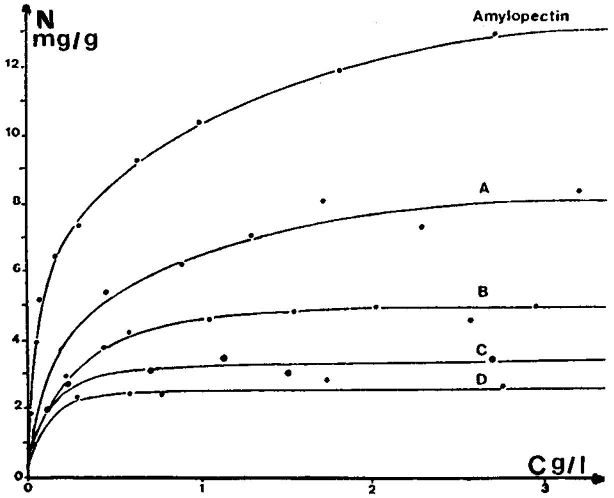

FIGURE 2 :

Adsorption isotherms of amylopectins in water ; dependence with the molecular weight : A,B,C,D are samples partially hydrolyzed in HCl 1 N during 15, 30, 60, 120 mn respectively.

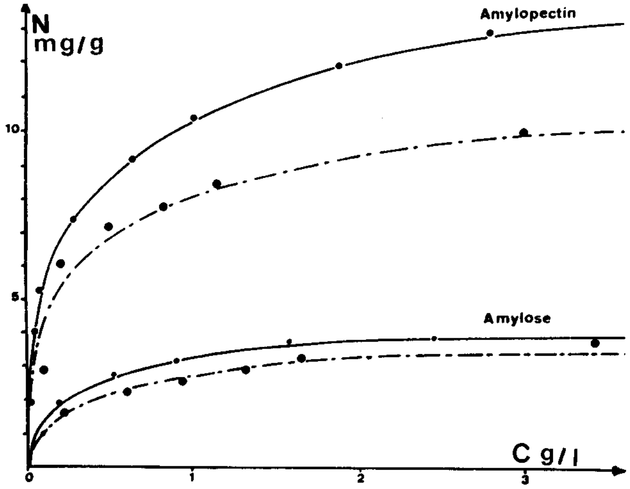

FIGURE 3 :

Adsorption isotherms of unlabelled and labelled amylose and amylopectin.

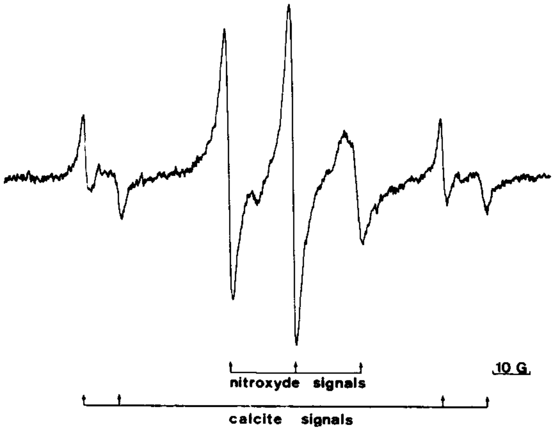

FIGURE 4 :

ESR spectrum on a calcite labelled amylose suspension in water (Q_s = 2.6 mg.g^{-1} ; gain 10 x 10^2 10.

CONCLUSION

In this work, the adsorption of neutral polysaccharides (amylose and amylopectin) on a negatively charged solid (the calcite) was investigated. The results demonstrate that the molecular structure modifies the mechanism of the adsorption : amylopectin forms much more loops i.e. a larger adsorbed layer than amylose. Both experimental methods used confirm this phenomenon.

With amylopectin, the mechanism is modified when the molecular weight decreases and tends to form a flat thin layer on the solid.

The preparation of nitroxyde labelled polysaccharides with controlled nitroxyde content is described ; the analysis of the ESR spectra confirms the conclusions drawn from adsorption isotherms.

REFERENCES

H. BJORNDAL, C.G., HELLERQUIST, B, LINDBERG, B, SVENSSON, S. Angew. Chem. Int. Ed. 9 610 (1970).

A.T. CLARK, I.D. ROBB and R. SMITH. J. Chem. Soc. Faraday I 72, 1489 (1976).

K.K. FOX, I.D. ROBB and R. SMITH. Trans. Faraday Soc. 70, 1186 (1974).

H. HOMMEL, L. FACHINI, A.P. LEGRAND and J. LECOURTIER. Polymer J. 14, 803 (1978).

S. OGAWA and H.M. Mac CONNELL Proc. Nat. Acad. Sci. U.S. 58, 19 (1967).

R. PERKEL and R. ULLMANN. J. Polymer Sci. 54, 127 (1961).

R.D. ROBB and R. SMITH. Eur. Poly. J. 10, 1005 (1974).

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