Theoretical water sorption energies by conformational analysis

Part 2: Amorphous cellulose and the sorption isotherm

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Summary. Values of the sorption energies of single molecules of water on all available sorption sites of amorphous cellulose I have been obtained by conformational analysis. The sorption energies are equated to the total energy (Etot) of interaction between the water molecule and all the atomic groups of the cellulose. Van der Waal, H-bond and electrostatic energies comprised the Etot. The interference of water molecules on two vicinal sorption sites were also obtained and sites in which such interference can occur were identified for amorphous cellulose. Curves relating Etot to percentage equilibrium moisture content are reported as well as exact sorption isotherms constructed as Etot as a function of humidity for the amorphous and crystalline cellulose I. These isotherms were constructed for different relative proportions of amorphous to crystalline cellulose and can be constructed for any of their relative proportions from the isotherms for amorphous-only and crystalline-only cellulose. The sorption energies of the monolayer were all calculated. Curves of energy of sorption of bound water were also obtained by introducing the calculated energy values in equations from already established sorption theories.

Sorption capacities of amorphous and crystalline Cellulose I were calculated and the respective isotherms constructed and discussed from the point of view of existing sorption theories.

Introduction

It is clear from comparative studies of the morphology and the chemistry of amorphous and crystalline cellulose that the two forms of cellulose behave very differently one from the other. This article repeats for amorphous cellulose the calculation of exact values of the energies of sorption of single molecules of water which was carried out for crystalline Celluloses and attempts to correlate the values obtained for the two forms of cellulose to the sorption isotherms.

Experimental

The computer programme and calculation techniques used in Part 5 of this study were used for the work presented in this article (Pizzi et al. 1986).
Discussion

The sorption sites on the helicoidal representation (Pizzi et al. 1986) of the amorphous cellulose have total energies of sorption as indicated in Fig. 1. All the sites appear to be strong sorption sites, except for one of the bridge oxygens, that forming the inter-cellobiose β-glucosidic linkage, which is poorer due to steric hindrance. The high percentage of strong sorption sites is a consequence of the more open structure of amorphous cellulose; it also agrees with the greater adsorptive capabilities experimentally determined for amorphous cellulose. In this respect it must be stressed that as regards sorption characteristics of amorphous

Fig. 1. Exact schematic examples of repetitiveness of sorption energy values on equivalent sites along an eight cellobioses amorphous cellulose chain in the (−49°, −130°)−(−58°, −171°) conformation of minimum total energy