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A. Pizzi[a]; N. J. Eaton[a]
[a] National Timber Research Institute Council for Scientific and Industrial Research, Pretoria, Republic of South Africa

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THE STRUCTURE OF CELLULOSE BY CONFORMATIONAL ANALYSIS. PART 5. THE CELLULOSE II WATER SORPTION ISOTHERM

A. PIZZI and N. J. EATON

National Timber Research Institute
Council for Scientific and Industrial Research
Pretoria 0001, Republic of South Africa

ABSTRACT

Exact values of the sorption energies of single molecules of water on all available sorption sites of crystalline cellulose II have been obtained by conformational analysis. The sorption energies are equated to the total energy (E_{tot}) of interaction between the water molecule and all the suitable atomic groups of the cellulose. E_{tot} is composed of van der Waals, H-bond, and electrostatic energies. The interferences of water molecules on vicinal sorption sites were obtained. Sites in which such interference can occur were identified for crystalline cellulose II. Sorption energy in crystalline cellulose II appears to depend only on the interaction of water with surface sorption sites of the crystal. There appears to be favorable sorption on 1) sites exerting high attractive forces, and 2) sites which are exposed and protrude from the crystal surface. Sites recessed from the crystal surface are generally repulsive due to strong interactions with neighboring groups. All the sorption energies of the "monolayer" were calculated. Very strong sorption sites cannot always form a second layer because of strong steric hindrance from vicinal groups. Sorption capacities of crystalline cellulose II were calculated, and the isotherm of the schematic five chain crystallite used was constructed by theoretical means. The results obtained were briefly compared with those for cellulose I crystallites and amorphous cellulose. The inflection points of the iso-

therm and the variability of Dent's k_1 constant for the water monolayer with relative humidity for the cellulose I and II isotherms were also calculated by theoretical means.

INTRODUCTION

Theoretical determination by conformational analysis of the energies of water sorption on available sites of amorphous cellulose and of cellulose I crystallites have been carried out [1, 2]. The amorphous cellulose/water isotherm obtained [2] may well be helpful in drying calculations and drying models for regenerated cellulose. The high level of crystallinity of regenerated cellulose fibers makes it important to supplement and complete this information by extending the same theoretical approach to the determination of the sorption isotherm of crystalline cellulose II. 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. It is also likely that the different crystallite structures of cellulose I and cellulose II could lead to noticeable differences in the number of sorption sites and in their capability and intensity of sorbing water. In this article the calculation of exact values of the energies of sorption of single molecules of water on sorption sites of crystalline cellulose II is carried out, and the values obtained are correlated with the sorption isotherm of the crystalline portion of regenerated cellulose fibers.

EXPERIMENTAL

The computer program, calculation method, and techniques used were identical to those already reported in the study of crystalline cellulose I and amorphous cellulose [3-5]. The detailed structure of crystalline cellulose II used as a water sorption substrate in this article and the detailed extent of the interatomic forces involved have already been reported [6].

The spatial positions for each molecule of water and its minimum energies (E_{tot}, E_{VdW}, $E_{H\text{-}bond}$, E_{elec}) of interaction with each possible sorption site on the surface of the cellulose II crystallite were calculated by rotating the molecule of water on a sphere according to Diagram 1, in which the three angles, 1, 2, and 3, were simultaneously rotated by 2° over 360°. As a consequence of this, all the possible positions and interactions with all atoms of the 20 glucose residues cellulose crystallite for 2° X 2° of the two hydrogens and oxygen of the water molecule on the surface of their own sphere were calcu-

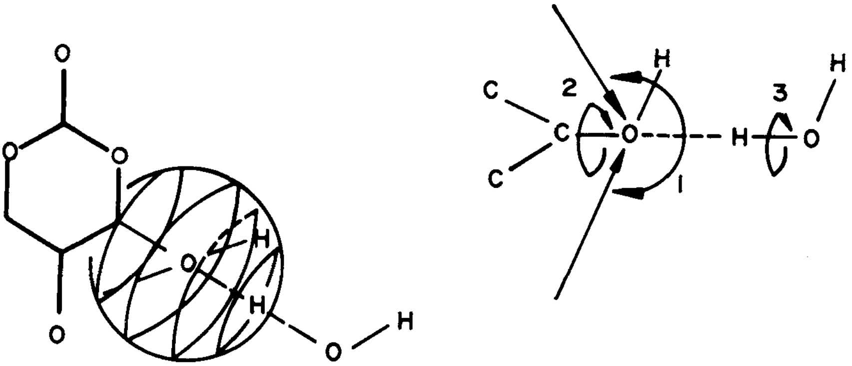


DIAGRAM 1.

lated as well as the relative position of the hydrogen of the hydroxyl group of the sorption site.

This thorough system of examination was obtained (Diagram 2) mathematically by creating an axis orthogonal to C_1C_2 and OC_2, creating an axis parallel to the previous one but centered on the hydroxyl O, positioning H_{W1} and O_W by extending the C_2O axis, extending the $H_{W1}O_W$ axis by 0.2404 Å, moving 0.9294 Å in the direction of the OD_1 axis and positioning H_{W2}, and rotating angles 1, 2, and 3.

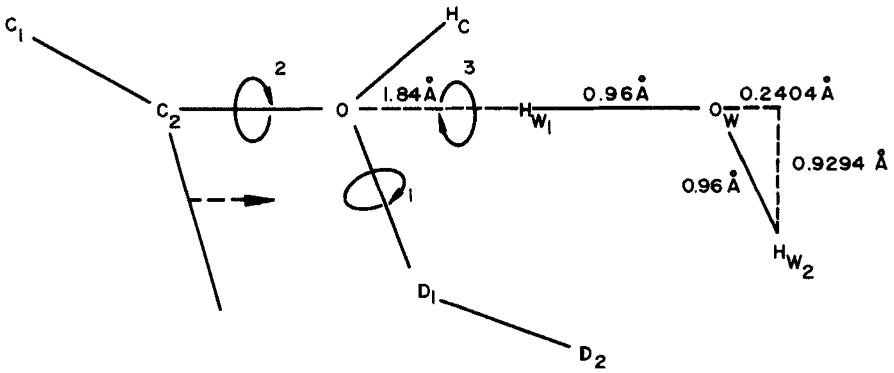
The water sorption isotherms were calculated by Dent's equations:

$$\begin{aligned} m_1 &= m_0 k_1 h/(1 + k_1 h - k_2 h), \\ m &= m_0 k_1 h/(1 - k_2 h)(1 + k_1 h - k_2 h), \end{aligned} \tag{1}$$

where m_1 is the monolayer water sorption, m_0 is the maximum value of water theoretically possible in monolayer sorption (which was available exactly for the first time), h is the relative humidity, and k_1 and k_2 are equilibrium constants related to the binding energies of the primary and secondary water layers. The latter were obtained from the expressions

$$\begin{aligned} E_{tot1} &= -(RT/18) \ln k_1, \\ E_{tot2} &= -(RT/18) \ln k_2, \end{aligned} \tag{2}$$

where E_{tot1} used was the most probable average sorption energy for the



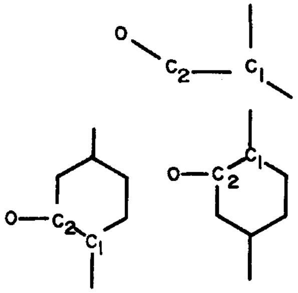


DIAGRAM 2.

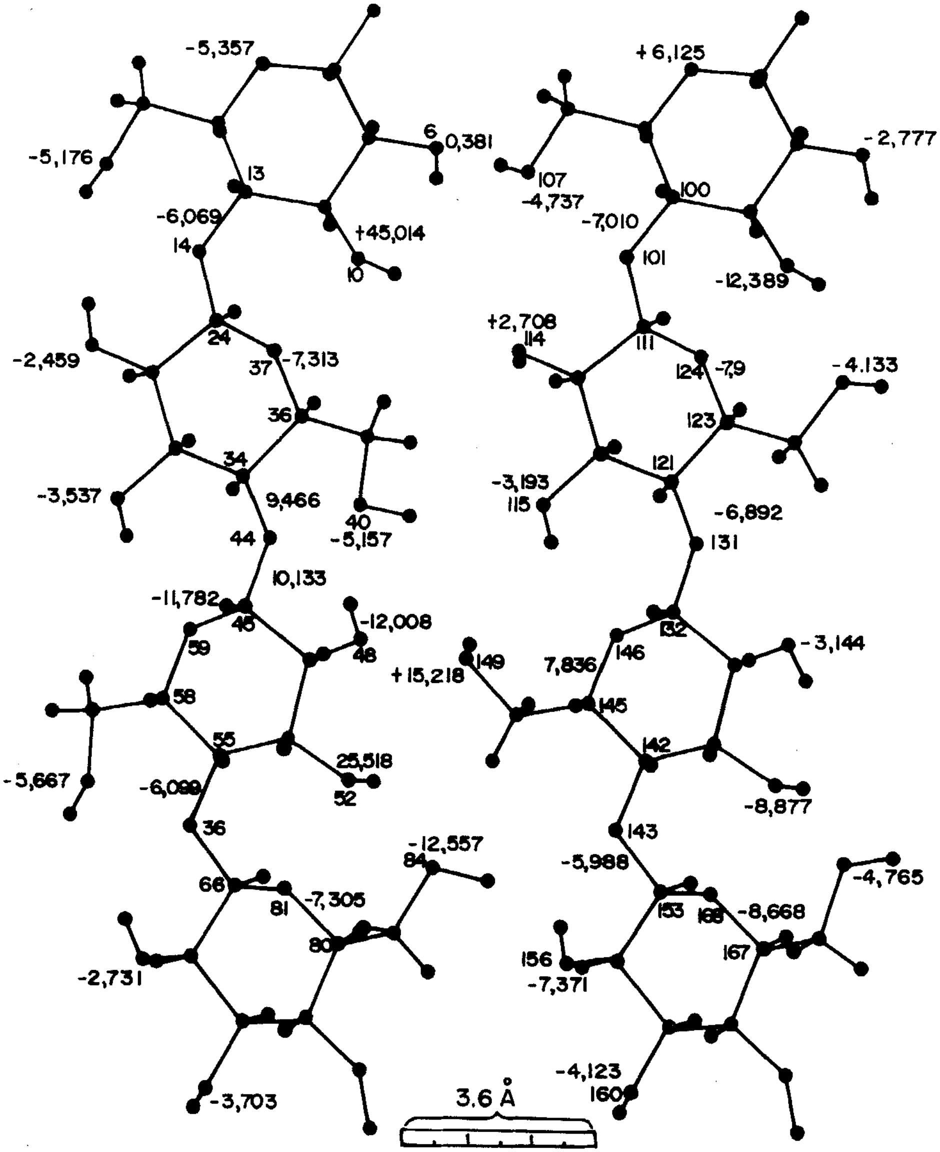
monolayer calculated by conformational analysis derived from its frequency distribution curve (cf. Fig. 5). (7.7 kcal/mol was used for E_{tot1} of cellulose II and 5.41 kcal/mol for cellulose I.) The value of k_2 was obtained in the same manner by using the E_{tot2} already obtained by conformational analysis [1, 2]. As it is known that k_1 and k_2 vary with relative humidity h, the m_1 curve was also calculated for each addition to the crystal of a water molecule with the single exact energies obtained for each specific sorption site involved (cf. Fig. 7). The knowledge of the exact sorption energy for each cellulose II site allowed the determination of the dependence of k_1 on the relative humidity for the first time. All the calculations were carried out for a temperature of 300 K. It was found that k_2 had very little variation [1], and the value of k_2 in the system of reference used in the calculation was 0.934.

DISCUSSION

All possible water sorption sites of the schematic crystallite of cellulose II (five chains of four glucose residues each according to the refined Kolpak, Weih, and Blackwell model [6, 7]) were tested for interaction forces with a single molecule of water per site. The total energies of interaction and their van der Waals, H-bond, and electrostatic contributions were obtained. The total energy values of the sorption sites and their locations are shown in Figs. 1 and 2 for the two top and bottom surface cellulose chains respectively. It must again be stressed that the two middle rings in each cellulose chain in Figs. 1 and 2 represent the conformation of minimum energy of anhydroglucose units along the length of the cellulose chain. The upper and lower terminal glucose units in each chain are in the conformation of the last anhydroglucose units of the cellulose II crystallites before the start of the amorphous zone and terminating the crystallite [6]. Attractive interactions (negative values), and hence the effective probable sorption sites and a few repulsive ones, are indicated in Figs. 1 and 2. The same values in order of decreasing sorption capability for a first molecule of water ("monolayer") and the values of the rotational angles involved (cf. Experimental) are reported in Table 1.

The antiparallel central chain did not present any sorption sites, and only in a few cases was weak H-bonding of between -0.10 and -0.30 kcal/mol found between central chain oxygens and a molecule of water strongly sorbed on one of the outer chains. This indicates that, in effect, the antiparallel central chain does not contribute to water sorption. Water sorption on the cellulose II crystallite appears then to be only a phenomenon limited to the surface chains of the crystal. Sorption sites on the side edges of the crystal had total energies very similar to those reported for cellulose I crystallites [1]. A few sites on the side edges of the crystal were tested for sorption of a second molecule of water per site. Table 1 reports the energies obtained. From these, it appears that very strong sorption sites often cannot accommodate a second molecule of water as a cause of strong steric hindrance and repulsive interactions (cf. Table 1, positive values) from groups vicinal to the site. Weaker attractive sites, due to lower steric hindrance and a higher degree of freedom, are more successful in sorbing a second molecule of water (second layer).

Sites groupings, where substantial interference between two or more water molecules sorbed on vicinal sites is apparent, were identified. These were: 1) attractive sites 48 and 118 on the top surface of the crystallite (cf. Figs. 1 and 3) (sorption site 40 did not contribute substantially to the interference between


-5,357
+6,125
-5,176
6
0,381
-2,777
13
107
-4,737
100
-6,069
-7,010
+45,014
14
10
101
-12,389
+2,708
114
111
24
-2,459
37
-7,313
124
-7,9
-4.133
36
123
121
34
-3,193
-3,537
9,466
115
-6,892
40
44
-5,157
131
10,133
-11,782
-12,008
132
46
-3,144
59
48
146
+15,218
149
7,836
58
145
-5,667
55
142
25,518
-6,099
52
-8,877
36
143
-12,557
84
-5,988
-4,765
66
81
-7,305
153
168
-8,668
80
167
156
-7,371
-2,731
-4,123
160
-3,703
3.6 Å

PLANE X

water molecules on the two other sites) and 2) attractive sites 228, 292, and 184 (214 did not participate substantially) on the bottom surface of the crystallite (Figs. 2 and 4). Energetically, interference takes two forms:

I. The combined sorption energy and interaction of two water molecules on two vicinal sites is much lower than the sorption energy of each single water molecule on its respective site. Two different cases of this type are shown in Table 2. *Sites 288/292*: The positions of the water molecules sorbed singly on these two sites are nearly coincidental. The two sites thus sorb only one water molecule between them. This is evident on comparing Figs. 4(a) and 4(b). Figure 4(c), supposed to show the alleged interference, instead depicts a nonexisting situation. The energy values in Table 2 indicate that the only water molecule to be sorbed is that on site 288 (Fig. 4b). *Sites 288/184*: The positions of the water molecules sorbed singly on these two sites are not coincidental. The final effect is, however, the same: only one water molecule will be sorbed, only on one site. This is likely to be the water molecule on site 288 both for energetic considerations and because the water molecule on site 188 rotates considerably when interfered with. The molecule on site 188 is not likely to be sorbed at all. An unstable situation, however, in which both molecules are sorbed and interfere with each other may well exist, but the extent of the interference is such that the molecule on site 188 is likely to eventually leave the site.

II. The combined sorption energy and interaction of two water molecules on two vicinal sites is higher than the sorption energy of each single water molecule on its respective site. This case is also shown in Table 2. *Sites 48/188*: Both molecules of water will remain sorbed on the two vicinal sites although strongly interfering with each other. The extent of the interference is shown by the difference in energy between the sorption energy sum of the

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FIG. 1. Sorption energies of a single water molecule on the planar projection of the upper surface of a schematic five-chains crystallite of cellulose II. Negative values indicate sorption sites. The positive values indicate some of the potential sorption sites which are repulsive and do not sorb water. The two middle rings in each chain represent the conformation of anhydroglucose units along the length of the cellulose chain. The upper and lower terminal glucose units in each chain are in the conformation of the anhydroglucose units of the cellulose II crystallite before the start of the amorphous zone.

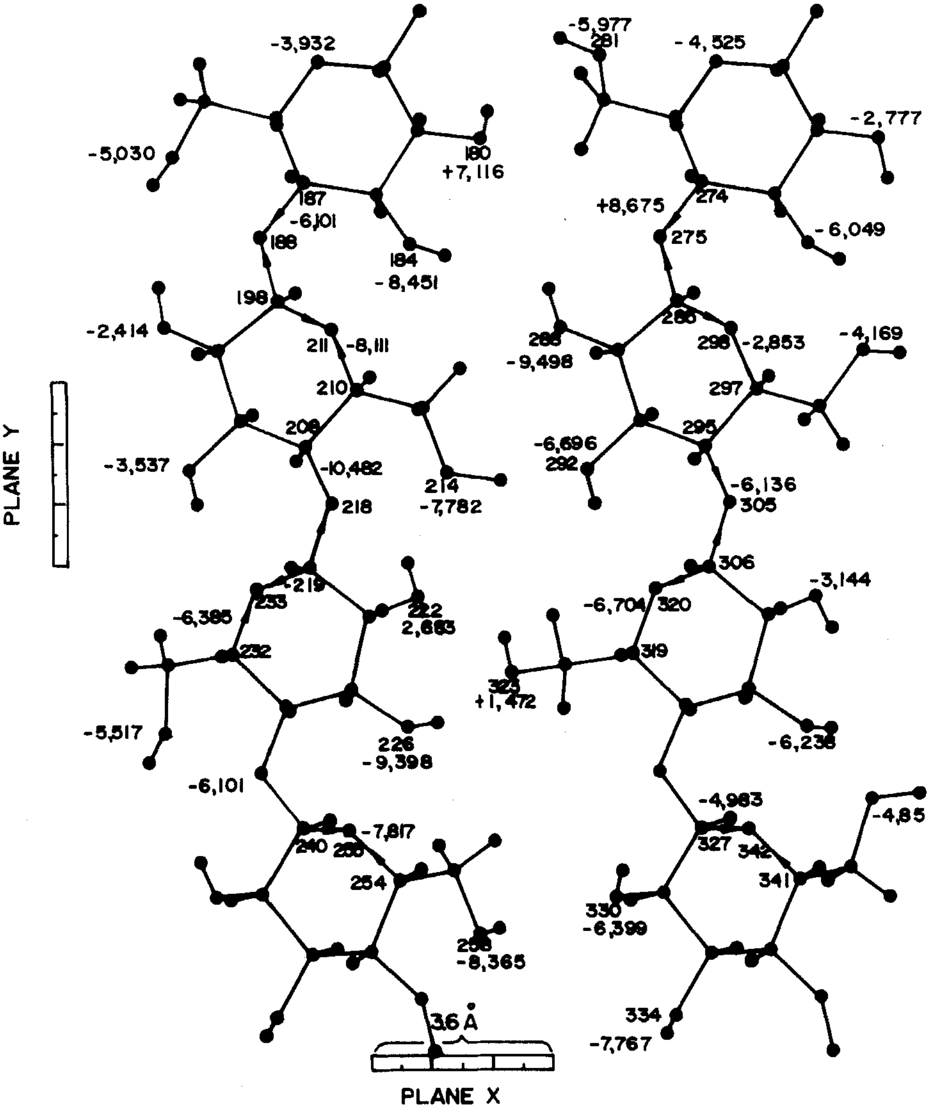

FIG. 2. Sorption energies of a single water molecule on the planar projection of the lower surface of a schematic five-chains crystallite of cellulose II. (See the comments in the Fig. 1 legend.)

two single molecules and the combined sorption energy of the two interfering molecules (Table 2). This case is depicted clearly in Figs. 3(a), 3(b), and 3(c).

When interference between two molecules on two vicinal sites does not exist, or is not substantial, the total energy of sorption of the system is equal or very similar to the sum of the single sorption energies. All the other sites fall in this category for the first water molecule sorbed.

In crystalline cellulose II monolayer sorption appears to occur only 1) on sites which exert high attractive forces due to favorable contributory positions of neighboring groups and 2) on sites exposed and protruding from the crystal surface. Recessed sites, which, in principle, could be good sorption points, appear to always be repulsive due to strong interaction of the water molecule with neighboring groups.

Figure 5 shows the energy frequency distribution of sorption sites for the five-chains elementary crystal examined and for a 17-chains crystal equivalent to the size of an elementary microfibril. The frequency distribution changes when crystals with an even greater number of chains are examined. The maximum for these, however, remains at the same value as for the 17 chains crystal.

Figure 6 show the water sorption isotherm (m) and monolayer water sorption isotherm (m_1) for the schematic five-chains crystal of cellulose II built according to Dent's equations [8] by using the theoretical energy values calculated by conformational analysis (cf. Experimental). The equivalent curves for the same size crystallite of cellulose I and for amorphous cellulose are reported in the same figure for comparative purposes. It must be clearly pointed out that this is only an example of how an isotherm can be built by using values calculated by theoretical means. The true isotherm will be somewhat different, as the reputed size of an elementary fibril [10] is of 17 chains and of a microfibril [9] of approximately 176 chains. Figure 6 indicates that when Dent's equations is used with exact energy values, the shape of the isotherm (m) is not a slightly sigmoid curve as when calculated with other data, and the shape of the monolayer isotherm (m_1) is a straight line. This behavior is due to 1) the available sorption sites of the monolayer being exhausted long before reaching equilibrium moisture content, 2) a marked tendency to sorb a second water molecule ("second layer") on already sorbed sorption sites, 3) variation in slope in bigger crystals as in nature, as obtained on adding water molecules to numerous strong sorption sites of the same value, and 4) the variation of k_1 with h in Dent's equations.

The first reason is supported by a number of primary sorption sites being eliminated by the interference effect already described, but this is not likely

TABLE 1. Total Interaction of Sorption Sites with a Single Water Molecule and Angles Describing the Position of the Water Molecule for Schematic Five Chains (four glucose residues each) Cellulose II Crystallite

1st H_2O contribution, kcal/mol	Angles, in degrees			1st H_2O contribution, kcal/mol	Angles, in degrees		
	1	2	3		1	2	3
-12.5575	-32	121	182	-4.9831[a]	130	71	25
-12.0079	-49	152	-80	-4.7373	-85	61	172
-11.7818[a]	-49	-1	32	-4.1229	-39	-54	-44
-10.4819	-57	117	-15	-3.1928	-51	-86	84
-9.4976	-63	141	-54	-2.8531[a]	-72	118	-35
-9.3979	30	88	-64	+0.3808	-64	6	-129
-8.6677[a]	35	-110	-49	Crystal sides (external corners)			
-8.4506	16	94	-118	1st H_2O contribution, kcal/mol[b]	2nd sorbed H_2O contribution, kcal/mol		
-8.3645	28	-92	78	-12.389			
-8.1107	35	-107	-47	-8.877			
-7.9839[a]	32	-118	-30	-6.238			
-7.8362	43	-104	83	-6.049			
-7.8167	45	-98	110	-5.667			
-7.7815	-49	51	-50	-5.517			

-7.7673	-49	-42	-59	-5.357	
-7.3701	37	-19	103	-5.176	
-7.3128	33	-116	-26	-5.030	
-7.3049	33	-116	-26	-4.850	
-7.0102	-52	85	-7	-4.765	+4.293
-6.8922[a]	47	-140	0	-4.169	+3.293
-6.7036	-42	91	-34	-4.133	
-6.6960	83	-111	43	-3.932	
-6.3989	31	34	36	-3.709	-2.255
-6.3847[a]	42	-88	144	-3.537	-2.275
-6.1355[a]	48	-143	-19	-3.537	
-6.1010[a]	51	-88	-160	-3.144	-2.275
-6.1006[a]	51	-88	-160	-3.144	
-6.0991[a]	51	-88	-160	-2.777	-2.275
-6.0693	51	-85	-160	-2.777	
-5.9887	62	-105	-37	-2.731	-2.275
-5.9772	-51	-7	-108	-2.459	-2.275
-5.1568	-39	-61	100	-2.414	-2.275

[a] For cellulose II only.

[b] For both cellulose II and cellulose I.

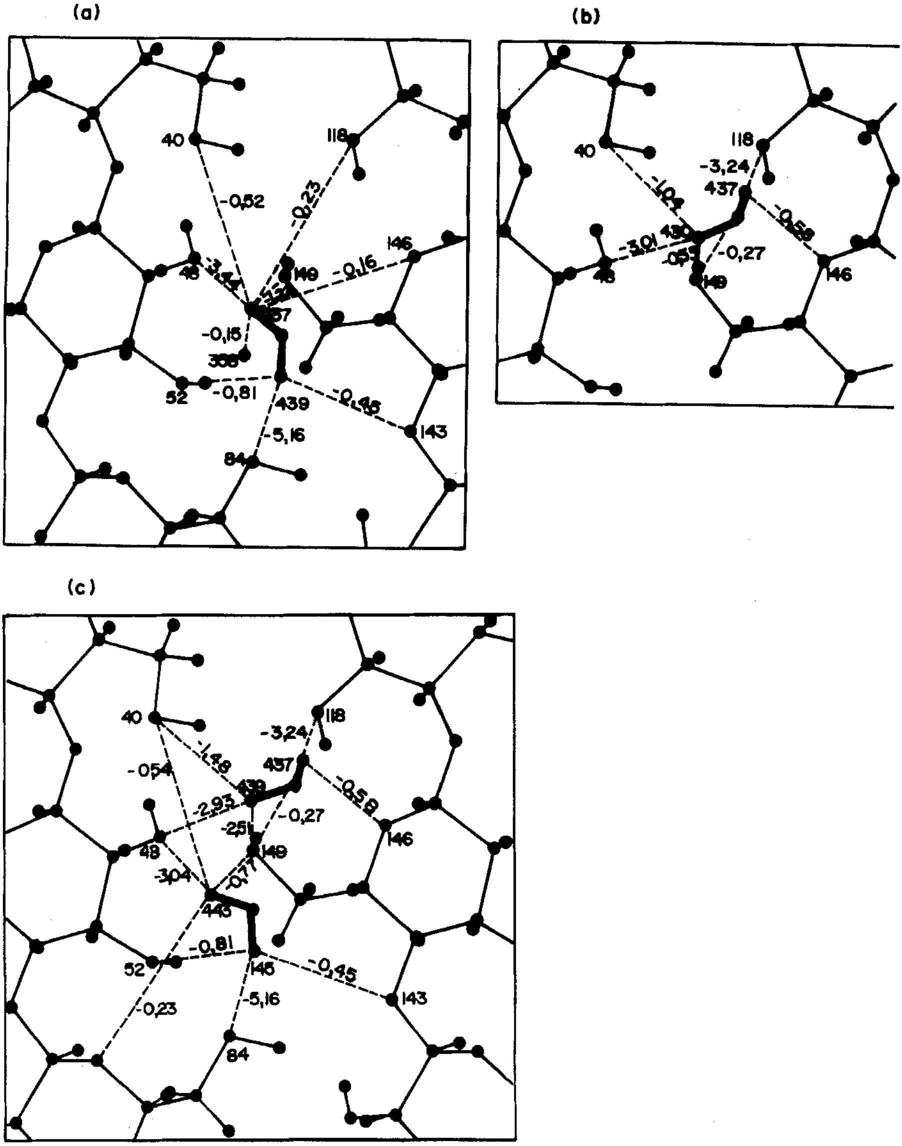

FIG. 3. Interference effect of water molecules on vicinal sorption sites. Segmented lines indicate the calculated H-bond location and values in kcal/mol. Planar projection of the upper surface of schematic crystallite. (a) Sorption site 48, single water molecule (note: H-bond with O atom 358, on central antiparallel chain). (b) Sorption site 118, single water molecule. (c) Interference of sorption sites 48 and 118, two water molecules. Water molecules drawn in heavier lines.

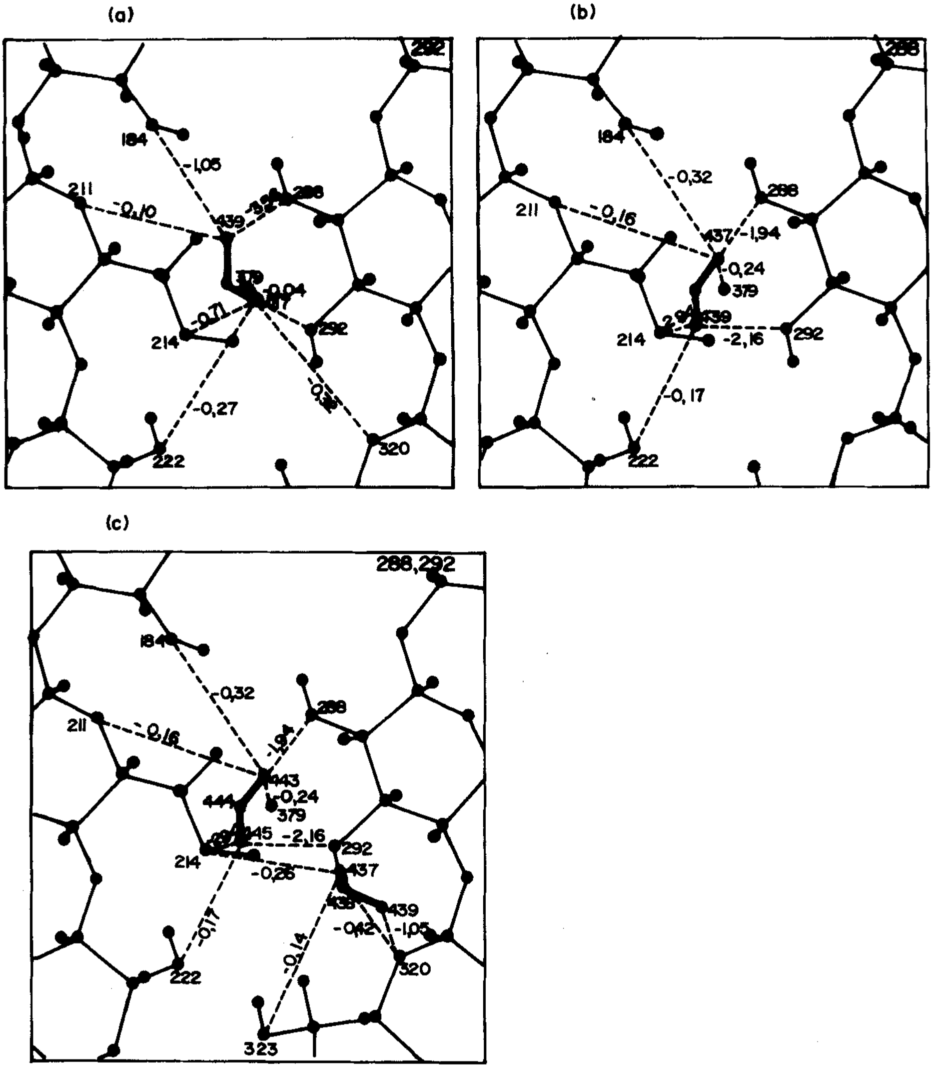

FIG. 4. Interference effect of water molecules on vicinal sorption sites. Segmented lines indicate the calculated H-bonds location and values in kcal/mol. Planar projection of the lower surface of schematic crystallite. (a) Sorption site 288, single water molecule. (b) Sorption site 292, single water molecule. (c) Interference of sorption sites 288 and 292 depicting nonexistent situation and confirming only one water molecule, on site 288, exists in this situation. Note the weak H-bond with oxygen atom 379 of the central antiparallel chain of the schematic five-chains crystallite.

TABLE 2. Effect of Interference on Sorption Energy of Water Molecules Sorbed on Two Vicinal Sites on the Surface of a Schematic Five-Chains Cellulose II Crvstallite

Case[a]	Sorption site (atom number)	Sorption energy of single site with one H_2O molecule only, kcal/mol (cf. Table 1)	Total sorption energy of combined sites with one or two H_2O molecules, kcal/mol (effective value)
1	48	-12.0079	
	118	-3.1928	
Totals		-15.2007	-12.683
2	184	-8.4506	
	288	-9.4976	
Totals		-17.9482	-7.8008
3	288	-9.4976	
	292	-6.6960	
Totals		-16.1936	-6.4346

[a] *Case 1*: Two molecules of water sorbed onto vicinal sites interfering with each other but both remaining sorbed. *Case 2*: Two molecules of water on two sites interfering to such an extent that one is likely to be shed from the surface or is not sorbed at all. *Case 3*: One molecule of water sorbed on two sites

to have an extensive influence. The second reason is likely to be caused by the internal and interassociative energy characteristics of water molecules in the vapor phase. When the associative energy of the water molecules is equal to or higher than the sorption energy of the still-available primary sites, sorption will become preferential on the first water molecule already sorbed on a site and water clusters will then start to form [11]. The monolayer sorption isotherm (m_1) will then reach a maximum at a certain h and stabilize at that level for any increasing value of h. This will cause the appearance of the known sigmoid shape of the m curve for lignocellulosic materials. If one considers the

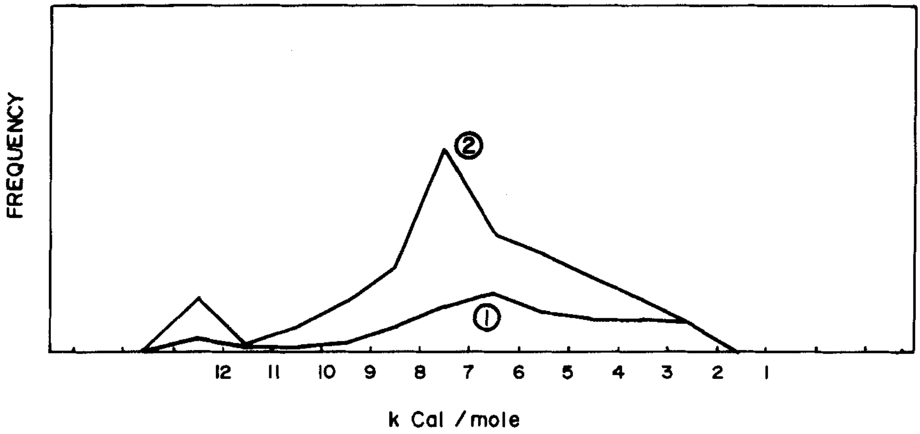

FIG. 5. Frequency distribution of sorption sites energy for (1) five-chains of schematic crystallite of four glucoses each, and (2) 17-chains of elementary crystallite of four glucoses each.

water clustering effect to become markedly evident at a sorption site energy of 5.5 to 6 kcal/mol, which is borne out by experimental evidence on wood isotherms [8], then the inflection point of the water sorption isotherm m can be foreseen to be at approximately 0.4 to 0.5 relative humidity for crystalline cellulose II and at 0.25 for crystalline cellulose I, in good accord with experimental evidence [8].

The calculation of the m_1 and m isotherms, molecule of water by molecule of water, presents the problem that the average energy of sorption obtained from Fig. 5 cannot be used. The sorption energy of each single site must be used instead. As this is variable, at least the monolayer constant k_1 in Dent's equations [8] also varies. This proved to be the case. The m_1 and m isotherms for crystalline cellulose I, at very low relative humidities, were then obtained by progressive addition of single molecules of water. The values obtained are shown in Table 3. Dent's equations were never conceived for variable constants but for use with average sorption energies. That Dent's equations need revision in this respect is shown in Table 3 where the equations predict water clustering (a difference exists between m_1 and m values) even after sorption of the first molecule of water. This is not possible. The m-m_1 values difference must be at least equal to the m_1 value for sorption of the first molecule of water to allow sorption of a molecule of water on the sec-

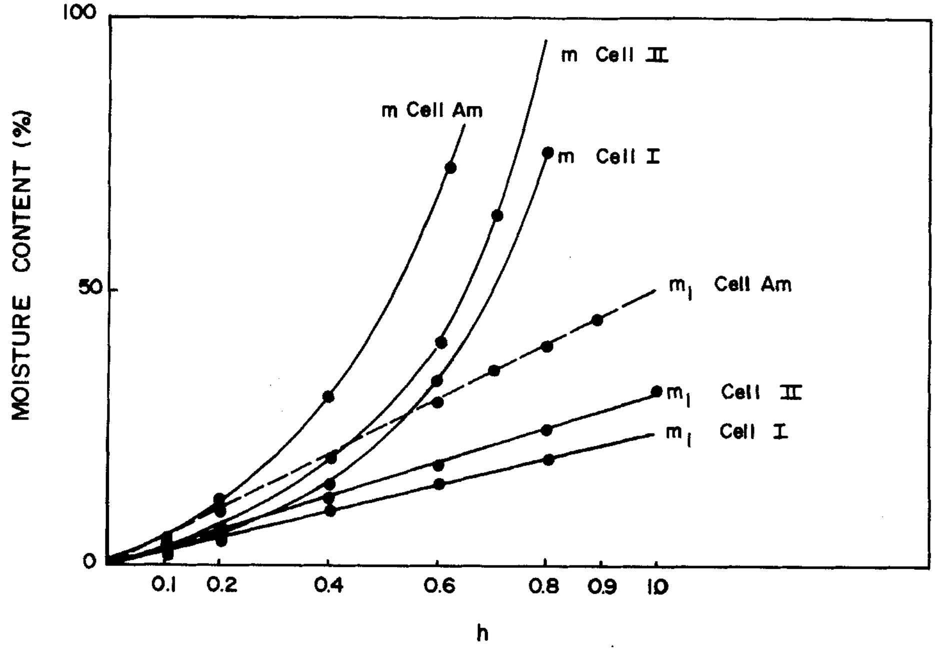

FIG. 6. Comparison of water sorption isotherms (m) and monolayer isotherms (m_1) calculated for amorphous cellulose (Cell Am), and the schematic five-chains crystals of cellulose I and cellulose II. Note the absence of inflection points when Dent's k_1 is taken as constant at different h values. These curves do not adequately describe water "clustering" and the start of further water layers. Clusters already form at $h = 0.1$ (2.6 to 3.0%). Cellulose II, $\Delta G_1 = 7.7$ kcal/mol, $m_0 = 33.82\%$; cellulose I, $\Delta G_1 = 5.41$ kcal/mol, $m_0 = 26.18\%$; cellulose amorphous, $\Delta G_1 = 6.48$ kcal/mol.

ond layer, hence the real start of water clustering. The values in Table 3 allow the forecast that, in the schematic case under consideration, clustering cannot start earlier than when the 7th molecule of water is sorbed, i.e., at a relative humidity h of 0.17 and 0.14 for cellulose I and II, respectively, or approximately 4% equilibrium moisture content for both types of cellulose.

The dependence of Dent's k_1 on h for the schematic five-chains crystallite under consideration can then be expressed (Fig. 7) as

$$\begin{aligned} k_1 &= 0.06261 \ln h + 0.92388 \text{ for cellulose I,} \\ k_1 &= 0.05178 \ln h + 0.85313 \text{ for cellulose II,} \\ k_1 &= 0.03228 \ln h + 0.84848 \text{ for amorphous cellulose.} \end{aligned} \tag{3}$$

TABLE 3. Theoretically Calculated Values of Dent's Constant k_1, Water Isotherm m, and Monolayer Isotherm m_1 at Low Relative Humidities h When Adding One Water Molecule at a Time to the Schematic Five-Chains Cellulose II

Crystalline cellulose I					Crystalline cellulose II					Amorphous cellulose		
k_1	m_1	h_1	m	$m - m_1$	k_1	m_1	h_1	m	$m - m_1$	k_1	m_1	h_1
0.688	0.00545	0.0300	0.00562		0.0684	0.00545	0.0234			0.790	0.0545	0.1242
0.763	0.0109	0.0539			0.688	0.0109	0.0463			0.792	0.1090	0.2437
0.765	0.0164	0.0803			0.696	0.0164	0.0685			0.818	0.1636	0.3517
0.781	0.0218	0.1042			0.701	0.0218	0.0900			0.823	0.2182	0.4612
0.804	0.0273	0.1265			0.729	0.0273	0.1083			0.824	0.2727	0.5687
0.804	0.0327	0.1508	0.03125	-0.00145	0.751	0.0327	0.1258			0.824	0.3279	0.6742
0.812	0.0382	0.1738	0.03850	0.0003	0.753	0.0382	0.1460	0.0442	0.00600	0.845	0.3818	0.7714
0.815	0.0436	0.1969	0.04624	0.00264	0.765	0.0436	0.1639			0.848	0.4364	0.8726
0.828	0.0491	0.2180			0.770	0.0491	0.1829			0.856	0.4909	0.9716
0.833	0.0545	0.2399			0.775	0.0545	0.2013					
					0.783	0.0600	0.2191					
					0.786	0.0655	0.2377					

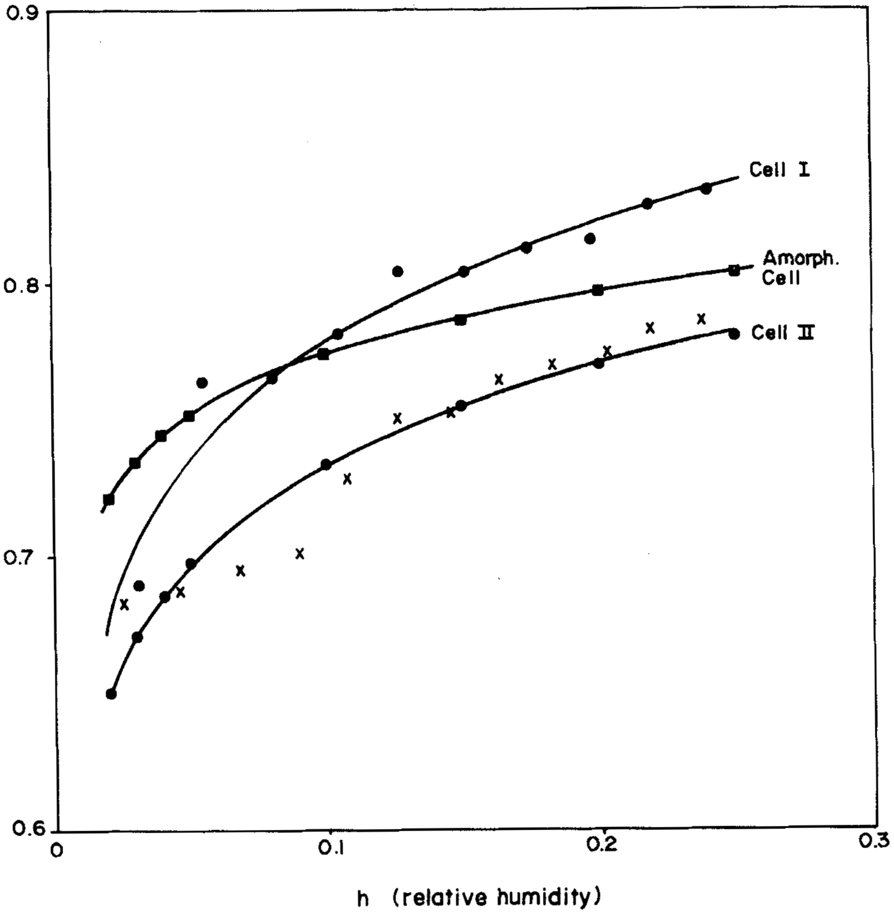

FIG. 7. Comparison of the variation of Dent's constant k_1 for the water monolayer isotherm as a function of relative humidity h for amorphous cellulose (Cell Am), and the schematic five-chains cellulose I and cellulose II crystallites. Values obtained by adding one water molecule at a time on the schematic cellulose crystallites.

The value of the Dent's k_2 was found to vary little with h, due to the very small sorption energy variation between water molecules sorbed as second layer (clustering) on different sorption sites [2].

CONCLUSIONS

1. The results obtained now render possible the construction of theoretical water sorption isotherms for cellulose II crystallites of any known size, one molecule of water at a time. This affords considerably higher precision at lower humidities than any previous method.
2. Water clustering appears to start very early, much earlier than previously thought, in water sorption by all three forms of cellulose.
3. The k_1 parameter for the water monolayer in Dent's equations has been shown not to be constant when calculated for each successive water molecule sorbed. Definite relations determine its variation with humidity for crystalline celluloses I and II and amorphous cellulose. This variability if one of the main causes of the sigmoid shape of experimental water isotherms.
4. The average sorption site energy for cellulose II crystallites is consistently higher than in cellulose I and amorphous cellulose [1, 2]. This indicates that the water monolayer is more strongly bound in cellulose II. It may also indicate that, in cellulose II, the water monolayer adsorbs more readily and desorbs less readily than in the other two forms of cellulose.
5. The cellulose II crystallite appears to be able to adsorb more water than cellulose I crystallites of identical molecular weight, but considerably less water than amorphous cellulose [1, 2] in direct relation to the respective number of sorption sites available. This is consistent with other experimental evidence.
6. Sorption sites interference appears to be more marked in cellulose II than in cellulose I crystallites [1].
7. As for cellulose I crystallites, the stronger "monolayer" sorption sites of cellulose II cannot always form a second layer due to strong steric hindrance from vicinal groups.
8. As in cellulose I, in crystalline cellulose II there appears to be favorable sorption on sites exerting high attractive forces and on sites which are exposed and protrude from the crystal surface.

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