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A New Interpretation of the Cellulose–Water Adsorption Isotherm and Data Concerning the Effect of Swelling and Drying on the Colloidal Surface of Cellulose[1,2]

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The great affinity of dry cellulose for water is today attributed to the hydrogen bonding capacity[3] of the alcoholic groups because progressive masking of the latter by esterification progressively reduces the amount of moisture absorbed from standard, humid surroundings.[4,5,6a] Although immersion in heavy water replaces the hydrogen in all alcoholic groups throughout the mass of cellulose by deuterium,[7] X-ray[8] and optical data[9] strongly suggest that the water molecule as a whole fails to penetrate the crystallites and that the absorption is a function of the amorphous portion. It is well known[10] that cellulose acquires an equilibrium moisture content when kept for a sufficiently long time in a humid atmosphere and that the adsorption isotherm is of the sigmoid type illustrated in Fig. 1, plots I and II. Flexed curves are also obtained by plotting the absorbed moisture, or the relative humidity, against other physical properties such as the rigidity,[11a] the electrical conductivity,[6,12] capacitance and power factor.[13] Moreover, similar relationships exist between the amount absorbed and the specific heat[14] and apparent specific volume[15] of the absorbed water, the heats of wetting by water, aqueous alkali and methanol,[12,16] the selective absorption of water, or of solute, from various solutions[17] and the absorption of gases[18,19] and alcohols.[5b,20,21] All the results are consistent with the view that the first avid adsorption of moisture (to region B, Fig. 1) is caused by the strong hydrogen bonding of single molecules to each of all the alcoholic groups accessible to water in the amorphous portion of the cellulose. The intermediate, nearly linear portions of plots I and II (region B to region D) correspond either to the formation of multilayers that are held with diminishing tenacity[3] or to the filling up of the finer capillaries.[19,22] There is agreement to the effect that the steep, final portion of the adsorption isotherm (from region D) at high humidities owes its shape to the swelling of the cellulose and to the condensation of "free" or "unbound" water in the coarser capillaries.[23] On this interpretation, the moisture content at B provides a measure of the amount of cellulose, or of the extent of its col-

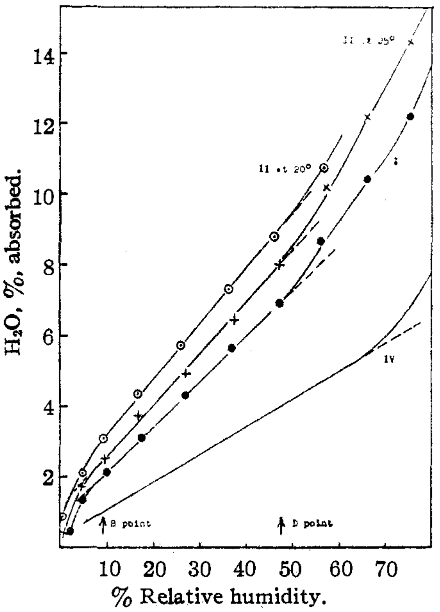

Fig. 1.—Moisture adsorption isotherms: Cellulose I at 25°, ●; Cellulose II at 20°, ○; Cellulose II at 25°, ×; Plot IV is Urquhart and Williams'[10] data for unswollen cotton at 80°.

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(2) Abstracted from Theses submitted to the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degrees of Doctor of Philosophy (A. G. A., May, 1942) and of Bachelor of Science (R. H. H., December, 1942).

(3) Babbitt, *Can. J. Research*, **20A**, 143 (1942), gave several literature references. See also the review by Barrer, *J. Soc. Dyers and Colourists*, **57**, 264 (1941).

(4) Urquhart, *J. Text. Inst.*, **20**, T125 (1929).

(5) Sheppard and Newsome (a) *Ind. Eng. Chem.*, **26**, 285 (1934); (b) *J. Phys. Chem.*, **36**, 2306 (1932).

(6) Walker, (a) *Textile Research*, **7**, 229, 289 (1937); (b) *J. Text. Inst.*, **24**, T145 (1933); (c) *J. Applied Phys.*, **8**, 261 (1937).

(7) Champetier and Viallard, *Compt. rend.*, **205**, 1387 (1937).

(8) Katz, *Physik. Z.*, **25**, 321 (1924); *Trans. Faraday Soc.*, **29**, 279 (1933).

(9) The researches of Nägeli and of Ambronn were reviewed by Steinbrinck. *Kolloid-Beihefte*, **23**, 6 (1926–1927).

(10) Urquhart and Williams, *J. Text. Inst.*, **15**, T559 (1924).

(11) Peirce, *ibid.*, (a) **15**, T501 (1924); (b) **20**, T133 (1929).

(12) Argue and Maass, *Can. J. Research*, **13B**, 156 (1935).

(13) Whitehead, "Impregnated Paper Insulation," Wiley and Sons, New York, N. Y., 1935, pp. 13–35.

(14) Shipley, Campbell and Maass, *Can. J. Research*, **17B**, 40 (1939).

(15) Maass and Campbell, *Pulp Paper Mag. Canada*, **40**, 108 (1939).

(16) Morrison, Campbell and Maass, *Can. J. Research*, **18B**, 168 (1940).

(17) Stamm and Hansen, *J. Phys. Chem.*, **42**, 209 (1938).

(18) Grace and Maass, *ibid.*, **36**, 3046 (1932).

(19) Stamm and Millett, *ibid.*, **45**, 43 (1941). A literature review is included.

(20) Russell, Maass and Campbell, *Can. J. Research*, **15B**, 13 (1937).

(21) Kanamaru and Chao, *Kolloid-Z.*, **84**, 85 (1938).

(22) Stamm, "Colloid Chemistry of Cellulosic Materials," U. S. Dept. Agric. Misc. Publ., No. 240 (1936).

(23) Marsh and Wood, "An Introduction to the Chemistry of Cellulose," Chapman and Hall, London, 2nd Ed., 1941, pp. 29–48. See also Bancroft and Calkin, *Textile Research*, **4**, 371 (1933–1934).

loidal surface, that is accessible to water, and similar information can be obtained by studying the adsorption of other vapors.[19] These views have the great merits of being intrinsically reasonable, of correlating a very large mass of information and of being not inconsistent with the work of Emmett and his collaborators on the adsorption of gases by inorganic catalysts.[24] Nevertheless, the validity of applying this interpretation to adsorption by cellulose does not appear to be supported by direct, experimental proof. The present research originated in an attempt to remedy this deficiency. As explained in the preceding article,[25] the fraction of the cellulose alcoholic groups wetted by a normal ether can be determined by using a thallous ethylate solution and by subsequently methylating the thallium cellulosate produced. The relationship between the percentage wetted and the molecular volume of the normal ether is linear and extrapolation to molecular volumes of 18 and 35[26] gives the percentages theoretically available for adsorption of vapors of water and nitrogen molecules, respectively. The weights of adsorbed layers were calculated from these amounts by assuming that each available alcoholic group bonded one molecule and the data were compared with those corresponding to the B and D points on the adsorption isotherms of the same cellulose samples. Although alteration in the colloidal surface of the samples during the adsorption of nitrogen and ethers could be assumed to be negligible, many quantitative results confirmed the fact that the sorption of water produced changes of great magnitude in unswollen cellulose. This effect was minimized, but not eliminated, in the comparative experiments by employing samples that were already highly swollen.

Experimental

Cellulose Samples.—The high grade cotton linters[27] were dewaxed, swollen in caustic soda and dried through methanol and benzene with all the precautions previously described.[25] Sample I contained 1.47% of moisture when examined, but samples II and III were thoroughly dried over concentrated sulfuric acid at room temperature and atmospheric pressure.

Estimation of Accessible Cellulose.—The thallations of approximately 0.3-g. samples of celluloses I, II and III were carried out with excess thallous ethylate dissolved in normal ethers exactly as already described, and the methylation of the thallium cellulosates was completed in the same way.[25] The methoxyl contents in duplicate or triplicate estimations of cellulose I were 11.5, 10.0 and 9.7% in diethyl, 8.1, 8.1% in dibutyl and 5.5, 7.4 and 6.7% in diamyl ether. Cellulose III gave values of 10.7, 12.6, 10.9; 9.7, 9.3, 9.5; and 7.5, 7.5, 7.5% methoxyl, respectively, with thallous ethylate dissolved in the same three ethers. The average methylation corresponding to each ether is plotted in Fig. 2 against the molecular volume of the ether and extrapolation to volumes of 18 and 35, respectively, gave the methylation theoretically corresponding to the penetration of the celluloses by water vapor and nitrogen gas. Ethyl ether values of 10.7, 11.6 and 11.1% methoxyl were the only ones available for cellulose II, but the line drawn through this point is approximately correct, since the slopes of the plots for highly swollen celluloses do not vary greatly. The difference between samples II and III, although obvious in Fig. 2, was in fact well within the experimental error. As previously explained,[25] multiplication of the methoxyl percentage by the factor 100/57.4 gave the percentage of cellulose, or of cellulose alcoholic groups, accessible to the penetrant (Fig. 2, Tables I and II). The product of the latter percentages and the factor 1.87 × 10^7 expressed the data as accessible colloidal surface in sq. cm. per g. of cellulose.

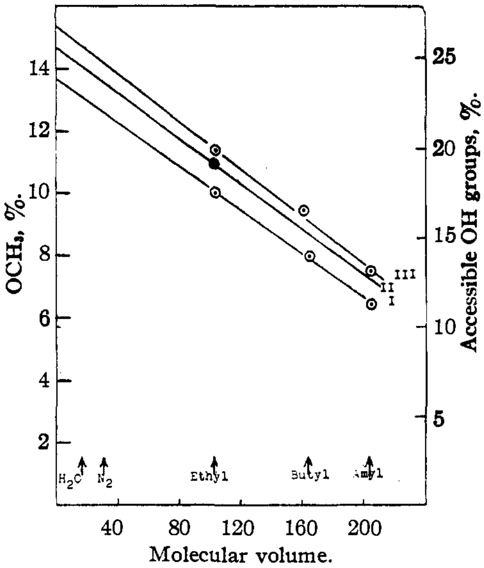

Fig. 2.—Superficial thallation-methylation of celluloses I, II and III, with thallous ethylate in normal ethers. Molecular volume of ether plotted against %OCH_3 and % accessible hydroxyl groups in the celluloses.

Sorption of Water Vapor at 20 and 25°.—The lower portions of twelve small desiccators, kept in a room whose temperature was constant at 20, or 25°, to within 1°, were filled with aqueous sulfuric acid of various definitely known concentrations. Published tables[28] gave the relative humidity within each desiccator at either temperature.

The cellulose sample, 1.5 to 1.7 g., held in an open weighing bottle, was kept in the desiccator containing concentrated sulfuric acid until the weight became constant, when the sample was assumed to be quite dry. It was then transferred to desiccators of increasing humidity, and daily weighings, quickly made on a magnetically damped balance, determined the moisture absorbed. The sample remained in each desiccator until weighings made on successive days did not differ by more than 1 mg. Three days at the lower humidities and five to seven days at the higher ones were required for equilibrium to be established within this weight limit. The best straight line was drawn through the observed points in the linear, intermediate portion of each adsorption isotherm (Figs. 1 and 4) and the moisture contents at the humidities where the plots commenced to diverge perceptibly from the extrapolation of this line were observed (Table I).[24] At ordinary temperatures, these humidities were 7 to 10% for the B, and 45 to 50% for the D point.

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[24] Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

[25] Assaf, Haas and Purves, *ibid.*, **66**, 59 (1944).

[26] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, give 0.808 g./cm.^{3} as the density of liquid nitrogen at −195.8°. This value was used in the calculation of the molecular volume.

[27] The authors wish to thank Dr. H. M. Spurlin and the Hercules Powder Company, Hopewell, Virginia, for the gift of this material.

[28] Wilson, *Ind. Eng. Chem.*, **13**, 326 (1921).

The desorption isotherms were obtained by transferring the cellulose samples through the desiccators in reverse order, but the data are omitted from Fig. 1. Sample I had 26.7% moisture at 100% relative humidity, when desorption was commenced, and the corresponding figure for sample II was 40.4% at 20°. The desorption of III and of II at 25° was from equilibrium at 56% relative humidity, or from just beyond the D point, when the moisture contents were 7.35 and 10.7%, respectively (Figs. 1 and 4). After desorption had been completed by standing over concentrated sulfuric acid, the standard estimation with thallous ethylate in ethyl ether gave methoxyl contents of 0.2, 0.2, 1.4 and 2.5% (latter in ethanol) for samples I, II at 20°, II at 25° and III, respectively. A value of 0.5% methoxyl (ethyl ether) was obtained when 2.06% moisture still remained in cellulose I.

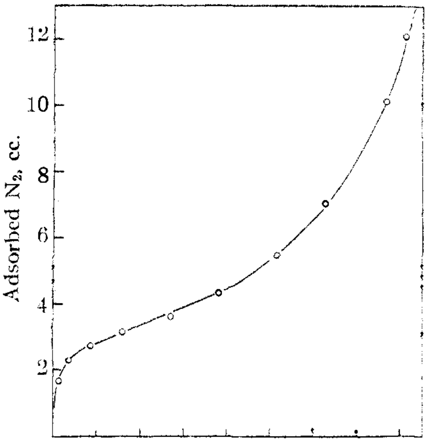

Fig. 3.—Nitrogen adsorption by an 0.3284 g. cellulose sample at −195.8°. The observed adsorption, after correction for "dead space" and to N.T.P., is plotted against the relative vapor pressure.

Adsorption of Nitrogen at −195.8°.—The isotherms for celluloses I and II were determined by the method of Brunauer, Emmett and Teller[29,30] with 0.2-g. samples. Helium was used to estimate the "dead space" in the apparatus and the data for the adsorption of nitrogen were corrected accordingly. The preliminary evacuation was at 80°. If v is the volume adsorbed at pressure p, and p_0 is the saturation pressure at the same temperature, v_m, the volume adsorbed at the first inflection of the isotherm (the B point) is given by the relationship

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{C - 1}{v_m C}\frac{p}{p_0}$$

where C is a constant.

Samples I and II had v_m values of 2.34 cc. and 2.83 cc., corrected to N.T.P. These results correspond to adsorptions of 11.6 cc. and 14.0 cc. per gram of cellulose, or to unimolecular layer surfaces of 53.0 × 10^4 sq. cm./g. and 64.6 × 10^4 sq. cm./g., respectively, if 17 sq. Å. is assumed for the area covered by a nitrogen molecule in the liquid condition. A complete isotherm for a different sample is reproduced (Fig. 3) to show that the shape is sigmoid and that the above method of calculating area was probably legitimate when applied to cellulose. The area computed for this sample was 34.8 × 10^4 sq. cm./g.

Results and Discussion

Suggested Interpretation of the Cellulose Moisture Adsorption Isotherm.—When swelling is neglected, the percentages of the cellulose samples I, II and III theoretically accessible to water vapor can be read from Fig. 2 and are recorded in Table I, column 2, as percentages of accessible alcoholic groups. If each of the latter is assumed to become hydrogen bonded to one water molecule, the calculated moisture content of the entire mass of cellulose is one-third of this percentage because fully hydrated cellulose, $C_6H_{10}O_5 \cdot 3H_2O$, has 33.3% water (column 3). The B and D points of inflection in the moisture adsorption–relative humidity plots at 20 or 25° (Figs. 1 and 4), are given in columns 5 and 6 of Table I. Comparison between columns 3 and 5 shows at once that the water adsorption calculated from the thallous ethylate-methylation data is far higher than that at the B point. Since the accuracy of the calculated values is thought to be well within ±15% and lines

Table I

Correlation of Accessible Alcoholic Groups with the Moisture Adsorption Isotherm of Cellulose

	Accessible[a] OH groups, %	H_2O[b] calcd., %	Water adsorbed Temp.	B[c] point, %	D[c] point, %	Ratio B point / D point
Cellulose I	22.8	7.6	25°	2.1	6.9	0.30
Cellulose II	24.4	8.1	25°	2.4	7.9	0.30 }
			20°	3.1	9.0	0.34 }
Cellulose III	25.6	8.5	20°	2.3	7.4	0.31
Unswollen			20°	2.0	6.0	0.33 }
cotton[d]	..	...	25°	1.9	5.8	0.33 }

[a] Data in Fig. 2 extrapolated to molecular volume 18. [b] Calcd. by assuming that one water molecule was adsorbed by each accessible alcoholic group. [c] From Figs. 1 and 3. [d] From Urquhart and Williams' data.[10]

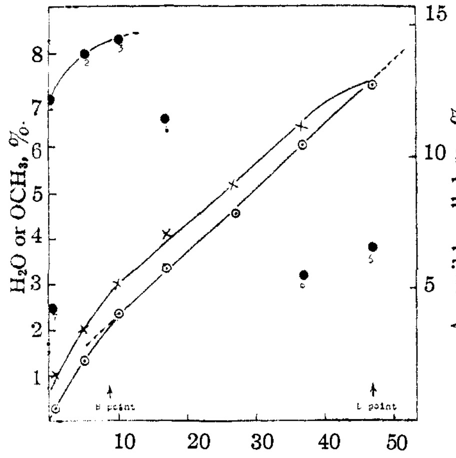

Fig. 4.—Water sorption isotherm of Cellulose III at 25°: adsorption, ⊙; desorption, ×; concurrent estimations of cellulose accessible to thallous ethylate in ethanol, ●.

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(29) Brunauer, Emmett and Teller, This Journal, **60**, 309 (1938).

(30) We wish to thank Dr. W. R. Smith and Mr. F. S. Thornhill, of the Godfrey Cabot Laboratories, Boston, Massachusetts, for their great kindness in determining all of the nitrogen isotherms and in calculating the results.

drawn through the isotherms to produce a similar variation are obviously misplaced, the total experimental error of perhaps ±30% is quite insufficient to reconcile the two sets of values. The same remark is true of the effect of any swelling during moisture adsorption because the observed B point would have already been increased, rather than decreased, by this contingency. On the other hand, the agreement between columns 3 and 6 of Table I is good, especially since the exact position of the D point cannot be read from the plots with accuracy and is probably sensitive to swelling. The conclusion reached is that a complete coverage of the accessible cellulose hydroxyl groups by water corresponds to the second region of inflection in the adsorption isotherms for ordinary temperatures, and not to the first, as has hitherto been supposed.

If this conclusion is entertained, it becomes desirable to find a new interpretation for the B point. Each glucose residue in cellulose contains three hydroxyl groups that differ markedly in chemical reactivity. Those in the primary or sixth positions of the glucose units are known to react more rapidly in esterification and deesterification,[31,32] etherification[33] and possibly nitration[34] than those in the two secondary alcoholic positions. Those in some sugar derivatives behave similarly.[35] Simple primary alcohols are considered to be more highly associated in benzene solution than their secondary isomers,[36,37,38,39] and their boiling points at atmospheric pressure are about 20° higher.[40] All these observations make it plausible to argue that primary alcohols form intermolecular hydrogen bonds, and, presumably, hydrogen bonds with water molecules, that are stronger than those pertaining to secondary alcohols. The initial strong adsorption of water by cellulose (up to the B region, Fig. 1) accordingly may be attributed for the most part to the primary alcoholic groups, and is identifiable with the powerful "*a*" absorption assumed by Peirce.[11b] The intermediate portion of the isotherm represents the weaker adsorption of the secondary alcoholic groups but is progressively distorted from the region of the D point onward by enlargement of surface through swelling and by the filling up of the capillaries. Since there is on the average one primary for every two secondary alcoholic groups accessible in the cellulose, the above interpretation requires that the moisture content at the B point should be approximately one-third of that at the D point. This deduction is supported by the most probable ratios observed both in our own experiments and in those of others[10] (Table I, column 7), although it is true that graphical manipulation of the data in Figs. 1 and 4 may give values ranging from 0.25 to 0.4.

Another deduction from the new interpretation is that the shape of the adsorption isotherm must be determined by the three equilibria

$$R_2OH + H_2O \rightleftarrows R_2OH{\cdot}H_2O$$
$$R_3OH + H_2O \rightleftarrows R_3OH{\cdot}H_2O$$
$$R_6OH + H_2O \rightleftarrows R_6OH{\cdot}H_2O$$

when both swelling and the slight affinity of water for acetal oxygens and hydrocarbon chains are neglected. R_2OH, R_3OH and R_6OH represent the equimolar amounts, m, of alcoholic groups in the second, third and sixth positions of the glucose residues accessible to moisture in the cellulose. If x_2, x_3 and x_6 moles are the equilibrium amounts of moisture adsorbed by the three kinds of alcoholic group at the vapor pressure p, the law of mass action states that

$$x_2/p(m - x_2) = \text{a constant } K_2, \text{ or } x_2 = K_2mp/(1 + K_2p)$$

with similar equations for x_3 and x_6. Since these equations are identical in form to those devised by Langmuir for unimolecular layer adsorption, cellulose may be regarded as a surface containing equal amounts of three kinds of elementary space, each adsorbing with different intensity.[41] The constant K_6 is so large that the primary alcoholic groups are extensively hydrated at a relative humidity of 7 to 10% (Fig. 1), but K_2 and K_3 are such that the hydration of the secondary alcoholic groups is very much less in the same conditions. It follows that the selective hydration of R_6OH is responsible for the 15.7 kcal. of heat evolved when one mole of water vapor at ordinary temperature is adsorbed by a very large mass of perfectly dry cellulose.[3,42] Since the latent heat of condensation of water vapor is 10.5 kcal., the difference of 5.2 kcal. may be attributed to the heat of formation of the $R_6OH{\cdot}H_2O$ hydrogen bond. This value is approximately half-way between those of 4.5 and 6.0 kcal. reported for the hydrogen bond strength in ice and aliphatic alcohols, respectively.[43,44] It is to be expected that the $R_2OH{\cdot}H_2O$ and $R_3OH{\cdot}H_2O$ bonds have a heat of formation smaller than 5.2 kcal. and this supposition, plus the utilization of energy to cleave pre-existing cellulose–cellulose hydrogen bonds during swelling, would explain

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(31) Cramer and Purves, THIS JOURNAL, **61**, 3458 (1939).

(32) Gardner and Purves, *ibid.*, **64**, 1539 (1942).

(33) Mahoney and Purves, *ibid.*, **64**, 9 (1942).

(34) Murray and Purves, *ibid.*, **62**, 3194 (1940).

(35) Hockett and Downing, *ibid.*, **64**, 2463 (1942).

(36) Biltz, *Z. physik. Chem.*, **29**, 249 (1899).

(37) Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

(38) Lassettre, *Chem. Rev.*, **20**, 259 (1937).

(39) Huggins, *J. Org. Chem.*, **1**, 407 (1936–1937).

(40) The normal heptyl alcohols, for example, have the following boiling points: heptanol-1, 176°; heptanol-2, 159°; heptanol-3, 157° (750 mm.), and heptanol-4, 154°.

(41) Langmuir, THIS JOURNAL, **40**, 1361 (1918).

(42) Neale and Stringfellow, *Trans. Faraday Soc.*, **37**, 525 (1941).

(43) Robertson, *ibid.*, **36**, 913 (1940). No distinction was made between the hydrogen bond energies of primary and secondary alcohols.

(44) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 307, mentions a bond energy of 6,200 cal. for methanol and ethanol.

the sharp decrease in the heat evolved by the adsorption of additional amounts of water.[3] The thermal effects connected with the adsorption of the lower alcohols[20] would be subject to similar considerations.

It is well known that moist cellulose rapidly becomes bone dry when heated in air to slightly more than 100°.[11b] This is, therefore, the temperature range in which even the most powerfully adsorbed moisture, $R_6OH{\cdot}H_2O$, is expelled and in which the corresponding hydrogen bond, like that in liquid water, becomes quite unstable. The hydrogen bonds holding the cellulose crystallites together resist far higher temperatures because their strength is additive in this case. Since the bond system in an associated liquid secondary alcohol disintegrates at a temperature about 20° lower than that in the primary isomer,[40] it is reasonable to suppose that the complexes $R_2OH{\cdot}H_2O$ and $R_3OH{\cdot}H_2O$ in moist cellulose have only a transient existence at 80° or more. In other words, the moisture-adsorption isotherms at such elevated temperatures should be a function of the primary alcoholic groups alone. Urquhart and Williams[10] determined isotherms at 80° and above, one of which is reproduced in Fig. 1, plot IV. An inflection corresponding to the B point at lower temperatures is scarcely perceptible and the plot remains practically linear until distorted upward by swelling. The linearity at lower humidities is consistent with Langmuir's adsorption isotherm for surfaces containing only one kind of elementary space. It follows that plots of similar shape may be expected at *all* temperatures with high molecular materials that swell but possess only one kind of hydroxyl or other adsorbing group. If some other physical properties of cellulose, such as elasticity or rigidity, happen to be connected with hydrogen bonding between secondary alcoholic groups in the amorphous regions, such properties may alter more or less abruptly about 80°.

These general principles may eventually throw fresh light upon the mechanism of some gelations. Heymann and his collaborators, for example, provided evidence that the gelation of aqueous solutions of methylcellulose (substitution 1.59) in the temperature range 40 to 50° is accompanied by a decrease in the solvation of the macromolecules.[45] Most of this decrease might be caused by the preferential, partial desolvation of the unsubstituted, secondary alcoholic groups, rather than to the decomposition of hydrated ether complexes, as was suggested. The pasting of starch in water kept at 65 to 85°[46] may be connected with the breakdown of hydrogen bonds uniting secondary alcoholic groups in the granule and with their inability to remain extensively solvated in this temperature range. When the paste cools, its rigidity increases[47] because these groups recover their ability to hydrogen bond with each other, with the primary alcoholic groups, and with water to form a random system in dynamic equilibrium.

The Cellulose Nitrogen Adsorption Isotherm.—The percentages of the celluloses I and II theoretically accessible to nitrogen (Fig. 2) are given in Table II, column 2, together with the adsorption calculated on the basis of three nitrogen molecules for each accessible glucose residue (column 4). Column 5 shows that the gas actually adsorbed at the B point, as found by Brunauer, Emmett and Teller's method[29] was *one-seventh to one-eighth of the calculated amount*, and the surfaces calculated by the thallous ethylate and the nitrogen methods were in practically the same ratio (columns 3 and 6). This coincidence originated in the fact that the former method of calculating surface assumed an area of 52 sq. Å. for a glucose residue, which in the second method would be almost completely covered by three nitrogen molecules forming a continuous film with a total area of 3 × 17 sq. Å., or 51 sq. Å. It therefore happened that the assumed adsorption at three discrete points in each glucose residue very nearly corresponded to a continuous film that was "unimolecular" in the accepted sense of the word.[29] Although the measurements are not extensive, they are in accord with Babbitt's[3] conclusion that it is necessary to assume *six or seven* superimposed, unimolecular water layers, calculated by Emmett, Brunauer and Teller's method, in order to account for the observed moisture content of cotton and spruce wood in the region of the 20° isotherms just above the D point. The agreement suggests that nitrogen as well as water molecules are adsorbed by the exposed alcoholic groups of the cellulose and in this event the first three of the "unimolecular" layers might represent adsorption on the three different

TABLE II

CORRELATION OF ACCESSIBLE CELLULOSE WITH NITROGEN ADSORPTION

	Available to N_2[a] Cellulose %	Surface[b] cm.²/g. × 10^{-4}	Calcd. N_2[c] cc./g.	N_2 adsorbed at B point Found cc./g.	Surface[d] cm.²/g. × 10^{-4}
Cellulose I	22.0	411	91.3	11.6	53.0
Cellulose II	23.7	443	98.3	14.0	64.6

[a] Extrapolated from thallous ethylate methylation data in Fig. 2. [b] From column 2 and 52 sq. Å. as area of glucose unit in cellulose. [c] From column 2 and $3N_2$ for a glucose residue. [d] From column 5 and 17 sq. Å. as area of a nitrogen molecule.

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(45) Heymann, Bleakley and Docking, *J. Phys. Chem.*, **42**, 353 (1938). The present authors thank Dr. S. L. Bass, of the Dow Chemical Company, Midlands, Michigan, for a private communication discussing Heymann's work in connection with the gelation of water-soluble methylcelluloses.

(46) Radley, "Starch and its Derivatives," D. Van Nostrand Co., New York, N. Y., 1940, pp. 29–47, discussed the literature.

(47) Caesar, *Ind. Eng. Chem.*, **24**, 1432 (1932).

kinds of alcoholic group present.[48] This assumption would render the areas calculated by Emmett, Brunauer and Teller's method about one half, instead of about one sixth, as large as those derived from the thallous ethylate technique. Further work is required to overcome the discrepancy. In the meantime, the suggestion that the D point, rather than the B point, of sigmoid adsorption isotherms corresponds to the complete monolayer must be restricted to the adsorption of water vapor by cellulose.

Changes in Accessible Surface Caused by Solvent-Exchange Drying and by Sorption of Water.—Samples of the highly swollen, dry cellulose II were permitted to absorb known equilibrium amounts of water before being submitted to the thallous ethylate-methylation determination. The solvents chosen for the ethylate were diethyl ether, in which water dissolves sparingly, 1,4-dioxane, which is miscible with water, and absolute ethanol, which competes effectively with cellulose for traces of moisture.[49] The usual large excess of thallous ethylate was increased to offset the decomposition of a portion by the water. Experiments 1 and 2, 5 and 6 (Table III) show that a moisture content of 9% made about three-quarters of the original surface inaccessible not only to ether, but also to dioxane. The preliminary removal of water by standard solvent-exchange drying procedures was also unsatisfactory (expts. 3 and 4) but comparison with experiments 7, 8 and 9, in which even a slight, final drying *in vacuo* was scrupulously avoided, showed that the latter step was the major cause of difficulty. The results support Kistler's conclusion that the formation of aerogels by the direct evaporation of liquids below their critical temperature must involve a collapse of surface.[50]

Figure 4 records an attempt to follow the surface changes exhibited by cellulose III during a moisture sorption cycle from zero to 47% relative humidity at 25°. The method employed thallous ethylate in absolute alcohol and involved no drying. Points 1, 2 and 3, determined during adsorption, are reliable and show that the adsorption of as little as 2.3% of moisture increases the accessible cellulose by at least one fifth, even although the original sample was highly swollen. Points 4 and 5, determined during adsorption, and point 6, after desorption was commenced, merely reveal the inadequacies of the experimental method at higher humidities because the surface was certainly not contracting during the adsorption of additional amounts of water. Point 7, determined when desorption was complete, is accurate, and comparison with point 1 shows that two-thirds of the original surface became inaccessible to ethanol during the complete sorption cycle. The experimental portion contains data showing that the obliteration of surface may amount to 98% as a result of desorption from 100%, instead of 47%, relative humidity.

TABLE III

THALLATION-METHYLATION OF MOISTURE-CONTAINING CELLULOSE

Expt.	Moisture, %	Pretreatment of sample	Solvent for TlOEt	OCH_3,[a] %
1	0.0	Original sample	Ether	11.2
2	9.0	None	Ether	3.5
3	17.2	Solvent-exchanged through 100% methanol and dry benzene. Dried over solid KOH *in vacuo*	Ether	0.9
4	24.1	Solvent exchanged through 100% methanol and dry ethyl ether. Kept *in vacuo* for five minutes	Ether	1.8
5	0.0	Original sample	1,4-dioxane	8.0
6	9.0	None	1,4-dioxane	2.0
7	0.0	Original sample	Ethanol	10.2
8	9.1	None	Ethanol[b]	7.8
9	9.5	Absolute ethanol for fourteen hours. Surplus removed without drying	Ethanol	7.4

[a] Averages of concordant duplicate or triplicate estimations. [b] Twenty, instead of the usual three, hours in excess of the 0.1 *N* solution of thallous ethylate.

A more detailed experiment on the effects of drying (Fig. 5) was carried out with cellulose I,

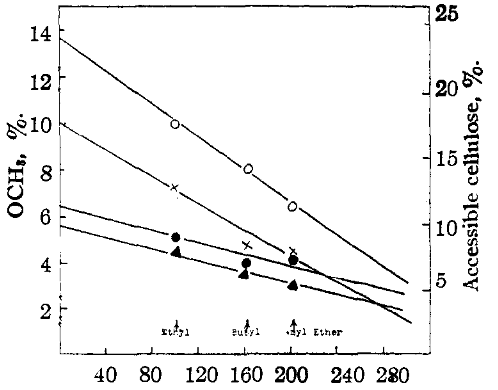

Fig. 5.—Progressive decrease in portion of Cellulose I accessible to thallous ethylate in normal ethers: initially, 1.47% moisture, ○; after 22 days over solid caustic potash, ×; after 53 days, ●, and after 99 days, ▲.

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[48] This idea is analogous to the opinion expressed by Brunauer and Emmett, THIS JOURNAL, **62**, 1732 (1940), concerning certain synthetic iron catalysts, the heterogeneity of whose surfaces was probably due to different developed crystal faces. See also the review by Emmett, "Twelfth Report of the National Research Council Committee on Catalysis," John Wiley and Sons, New York, N. Y., 1940, pp. 53-67.

[49] Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 390 (1940).

[50] Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

whose initial moisture content of 1.47% was not sufficient to render the thallation method with ethers inaccurate. When stored in the dark and *in vacuo* over solid caustic potash, the moisture content diminished during ninety-nine days to 0.43%, while the accompanying change in the amount of cellulose accessible to an ether of zero molecular volume (amorphous cellulose[25]) was from 24% to 10%. Although experimental inaccuracies make the intermediate plots doubtful, the slopes of the initial and final plots are such as to render the percentage decrease in accessible cellulose almost independent of the molecular volume of the ether. The drying process, therefore, seems to obliterate the larger and smaller capillaries of molecular dimensions to almost the same extent. The magnitude of the effect suggests that the removal of a water molecule from the more confined spaces may make possible the formation of a hydrogen bond between two glucose residues on opposite sides of the fissure, and that the corresponding macromolecules, held together in this way at one point, then crystallize imperfectly but extensively against each other.[15,51] In this event, the mechanism may be compared to the action of the domestic "slide fastener" as it unites two serrated edges. The removal of adsorbed liquid appears to be essential for the contraction in surface because the thoroughly dry cellulose II retained its original, superficial methylation of 11.2% unchanged during storage for three months over concentrated sulfuric acid.

Interpretation of the "Mercerization Ratio" of Cellulose.—Data in this and the preceding article[25] show that the accessibility of cellulose to thallous ethylate dissolved in normal ethers may be increased perhaps a hundredfold by appropriate swelling and drying. The value of the "mercerization," "activation" or "reactivity" ratio[23] is therefore of the order of 100 in this case and ratios of similar magnitude probably describe the behavior of cellulose toward other non-swelling reagents. For example, oxidations with chromic anhydride dissolved in glacial acetic acid fall in this category.[52]

Since the amount of unswollen cotton accessible to thallous ethylate in ether is about 0.5%, an adsorption of one water molecule by each available alcoholic group would correspond to a moisture content of the order of 0.2% if swelling did not occur. The value of 6% observed at the D point (Table II) indicates that swelling does in fact multiply the original, minute surface some thirty times. When aqueous solutions of oxidants, mineral acids or dyestuffs[23] are used to measure reactivity, the results for *unswollen* cellulose are probably too large by a factor of similar size. After the specimen has been highly swollen in caustic soda, the water-wet product is usually directly dried before its reactivity is measured. The drying processes used obliterate by far the greater part of the original, swollen surface, which is then regenerated to a considerable extent during the final measurement. It follows that the reactivity ratios of approximately 1.5 obtained by these methods record only the net effect of swelling and contracting changes of much greater magnitude.

This article has profited greatly from constructive suggestions made by Professors P. H Emmett and G. Scatchard, although responsibility for the opinions expressed remains entirely with the authors.

Summary

1. Three highly swollen samples of cotton linters were immersed in solutions of thallous ethylate in normal ethers of different molecular volume. Methylation of the resulting thallium cellulosates gave products whose methoxyl contents were accepted as proportional to the penetration of the ether into the celluloses. Extrapolation of the linear methylation-molecular volume plots to volumes of 18 and 35 gave the respective percentages of cellulose theoretically accessible to water vapor and nitrogen gas.

2. The moisture adsorption isotherms, at 20 or 25°, of the same swollen samples were determined. The moisture content at the second region of inflection in the sigmoid shaped plots, occurring at a relative humidity of about 50%, was approximately that predicted from (1) by assuming the adsorption of one water molecule by each accessible alcoholic group. This region in the isotherm was considered to be approximately equivalent to a unimolecular water layer completely covering the accessible surface of the cellulose.

3. The moisture content at the first region of inflection in the isotherm, occurring at a relative humidity of about 10%, was approximately one-third of the value at the second inflection. This fact, together with other considerations cited, suggested that the avid adsorption of water up to the first inflection was mainly a function of the strong hydrogen bonding capacity of the accessible, primary alcoholic groups. The flat, intermediate portion of the isotherm represented the water less strongly hydrogen-bonded to the secondary alcoholic groups, but its shape was influenced at the higher humidities by the effects of swelling and by capillary condensation. Some physical-chemical implications of these ideas were discussed, particularly the inference that the moisture sorption characteristics of cellulose and starch at 80° or more must be those of the primary alcoholic groups exclusively.

4. Up to 98% of the surface of moist, swollen cellulose was obliterated by direct drying, but up to 75% was preserved during solvent-exchange with ethanol. The absorption of 6% to 9% of

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(51) Kratky, *Angew. Chem.*, **53**, 153 (1940).

(52) Gladding and Purves, *Paper Trade J.*, **116**, No. 14, 26 (1943).

water increased the colloidal surface of highly swollen cellulose by at least 20%, but the increase for unswollen samples was perhaps thirty fold. These data threw fresh light upon the significance of the "mercerization" or "reactivity" ratio of cellulose, which is usually given as about 1.5.

5. The surfaces of two of the swollen cellulose samples were estimated by a standard method involving the determination of the nitrogen adsorption isotherm at −195.8° but the correlation of this method with the thallous ethylate technique requires further study.

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Diacetone Xylitol (2,3,4,5-Di-isopropylidene-D,L-xylitol)

BY RAYMOND M. HANN, A. T. NESS AND C. S. HUDSON

Tipson and Cretcher[1] have recently prepared a crystalline diacetone xylitol by condensing the components under suitable conditions. The substance contains one free hydroxyl group and they prepared its crystalline monotosyl derivative and subjected this substance to the action of a solution of sodium iodide in acetone at 100° for two hours, conditions which have been recommended by Oldham and Rutherford[2] for use in their method of distinguishing primary and secondary hydroxyl groups in the case of the aldohexosides, where it appears to be a general rule that a tosyl group is replaced by iodine only when it is attached at the primary hydroxyl of carbon atom 6. Tipson and Cretcher found that tosyl diacetone xylitol reacts with sodium iodide, as is shown by their isolation of sodium tosylate in nearly quantitative yield; it is not mentioned whether the isolation of the expected iodo diacetone xylitol was attempted. They found on the other hand, that all four tosyl groups of tetratosyl-erythritol are removable as sodium tosylate by the acetone solution of sodium iodide under the same conditions and that the erythritol moiety undergoes extensive change to volatile products, a component of which appears to be butadiene, as shown by a test for conjugated double bonds. They concluded therefore that "Oldham and Rutherford's rule apparently does not apply to tosyl esters of the sugar alcohols." Drawing this conclusion, the position of the free hydroxyl group in diacetone xylitol was left undecided.

We have used the Oldham–Freudenberg technique for the preparation of iodo derivatives of the sugar alcohols on numerous occasions. In all but two cases, the tosyl groups of the substances which we studied were attached only to primary hydroxyl groups; these tosyl groups were replaceable by iodine in conformity with the Oldham–Rutherford rule. However, in these cases the general question of the applicability of the Oldham–Rutherford rule did not arise, because we determined the position of the iodine atom in the iodo derivative by an independent and conclusive method, namely, the replacement of the iodine by hydrogen to yield a desoxy compound, the structure of which was then determined through oxidation by per-iodic acid or lead tetraacetate and the estimation of the resulting acetaldehyde. In one of the excepted cases,[3] the 1,4-ditosyl derivative of 2,3,5,6-di-isopropylidene-D,L-galactitol has been shown to give a nearly quantitative yield of a mono-iodo monotosyl derivative, a result which agrees with the Oldham–Rutherford rule in an appropriate test case. In the second excepted case,[4] it has been shown that the substance which has the structure 1,6-ditosyl-2,3,4,5-dimethylene-D-mannitol (as proved conclusively by per-iodic acid oxidation of an appropriate derivative and the estimation of acetaldehyde) reacts with sodium iodide according to the Oldham–Rutherford directions to give the expected 1,6-di-iodo-2,3,4,5-dimethylene-D-mannitol in 98% yield. A second substance which is also a di-tosyl-dimethylene-D-mannitol, was found to be entirely unreactive toward sodium iodide even under more drastic conditions; it seems highly improbable that this second closely similar substance can have either of its tosyl groups at a primary position. We assumed from their lack of reactivity, as contrasted with the proved reactivity of the 1,6-tosyl groups in the isomer, that they are attached to secondary hydroxyl groups; our interpretation of this case is that it follows the Oldham–Rutherford rule.

In the course of studies on methylene acetals of sugar alcohols we have obtained a dimethylene-L-xylitol (m. p. 215–217° (cor.), $[\alpha]^{20}\mathrm{D}$ $-25.3°$ in water) and a crystalline desoxy-dimethylene-D,L-xylitol (m. p. 155–156°), which will be described further in later publications; it became important in the study of these substances that the desoxy-xylitol which would be expected to be obtainable from Tipson and Cretcher's diacetone xylitol, be prepared. Our results confirm their work in the preparation of the diacetone xylitol and its tosyl derivative. The replacement of the tosyl group by iodine was accomplished

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[1] Tipson and Cretcher, *J. Org. Chem.*, **8**, 95 (1943).

[2] Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932); *cf.* Oldham, *J. Chem. Soc.*, **127**, 2840 (1925); Freudenberg and Raschig, *Ber.*, **60**, 1633 (1927).

[3] Hann, Maclay and Hudson, THIS JOURNAL, **61**, 2440 (1939).

[4] Haskins, Hann and Hudson, *ibid.*, **65**, 67 (1943).