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A Study of the Amorphous Portion of Dry, Swollen Cellulose by an Improved Thallous Ethylate Method[1,2]

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Several recent reviews[3] summarize in detail the modern concept of the structure of fibrous cellulose. It is only necessary to remark here that the linear macromolecules are crystallized together along intermittent portions of their length to form elongated, dense crystallites, or micelles, that are of submicroscopic dimensions and produce a well-defined X-ray diffraction pattern. Other portions of the macromolecules have a more confused relationship in space to one another, give rise to a diffuse or "amorphous" X-ray background and form a less dense, highly porous system of great absorptive capacity. The coarsest flaws and discontinuities in the fiber are visible in the microscope and electron microscope.[4] X-Ray studies of fibers impregnated with colloidal metals have revealed the presence of intercommunicating, elongated channels ranging in diameter from 50–120 Å.[5] The great majority of the submicroscopic faults in the crystal structure, however, are of the order of 10 Å. in cross section, or have molecular dimensions. These ideas make it easy to understand that the amount of amorphous cellulose might be increased at the expense of the less perfectly organized crystallite portion by swelling the fiber in a suitable liquid and be decreased by subsequent drying, particularly under tension.[6a,6b,7] There is evidence that such changes have an important influence upon the elasticity, the absorptive capacity and other industrially valuable physical properties of the fiber.[6b]

One method of estimating the amount of amorphous cellulose is to measure the intensity of the diffuse "background" radiation in the X-ray diffraction pattern of the fiber.[6b] In other methods, the solid cellulose is submitted to a suitable chemical change and the percentage of the more accessible, amorphous portion is calculated from the extent of the initial, more rapid reaction. The rate plots of various heterogeneous reactions[8,9] have been interpreted in this way. These chemical procedures suffer from the disadvantage that the reagents either do, or possibly may, penetrate the cellulose crystallites and may also cause swelling during the estimation. Both eventualities would tend to make the results high by an undetermined amount. In an endeavor to avoid this difficulty, Harris and Purves studied the thallation produced in ramie fiber by thallous ethylate dissolved in ether or benzene, which are non-hydroxylic, non-swelling liquids.[10] Since thallous ethylate is a strong base like its sodium analog, cellulose hydroxyl groups that came into contact with the reagent were changed to thallium alcoholates

$$\text{Cellulose OH} + \text{TlOEt} \longrightarrow \text{Cellulose OTl} + \text{EtOH}$$

The reaction was considered to be restricted to the amorphous cellulose because the thallation of finely powdered sucrose crystals, or unswollen ramie fiber, was very small and because the X-ray diffraction pattern of thallium cellulosate had no signs of a regularly oriented thallium crystal lattice. The thallium cellulosate was heated with excess methyl iodide,[11] or dimethyl sulfate, in benzene and, after purification, the methoxyl content

$$\text{Cellulose OTl} + \text{MeI} \longrightarrow \text{Cellulose OMe} + \text{TlI}$$

of the resulting partly methylated cellulose was determined. Since the thallation and methylation of some fructosides proceeded almost quantitatively with sufficient excess of the reagents,[12] the methoxyl substitution of the partly methylated cellulose was accepted as proportional to the number of hydroxyl groups that had come into contact with the thallous ethylate reagent. The present article describes substantial improvements in the technique of the estimation, together with the behavior of dry, highly swollen cotton linters toward thallous ethylate dissolved in several organic liquids. A new definition of amorphous cellulose is suggested and the measurements show that its absolute amount varies greatly.

Experimental

The methods are described in detail. Although straightforward enough in principle, they can be used successfully only by avoiding many manipulative errors that are not so unimportant as they may seem.

(1) Presented at the February, 1943, meeting in Cumberland, Maryland, of the Western Maryland Section of the American Chemical Society.

(2) Abstracted from Theses submitted to the faculty of 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) See, for example, Marsh and Wood "An Introduction to the Chemistry of Cellulose," 2nd ed., Chapman and Hall, London, 1942, pp. 380–405.

(4) Barnes and Burton, *Ind. Eng. Chem.*, **35**, 120 (1943). Earlier references are cited.

(5) Frey-Wyssling, *Protoplasma*, **25**, 261 (1936); **27**, 372 (1937). The fine structure of fibrous cellulose is discussed.

(6) (a) See, for example, the reviews by Mark, *Ind. Eng. Chem.*, **34**, 449 (1942); (b) *J. Phys. Chem.*, **44**, 764 (1940).

(7) Kratky, *Angew. Chem.*, **53**, 153 (1940), a review.

(8) Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1931–1932); *Kolloid-Z.*, **68**, 168 (1934).

(9) Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85, 1480 (1942).

(10) Harris and Purves, *Paper Trade J.*, **110**, 29 (Feb. 8, 1940).

(11) Fear and Menzies, *J. Chem. Soc.*, 937 (1926).

(12) Purves and Hudson, THIS JOURNAL, **59**, 49 (1937).

Preparation of Cellulose Samples.—Thoroughly dewaxed, air-dried, high grade cotton linters,[13] 15 g., were immersed in 540 cc. of 10% caustic soda kept at 5°,[14] and after three hours the loose, swollen mass was diluted with 540 cc. of 2% caustic soda. Thirty minutes later the cotton was recovered by filtration and was washed thoroughly and in succession with water, with 1% acetic acid and with distilled water. Slight squeezing quickly removed most of the excess moisture before the wet mass was dispersed in a liter of 99+ % methanol. The methanol was removed and replaced by a fresh amount after fifteen minutes. A third immersion, this time in magnesium-dried methanol, was followed by two more, each of thirty minutes duration, in one-liter volumes of sodium-dried, thiophene-free benzene. The supernatant liquors were easily reclaimed and purified. Great care was taken to avoid letting the cellulose dry out even superficially, by keeping it completely covered by the methanol or benzene, and by quick manipulation during the transfers. Neglect of this precaution resulted in non-uniform preparations.

The swollen linters, now moist with benzene, were dried for several days in a desiccator containing solid paraffin wax. The desiccator was evacuated at intervals to 25 mm. pressure, but the use of a higher vacuum was avoided because a too rapid, irregular evaporation of the benzene produced a non-uniform product. This mishap was signalized by the appearance of white patches on the surface of the rather translucent mass. Although up to 15 g. of linters could be swollen and dried in a uniform way with available laboratory equipment, the degree of swelling could not be exactly duplicated in successive preparations. The dried, swollen linters were stored for ten days or more over concentrated sulfuric acid in a desiccator that was *not* evacuated and were then ready for thallation. Solid caustic potash *in vacuo* was a less efficient desiccating agent. The effect of this final drying on moisture-containing preparations is discussed in another article.[15]

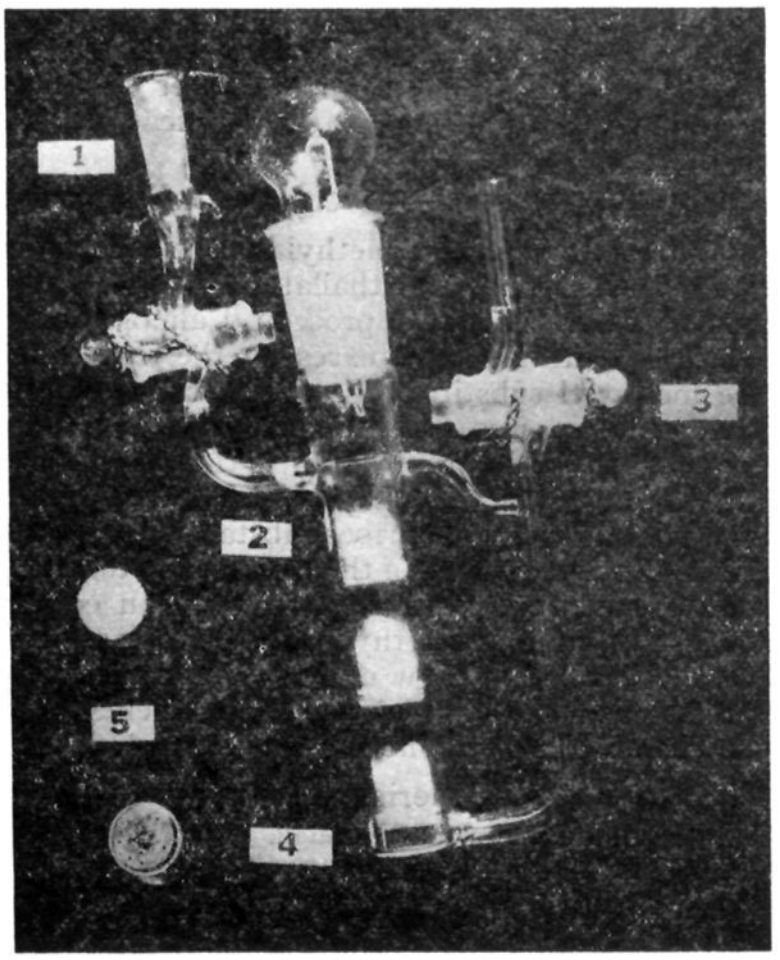

Fig. 1.—Apparatus used for thallation of cellulose.

Solvents.—The ready decomposition of thallous ethylate by moisture, by peroxides and other catalysts made it essential to purify all solvents carefully. Standard methods were used.[16]

Commercial 1,4-dioxane was freed from any acetals by refluxing with dilute hydrochloric acid in the presence of a stream of air. Thiophene was removed from benzene by bubbling the vapors, at 80°, through concentrated sulfuric acid. Other solvents were given suitable preliminary purifications when necessary. All hydrocarbons and ethers were dried with sodium before fractional distillation and were stored over sodium wire in brown glass bottles to avoid the formation of peroxides. These solvents were decanted from the sodium when required. All alcohols were dried either by adding small pieces of sodium or by refluxing with clean magnesium ribbon, and were recovered by distillation just before use. Methyl iodide was redistilled from phosphorus pentoxide.

Preparation of Thallous Ethylate Solutions.—Thin slices of clean, silvery thallium metal, 2 g., contained in a 125 cc. glass-stoppered, thick-walled Erlenmeyer flask, were covered with 50 cc. of absolute ethanol, and a stream of dry oxygen gas was played over the surface of the liquid for one or two minutes.[17] The flask was then stoppered, shielded from light and shaken mechanically. Solution of the metal was complete within two hours if the oxygen atmosphere was renewed at fifteen minute intervals. It was inadvisable to use thallium pellets in the preparation unless their surface was quite free from the insoluble brown crust formed by prolonged exposure to the air. The use of a trace of iodine to hasten the solution of the metal[10] was abandoned because iodine also catalyzed the decomposition of the thallous ethylate.

A small piece of porous porcelain was added to the solution to promote uniform boiling during the removal of ethanol in the vacuum of a water pump. The latter part of the distillation was from a warm water-bath but an excessive use of the pump was avoided lest moisture reach the ethylate when the vapor pressure of the residual alcohol became low. When the flask was shielded from light and the technique of distillation was satisfactory, the residual thallous ethylate formed about 1 cc. of a heavy, pale yellow oil. The oil was kept at room temperature for ten minutes in a high vacuum to remove any traces of ethanol and was dissolved in 50 cc. of the pure, anhydrous solvent to be used. Glass-stoppered graduates of 100-cc. capacity were convenient receptacles for these solutions.

The normality of the thallous ethylate was determined by pipeting 5 cc.[18] into a mixture of 20 cc. of methanol and 10 cc. of 0.1 *N* hydrochloric acid, the excess of which was then titrated with standard caustic soda. Dilution of the thallous ethylate solution to 0.1 *N* was made with the appropriate volume of the pure solvent. These solutions did not change their normality during several weeks if kept near 0° in the dark, but exposure to light caused a rather rapid formation of a spongy, brown decomposition product. Thallous ethylate oil was also fairly stable when properly stored.

Apparatus.—The all-glass Pyrex apparatus (Fig. 1) was designed for triplicate cellulose samples and was made from 20-mm. tubing about five inches long. The top carried a no. 20 female joint and could be closed with a well-fitting, lightly greased, ground stopper. Liquids introduced through the no. 7 female joint (1) from a 30-cc. separatory funnel passed through a stopcock and a sintered glass filter (2) before entering the tube a short distance below the stopper. Solutions were withdrawn through the stopcock (3) which was attached to the side of

(13) The authors wish to thank Dr. H. M. Spurlin and the Hercules Powder Company, Hopewell, Virginia, for the gift of this material.

(14) Richter and Glidden, *Ind. Eng. Chem.*, **32**, 480 (1940).

(15) Assaf, Haas and Purves, THIS JOURNAL, **66**, 64 (1944).

(16) Weissberger and Proskauer, "Organic Solvents," The Clarendon Press, Oxford, 1935.

(17) Lamy, *Ann. chim. phys.*, [4] **3**, 373 (1864).

(18) Although thallous ethylate is practically non-volatile and produced no ill effect on health during the research, the reader is reminded that many thallium compounds are cumulative poisons.

the tube by a solid glass support and to the flat bottom (4) by capillary tubing. Both stopcocks were of the 2-mm. slant-bore type.

The cellulose samples were contained in three glass cups, one inch in height, that fitted rather closely, one above the other, into the 20-mm. tube. These cups, shown separately at (5), had sintered glass bottoms for finely divided samples and perforated bottoms for fibrous ones. An annular segment of glass rod raised the lowest cup from the bottom of (4) so that liquid passed without obstruction into the capillary exit tube.

Procedure for Thallation and Methylation.—The cotton samples, 0.1 to 0.3 g., were transferred from a desiccator into the tared cups and were quickly weighed on a magnetically damped balance prior to insertion into the apparatus (Fig. 1). The stopper was replaced promptly to prevent access of moisture and the apparatus was at once evacuated with an oil pump attached to (3). A low result was obtained when this evacuation was neglected. Stopcock (3) was then closed and (1) was opened to permit 0.1 *N* thallous ethylate solution to be sucked into the apparatus from the separatory funnel. About 20 cc. of solution was sufficient to fill all three cups and immerse them completely. After standing in the dark at room temperature for one hour, the partly exhausted solution was sucked out through stopcock (3), with a minimum use of a water pump, and the thallation was repeated with fresh solution drawn in through (1). Samples thallated in ethers or hydrocarbons were colored yellow and, the deeper the color, the greater the thallation. When the thallous ethylate was dissolved in an alcohol, no color developed, although thallation occurred. The thallous ethylate solution was withdrawn at the end of the second hour in the dark and residual amounts were washed from the samples by filling the apparatus with pure, dry benzene. Four or five benzene extractions, the first of fifteen and the others each of five minutes duration, were sufficient. The wet samples were then prepared for methylation by filling the apparatus with benzene containing a large excess, 2 cc., of methyl iodide. The no. 20 ground-glass stopper (Fig. 1) was replaced with a glass-jointed reflux condenser whose upper end was equipped with a calcium chloride tube, stopcocks (1) and (3) were closed and the entire apparatus was immersed up to the level of the upper sample cup in a water-bath kept at 80°. No exclusion of light was necessary during the methylation, which was complete within three and one-half hours. Since thallous iodide was a by-product of the reaction, the methylation was attended by a color change in the samples from yellow or white to orange, the final depth of which was a rough measure of the amorphous cellulose. An experienced operator could complete the thallation and methylation of twenty-one cellulose samples, contained in seven sets of equipment, during one long working day. The condenser was then exchanged for the glass stopper, the excess methyl iodide–benzene mixture in the cell was sucked out by the water pump and pure benzene was sucked in. The first two benzene extractions, each of fifteen minutes' duration, were followed by six more each lasting for five to ten minutes. Thoroughness was essential in this extraction lest traces of residual methyl iodide invalidate the final methoxyl estimation. The apparatus was then connected to a vacuum pump but in the beginning stopcock (3) was kept open only momentarily in order to avoid scattering of the samples by a too sudden evaporation of the residual benzene. After a final drying in high vacuum at 80° for two hours, the whole of each sample, with its occluded thallous iodide, was analyzed at leisure for its methoxyl content. Clark's procedure[19] was followed except that 5 g. rather than 2 g. of phenol was added to the hydriodic acid to promote more regular ebullition, and the sample was dissolved in the reagent by a preliminary heating for a few minutes in a boiling water-bath.[20] The methoxyl content was expressed as a percentage of the original, *unsubstituted* cellulose, and multiplication by the factor 100/57.4 gave the percentage of the cellulose hydroxyl groups that had been methylated.[21] This value was assumed to be equal to the percentage of the cellulose wetted by the solvent for the thallous ethylate.

TABLE I

THALLOUS ETHYLATE METHYLATIONS OF DIFFERENT SAMPLES OF DRY, SWOLLEN LINTERS

Solvent for $TlOC_2H_5$	Methoxyl introduced[a] % Cup 1	Cup 2	Cup 3	Mean %	Hydroxyl groups %[b]	Error ± %
Benzene	6.1	5.7	5.7	5.8	10.1	5
Decalin	3.4	2.2	2.9	..	..	25
Decalin	4.1	4.1	...	..	..	0
Decane	5.7	5.7	...	5.7	9.9	0
Ethyl ether	11.5	10.0	9.7	10.4	18.1	10
Ethyl ether	7.4	6.6	7.7	7.2	12.5	8
Isoamyl ether	5.0	4.2	3.9	..	..	14
Methanol[c]	4.8	4.7	4.9	4.8	8.4	2
Ethanol[c]	6.5	6.5	6.4	6.5	11.3	1.5
Propanol[c]	4.8	5.3	5.2	5.1	8.9	4
n-Amyl ether[c]	7.5	7.5	7.5	7.5	13.0	0

[a] Based on weight of original cellulose sample. [b] Mean methoxyl percentage × 100/57.4 = percentage of cellulose hydroxyl groups methylated. [c] Extraction of last traces of methyl iodide as described in experimental portion.

Reproducibility of the Estimation.—Table I contains a representative portion of the data, which included more than two hundred and fifty individual estimations. Cups 1, 2 and 3 refer to triplicate analyses carried out simultaneously in the top, middle and bottom cups of a single piece of apparatus. If the observed methoxyl content decreased markedly and steadily from the top to the bottom cup, as in the case quoted for thallous ethylate in isoamyl ether, incomplete thallation was at once suspected and the analyses were repeated. The other serious cause of divergence between triplicates was failure to extract the last traces of methyl iodide from the methylated samples prior to the methoxyl estimation. Most of the present data were obtained before this fact was fully appreciated and the divergence from the averages quoted below was sometimes as much as ± 10%. When the method of extraction already described was rigidly followed, the agreement between triplicates was usually better than ± 5%. The third analysis on samples known to be uniform was sometimes omitted when the first two gave the same result. Wide fluctuations that persisted in a second series of analyses were characteristic of samples that were not uniform and were usually connected with poor technique during the drying of the swollen cellulose.

Estimation of Cellulose Hydroxyl Groups by Means of Methylmagnesium Iodide.—Use was made of a modified Zerewitinoff apparatus that had been extensively tested during the determination of active hydrogen in insulating and other oils.[22,23] A thoroughly dried specimen of highly swollen linters, 0.117 g., was brought into contact with excess of an approximately 0.4 *M* solution of methylmagnesium iodide in isoamyl ether[24] and 4.96 cc. of methane (cor. to N.T.P.) was collected. This amount corresponded to the active hydrogen in 10.2% of the hydroxyl groups in the sample. A preliminary result of 5.7% was rejected as erroneous. Parallel estimations by the thallation-methylation method, giving 6.8, 6.5 and 6.5% methoxyl with thallous ethylate dissolved in the same

(19) Clark, *J. Assoc. Official Agr. Chem.*, **15**, 136 (1932).

(20) Arndt and Neumann, *Ber.*, **70B**, 1835 (1937).

(21) Trimethyl cellulose has a methoxyl content of (3 × 31 × 100)/162, or 57.4% on this basis, and the figure for lower methylated derivatives is directly proportional to their substitution.

(22) Assaf and Gladding, *Ind. Eng. Chem., Anal. Ed.*, **11**, 164 (1939).

(23) Larsen, *ibid.*, **10**, 195 (1938).

(24) Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

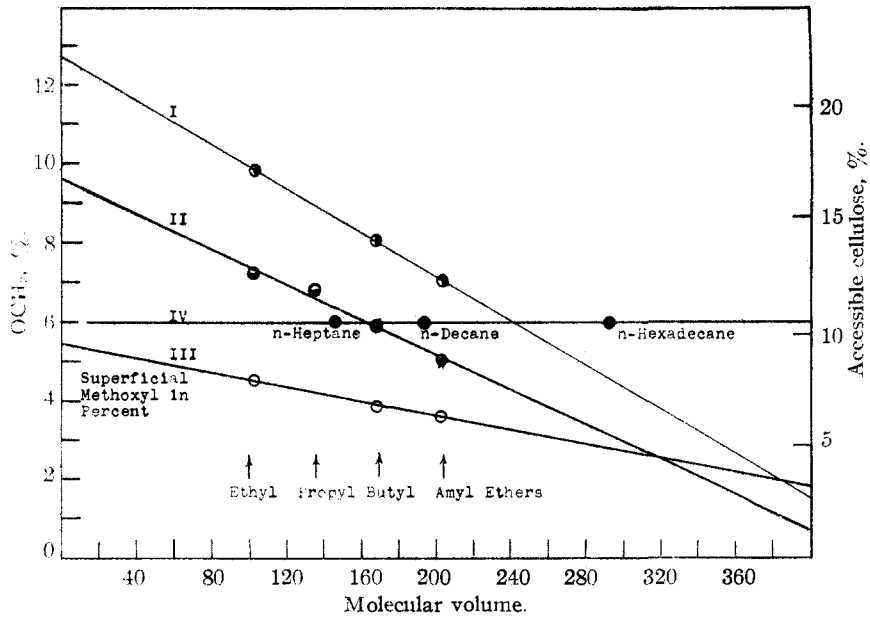

Fig. 2.—Superficial methylation and accessible cellulose plotted against molecular volume of thallous ethylate solvent: ethers, O, ◑ and ◒; hydrocarbons, ●.

solvent, indicated that 11.5% of the hydroxyl groups had been methylated. The latter figure was 20% with thallous ethylate in diethyl ether. Although the Zerewitinoff method checked the thallous ethylate technique, the utility of the former for present purposes was limited by its sensitivity to traces of moisture in the sample and by the necessity of employing a solvent with a low vapor pressure.

Results and Discussion

In Fig. 2, the percentage of methoxyl introduced into three different samples of uniformly swollen, dried linters by the thallation-methylation technique is plotted against the molecular volume of the liquid in which the thallous ethylate was dissolved. Each point is the average of duplicate or triplicate estimations that agreed with the mean to within ±10% and all thallations of each cellulose sample were made simultaneously in order to avoid the effects of possible change in the specimen.[15] These precautions were taken throughout the work. The points for ethyl, *n*-propyl (Fig. 2, plot II), *n*-butyl and *n*-amyl ethers fall on three straight lines whose slope and position are characteristic of the cellulose sample. Although the decrease in the degree of methylation with increasing molecular volume could have been predicted from the work of others,[25,26,27] the closely linear nature of the relationship suggests that the cross-section of the capillaries in the amorphous portion of the linters diminishes in a regular way as a crystalline region is approached. Plot IV, obtained with the same cellulose and at the same time as the ether plot II, demonstrates that the extent of thallation with the normal hydrocarbons is entirely independent of their molecular volume. Attempts were made to reconcile the data in the two series by plotting the per cent. of methylation against some other physical property, such as the viscosities or the molecular weights, of the liquids in question. These attempts revealed no regular relationship and the results with normal hydrocarbons require amplification. Their curious behavior may be connected with the fact that they differ from ethers in having no dipole moment and no residual affinity for hydroxyl groups. Since branched chain and cyclic molecules are more limited in shape configurations than their normal analogs, it is to be expected that they would have greater difficulty in entering the finest capillaries and would permeate the amorphous portion of cellulose less efficiently. Figure 3 shows that the methoxyl contents produced with thallous ethylate in isoamyl ether, 1,4-dioxane and decalin were lower than those obtained with *n*-amyl ether, diethyl ether and *n*-decane, respectively, although each pair had approximately the same molecular volume. The figure for dioxane is interpolated from similar experiments.

The data summarized in Fig. 4 are strictly comparable with the exception of those for methanol, which were obtained with an 0.056 *N*, instead of the usual 0.1 *N*, thallous ethylate solution.[28] Individual estimations are recorded because those for the ethers were unusually discordant. Although the results with the normal alcohols from ethyl to heptyl are regular and reproducible, the molecular volume plot is not linear and lies below that of the ethers. Since

(25) Sheppard and Newsome, *J. Phys. Chem.*, **36**, 2306 (1932).

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

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

(28) The addition of methanol to liquid thallous ethylate caused the prompt deposition of the sparingly soluble, crystalline methylate.

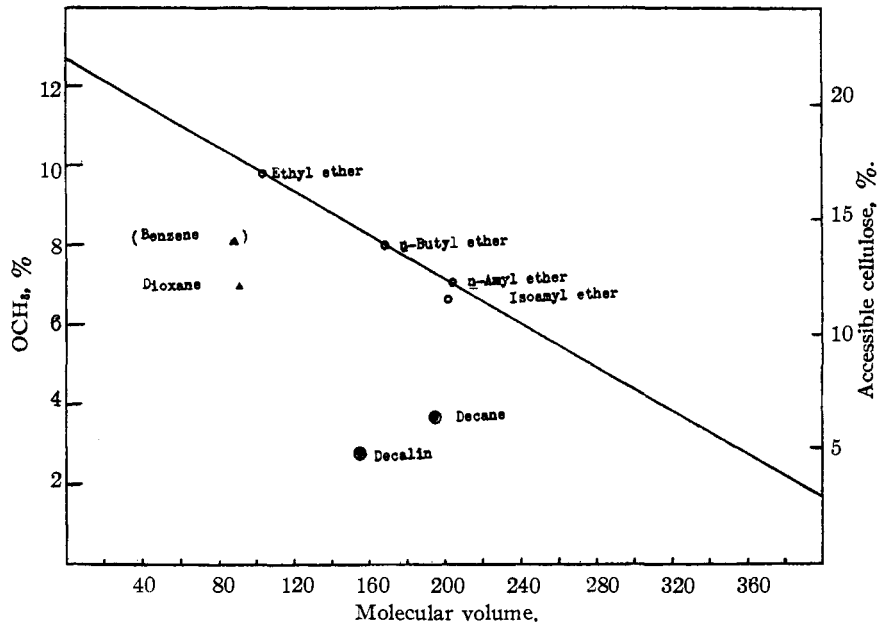

Fig. 3.—The superficial methylation of a uniform, swollen cellulose by thallous ethylate dissolved in various liquids.

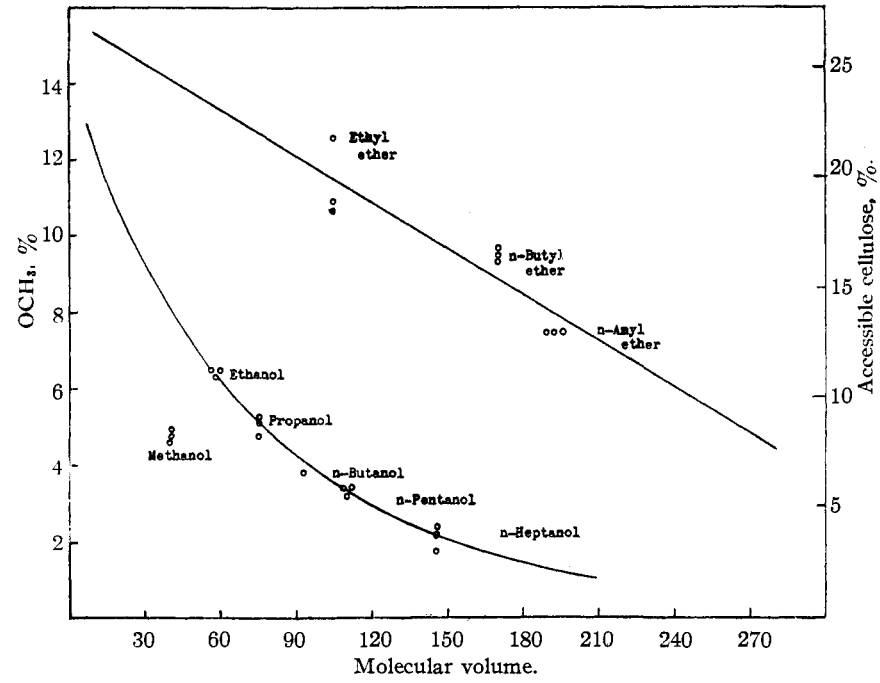

Fig. 4.—The superficial methylation of a uniform, swollen cellulose by thallous ethylate dissolved in various normal alcohols and ethers: triplicate estimations shown.

alcohols swell cellulose somewhat, they should penetrate the amorphous portion more readily than ethers of comparable molecular volume and lead to more, rather than less, thallation and methylation. This discrepancy strongly suggests that thallation in alcohols was incomplete, probably because the large number of hydroxyl groups they contain competed effectively with those in the cellulose for the thallium. There is also a possibility that molecular association rendered the effective volumes of the alcohols three to seven times larger than those calculated.[29]

The thallous ethylate molecule has a calculated molecular volume of about 69 (density about

(29) Fox and Martin, *Trans. Faraday Soc.*, **36**, 897 (1940), express the opinion that up to four benzyl alcohol molecules may form hydrogen bonds with each other. The resulting, unstable, cyclic structure may have the hydrocarbon groups on the outside.

3.6,[17] mol. wt. 249) and any part it played in the above experiments was a matter of importance. A consideration of Figs. 2 to 4 strongly suggests that the ethylate functioned merely as a delineator of the penetration of the liquid in which it was dissolved, because otherwise the dependence of the methylation data upon the molecular volume of the solvent would be incomprehensible. This conclusion was supported by parallel experiments with solutions of methyl magnesium iodide and thallous ethylate in isoamyl ether. The methane liberated in the first case corresponded to 10.2% of the cellulose hydroxyl groups and 11.5% reacted in the control experiment. The approximate equality of these figures shows that the extent of the reaction was independent, or nearly so, of the nature of the reactive solute. When this view is accepted, the extrapolation of the normal ether plots to zero methylation (Figs. 2 to 4) theoretically gives the maximum molecular volume a liquid may have if it can enter the fiber at all. These limiting volumes range from 360 upward and are large enough to accommodate molecules as bulky as those of many dyestuffs. Such molecules, however, would come into contact with the visible external surface and would enter the coarsest channels of the submicroscopic capillary system.[5] Since the wetting of these minute portions of the fiber would be independent of the molecular volume of the liquid, the above extrapolation must become asymptotic to the abscissa at a small methoxyl percentage.

Extrapolation of the normal ether plots in the other direction gives the theoretical methylation, or thallation, produced by thallous ethylate dissolved in a liquid of zero molecular volume. This observation suggests that the amorphous portion of cellulose can be defined as the percentage accessible to a liquid of zero molecular volume and with no tendency to swell the cellulose or penetrate its crystallites.[30] If this definition has any validity, the result should be independent of the particular homologous series of liquids in which the thallous ethylate is dissolved. Figure 4 shows that this inference is probably true for the normal ethers and alcohols (omitting methanol) and that the methylation at zero molecular volume lay between 14.5 and 16.5%. The amorphous cellulose in this sample was therefore 15.5 × 100/57.4 or 27%, with an absolute error of the order of ±2%. Since the extrapolation was a large one, an attempt was made to determine the data for dimethyl ether (mol. vol. 40) which falls at an intermediate point on the plot. The estimation was tried at atmospheric pressure and −30° but was not completed because the thallous ethylate crystallized rapidly from solution at this low temperature. Another attempt with water (mol. vol. 18) was more successful and led to a new and reasonable interpretation of the cellulose-moisture adsorption isotherm.[15] The above definition of amorphous cellulose has at least the merit of practicality, although the anomalous behavior of the normal hydrocarbons (Fig. 2) makes it advisable at present to use only ethers or alcohols in the estimation.

Table II, column 3, summarizes the results of the present research and includes other relevant data. The infrared absorption study[31] showed that all, or nearly all, of the hydroxyl groups in dry, unswollen ramie are hydrogen bonded and presumably are present in the molecular lattice of the crystalline portion. Neither the infrared study, nor statements based upon the X-ray method,[6b,7,32,33] are considered to be necessarily in conflict with the very small percentages of amorphous cellulose revealed in unswollen samples by the thallous ethylate technique, or by methylation with an ethereal solution of diazomethane.[34] If these percentages are accepted as approximately correct, it follows that suitable swelling and drying procedures increase the amorphous fraction fifty or even an hundredfold and therefore increase the accessibility of fibrous cellulose to non-swelling reagents by a factor of similar magnitude. Another article[15] discusses this matter in greater detail. It also follows from column 3 that estimations of the amorphous fraction by acetylation[8] or by oxidation with ferric chloride in aqueous hydrochloric acid[9] involve a surprisingly large degree of swelling, and record the amounts present in swollen products rather than those in the initial samples. This characteristic, of course, may enhance the utility of such methods as control estimations for celluloses destined for industrial processes in which swelling plays a prominent role.

If it be assumed from X-ray data that a single glucose residue has an area of 52×10^{-16} sq. cm.,[35] a continuous, unimolecular film of cellulose weighing 1 g. covers $52 \times 10^{-16} \times 6.02 \times 10^{+23}/162$ or $1.87 \times 10^{+7}$ sq. cm. The colloidal surfaces (Table II, column 4) corresponding to the amorphous fractions found by the thallous ethylate method range up to 520×10^4 sq. cm. per gram and their extent approximates those developed by good grades of carbon black.[36] The order of magnitude of these surfaces is also in agreement with the general value of 300×10^4 sq. cm. per gram derived for swollen celluloses

(30) We are indebted to Dr. R. F. Conaway, of E. I. du Pont de Nemours and Company, for suggesting this definition.

(31) Ellis and Bath, THIS JOURNAL, **62**, 2859 (1940).

(32) Meyer, *Ber.*, **70**, 266 (1937).

(33) Kratky, *Silk and Rayon*, **13**, 480, 571, 634, 638 (1939); *C. A.*, **33**, 6041 (1939); **34**, 259 (1940), a review.

(34) Reeves and Thompson, *Contrib. Boyce Thompson Inst.*, **11**, 55 (1939); *C. A.*, **34**, 3923 (1940). The degree of methylation increased with the moisture content.

(35) Adam, *Trans. Faraday Soc.*, **29**, 90 (1933), found 52 sq. Å. from a model built to scale and 55 to 60 sq. Å. from measurements of unimolecular films. A value of 42 sq. Å. was assumed by one of the present authors in the earlier article.[10]

(36) Brown and Smith, *Ind. Eng. Chem.*, **34**, 352 (1942).

TABLE II

THE AMORPHOUS FRACTION AND COLLOIDAL SURFACE OF VARIOUS CELLULOSE SAMPLES

Swollen samples[a]	Method	Amorphous cellulose, %	Colloidal surface sq. cm./g. × 10^{-4}
Linters, Fig. 2, Plot I	TlOEt	22	420
Linters, Fig. 2, Plot II	TlOEt	17	330
Linters, Fig. 2, Plot III	TlOEt	9	170
Linters, Fig. 4	TlOEt	27	520
Linters, regenerated	TlOEt[10]	3.3	60
Ramie	TlOEt[10]	18	360
Unswollen samples[b]			
Linters	TlOEt	0.4	8
Ramie	TlOEt[10]	0.25	5
Ramie	Infrared absorption[31]	Very small	
Linters	X-Ray diffraction[33]	Practically none	
"Cellulose"	X-Ray diffraction[32]	10	190
Viscose rayon, unstretched	X-Ray diffraction[6b]	60	1150
Viscose rayon, stretched	X-Ray diffraction[6b]	30	580
Viscose rayon	$FeCl_3$ in aqueous HCl[9]	21	400
Linters, unmercerized	$FeCl_3$ in aqueous HCl[9]	5	100
Cellulose	Diazomethane[34]	0.4	8
Linters, mercerized	$FeCl_3$ in aqueous HCl[9]	11	210
Ramie	Esterification, X-ray diffraction[8]	30–50	580–960

[a] Swollen in caustic soda and dried by solvent exchange. [b] Dried directly, at 25° or 105°, whether previously swollen or not.

from the areas covered by various adsorbed films.[37] The latter investigations, however, assign a cross-sectional area to the adsorbed molecule, rather than to the cellulose itself, and assume the adsorbed film to be monomolecular and continuous. A close comparison of these data with the results of the present work is therefore hardly possible. As might be expected, the microscopically visible surface of about 2×10^3 sq. cm. per gram assigned to unswollen fibers[37] is considerably smaller than the 5×10^4 sq. cm. per gram available to an ether of zero molecular volume (Table II).

Summary

1. Cotton linters, highly swollen in caustic soda and dried through methanol and benzene, were immersed in a large excess of 0.1 *N* thallous ethylate solution. The thallium cellulosate so formed was methylated with excess methyl iodide in benzene. The methoxyl content of the product was accepted as proportional to the percentage of the cellulose wetted by the particular liquid in which the thallous ethylate was dissolved.

2. The extent of the methylation did not depend upon the molecular volume of normal hydrocarbon solvents for the thallous ethylate, but the relationship was inverse and linear for the normal ethers from diethyl to di-*n*-amyl. Branched chain or cyclic ethers and hydrocarbons penetrated the cellulose less efficiently than their normal analogs and thallations in alcohols, although reproducible, were thought to be incomplete.

3. "Amorphous" cellulose was defined to be the percentage wetted by an ether of zero molecular volume and was estimated by extrapolating the linear methylation-molecular volume plots of three or more straight chain ethers. An extrapolation of the similar plot for the normal alcohols from ethyl to hexyl tended to confirm the result, which was probably accurate to ±10%.

4. The amorphous fractions of swollen linter samples were as high as 27 ± 2% but the amount present in unswollen fibers was of the order of 0.25 to 0.5%. The corresponding colloidal surfaces, ranging from 520×10^4 to 5 or 10×10^4 sq. cm. per gram, were not inconsistent with published estimates based upon other experimental methods.

(37) Stamm and Millett, *J. Phys. Chem.*, **45**, 43 (1941). Includes a review of the literature.

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