351. *The Absorption Spectra of Some Cellulose Derivatives in the 3-μ. Region.*

By L. Brown, P. Holliday, and I. F. Trotter.

The infra-red absorption spectra of native and regenerated cellulose and of a number of cellulose derivatives have been measured in the region 2·5—4·0 μ. The results show that the shape and frequency of the absorption band associated with the fundamental hydroxyl stretching mode give considerable information about the hydrogen-bonding conditions, and in particular may be used as a criterion of uniformity of substitution along the cellulose chains. The possibility of using the intensity of the hydroxyl band as a measure of the hydroxyl content of cellulose derivatives is discussed. Preliminary infra-red measurements are described on the water imbibition of some cellulose ethers and esters.

It is generally accepted that a reaction involving fibrous cellulose will proceed more rapidly in the less crystalline regions, and the highly crystalline material will only react to an equivalent extent if one of three conditions is fulfilled, namely: (i) the reaction goes to completion, giving a trisubstituted derivative; (ii) an equilibrium is set up, the extent of the reaction depending on the concentration of reagents; (iii) the cellulose passes into solution or becomes so highly swollen that all distinction between the regions of varying crystallinity is lost.

In the preparation of incompletely substituted cellulose esters of organic acids the first and third of these conditions are used, a substantially completely substituted product, the primary ester, being subjected to partial hydrolysis in solution, thus ensuring a uniformly substituted secondary ester. If, however, the substitution stops short of the triester, the unesterified material will consist largely of the more crystalline parts of the cellulose, and in the resulting

secondary ester the degree of substitution will vary for different portions of the same chain. Such non-uniform substitution will have a marked effect on the solubility properties, since the normal solvents for cellulose esters are incapable of solvating those portions of the chain where the packing differs little from that found in crystalline cellulose. Where, however, these regions are small compared with the substituted regions, it is possible that the material will dissolve in the normal solvents, but that the resulting solution will show poor flow properties and give an apparent viscosity greater than that indicated by the average molecular weight of the solute. Similar considerations apply to the solubility of cellulose ethers.

As there are other explanations of the anomalous solubility properties of certain cellulose derivatives, a method was sought for the direct detection of non-uniform substitution as distinct from the chemical methods used by Purves and his collaborators (*J. Amer. Chem. Soc.*, 1939, **61**, 3458, 3463; 1942, **64**, 9, 15, 1539). The measurement of the infra-red absorption spectra seemed to offer some hope of an unambiguous solution, as non-uniform substitution will cause variations in the hydrogen-bonding conditions around the residual hydroxyl groups and such variations should affect the hydroxyl-stretching frequency near 3 μ.

Experimental.

The spectra were measured on a Hilger D.209 double-beam recording spectrometer fitted with a lithium fluoride prism. The slit width used was 0·2 mm. and the accuracy of the frequency measurements was probably better than ±3 cm.$^{-1}$. The quantitative measurements on the intensity of the hydroxyl absorption were made on a Grubb–Parsons S-3 single-beam spectrometer, a sodium chloride prism and slit width of 0·026 mm. being used.

The cellulose derivatives were studied in the form of films of suitable thickness cast from the appropriate solvents on glass plates. The regularity of most of the films cast this way is so great as to give interference fringes in the infra-red, which appear as spurious absorption bands. The production of these undesirable fringes was eliminated by casting the films on finely ground glass plates.

To avoid the effects of absorbed water, the films were measured in the dry state. The water content of fibres and films of thicknesses suitable for infra-red investigation reaches equilibrium with the surrounding atmosphere in a matter of a minute or so. To obtain the spectrum of a dry sample it is therefore essential that the atmosphere in contact with the specimen should be kept dry throughout a measurement. This can be achieved in several ways: (i) by mounting the film in a cell which can be evacuated; (ii) by mounting the film in a sealed cell containing phosphoric oxide or magnesium perchlorate; or (iii) by mounting the film in a cell through which a stream of dry nitrogen can be passed. It was found that a combination of (i) and (ii) gave the most rapid drying. The cell used was made of brass, with rock-salt windows, and was small enough to be located at the primary focus of the Grubb–Parsons S-3 spectrometer. A small tray of phosphoric oxide was included in the cell, and an outlet tube attached to a pump allowed the cell to be kept under vacuum throughout an experiment. Under these conditions no further change in the spectrum of any of the samples could be detected after about 5 minutes. The position of the film mount could be adjusted externally by means of a screw, so that measurements could be made through various portions of the film without breaking the vacuum.

Results and Discussion.

(a) *Native and Regenerated Cellulose.*—The spectrum of native cellulose from 2700 to 3700 cm.$^{-1}$ is shown in Fig. 1, No. 1. The results, obtained from two different thicknesses of the cell wall of *Valonia ventricosa*, refer to undried samples but it was found that subjection of the films to an intensive drying treatment produced no detectable change in the spectrum. When the sample was heated in a stream of hot, dry nitrogen the bands were reduced in intensity and shifted to higher frequencies, a shift of some 20 cm.$^{-1}$ being observed for the 3350-cm.$^{-1}$ band at about 150°, but when the nitrogen stream was cooled the spectrum reverted to that of an undried sample. The CH band shows three well-resolved peaks, and the hydroxyl band three peaks at 3245, 3274, and 3350 cm.$^{-1}$ with a shoulder on each side of the 3350-cm.$^{-1}$ band.

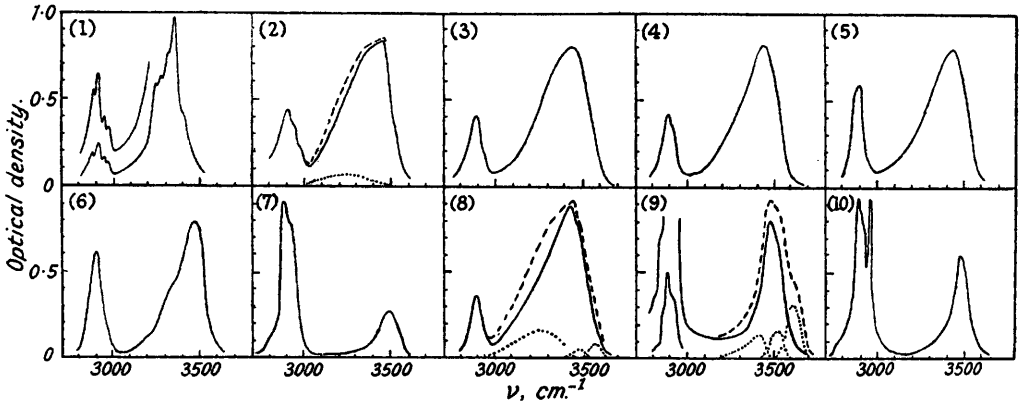
The spectrum of regenerated cellulose (Fig. 1, No. 2), obtained from a sample of viscose film, is in marked contrast to that of *Valonia*, the CH absorption being less well resolved and the OH band broad and ill defined. Further, there is a detectable change in the OH absorption on drying. It is known from *X*-ray diffraction results, and in particular from the measurements by Hermans and Weidinger (*J. Polymer Sci.*, 1949, **4**, 135), that *Valonia* is much more crystalline than regenerated cellulose. It is also known that water cannot be absorbed in the lattice of native cellulose, but that regenerated cellulose readily forms a hydrated lattice in moist air (*idem*, *J. Colloid Sci.*, 1946, **1**, 185). The sharpness of the OH and CH bands in *Valonia*, and the apparent absence of absorbed water, agrees with these results. The less well-resolved CH bands and the broad OH absorption in the viscose film are in agreement with a much lower degree of crystallinity. The spectrum of the absorbed water is discussed in the next section.

(b) *Cellulose Cyanoethyl Ethers.*—The possibility of obtaining a correlation between the

solubility and the hydroxyl absorption of cellulose derivatives was first investigated for a series of cyanoethyl ethers, this class of compound being chosen because samples prepared by MacGregor's method (B.P. 588,751, 605,357) were available over a wide substitution range. The cyanoethyl celluloses do not, however, constitute an ideal case for an investigation of this type, because in their preparation some hydrolysis of the cyano-groups always occurs. Spectroscopic measurements have shown that this hydrolysis usually stops at the amide stage and involves only a small proportion of the cyano-groups. In the present considerations the presence of amido-groups may be ignored.

The degree of substitution of a cellulose derivative may be defined as the average number of hydroxyl groups substituted per anhydroglucose residue. On this basis the degree of substitution of a fully substituted cellulose derivative is 3. At low degrees of substitution the cyanoethyl celluloses are soluble in dilute solutions of sodium hydroxide and the hydroxyl absorption is similar to that of regenerated cellulose. This is illustrated in Fig. 1, Nos. 8 and 3, where the spectra of two derivatives of degree of substitution 0·15 and 0·66 are shown. At the higher degree of substitution it is possible to prepare water-soluble derivatives, the spectrum of

FIG. 1.



Curve no.	*Substance.*	*Curve no.*	*Substance.*
1	Valonia ventricosa.	6	*Cyanoethyl cellulose* (2·12).
2	*Regenerated cellulose.*	7	*Cyanoethyl cellulose* (2·96).
3	*Cyanoethyl cellulose* (0·66).	8	*Cyanoethyl cellulose* (0·15).
4	*Cyanoethyl cellulose* (0·77).	9	*Cyanoethyl cellulose* (2·92).
5	*Cyanoethyl cellulose* (2·00).	10	*Cellulose ether.*

Figures in parentheses refer to degree of substitution.

- - - - *Undried samples.* ——— *Dried samples.*

such a substance of degree of substitution 0·70 being shown in Fig. 1, No. 4. The maximum of the OH absorption is a few wave-numbers higher for the water-soluble cyano-ether and the band is more symmetrical than that of the alkali-soluble cyano-ether. In cellulose and its derivatives, where there are regions of varying crystallinity, corresponding hydroxyl groups will not all be similarly environed even for a uniform distribution of substituent groups, and the resulting OH band may probably be regarded as a type of distribution curve showing the proportions of hydroxyl groups with the various possible degrees of hydrogen bonding. The shape of the OH band is clearly of importance, as a small proportion of strongly hydrogen-bonded OH groups will have a considerable influence on the solubility characteristics. Some measure of the symmetry of the OH absorption bands may be obtained from the ratio of the band widths on the low- and on the high-frequency side of the maximum at half the peak optical density. This designation for symmetry being used, the symmetry index for a symmetrical band is unity and is greater than unity for bands which are broadened on the low-frequency side. The results obtained for a number of cyanoethyl celluloses are summarized in the table, from which it can be seen that the water-soluble derivatives show an OH frequency in the range 3450 ± 3 cm.$^{-1}$ and a symmetry index of between 1·5 and 1·9. For the alkali-soluble derivatives the corresponding figures are 3434 ± 12 cm.$^{-1}$ and 2·0—2·5, respectively. Regenerated cellulose has an OH frequency of 3443 cm.$^{-1}$ with a symmetry index of about 2·6. It is evident that the water-soluble cyanoethyl celluloses are less like regenerated cellulose in their state of

hydrogen bonding than are the alkali-soluble derivatives. This implies a greater penetration of the highly crystalline regions of the cellulose by the substituent groups in the former case; *i.e.*, the water-soluble cyano-ethers are more uniformly substituted than the alkali-soluble cyano-ethers.

Degree of substitution.	Solubility.	ν_{OH}, cm.$^{-1}$.	Symmetry index.	Degree of substitution.	Solubility.	ν_{OH}, cm.$^{-1}$.	Symmetry index.
0·00 *	—	3443	2·6	1·28	Aq. NaOH	3429	2·0
0·15	Aq. NaOH	3443	2·5	1·38	Aq. NaOH	3435	2·1
0·57	Aq. NH_3	3432	1·7	1·70	Aq. NaOH	3422	2·0
0·66	Aq. NaOH	3440	2·0	2·00	Aq. NaOH/ acetone	3430	2·3
0·70	Water	3448	1·7				
0·84	Water	3451	1·5	2·12	Aq. acetone	3460	1·7
0·90	Water	3453	1·8	2·70	Acetone	3476	1·1
1·05	Water	3448	1·9	2·79	Acetone	3477	1·0
1·05	Aq. NaOH	3437	2·1	2·92	Acetone	3484	1·1
1·10	Water	3453	1·5	2·92	Acetone	3481	1·0
1·21	Aq. NaOH	3435	2·5	2·96	Acetone	3481	1·0

* Regenerated cellulose.

When the degree of substitution exceeds a value of about 2, solubility in a purely aqueous medium would no longer be expected, and over the substitution range 2·0—2·5 it was found that the majority of the cyano-ethers were soluble in aqueous acetone; some, however, required the addition of alkali before dissolution would occur. The OH absorption of these two types of derivative is shown in Fig. 1, Nos. 5 and 6. The shapes of the two bands differ in the same way as was found in the lower substitution ranges, and the maxima differ by about 30 cm.$^{-1}$, the frequency of the alkali-soluble derivative being the lower one. Above a degree of substitution of about 2·6 the cyanoethyl celluloses are soluble in dry acetone and show an OH frequency of 3480 $\pm$ 4 cm.$^{-1}$ (Fig. 1, No. 7). The hydroxyl bands for these derivatives are almost symmetrical, the symmetry indices differing little from unity.

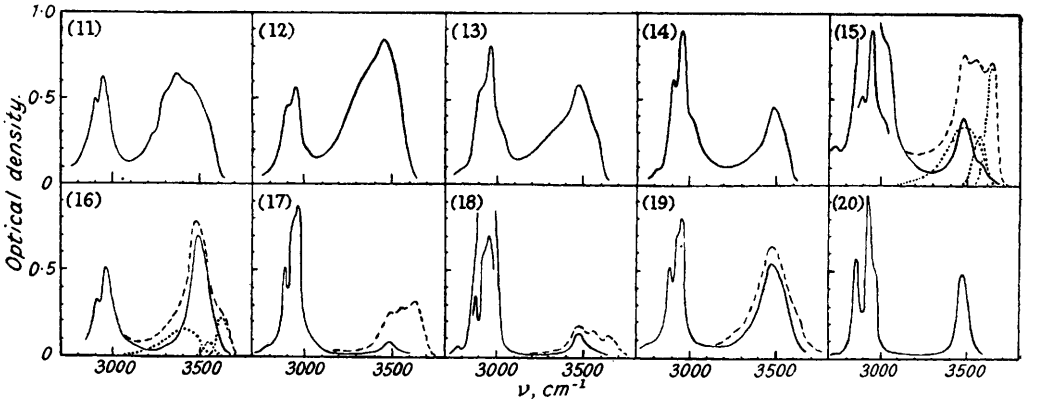
All the cyanoethyl celluloses readily absorb water vapour, and the spectra of the dried samples, referred to above, are appreciably different from those of the corresponding samples measured in moist air. The difference between the absorption spectra of a dry and an undried sample, plotted on an optical density versus frequency basis, gives the spectrum of the absorbed water. Graphical separation of the resulting curve shows it to consist of three bands, a very broad band extending to low frequencies and two sharper bands at higher frequencies. This is illustrated for two extreme samples in Fig. 1, Nos. 8 and 9. The broad low-frequency band is similar to that obtained with liquid water. The two high-frequency bands probably correspond to the symmetrical and antisymmetrical stretching frequencies of water molecules hydrogen-bonded to the hydrogen atoms of the cellulosic hydroxyl groups. It is difficult to make an accurate determination of the precise contour of the water absorption band, and from the nature of the graphical separation it is not possible to attach any great significance to variations in the frequencies of these three bands. It is, however, of interest that the absorption spectrum should serve to distinguish between bonded and non-bonded water. No evidence of the two high-frequency bands was obtained in the spectrum of regenerated cellulose. This difference between cellulose and the cyanoethyl celluloses is probably to be attributed to the fact that introduction of substituent groups must increase the spacing between adjacent chains. This will leave a number of unbonded hydroxyl groups which could form hydrogen bonds with water molecules. If this explanation of the observed differences is correct, it would seem that there can be very few unbonded OH groups in regenerated cellulose even in the less crystalline regions. This may be compared with the state of affairs found in polyamides where there is no spectroscopic evidence for any unbonded NH groups.

(c) *Cellulose Ethyl Ethers.*—All the cellulose ethyl ethers measured were in the substitution range 2·2—2·6. These samples showed similar solubility characteristics and in the dry state all showed a single OH band at 3479 cm.$^{-1}$. The spectrum of a typical cellulose ethyl ether is shown in Fig. 1, No. 10, and it can be seen that the CH absorption is appreciably different from that of a cellulose cyanoethyl ether.

(d) *Primary Cellulose Acetates.*—The results described for the cyanoethyl celluloses refer to the complete range of degrees of substitution. In order to obtain more detailed information about the hydrogen-bonding conditions, an investigation was made of a number of derivatives containing relatively few hydroxyl groups. This was done by studying the absorption spectra of a series of primary cellulose acetates, *i.e.*, cellulose acetates isolated during the later stages of the acetylation of cellulose.

The cellulose acetates investigated were isolated at hourly intervals from a fibrous acetylation. After the first hour the conditions of acetylation were such that the degree of substitution was of the order of 2·5, and thereafter it rose more slowly to a value of about 2·95. The early samples gave solutions in methylene chloride–alcohol which were of high viscosity and showed poor flow properties, whereas the later samples gave clear, oily solutions of progressively decreasing viscosity. The spectra of a selection of these acetates are shown in Fig. 2, Nos. 11—15. T_1, the earliest sample to be isolated, shows OH maxima at 3343 and at about 3455 cm.$^{-1}$ with shoulders at 3210 and 3290 cm.$^{-1}$. Comparison with the hydroxyl absorption in regenerated cellulose (Fig. 1, No. 2) shows that the main absorption at 3343 cm.$^{-1}$ is at a considerably lower frequency than that found in regenerated cellulose and is nearer to that found in native cellulose. This implies that the hydrogen-bonding conditions in some of the unesterified regions of T_1 must approximate closely to those found in the more highly crystalline parts of cellulose, and the presence of such regions of unattacked crystalline cellulose would account for the poor flow properties of T_1 in solution. T_2 and T_3 both show broad OH absorption bands with maxima at 3465 and 3470 cm.$^{-1}$, respectively. Both bands are

FIG. 2.



Curve no.	*Substance.*	*Curve no.*	*Substance.*
11	*Cellulose acetate T1 (2·5).*	16	*Secondary cellulose acetate (2·47).*
12	*Cellulose acetate T2 (2·84).*	17	*High-acetyl acetate butyrate.*
13	*Cellulose acetate T3 (2·87).*	18	*Low-acetyl acetate butyrate.*
14	*Cellulose acetate T4 (2·91).*	19	*Secondary acetate butyrate.*
15	*Cellulose acetate T5 (2·95).*	20	*Cellulose laurate.*

Figures in parentheses refer to degree of substitution.

– – – – *Undried samples.* ——— *Dried samples.*

considerably broadened on the low-frequency side and show shoulders at about 3350 cm.$^{-1}$, and this again can be taken as evidence of the presence of crystalline cellulose, though in smaller quantity than in T_1. In T_4 the OH maximum is at 3480 cm.$^{-1}$ with shoulders at 3384 and 3558 cm.$^{-1}$. T_5 again shows a maximum at 3480 cm.$^{-1}$, but apart from the shoulder at 3558 cm.$^{-1}$ the absorption band is symmetrical and this type of hydroxyl absorption is typical of all the later members of the series. Hence, the spectroscopic results indicate a decrease in the amount of crystalline cellulose in passing from T_1 to T_4 and the absence of any such regions in T_5 and the subsequent members of the series, a decrease which is paralleled by the improved flow properties of solutions of these acetates in methylene chloride–alcohol.

In Fig. 2, No. 15 is shown the absorption spectrum of T_5 from 2700 to 3800 cm.$^{-1}$ for dried and undried samples. The undried sample shows three maxima of approximately equal intensity at 3485, 3560, and 3635 cm.$^{-1}$, while the dried sample only shows a single maximum at 3480 together with a shoulder at 3558 cm.$^{-1}$. Subtraction of the two absorption curves gives the absorption spectrum of the absorbed water, and graphical separation of this curve gives three peaks, as found with the cyanoethyl ethers. Again, it is probable that the two high-frequency bands are to be associated with hydrogen-bonded water, and the broad low-frequency band with absorbed liquid water. Although the shoulder at 3558 cm.$^{-1}$ in the spectrum of the dried sample is at the same frequency as one of the water bands, this shoulder cannot be removed on drying, and as the spectra of dried acetates show no evidence of the more intense water band

at 3635 cm.$^{-1}$, the shoulder must be due to some structural feature of the cellulose acetate molecule. From the frequency of this shoulder it is probably to be associated with unperturbed hydroxyl groups.

Examination of a molecular model of a portion of a cellulose acetate chain shows that if in any anhydroglucose unit the OH group in the 6 position is unsubstituted, the remaining two OH groups being substituted by acetyl radicals, then only a weak internal hydrogen bond with the bridge oxygen atom is possible. If, however, the free OH group is in the 2- or the 3-position, an internal hydrogen bond can be formed between the OH group and the adjacent carbonyl group. The existence of such an internal hydrogen bond would cause a certain stabilisation of the structure, and this stabilisation would probably account for Purves's results (*loc. cit.*) on the distribution of the unesterified hydroxyl groups in secondary cellulose acetates. He found that the number of glycol units in a secondary acetate was less than could be accounted for by a purely random hydrolysis, and concluded that in the partial hydrolysis from triacetate, the loss of an acetyl residue from the 2- or the 3-position tended to stabilise the adjacent group in the anhydroglucose residue. Thus it is possible that the shoulder at 3558 cm.$^{-1}$ is due to hydroxyl groups in the 6-position which are so environed as to be incapable of hydrogen bonding on to adjacent chains.

(e) *Secondary Cellulose Acetates.*—When a primary acetate is hydrolysed, the increase in the intensity of the OH band relative to that of the CH bands is accompanied by a gradual shift in the OH frequency from 3480 to about 3490 cm.$^{-1}$. The shoulder at 3558 cm.$^{-1}$ is less marked in the spectra of the secondary acetates, as would be expected if this band is due to relatively unperturbed hydroxyl groups. The shift of the main OH absorption band to higher frequencies is probably to be explained by an increasing amount of inter-chain hydrogen bonding which may be weaker than the intra-chain bonding because of the steric effects of the acetyl groups. Such an explanation would be in accordance with the observed solubilities, triacetates being soluble in methylene chloride and the secondary acetates in acetone.

It has been shown that for primary acetates containing relatively few hydroxyl groups it is possible to detect non-uniformity of substitution by means of the contour of the OH absorption band. With secondary acetates the detection of small regions of non-uniformity is more difficult because the number of strongly bonded hydroxyl groups is a smaller proportion of the total number. However, by analogy with the cyanoethyl celluloses, measurement of the symmetry indices of the OH bands would be expected to give some information on the uniformity of substitution. Several secondary acetates with a degree of substitution between 2·4 and 2·5 have been studied. Some of these were soluble in dry acetone and some in aqueous acetone, and although the OH frequency varied little from 3490 cm.$^{-1}$ the symmetry index of those soluble in aqueous acetone was appreciably greater than the value of unity found for acetone-soluble derivatives. The spectrum of a typical acetone-soluble secondary cellulose acetate in the dried and in the undried state is shown in Fig. 2, No. 16, and, as with the primary acetates, graphical separation gives three bands due to absorbed water.

(f) *Cellulose Acetate Butyrates.*—In the undried state primary acetate butyrates show three OH bands at 3490, 3553, and 3631 cm.$^{-1}$, and in this respect are analogous to the primary cellulose acetates. However, the relative intensities of these three bands vary with the acetyl : butyryl ratio, the intensity of the 3490 cm.$^{-1}$ band increasing relatively to the intensities of the 3553 and 3631 cm.$^{-1}$ bands with increasing butyryl content. This intensity variation is in accordance with the decrease in water imbibition which accompanies an increase in the butyryl content. In the dry state the primary acetate butyrates show a single OH frequency at about 3486 cm.$^{-1}$ with a weak shoulder at about 3560 cm.$^{-1}$. As with the secondary cellulose acetates, the OH frequency of a secondary acetate butyrate is a few wave-numbers higher than that of the corresponding primary ester and is found at 3495 cm.$^{-1}$. The spectra of two primary acetate butyrates of high and low acetyl content are shown for dried and undried samples in Fig. 2, Nos. 17 and 18, and the spectrum of a secondary cellulose acetate butyrate is shown in Fig. 2, No. 19.

At low butyryl values the CH absorption of a cellulose acetate butyrate is similar to that of a cellulose acetate, but with increasing butyryl content several changes take place, *viz.*, (i) the 2956 cm.$^{-1}$ band splits into two components at 2944 and 2964 cm.$^{-1}$; (ii) the 2898 cm.$^{-1}$ band is shifted to 2881 cm.$^{-1}$; (iii) the intensity of the shoulder at about 3024 cm.$^{-1}$ is reduced.

(g) *Miscellaneous Cellulose Esters.*—The spectra of cellulose laurate, cellulose laurate naphthenate, and cellulose acetate stearate are all very similar in the 3-μ. region, and the presence of the large non-polar side chains reduces the water absorption to such an extent that no changes could be observed between the spectra of samples which had been subjected to intensive drying

and those which had been measured in moist air. The OH frequencies observed for highly substituted esters of this type are: cellulose laurate, 3476 cm.$^{-1}$, cellulose laurate naphthenate, 3480 cm.$^{-1}$, and cellulose acetate stearate, 3485 cm.$^{-1}$. The spectrum of cellulose laurate is illustrated in Fig. 2, No. 20. From the nature of the side chains and the fact that these esters are soluble in benzene it is unlikely that there is any inter-chain hydrogen bonding, so that any hydrogen bonding must be intra-chain in character, probably taking place between hydroxyl and carbonyl groups in the adjacent 2- and 3-positions. No evidence was found for relatively unperturbed hydroxyl groups in the spectra of any of these esters. This may be due to the effect of the large acyl radicals, substitution in the 6-position being easier than substitution in both the 2- and the 3-position. If this is so, then in a highly substituted ester there would be fewer OH groups in the 6-position than in the 2- and 3-positions, and because of the lower extinction coefficient of non-hydrogen bonded OH groups the detection of such groups would be difficult. It is of interest that the value of the OH frequency is affected to a slight extent by the nature of the acyl groups.

(h) *Quantitative Measurements on the Hydroxyl Absorption of Cellulose Acetates.*—As the intensity of the hydroxyl band is a function of the number of hydroxyl groups, it should be possible to devise a semi-empirical method for the determination of the degree of hydrolysis of a secondary cellulose acetate providing that the ester does not show any gross irregularities of

FIG. 3.

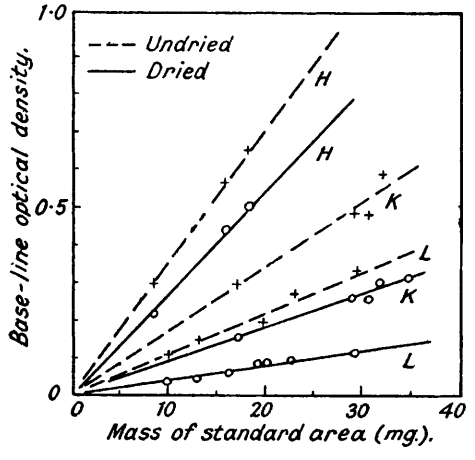
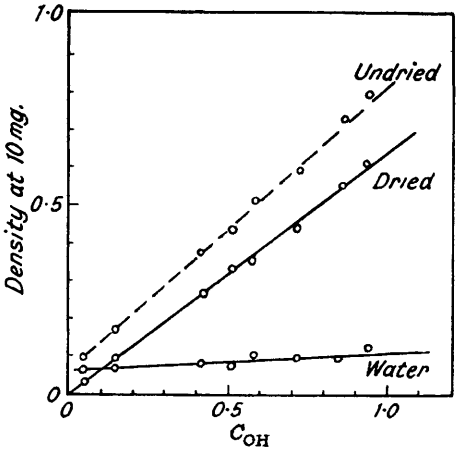


FIG. 4.



substitution. There are two ways in which such an analysis can be carried out in the 3-μ. region: in the first, the film thickness is eliminated by taking the ratio of the optical densities of the OH and one of the CH bands; in the second, the optical density of the OH band alone is measured together with the film thickness. Measurements are made for a number of cellulose acetates of known degrees of substitution and an empirical calibration curve is set up from which the hydroxyl content of any cellulose acetate can be read off. The difficulty in the first method lies in the elimination of scattering and reflection losses at the film surfaces. Although these losses can be reduced by mounting the film in Nujol, this masks the CH absorption. A good match for the refractive index of cellulose acetates can be obtained by a suitable mixture of carbon tetrachloride and carbon tetrabromide, both of which are transparent in the 3-μ. region. Both these substances, however, cause a limited swelling of cellulose esters, with consequent modification of the hydroxyl absorption. It is possible that a fluorocarbon could be used but this has not been tried. A further disadvantage of the method is that it could only be applied to simple esters, because with mixed esters the CH absorption varies with the relative amounts of the various acyl groups. In the second method the scattering and reflection losses may be eliminated by using a base-line optical density method. The simplest way of obtaining a measure of the film thickness is by cutting a standard area of film with a template and weighing it. Since the density of a cellulose ester is almost independent of the hydroxyl content, the mass of the standard area of the film may be used as a measure of the film thickness. The error introduced by day-to-day variations in the relative humidity of the atmosphere and the consequent variations in the moisture content and mass of the films will be small. To avoid

errors due to variations in the thickness of the films, a number of readings can be taken of the absorption at different parts of the film, and the resulting optical densities averaged. Alternatively, the film can be mounted off-focus so that the radiation passes through almost the entire sample. These two methods give the same results provided that the variations in thickness are small.

A number of measurements have been made of the base-line optical densities of the hydroxyl band for several cellulose acetate films of varying acyl content both in the dry state and at some constant relative humidity, namely, the relative humidity at the primary focus of the Grubb–Parsons S-3 spectrometer under standard operating conditions. The measurements were made by using the relatively low dispersion of a sodium chloride prism, and it was shown that the band area was the same linear function of the peak optical density both for dried and for undried samples, so that the difference between the measurements on undried and dried samples should be a measure of the water content. In Fig. 3 is plotted base-line optical density against the mass of a standard area of film for three cellulose acetate samples in the dried and in the undried state. In each case straight lines were obtained which passed through the origin. Similar measurements were carried out on a number of cellulose acetates and the results are summarized in Fig. 4 which shows a graph of base-line optical density at constant mass (10 mg.) against the hydroxyl content for a series of cellulose acetates (C_{OH} = 0·04—0·94) in the dried and in the undried condition. The difference between these two curves is also plotted and this, as explained above, must be related to the water absorption of the sample. One possible explanation of the shape of these curves is the following : if the curve for the optical density of undried samples is extrapolated to cut the optical density axis, the intercept may represent the non-bonded water in a cellulose triacetate. If the amount of non-bonded water is roughly independent of the degree of substitution, then the bonded water would be a linear function of the number of hydroxyl groups. No attempt has yet been made to correlate the water absorption band with the total amount of absorbed water.

The fact that the graph shown in Fig. 4 for dried cellulose acetates passes through the origin shows that there can be no appreciable contribution to the hydroxyl band from the first overtone of the stretching frequency of the ester carbonyl group.

Some measurements have also been made on the intensity of the hydroxyl absorption of cellulose acetate butyrates, and the results so far obtained show that, provided the measurements be carried out on dried samples, the calibration curves obtained for dried cellulose acetates can be used, *i.e.*, that the extinction coefficient of the OH absorption band in cellulose acetate butyrates is not very different from that in cellulose acetates. The results obtained in this way for a number of cellulose acetate butyrates agree with the chemical determinations of the hydroxyl content within the limits of error of the latter, but as this error is rather large this does not constitute a reliable test.

It is also possible to obtain calibration curves for the analysis of cellulose ethyl ethers, and there seems to be no reason why the method should not be perfectly general for cellulose derivatives.

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