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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIX. THE CONSTITUTION OF ALKALI CELLULOSE[1]

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Introduction

The determination of the composition of the solid phase when cellulose is brought into contact with solutions of sodium hydroxide of varying concentrations has been the subject of numerous researches extending over a period of more than eighty years.

The main purpose of this investigation is to show whether the effect is chemical, physical or physico-chemical, or due to a combination of these possibilities.

As early as 1844 Mercer[4] assumed that a chemical compound was formed between the cellulose and sodium hydroxide at a certain optimum concentration. This idea received experimental support from the researches of Gladstone,[5] Thiele,[6] Vieweg,[7] Lindemann,[8] Normann,[9] Traube[10] and Hess.[11] Other more recent investigators include d'Ans and Jaeger,[12] Dehnert and Koenig,[13] Heuser and Niethammer,[14] Heuser and Bartunek,[15] Karrer[16] and Liepatow.[17]

A thorough review of the literature is to be found in papers by Blanco[18] and Clibbens.[19] Gladstone,[5] Karrer,[16] Hübner and Teltscher,[20] Heuser

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[4] J. Mercer, English Patent, 13,296 (1850).

[5] J. H. Gladstone, *J. Chem. Soc.*, **5**, 17 (1852).

[6] E. Thiele, *Chem.-Ztg.*, **25**, 610 (1901).

[7] W. Vieweg, *Ber.*, **40**, 3876 (1907).

[8] O. K. Lindemann, "Dissertation," Dresden, 1909.

[9] W. Normann, *Chem.-Ztg.*, **30**, 584 (1906).

[10] W. Traube, *Ber.*, **55**, 1899 (1922).

[11] K. Hess, *Ann.*, **435**, 1 (1923); *Z. angew. Chem.*, **38**, 320 (1925).

[12] J. d'Ans and A. Jaeger, *Cellulosechemie*, **6**, 137 (1925).

[13] F. Dehnert and W. Koenig, *ibid.*, **5**, 107 (1924); **6**, 1 (1925).

[14] E. Heuser and W. Niethammer, *ibid.*, **6**, 13 (1925).

[15] E. Heuser and L. Bartunek, *ibid.*, **6**, 14 (1925).

[16] P. Karrer, *ibid.*, **2**, 124 (1921).

[17] S. Liepatow, *J. Russ. Phys.-Chem. Soc.*, **57**, 48 (1925).

[18] G. W. Blanco, *Ind. Eng. Chem.*, **20**, 926 (1928).

[19] D. A. Clibbens, *J. Text. Inst.*, **14**, T217 (1923).

[20] J. Hübner and F. Teltscher, *J. Soc. Chem. Ind.*, **28**, 641 (1909).

and Niethammer[14] and Rassow and Wadewitz[21] attempted to wash the soda cellulose free from adhering alkali with alcohol. In the first two instances, the existence of a compound $(C_6H_{10}O_5)_2\cdot NaOH$ is claimed, while the other workers find the method unsatisfactory.

Vieweg[7] initiated the "indirect method," namely, the evaluation of data obtained from titration of the final equilibrium solutions.

It was found that a decrease in the alkali concentration always took place, and from this Vieweg calculated the absorption. From the data he concluded that the existence of two compounds was proved, *viz.* $(C_6H_{10}O_5)_2\cdot NaOH$ and $(C_6H_{10}O_5)_2\cdot 2NaOH$.

Similar investigations have been carried out with various modifications by Heuser,[14,15] Miller,[22] Joyner,[23] Dehnert and Koenig,[13] Karrer and Nishida,[24] Liepatow,[17] d'Ans and Jaeger,[12] Kolthoff,[25] Rumbold[26] and others.

Dehnert and Koenig,[13] as well as d'Ans and Jaeger,[12] also confirmed the formation of Vieweg's second compound at high alkali concentrations, while Karrer,[16] Hess,[11] Heuser and his co-workers[14,15] deny this.

From a consideration of the various curves obtained by using the "indirect method," in which concentrations of sodium hydroxide solution were plotted against weight of sodium hydroxide removed, the weight of evidence seems to show that there is some abnormal condition prevailing where the discontinuities of the curves occur. However, in all of these investigations, little or no attention has been paid to the absorption of water by the cellulose. Unless this takes place in constant amount, or in quantities so small that the effect would not be noticed, no definite conclusions can be drawn from the absorption curves obtained.

Leighton,[27] and Coward and Spencer,[28] used a centrifugal method to remove superfluous sodium hydroxide, in this way claiming to separate the amount of absorbed water from that of the absorbed or combined alkali. From their results they conclude that the phenomenon is due to absorption. Nevertheless the weight of evidence from other sources, as well as that obtained by most investigators using the "indirect method," tends to strengthen the belief that a chemical compound is formed.

Although the alcohol washing method, as developed by various investigators, has not led to definite conclusions as to the nature of the absorption process, the authors believe that the fault lies for the most part in its application rather than in an inherent inconsistency of the method.

[21] B. Rassow and M. Wadewitz, *J. prakt. Chem.*, **106**, 266 (1923).

[22] O. Miller, *Ber.*, **40**, 4903 (1907); **41**, 4292 (1908); **43**, 3430 (1910); **44**, 728 (1911).

[23] R. A. Joyner, *J. Chem. Soc.*, **121**, 2395 (1922).

[24] P. Karrer and K. Nishida, *Cellulosechemie*, **5**, 69 (1924).

[25] I. M. Kolthoff, *Pharm. Weekblad.*, **58**, 46 (1921).

[26] J. A. Rumbold, THIS JOURNAL, **52**, 1013 (1930).

[27] A. Leighton, *J. Phys. Chem.*, **20**, 32 (1916).

[28] H. F. Coward and L. Spencer, *J. Text. Inst.*, **14**, T32 (1923).

With this idea in view a systematic method of attack has been developed which seems to lead to consistent and comprehensible results.

Experimental Procedure

After immersion of the cotton cellulose in sodium hydroxide solution under conditions which will be described later, the sample was removed by means of a glass rod and filtered under suction in a Büchner funnel. The wet mass was well pressed by a flattened glass rod for three minutes, at the end of which period it was quickly transferred to a beaker containing 100 cc. of 95% alcohol, with which it was thoroughly mixed for two minutes.

The supernatant liquor was poured off into a dry flask and most of the solution pressed out of the cotton by means of a flattened glass rod, the operation requiring one minute. The washed fiber was then placed under suction, where it was pressed carefully for one minute and allowed to stand under suction for one minute longer. At the end of this time the material was again transferred to 100 cc. of alcohol, agitated for two minutes (not sufficiently vigorously to break up the fiber), pressed for one minute, the liquid collected and again placed under suction. This process was repeated for every washing.

An aliquot portion of each of the washing solutions was then transferred to a beaker, the alcohol removed by gentle boiling, and the alkali present determined by titration against standard sulfuric acid using methyl orange as indicator. The removal of alcohol by boiling eliminated the indicator difficulties experienced by Heuser.[14] After completing the last washing the cotton was stirred with distilled water and titrated with acid to determine the remaining alkali.

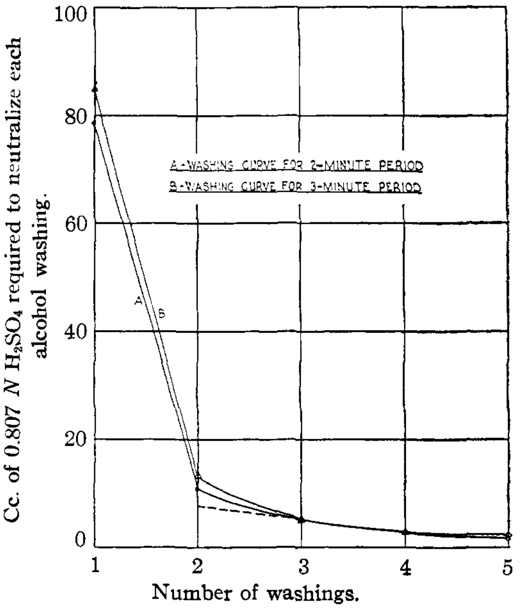

Fig. 1.

Repeated experiments showed that this method gave reproducible results, and established the fact that variations in the method, such as washing for a longer time, or with different amounts of alcohol, gave the same final result.

The following data (shown in Fig. 1) illustrate the calculation of the results.

Initial strength of sodium hydroxide solution = 23.2% by weight; washing period two minutes.

No. of washing	1	2	3	4	5
0.807 N H_2SO_4 required to neutralize each washing, cc.	78.6	10.82	5.14	2.77	1.65

Equiv. of alkali remaining in the cellulose = 22.10 cc. Extrapolated value to the *second* washing from Graph (I) 7.5 cc.

Then 22.10 + 7.50 + 5.14 + 2.77 + 1.75 = 39.16 cc. of 0.807 *N* acid are equivalent to the caustic alkali directly associated with 4.332 g. of cellulose, *i. e.*, 29.3 g. of NaOH to 100 g. cellulose.

For a washing period of three minutes the value found was 29.5 g. of NaOH per 100 g. of cellulose.

The agreement is within the limit of experimental error. Similar agreement was obtained when 150 cc. of alcohol, instead of 100 cc., was used for the washing. Therefore the conclusion was reached that the method could be applied to determine the amount of alkali combined with, or absorbed in, the fiber.

The absorption experiments were carried out at 25 ± 0.02° in a water thermostat. For the absorption vessel a cylindrical glass jar of about 300 cc. capacity was used, which was coated internally with a thin layer of paraffin wax and fitted with a rubber stopper provided with an exit tube and a tube dipping nearly to the bottom of the vessel.

During an experiment, nitrogen was bubbled gently through the mixture of cellulose and alkali to ensure thorough mixing, and to prevent oxidation and the absorption of carbon dioxide. The gas was passed through sodium hydroxide solution of the same strength as that contained in the experimental vessel in order to remove all carbon dioxide.

Pure "absorbent cotton" was used in these experiments. The α-cellulose value was 99.1%, the ash 0.05%. Before use it was dried in a vacuum for six hours at 60–70° and kept in a vacuum desiccator over phosphoric anhydride.

The sodium hydroxide was Schuchardt's, purified by means of alcohol; 1 kg. was dissolved in 1 liter of water and allowed to stand for ten days. The clear liquid was then forced out of a delivery tube, by means of carbon dioxide-free air, into a measuring cylinder, from which it was transferred in the same way to a flask containing the appropriate volume of air-free water. It was then a simple matter to fill a pipet with the carbonate free solution, and to transfer it to the reaction vessel. In this way a soda solution containing less than 1 part in 600 of carbonate was prepared.

The determination of the indirect absorption was carried out as follows. Dry cellulose (5 g.) was accurately weighed out and placed in the vessel, and 75 cc. of the sodium hydroxide solution added, during the passage of a slow stream of nitrogen. The concentrations of the initial and final solutions were determined, and from the difference between these at equilibrium, values for the indirect absorption were calculated according to Vieweg's procedure.

The cellulose was allowed to remain in contact with the soda solution for four hours, an interval of time which in the experience of other workers, *e. g.*, Miller,[22] would appear to be ample time for equilibrium to be established.

The wet fiber was then dried for three minutes using suction and subjected to a washing process at the end of which the residual alkali was found by titration. Thus it was possible to calculate a value for the alkali directly associated with the fiber over a wide range of concentrations according to the method of alcohol washing which has been outlined.

The results for the absorption as determined by the Indirect and Direct Methods are included in Table I.

Discussion of Results

The Method of Washing.—A consideration of the alcohol washing diagrams, Fig. 1, shows that undoubtedly the sodium hydroxide associated

TABLE I

ABSORPTION RESULTS

Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/ 100 g. of cellulose	Direct Detn., g. of NaOH/ 100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/ 100 g. of cellulose	Direct Detn., g. of NaOH/ 100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	"Indirect Detn.," g. of NaOH/ 100 g. of cellulose	Direct Detn., g. of NaOH/ 100 g. of cellulose
0.32	0.7	1.1	13.4	13.0	25.7	23.2	18.2	29.5
0.85	1.0	...	14.15	12.8	25.6	25.1	19.7	31.7
2.05	0.9	1.7	14.15	12.9	25.3	26.25	19.3	32.5
3.23	1.75	2.4	15.10	13.1	25.4	26.9	21.3	..
3.70	2.2	3.1	15.25	12.7	..	27.05	..	32.8
5.00	2.4	2.8	16.5	13.2	25.3	29.7	21.9	..
5.80	2.5	3.0	17.5	13.1	..	30.6	22.8	34.2
7.05	3.3	3.75	18.65	14.5	24.9	34.35	23.7	..
8.05	4.15	6.9	18.8	14.4	..	35.3	..	37.8
9.30	5.3	8.3	20.7	..	25.1	37.5	23.5	40.8
10.25	6.75	11.25	20.7	..	25.4	41.5	29.6	45.0
11.2	..	18.8	21.6	..	25.5	42.15	..	50.7
12.0	10.15	23.1	21.4	16.5	25.7	44.4	27.0	52.3
13.3	12.9	..	23.2	18.2	29.3	46.8	32.4	56.5
12.35	..	24.9						

with the fiber after it has been partially dried at the pump is not removed regularly, but that a large part is taken out in the first washing. After this, each washing removes a definite portion and in every case after the second washing the alkali is removed in small, gradually decreasing amounts. It would appear therefore that each washing diagram consists of two parts, the first indicating a rapid, and the second a much slower, removal of sodium hydroxide by the alcohol.

After obtaining a large number of diagrams of essentially the same form (particularly of type B) which seem to show a sharp break, it was concluded that they might be interpreted by assuming that the first portion represented easily removable alkali which was not combined with, or adsorbed on the fiber, while the second portion might be considered as adsorbed, or combined alkali which is removed slowly. The discontinuity in the diagram then is presumed to mean that point where adhering liquid, and superfluous solution entering the interior of the fibers due to osmotic effects, is removed.

The meaning of the extrapolation is best made clear by considering Curve B, Fig. 1 which holds for a range of concentrations 2–34% sodium hydroxide by weight. By analogy with washings 3, 4 and 5, it appears logical to regard the second washing as made up of part derived from the alkali present in the first washing liquor and part derived from the fiber. Assuming then that washing 3, 4 and 5 represent the general trend of removal of absorbed sodium hydroxide it is to be anticipated that the second washing is made up of a proportional amount derived from the fiber and extrapolation to this point therefore was employed. The extrapolation was not continued to the first washing, since it was thought that in the presence of such a large amount of easily removed alkali, none of the firmly bound sodium hydroxide would be taken out.

A different extrapolation was employed for very concentrated alkali solutions (34–47% by weight), A, Fig. 2. More washings are required to remove a more concentrated adhering solution, which, with the correspondingly higher viscosity, must be intrinsically greater in amount. From the curves the break was indicated at the third washing and therefore extrapolation to this point was carried out. Further, in the use of very dilute solutions (0–2%) it is apparent that the first washing might remove alkali from the interior of the fiber itself and this was also indicated by the graph, C, Fig. 2. Accordingly extrapolation was carried to the first washing.

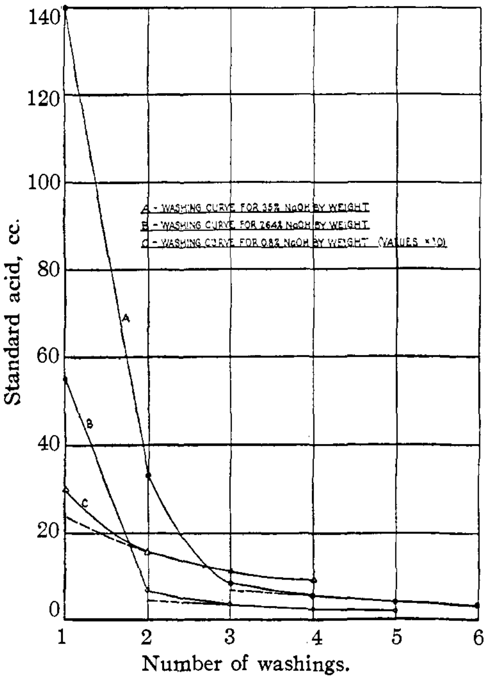

Fig. 2.

It is to be noted that the washing period is short. This has been so made purposely in order to accentuate the point at which the direction of the curve changes. It may be pointed out, however, that a ten-minute washing interval led to the same absorption value within 1%.

According to a recent paper by Neale,[29] swelling in the case of cellophane is due to osmotic effects arising from a Donnan Membrane Equilibrium; if this is indeed the case, alcohol would in all probability upset this so far as the "osmotically transferred" alkali and water are concerned, but it does not necessarily follow that the combined or adsorbed alkali is appreciably affected.

Interpretation of the Absorption Curve.—Curve I, Fig. 3, shows the relation between the amount of caustic alkali associated with the fiber and the concentration of the solution producing the absorption. The most significant feature of the curve is the almost vertical portion showing a discontinuity at a concentration of 12.5 g. of sodium hydroxide per 100 g. of solution,[30] and continuing horizontal to the concentration axis until a

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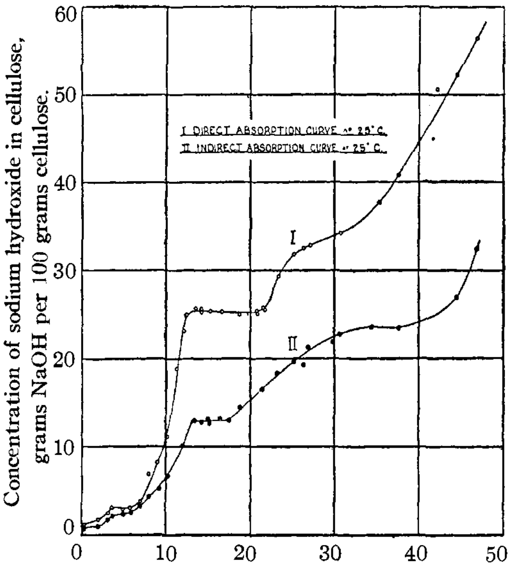
[29] S. M. Neale, *J. Text. Inst.*, **20**, T373 (1929).

[30] While the authors realize that from the standpoint of the phase rule, final, *i. e.*,

concentration of 21.5 g. of sodium hydroxide per 100 g. of solution is reached.

The break occurs where the mole ratio of sodium hydroxide to cellulose is 1:1, *viz.*, a concentration of alkali in the solid phase of 25.3 g. of sodium hydroxide per 100 g. of cellulose as compared to a theoretical value of 24.7% for a compound of the type $(C_6H_{10}O_5)\cdot NaOH$.

This is in harmony with the formation of a compound of that composition when interpreted on the basis of the phase rule. If the system in question were merely cellulose–soda cellulose–sodium hydroxide, then the approximately vertical portion of the curve would indeed be perpendicular. A classic example of this is given by Appleyard and Walker[31] for the system diphenylamine–picric acid–diphenylamine picrate.



Initial concentration of sodium hydroxide in liquid phase, grams NaOH per 100 grams solution.

Fig. 3.

In the case under review, however, it is believed that superimposed adsorption causes the deviation of the almost upright portion from the vertical. This point of view is substantiated by Biltz,[32] who used Fe_2O_3–sodium alizarate and Fe_2O_3–sodium arsenite. That part of the curve horizontal to the concentration axis simply indicates that only a 1:1 compound exists and that there is no superimposed adsorption until a concentration of 21.5% is reached.

The discontinuity, therefore, is in harmony with the concept of the formation of some compound between cellulose and sodium hydroxide in equal stoichiometric proportions, within the limit of experimental error, which is estimated as about 3% for this section of the curve.

Significantly enough the discontinuity in Curve II, Fig. 3, which represents the results of the indirect method of measurement, starts at almost the

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equilibrium, concentrations should have been plotted, the change in concentration of the solutions employed is so small as to render any effect in changing the shape of Fig. 2 negligible.

[31] J. R. Appleyard and J. Walker, *J. Chem. Soc.*, **69**, 1334 (1896).

[32] W. Biltz, *Ber.*, **38**, 4143 (1905).

same concentration of alkali, and it would seem that this too indicates compound formation, as Vieweg stated, although the composition, neglecting the effect of water absorption, is given by him as $2(C_6H_{10}O_5)\cdot NaOH$.

Further inspection of Curve I reveals also the possibility of the existence of a compound between the concentrations of 4 to 6% alkali by weight, and also on Curve II between these limits. Rumbold[26] also found a similar halt in his titration curve in this region. If such a compound does exist, the composition would be $(C_6H_{10}O_5)_8\cdot NaOH$, corresponding to the observed value of 3%, theory demanding 3.07% alkali in the cellulose.

The second break in Curve II, Fig. 3, at the higher concentrations has no analog in Curve I and the evidence for a second compound as proposed by Vieweg[7] is therefore discounted. A 1:1 compound between cellulose and sodium hydroxide is indicated within the limits of experimental error, which is estimated at about 3%. The idea of compound formation is in harmony with the chemical evidence.

Karrer[24] supports this view by a consideration of the analogous cases of other polyhydric alcohols. He points out that it is a general property of the alcohols to form compounds with alkalies, not only of the simple alcoholate type but in the case of polyhydric alcohols, compounds of a complex nature, as for example the compounds between glycerol and alkali, alkaline earth and heavy metal hydroxides.

Blanco[18] states that the phenomenon of the esterification of alkali cellulose with carbon disulfide, or benzoyl chloride, supports the idea that alkali cellulose has alcoholate properties. Herzog[33] has shown that the absorption bands in the infra-red region of the spectrum of cellulose and mercerized cellulose are distinctly different. The conception that alkali cellulose is a definite compound is further substantiated to some extent by x-ray analysis.

Taking the hydroxides of lithium, sodium and potassium, Katz[34] showed that abnormalities in the x-ray diagram coincide with the first break in the "Vieweg curve," the cellulose spectrum disappearing and new lines being formed by the absorption of nearly equimolecular amounts of these alkalies.

Whether the compound formed, and showing the new spectrum, is alkali-cellulose or an isomer of cellulose is, in his opinion, undecided.[35] The original lines disappear at 10.6% LiOH, 16% NaOH and 24% KOH, which are the concentrations at which the formation of alkali celluloses is most marked.

The difference observed between Curves I and II is due essentially to the fact that cellulose has absorbed water as well as alkali, and therefore the results as determined indirectly will be too low.

[33] R. O. Herzog, *Z. physik. Chem.*, **121**, 136 (1926).

[34] J. R. Katz, *Cellulosechemie*, **6**, 35 (1925).

[35] J. R. Katz, *Z. Elektrochem.*, **31**, 157 (1925).

The Absorption of Water.—It is a simple matter to calculate the water taken up by the fiber.

Let m = mass of cellulose
v = volume of original sodium hydroxide solution of density d
b = number of grams of sodium hydroxide in this solution
x = amount of alkali absorbed, or combined with m grams of cellulose as directly determined
y = mass of water absorbed in grams
c = final concentration in grams of sodium hydroxide per 100 grams of solution

Then weight of alkali in solution at equilibrium $= b - x$ and total weight of solution $= vd - x - y$

$$\frac{c}{100} = \frac{b - x}{vd - x - y}$$

x having been determined, y is readily calculated since all the other factors are known.

$$\text{Then \% water absorbed} = \frac{100y}{m}$$

The results of this calculation are contained in Table II and are plotted in Fig. 4. *The curve is remarkable from the point of view that the maximum absorption of water takes place at about 14% alkali concentration by weight, which is the point of maximum swelling as determined by Collins and Williams.*[36] In general maximum swelling is taken as the point where total maximum absorption occurs.

Table II

Results of Calculations

Init. concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g./H_2O/100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g./H_2O/100 g. of cellulose	Init. concn. of NaOH in g./100 g. of soln.	Final concn.	Water absorbed, g./H_2O/100 g. of cellulose
0.32	0.28	122	10.25	9.90	78.7	23.2	22.50	30.8
2.05	2.00	83.9	12.00	11.50	97.5	25.1	24.2	36.7
3.23	3.10	62.8	13.4	12.75	92.8	26.25	25.5	42.3
3.70	3.55	44.9	14.15	13.80	113	30.6	29.7	19.7
5.00	4.90	31.3	15.1	14.55	66.8	27.5	36.8	30.0
5.80	5.60	10.2	16.5	15.70	50.3	41.5	41.0	36.7
7.05	6.85	1.3	18.65	17.95	44.0	44.4	43.3	24.7
8.05	7.65	15.2	21.4	20.70	23.0	46.8	46.4	43.6
9.30	9.05	24.7						

Quantitative Analysis of the "Soda Cellulose."[37]—A series of quantitative experiments to determine whether the compound was in reality a

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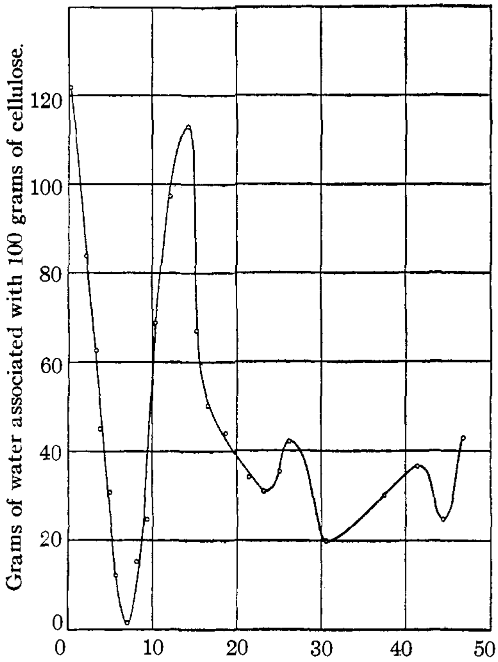
[36] G. E. Collins and A. M. Williams, *J. Text. Inst.*, **14**, T287 (1923).

[37] After the completion of this manuscript, there appeared the interesting communication of Rassow and Wolf [*Ber.*, **62**, 2949 (1929)]. These authors from the results of their analysis of a soda cellulose obtained by washing with absolute alcohol to neutrality, using alizarin yellow as indicator, claim to have obtained a definite compound of the formula $C_{12}H_{20}O_{10}\cdot NaOH$. The present authors, however, see no reason either for the arbitrary choice of this indicator, or the lengthy washing period employed, which must in their experience remove far more sodium hydroxide than is present in the adhering surface layer, *i. e.*, the uncombined material.

cellulosate, or a loose addition compound, was initiated. Following the same technique by which the values in Curve I, Fig. 2, were obtained, cotton was immersed in solutions of alkali having concentrations ranging between 13 and 20% by weight. Since as indicated on the curve (Fig. 1), the surface layer of alkali is practically entirely removed by one washing, the product was therefore submitted to a simple washing prior to analysis.

Analyses were carried out in the following way. The alkali-cellulose having been dried at 70° for six hours to constant weight in a vacuum over phosphoric anhydride and calcium chloride, was rapidly transferred to a stoppered weighing bottle, weighed and the alkali present determined directly by titration. Direct determinations of sodium as sulfate were carried out in a platinum crucible, but since the results were identical with those found by titration, this latter method was generally used because of its simplicity.



Initial concentration of sodium hydroxide in liquid phase, grams of NaOH per 100 grams of solution.

Fig. 4.

Carbon and hydrogen were found thus: the dried "soda cellulose" was placed in a platinum boat, the weight of which, when contained in a stoppered bottle, was known. The boat was heated at 78° for six hours in a vacuum in the presence of phosphoric oxide to constant weight, quickly transferred to the weighing bottle, weighed and then subjected to a macro combustion in oxygen in the usual way. Assuming that the sodium hydroxide quantitatively removed carbon dioxide to form carbonate, a correction was applied to find the percentage of carbon. This assumption has previously been used with success in the combustion of complex cobalt oxyoxalates and malonates when potassium

TABLE III

ANALYTICAL RESULTS

NaOH, initial concn. in g./100 g. of solution	13.5	15.5	17.0	18.3	19.65
Na	12.40	12.35	13.10	13.31	13.51
C	37.2	36.9	36.2	36.5	35.6
H	4.9	5.1	5.0	5.0	5.0

and alkaline earth metals were present (Percival and Wardlaw).[38] The results are given in Table III.

Is the Product a "Cellulosate" or an "Addition Compound"?—The attempt was made to decide whether the 1:1 compound is an addition compound or an alcoholate. The analytical figures which would be obtained for each are given below.

		Na	C	H
$C_6H_9O_5Na$	(Calcd.)	12.50	39.13	4.89
$C_6H_{10}O_5 \cdot NaOH$	(Calcd.)	11.36	35.64	5.44

From the results of the experiments portrayed in Graph I, Fig. 2, it was concluded that the mean probable error between concentrations of alkali of 13 and 20%, if the first washing value had been taken instead of extrapolating back to that point, was 6%. Thus it would be expected that the value for sodium obtained on analysis, if only one washing were carried out, would be high and the other percentages correspondingly low. The mean values from Table III are Na, 12.03; C, 36.5; H, 5.0. Applying the mean value for the correction, namely, 6%, these percentages become: Na 12.16; C, 36.9; H, 5.07.

The fact that the corrected values occupy an intermediate position between those demanded by theory for the two formulas, allows the assumption to be made that a mixture of the two forms may be present, *viz.*, $(C_6H_9O_5Na)_x$ and $(C_6H_{10}O_5 \cdot NaOH)_x$. The tentative suggestion is now put forward that an equilibrium of the following type may exist

$$(C_6H_{10}O_5 \cdot NaOH)_x \leftrightarrows (C_6H_9O_5 \cdot Na)_x + xH_2O$$

The present method involves subjecting the cellulose to the action of an alkaline solution and a "direct" determination of the amount of absorbed alkali by a standard washing procedure. In previous investigations the washing has been carried out by a variety of methods, involving in general the use of one or other indicator in alcoholic solution, a procedure criticized by many workers due to "end-point" difficulties and the arbitrariness of the method.

By replacing the use of an inductive, and employing a graphical, statistical method of extrapolation, it has been found possible, as indicated above, to determine accurately the amount of sodium held in chemical union.

The results establish the fact that "soda cellulose" is formed from the interaction of one mole of sodium hydroxide with *1* (not *2*) anhydroglucose units. At the present time it is not possible to state definitely either the structure of the addition compound first formed, or the type of cellulosate into which it apparently changes, although the changes may possibly take place as shown below

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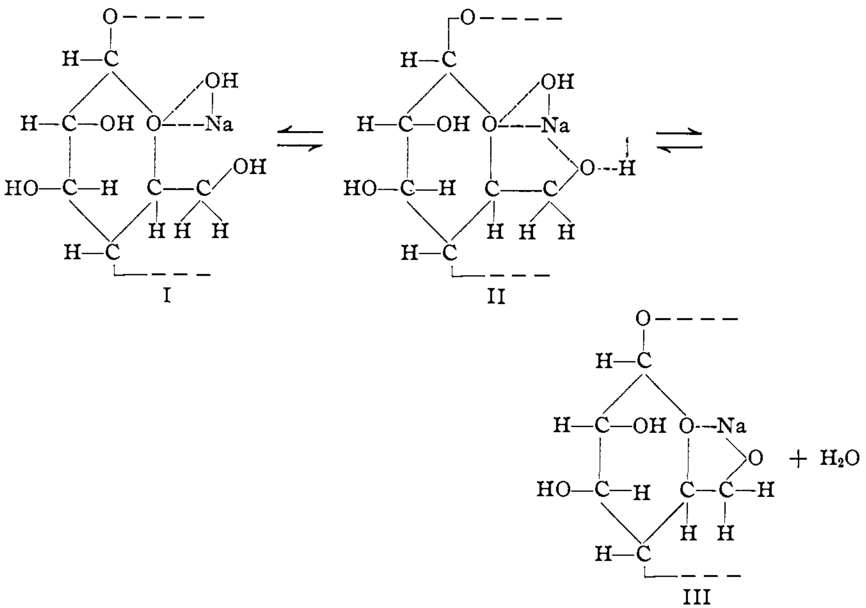
[38] E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, 2628 (1929).



I II III

In this scheme it is assumed that the sodium hydroxide first attaches itself to the oxygen atom. In the second phase, the sodium, through the exercise of subsidiary valency forces, attaches itself also to the oxygen atom of the primary alcohol group. This compound may then be assumed to lose a molecule of water, yielding the product III, which is the substance from which cellulose xanthogenate is formed.

It is also considered likely that "coördination compounds" of this type may be formed from the sodium hydroxide addition compound involving an anhydroglucose unit of one "cellobiose chain" and the primary alcohol group of a second one. Such an assumption may possibly have some bearing on the nature of "swelling" and hydration resulting from the effect of alkalies on cellulose.

Summary

1. The absorption of sodium hydroxide by cellulose has been studied over a wide range of concentrations at 25° by a carefully controlled method of washing, thus avoiding the inaccuracies associated with the use of indicators.

2. Evidence of chemical compound formation between alkali concentrations of 12.5 and 21.5% by weight is found.

3. *The compound may be regarded as resulting from the interaction of one molecule of sodium hydroxide with each anhydroglucose unit of the cellulose.* There would seem to be no definite proof of the existence of the compound $(C_6H_{10}O_5)_2{\cdot}NaOH$ as the main product formed.

4. The absorption of water by cellulose during the action of the alkali

solutions was studied, being calculated from a knowledge of the "direct" and "indirect" figures.

5. Maximum absorption of water is shown to occur at a concentration of alkali of about 14% by weight at 25°, *which corresponds with that concentration at which maximum swelling has been observed by other workers.*

6. Direct quantitative analysis of a soda cellulose which has been washed once with alcohol leads to the assumption that the product formed may be the result of an equilibrium reaction of the nature of $(C_6H_{10}O_5\cdot NaOH)_x \rightleftarrows (C_6H_9O_5Na)_x + xH_2O$. The nature of the structure of each of these compounds is uncertain but possibly in each case inter-micellary and residual-valence forces are involved.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE CLEAVAGE OF CARBONYL COMPOUNDS BY ALKALIES.
I. TRIHALOMETHYL KETONES OF THE MESITYLENE SERIES

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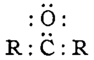
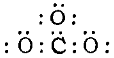
The large number of carbonyl compounds which undergo cleavage of the carbon chain when treated with alkalies suggests a cleavage mechanism arising from some property inherent in the carbonyl group. If we consider the cleavage of β-diketones, β-keto acids, nitromethyl, cyanomethyl and trihalomethyl ketones, for example, it is apparent that the carbonyl group is the structural element characteristic of the type. It is true also that the carbon atom which separates from the carbonyl carbon atom in the cleavage bears in each case one or more so-called negative groups, but the wide variety of these which are effective shows that this influence is of a very general nature. It seemed probable, therefore, that the explanation of this type of chain cleavage would be found in the properties of the carbonyl group. The purpose of the present paper is to present a theory developed on this basis.

It is assumed, in the first place, that in the *active form* of the carbonyl group the oxygen atom is singly bound to the carbon atom. The latter has, therefore, only six electrons in its valence shell (A). This idea has been used by Carothers[1] and by Latimer and Porter.[2] Latimer and Rodebush[3] have called attention to the fact that the carbon atom in solid carbonates probably has only six electrons in its shell (B). As Carothers has pointed out, this picture of the carbonyl group furnishes a satisfactory basis for the interpretation of addition reactions. The carbonyl carbon has a tendency to complete its octet of electrons by coördinating with an


(A)


(B)

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[1] Carothers, THIS JOURNAL, **46**, 2226 (1924).

[2] Latimer and Porter, *ibid.*, **52**, 206 (1930).

[3] Latimer and Rodebush, *ibid.*, **42**, 1419 (1920).