in other cyanide complexes, which are known to exist. The accuracy of the determination is within 5%.

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THE ACTION OF SODIUM HYDROXIDE ON CELLULOSE

BY J. S. RUMBOLD

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Introduction

When a sample of cellulose is steeped in an aqueous solution of sodium hydroxide, the concentration of the sodium hydroxide is diminished by an amount which depends on the temperature and the concentration. Some of the previous work on the mechanism of this interesting effect has been summarized recently by G. W. Blanco.[1] The evidence seems to favor the explanation which assumes the formation of a compound, but although many investigators agree that above a concentration of 16% the amount of caustic alkali absorbed by a given weight of cellulose is constant, the literature contains a remarkable variety of curves for the absorption from the more dilute solutions.

Cellulose is a very variable material, and the discrepancy between the results obtained by different investigators suggests that the absorption from dilute solutions may be a physical rather than a chemical process. It was, therefore, thought desirable to attempt to correlate absorption of sodium hydroxide from dilute solutions and certain physical properties of the cellulose. No results have yet been obtained from work in this direction since most of the celluloses selected for the purpose were found to be unsuitable on account of unexpected difficulties in filtration, and the present work is confined to a highly resistant cotton cellulose. The results so far indicate that there is a chemical reaction between cellulose and sodium hydroxide even when the latter is present in dilute solution. However, experiments are being continued with other varieties of cellulose, and it is hoped to deal with these in a later paper.

Description and Preparation of Materials.—The moisture content of the cotton, determined by heating to constant weight at 100°, was 6.96%, and the ash content was 0.035%. Its resistance to the peptizing action of strong alkali indicated that it was probably free from the organic impurities present in certain other celluloses, and except for a trace of ammonia no detectable amount of impurity could be removed by washing

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[1] Blanco, *Ind. Eng. Chem.*, 20, 926 (1928).

it with water or hydrochloric acid. It was, therefore, considered pure enough to be used without preliminary treatment. In order to obtain a uniform moisture content, enough for the whole investigation was stored for several weeks in an air-tight bottle and the moisture content was checked from time to time during the course of the work; the variation was negligible.

The sodium hydroxide solutions were made from sodium in a platinum dish and usually gave no reaction for carbonate, although some contained a trace; all were free from sulfate and chloride. They were always prepared immediately before they were required.

Determination of the Sodium Hydroxide Absorbed.—To determine the concentration of the sodium hydroxide solutions, portions were measured from weight burets into platinum dishes, slightly acidified with hydrochloric acid and evaporated to dryness in an oven at 100°. The residues were heated for one to two hours at 250° and then at 650° in an electric furnace in covered dishes to constant weight. When the work was almost complete, a paper by Richards and Hall[2] appeared in which it was concluded that nothing short of fusion would yield the anhydrous salt. The residues, of course, could not be fused, since loss by vaporization would result; to decide the matter weighed amounts of pure anhydrous sodium chloride were dissolved in water, made slightly acid with hydrochloric acid, and then treated exactly as described. In no case did the weight of residue differ by more than one unit in the fourth place from the weight of anhydrous salt, and it was concluded that a final treatment at 650° is as effective as a fusion in removing the last trace of moisture. The residues lost 0.15 to 0.20% of their weight by the heating in the electric furnace.

Each absorption experiment was carried out in the following way. Weighed amounts of solution and cotton were placed in a test-tube, which was then closed by a rubber stopper and well shaken. The contents of the test-tube were transferred to a Gooch crucible, in which the cotton was pressed to form a compact filtering medium, and the solution was poured through two or three times. The filtration seldom occupied more than a minute or two, so that it was unnecessary to take special precautions to protect the solution from contact with the carbon dioxide of the air. The filtrate was then analyzed by the method described above.

The amount of sodium hydroxide absorbed was calculated as follows. Let W = weight of original solution, w = weight of sodium hydroxide which it contains and a = weight of sodium hydroxide absorbed. Then, if an amount W' of the filtrate is found by analysis to contain w' of sodium hydroxide, $W - a = (w - a)(W'/w')$; and hence $a = (wW' - w'W)/(W' - w')$. The same amount of cotton was not used for each experiment, but usually about 0.4 g. was treated with 50 to 60 g. of solution. After removal of the cotton, about 30 g. was employed to determine w'.

The last trace of cotton could not be removed by the method of filtration; the amount which passed into the filtrate slightly increased with increase in concentration of sodium hydroxide. Since it was never more than a trace, and was completely burned in the treatment of the sodium chloride residues, no importance was attached to it.

The Effect of Time.—It has been previously shown[3] that equilibrium

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[2] Richards and Hall, This Journal, **51**, 709 (1929).

[3] Karrer, *Cellulosechemie*, **2**, 216 (1921); Dehnert, *ibid.*, **5**, 19 (1924); Liepatoff, *Kolloid-Z.*, **36**, 149 (1925).

is established very rapidly. A number of determinations were made in which the time of contact of the cotton with the solution was varied. For periods longer than half an hour, weighed amounts of solution and cotton were placed in paraffined test-tubes, which were than sealed and left in a thermostat for the desired time. The same amount of cotton and as nearly as possible the same amount of solution were used for each experiment of a series.

It appears from the results given in Table I that the time of contact, beyond a few minutes, has practically no influence on the absorption; and in subsequent determinations the cotton was well shaken with the solution, allowed to stand for a few minutes, and then removed.

TABLE I

EFFECT OF TIME ON THE AMOUNT OF SODIUM HYDROXIDE ABSORBED BY ONE GRAM OF COTTON AT 20°

Time, hours	Final concn. of NaOH, g. per 100 g. of soln.	NaOH absorbed by 1 g. of cotton, g.	Time, hours	Final concn. of NaOH, g. per 100 g. of soln.	NaOH absorbed by 1 g. of cotton, g.
Series 1. (Initial concn. of NaOH, 8.103 g. per 100 g. of soln.)			Series 3. (Initial concn. of NaOH, 4.952 g. per 100 g. of soln.)		
0.05	8.074	0.0240	0.05	4.912	0.0209
2.5	8.077	.0234	.5	4.909	.0210
64.0	8.076	.0240	63.0	4.911	.0206
Series 2. (Initial concn. of NaOH, 3.631 g. per 100 g. of soln.)			Series 4. (Initial concn. of NaOH, 2.011 g. per 100 g. of soln.)		
0.5	3.610	0.0206	4.75	2.005	0.0061
14.5	3.608	.0204	20.0	2.005	.0059
42.0	3.607	.0204	73.0	2.003	.0054

The Effect of Mercerization.—Preliminary experiments showed that over the concentration range 4 to 8% the absorption was practically constant, but a relatively large increase occurred when the concentration of alkali was raised to 11%. It seemed desirable to attempt to determine whether the absorptive power of the cotton had been irreversibly increased by treatment with alkali of this concentration.

Samples were, therefore, steeped in solutions of various strengths up to 30% and washed free of alkali. The cotton which had been treated with the more concentrated solutions showed a marked increase in absorptive power. The data, plotted as curves in Fig. 1, show that previous treatment with 5% alkali has no effect on the power of absorption, but stronger solutions cause an apparently permanent increase, which reaches a maximum when the concentration of the modifying solution is about 20%.

These results may be correlated with those of x-ray investigations of cellulose. Katz[4] found that the x-ray spectrum of mercerized cotton differs from that of native cotton, but this effect is not produced when

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[4] Katz, *Z. Electrochem.*, **32,** 273 (1926).

alkali of concentration less than 8% is used. Meyer and Mark[5] have shown that mercerization causes an increase in the volume of the space lattice, which is explained by a spatial rearrangement of the parallel cellobiose chains. It is assumed that the chains are held together laterally by secondary valences, and that the broadening of the space lattice is accompanied by a weakening of these micellar forces and a corresponding increase in the reactivity of the cellulose. The latter authors point out that the strong inter-micellar forces are probably due to the attraction of the (OH) groups. With these assumptions it might be expected that the increase in the volume of the space lattice, produced by the action of the more concentrated solutions, would result in a stronger attraction for sodium hydroxide. Further, the weakening of the inter-micellar forces is probably brought about by penetration of the space lattice by the alkali; and it may be supposed that up to a concentration of 5% the amount of absorbed alkali is insufficient to produce a permanent distortion of the lattice.

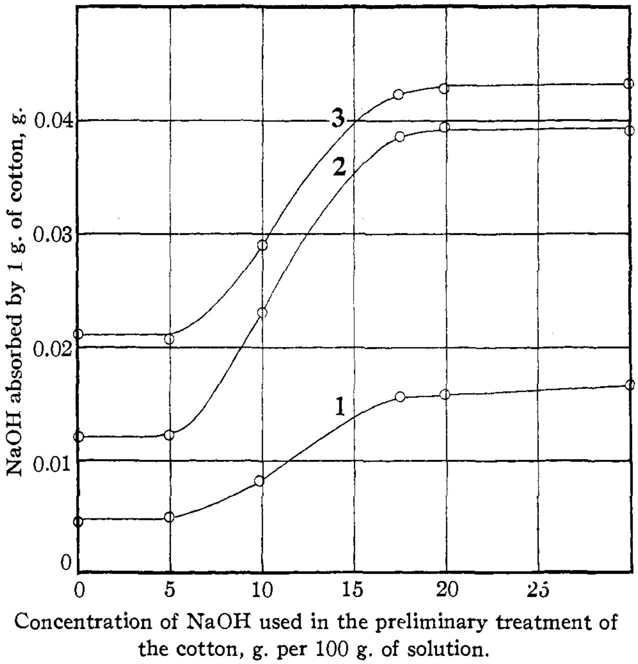

Fig. 1.—Absorption of NaOH by cotton at 20° after preliminary treatment with NaOH solution.

In order to study the action of dilute alkali on the mercerized product, about 20 g. was prepared from the native cotton by means of a 20% mercerizing solution, and the absorption of sodium hydroxide from solutions of various strengths was determined in the manner previously described.

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[5] Meyer and Mark, *Ber.*, **61**, 593 (1928).

Results and Conclusions

The experimental results are shown graphically in Fig. 2. The most striking point about the curves is the presence of the "breaks," which occur in both when the concentration is about 4%. At this concentration the compositions of the absorption complex are almost exactly expressed by $(C_6H_{10}O_5)_{12}\cdot NaOH$ (calcd., 0.0206 g. of NaOH per gram of cellulose) for the native cotton, and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ (calcd. 0.0412 g. of NaOH per gram of cellulose) for the mercerized cotton. The general character of the curves shows that the effect is not one of adsorption; and it is, therefore, improbable that the imbibition by the cotton takes place between colloidal particles. Moreover, the profound modification produced by the action of concentrated alkali indicates that an intimate penetration of the cellulose occurs, and there is no reason to suppose that the penetration of the lattice is confined to a particular concentration range. The speed with which equilibrium is attained is, however, not in accordance with the formation of solid solutions, and it is concluded that the absorption is a chemical process analogous to the formation of molecular com-

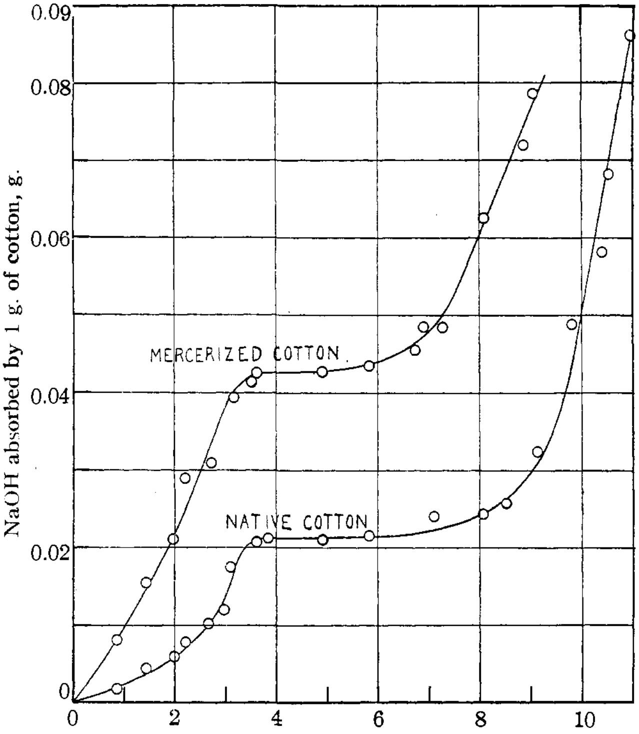

Fig. 2.—Absorption of sodium hydroxide by cotton.

pounds. According to this view, the horizontal parts of the curves indicate that the residual fields present in the cellulose are temporarily neutralized by the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

Summary

1. The absorption of sodium hydroxide by cotton has been shown to take place very rapidly, and to change only slightly over a period of two or three days.

2. Previous treatment of the cotton by sodium hydroxide solution of concentration greater than 5% increases its power of absorption. The maximum effect is produced when the concentration of the modifying solution is 20% or greater.

3. The absorption curves indicate that the action of sodium hydroxide solution of concentration 4 to 5% is the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

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A NEW METHOD OF PREPARING ACETALS

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Boron and silicon fluorides react readily with methyl or ethyl alcohols, forming heavy, fuming, almost colorless, and strongly acid liquids. These solutions have been studied by Liebig and Wöhler,[1] W. Knop,[2] Gay-Lussac and Thénard,[3] Kuhlman,[4] and V. Gasselin.[5] Due, however, to the complexity of the mixtures and to the instability of the compounds when isolated, the acids present have never been definitely identified. By distilling a solution of one mole of boron fluoride in one mole of methyl alcohol, Gasselin obtained an acid residue and the neutral compounds CH_3OBF_2 and $(CH_3O)_2BF$; but these in turn are decomposed by more alcohol with the liberation of acid. In the case of boron fluoride, the acid is probably HBF_4, or possibly H_3BF_6 or an ester acid, dissolved and ionized in absolute alcohol or some other constituent of the mixture. Orthoboric ester, which may be present, was shown by Walden[6] to be a

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[1] Liebig and Wöhler, *Pogg. Ann.*, **24**, 171 (1832).

[2] W. Knop, *J. prakt. Chem.*, [1] **74**, 41 (1858).

[3] Gay-Lussac and Thénard, "Recherches physico-chimiques," Vol. II, p. 39.

[4] Kuhlman, *Ann.*, **33**, 205 (1840).

[5] V. Gasselin, *Ann. chim. phys.*, [7] **3**, 5–83 (1894).

[6] Walden, *Z. physik. Chem.*, **54**, 175 (1906).