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Studies in Chemically Modified Celluloses. III. Estimation of Free Carboxylic Acid Groups in Oxycellulose

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Synopsis

Various methods suggested for the determination of carboxyl groups in chemically modified celluloses suffer from some drawbacks. Attempts have been made to overcome the drawbacks of some of these methods. The influence of alkali-sensitive reducing groups, enediol groups, and lactones on the carboxyl estimation is discussed and the importance of borohydride treatment of the oxycelluloses before the estimation of carboxyl groups by alkali titration method or by iodometric method is stressed. The usefulness and the limitations of both methods are pointed out.

INTRODUCTION

During the oxidative degradation of cellulose, reducing groups and acidic groups are formed in different positions of the anhydroglucopyranose units of cellulose macromolecules, depending on the conditions of degradation. The products of oxidation are generally more acidic in character and also possess greater reducing power than the undegraded cellulose. A number of methods[1–16] have been proposed for the quantitative estimation of carboxyl groups formed in cellulose during oxidation, and these depend on the ability of the acidic groups to bind either organic cations or metal cations. The cation exchange capacity of the oxidized products has been assessed by colorimetric, acidimetric, or complexometric titration. It has been found that none of these methods is suitable for every type of oxycellulose, since each of them suffers from some handicaps owing to the interference of alkali-sensitive reducing groups and to the existence of some of the carboxyl groups bound in the form of lactones. Also, lactones such as gluconic and glucuronic lactones are saponified under alkaline conditions at different rates and, depending on the conditions of carboxyl estimation, discrepancy in the results is likely to arise. Thus it was shown by Samuelson and Tornell[12] in the case of alkali-cooked cellulose that the calcium acetate method[10] gives 35%–40% lower values than the alkalimetric method of Samuelson and Wennerblom.[11] This has been ascribed to the presence of lactones not saponified during treatment with calcium acetate solution. They have also shown that after a pretreatment with alkaline salt solution

(to saponify the lactones present), a marked increase in calcium uptake takes place.

In view of what has been mentioned above, it was considered of importance of examine the problem more closely so that a suitable procedure, which would be applicable to all types of oxycellulose for the estimation of carboxyl groups present therein, is made available. The present communication deals with an investigation carried out for achieving these objectives.

EXPERIMENTAL

Standard Cellulose

Carefully purified 20s single yarn made from Indian cotton was used as standard cellulose. It had the following properties: copper number,[17,18] 0.01; cuprammonium fluidity[19] (0.5% solution), 3.0 r.poises; iodometric carboxyl value[8] 1.1 mEq per 100 g dry sample; alkalimetric carboxyl value,[3] 0.9 mEq per 100 g dry sample.

Preparation of Oxycelluloses

Sodium Hypochlorite Oxycelluloses. The oxidation of cellulose was carried out for 4 hr at 30°C in the dark, using sodium hypochlorite solution containing 3 g/l. available chlorine at pH 5.0 and 7.0, with a liquor ratio of 50:1. At the end of the reaction period, the samples were washed, treated with dilute sodium thiosulfate solution, and washed again.

Sodium Hypobromite Oxycelluloses. Cotton cellulose was treated with $N/25$ sodium hypobromite solutions buffered to pH 5.88 and 9.70 at 30°C, for 3 hr in the dark.

Potassium Permanganate Oxycelluloses. Cotton cellulose was treated with $0.1N$ potassium permanganate, buffered to pH 4.90 and 6.07 at 30°C, for 24 hr. This was followed by washing and treatment of the oxycelluloses with acidified hydrogen peroxide (1 vol) to remove the precipitated manganese oxides.

Accelerated Oxidation Oxycellulose. Cotton cellulose was oxidized with sodium hypochlorite solution buffered to pH 7.0, in presence of different leuco vat dyes by the method described by Turner, Nabar, and Scholefield.[20]

Potassium Dichromate–Oxalic Acid Oxycelluloses. Six grams of standard cellulose was suspended in 150 ml of $2N$ oxalic acid solution. Different amounts (20 ml and 40 ml) of $2N$ potassium dichromate solution (diluted to 750 ml with distilled water) were rapidly added and kept for 3 hr at room temperature.

Potassium Dichromate–Sulfuric Acid Oxycelluloses. The oxidation of cellulose was carried out with $0.1N$ potassium dichromate in the presence of $0.2N$ sulfuric acid at 30°C for 8 hr and 24 hr.

Nitrogen Dioxide Oxycelluloses. The oxycelluloses were prepared by the method followed by Nabar and Padmanabhan.[21] The cellulose was

treated with 3.4 ml of liquid nitrogen dioxide for 16 hr and 48 hr, in a stoppered glass flask.

Periodate Oxycelluloses. The oxycelluloses were prepared by steeping cotton cellulose in a solution of potassium metaperiodate (0.01*M*) buffered to pH 5.6 at 30°C for 4 hr and 9 hr, keeping a liquor ratio of 50:1.

Treatment of Oxycelluloses with Sodium Borohydride Solution[21]

Different oxycellulose samples were treated with unbuffered 0.01*M* sodium borohydride solution at 30°C for 24 hr. For highly oxidized samples, higher concentrations of the borohydride were selected.

After all the treatments described above were completed, in each case the sample was washed free from impurities with repeated changes of distilled water and dried at room temperature (30°C) and analyzed for its properties.

Analysis of Oxycelluloses and their Borohydride-Reduced Products

Copper number and cuprammonium fluidity of these samples were determined by standard methods.[17–19] For the estimation of carboxyl value, all oxycellulose samples were rendered cation free by steeping them in 0.5*N* HCl for 2 hr at 30°C, followed by washing free of acid and drying at room temperature. The carboxyl values were determined both by iodometry[8] and by alkalimetry[3] before and after borohydride treatment of the oxycellulose samples. In the latter method, the time of contact of the samples with alkali was varied (1, 4, and 20 hr).

RESULTS AND DISCUSSION

The different properties such as copper number, cuprammonium fluidity, and carboxyl content of the oxycellulose samples determined before and after sodium borohydride treatment are given in Table I.

Since most of the oxidizing agents are nonspecific in their action on cellulose, they oxidize the hydroxyl groups of cellulose to different stages of oxidation, depending on the conditions chosen, resulting in the possible formation of groups such as aldehyde or carboxyl at C_6 position; monoketo, diketo, dialdehyde, or enediol at C_2–C_3 position; gluconic acid group at one end of the molecular chain; keto group at C_4 at the other end, etc. Under acidic conditions, the carboxyl groups formed may be present partly bound as lactones and partly as free carboxyl groups. The lactones are saponified in an alkaline medium. Thus two types of groups, viz., carboxyl (free as well as lactonized) and enediol groups (which also react as acidic groups under certain conditions), may be present simultaneously in the products of oxidation. The estimation of carboxyl groups is likely to be adversely affected by the presence of enediol groups and lactonized carboxyl groups.

Of the various methods developed for the estimation of carboxyl groups in cellulose and modified celluloses, the carbon dioxide evolution method of Hess[1] appears to be the first one to be mentioned in the literature. How-

ever, this method is applicable only to oxycelluloses containing uronic acid groups. Schmidt and co-workers[2] have described a conductometric method for estimating carboxyl groups in cellulosic materials. Neale and Stringfellow,[3] however, found that this method does not give sharp inflection points in the titration curves. The method developed by Lüdtke[4] depends on the alkalimetric titration of acidic groups in the presence of a large excess of calcium acetate. Neale and Stringfellow[3] found this method unsatisfactory owing to the buffering effect of the acetate, resulting in an error with a range of 4–6 mEq COOH/100 g cellulose. Based on these observations, they[3] worked out a direct alkalimetric titration method for the determination of carboxyl groups in cellulose. This method has also certain disadvantages. It has been subsequently demonstrated that when the time of contact of an oxycellulose with alkali during the estimation is progressively increased beyond the recommended period of 1 hr, the carboxyl value obtained also increases.[23]

Sookne and Harris[5] suggested the use of metal ion binding capacity of weak acids for the estimation of carboxyl groups using calcium acetate. The calcium acetate method has been found by Heymann and Rabinov[6] to be suitable only if cellulose is removed from the system before the titration is carried out. They attempted to determine the acidic groups by a potentiometric method, but could not obtain definite values. The methylene blue absorption method of Davidson[7] appears to estimate true carboxyl groups and the presence of enediol groups is not likely to interfere with the estimation. This is confirmed by the observation that in the case of periodate oxycelluloses, acidity as measured iodometrically is completely removed by borohydride treatment, but the methylene blue method does not show any difference between the acidity value of these oxycelluloses before and after their borohydride treatment[24] (vide infra). The carboxyl value of these oxycelluloses obtained either by the iodometric method[8] after borohydride tratment or by the methylene blue absorption method[7] before and after borohydride treatment is the same as that of the original unoxidized cellulose. This suggests that carboxyl groups are not formed during periodate oxidation of cellulose and that the acidity measured by the iodometric method is solely due to the presence of enediol groups. It may be mentioned that the methylene blue absorption method gives reproducible results only under strictly standardized conditions and even small variation in these conditions leads to changes in the carboxyl value.

Nabar and Padmanabhan[8] developed an iodometric method for the estimation of carboxyl groups in cellulose by treating the latter with a solution containing potassium iodide, potassium iodate, sodium chloride, and a known excess of sodium thiosulfate for 24 hr at room temperature and back-titrating the residual thiosulfate with standard iodine in the presence of the sample. This method has been subsequently modified by raising the temperature to 60°C so that the treatment period can be reduced to 1 hr.[9] The above authors[8] have claimed that the iodometric method gives reproducible and reliable carboxyl values for various types of oxycellulose,

including the alkali-sensitive type, as the estmation is carried out at pH 7.0–7.3. Subsequent work[24] has however shown that enediol groups, if present in the sample, also take part in the estimation by behaving as dibasic acids. It was pointed out that the iodometric method estimates the total acidity of an oxycellulose and not that due to carboxyl groups alone. Therefore this method gives higher carboxyl values than those represented by true carboxyl groups.

It has been shown[15,16] that lactones of oxy acids are cleaved by a mixture of potassium iodide and potassium iodate and that this mixture enables one to determine uronic, aldonic, and saccharinic acids in lactone form also if present in cellulose. It is claimed that cleavage of lactones can be carried out at pH 7 (by using this solution) as compared to other methods where alkaline solutions (pH 8.5–12.0) are used for the saponification of the lactones. Among the possible types of lactones, dicarboxylic acid (at C_2–C_3) lactones were shown to be cleaved most easily. Aldonic and uronic acid lactones are cleaved with moderate ease.

It may be inferred that in the iodometric method of Nabar and Padmanabhan,[8] since the oxycellulose sample is in contact with potassium iodide–potassium iodate mixture (in presence of sodium chloride and sodium thiosulfate) for a fairly long period (24 hr), all the lactones undergo cleavage and hence all the carboxyl groups present in the oxycellulose sample, either free or bound as lactones, along with all the enediol groups are estimated.

Samuelson and Wennerblom[11] were perhaps the first to quantitatively determine lactones in cellulose. In their method, the total carboxyl content is determined by adding an excess of alkali to deionized sample and after complete saponification of the lactones, the remaining alkali is titrated with an acid in the presence of the sample. This method is applicable to samples having very low carbonyl content, as these groups interfere seriously. An attack on the carbonyl groups followed by peeling reaction forming organic acids, which consume a part of the alkali, leads to further errors in the results. The method of Samuelson and Tornell[12] of determining carboxyl content of cellulose consists in washing the sample with sodium chloride solutions at pH 7.5–8.0 (with sodium hydroxide) until free from excess alkali, followed by washing with CO_2-saturated water to displace sodium chloride, and finally elution with 0.01*M* HCl, followed by washing with deionized water. The effluent is titrated with standard barium hydroxide solution after boiling to expel carbon dioxide. Since the sample does not come into contact with excess alkali, this method is suitable for samples containing carbonyl groups.

Recently, Wilson[13] stuided the cation exchange capacity of cellulose by treating the sample with sodium and magnesium salt solutions and found that the capacity was more dependent on the cation concentration than on the ion valency. In this method the sample is treated with 0.1*N* sodium chloride buffered with sodium bicarbonate to pH 8.0 and, after elution with CO_2-saturated water, the sodium ions bound to the carboxyl groups are

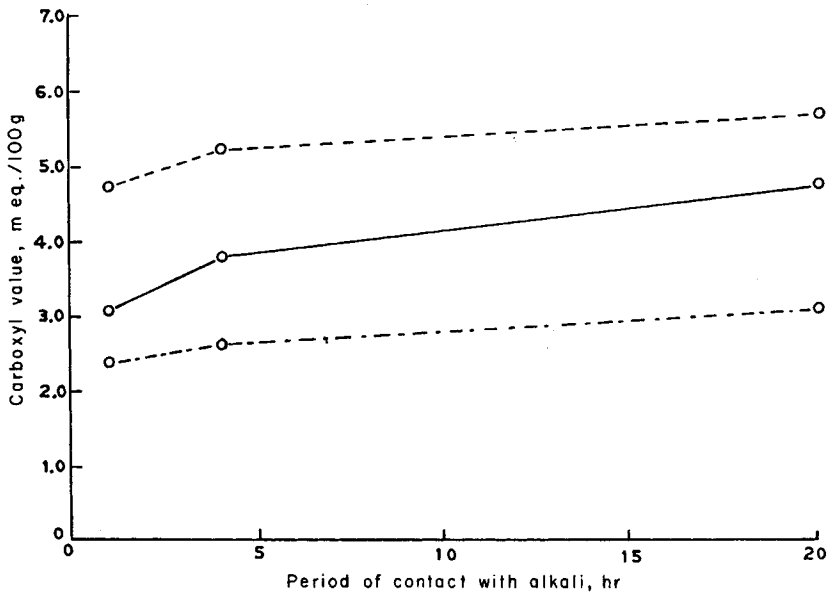

Fig. 1. Alkali sensitivity of oxycellulose and modified oxycellulose: (——) leuco vat/hypochlorite oxidation of cellulose; (– – –) chlorous acid-treated oxycellulose; (·—·—·) borohydride-treated oxycellulose.

titrated acidimetrically. He found that a pretreatment with 0.01*N* NaOH for 30 min completely hydrolyzed the lactones. When this was followed by 0.1*N* HCl treatment for 30 min, lactones were reformed.

Sodium borohydride in water or methanol solution has been found to be a very effective reagent for the conversion of aldehydes and ketones into the corresponding alcohols and is found to be much superior to lithium aluminum hydride in that it, being a less powerful reducing agent, can perform selective reductions.[25] Borohydride reduces acid chlorides to primary alcohols in nonaqueous media but carboxylic acids, anhydrides, esters, and nitriles are practically unaffected. Wolfrom and Wood[26] have shown that sodium borohydride is an efficient and convenient reagent for reducing aldonic acid lactones. Thus D-gluco-D-gulo-heptonic γ-lactone is reduced to D-gluco-D-gulo-heptose by sodium borohydride at pH 3–4 (with sulfuric acid) and to D-gluco-D-gulo-heptitol at pH 8.0 (aqueous solution of sodium borohydride). Wolfrom and Anno[27] have shown that lyxono-γ-lactone is reduced to lyxose at pH 3–4 (with acetic acid) and to arabitol under alkaline conditions (aqueous solution). Samuelson and Tornell[12] found that the carboxyl content of alkali-cooked cellulose determined by the Samuelson and Wennerblaum[11] method after treatment of the sample first with alkaline salt solution (this saponifies lactones) and then with borohydride solution did not decrease significantly (it decreased only by 2.5%). When the alkaline salt pretreatment is not given (i.e., the lactones are left unsaponified), a borohydride treatment alone is found to

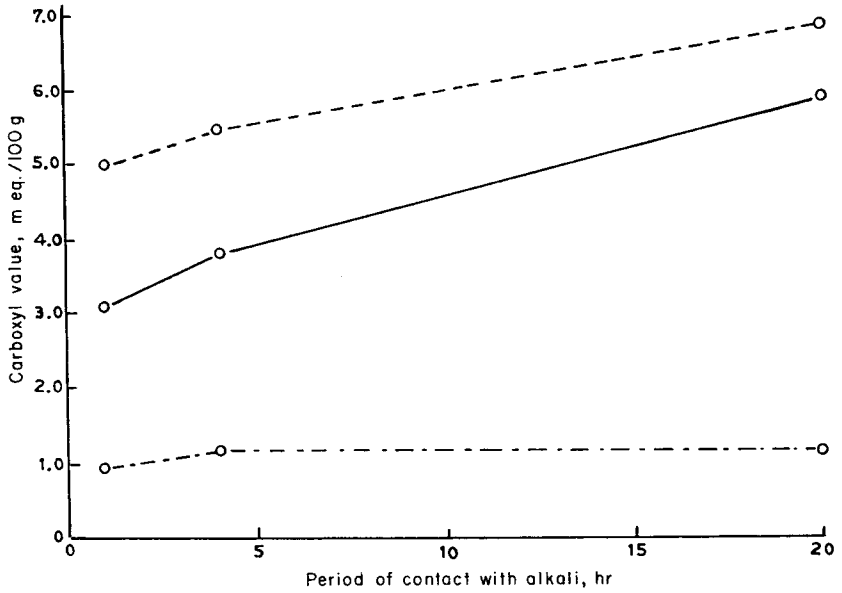

Fig. 2. Alkali sensitivity of oxycellulose and modified oxycellulose: (——) photochemically oxidized vat-dyed cellulose; (– – –) chlorous acid-treated oxycellulose; (-·-·-·-) borohydride-treated oxycellulose.

decrease the carboxyl content by about 20%, suggesting that borohydride reduces the lactones present in cellulose samples.

From what has been said above, it may be inferred that most of the methods suggested or recommended for the estimation of carboxyl groups in an oxycellulose do not appear to be suitable for applying to all types of oxycellulose.

Attempts have been made by several investigators to overcome the defects of these methods. For example, oxidation of aldehyde groups by chlorous acid or reduction by sodium borohydride treatment have been suggested to remove the alkali sensitivity of an oxycellulose, so that alkali titration methods can be used for the estimation of carboxyl groups.[23]

While studying the photochemical and allied tendering activity of vat dyes, Nabar and Shenai[23] prepared oxycelluloses by oxidizing leuco vat dyes, while present on cotton, with sodium hypochlorite and also by exposing vat-dyed cotton cloth to sunlight. They reported the presence in these oxycelluloses of certain groups which are not true carboxyl groups but have acidic properties (the groups liberated iodine from KI–KIO_3 mixture) and at the same time are reducible by a borohydride treatment. True carboxyl groups are not reduced by this treatment. They[22] determined the alkalimetric carboxyl values of these oxycelluloses before and after, separately subjecting the samples to chlorous acid and borohydride treatments. These results are reproduced in Figures 1 and 2. It can be seen that as the time of contact of the sample with alkali increases, the carboxyl value

TABLE I
Properties of Differently Modified Cellulose Samples

Oxidant	Conditions of oxidation	Sample number	Copper number	Cuprammonium fluidity, r. poises	Carboxyl value, mEq/100 g dry sample			
					Iodometry, 24 hr	Alkali titration method		
						1 hr	4 hr	20 hr
NaOCl	pH 5.00	1(OXY)	1.65	7.6	1.70	2.20	2.90	4.10
		1($NaBH_4$)	0.05	2.9	1.43	0.93	0.93	1.10
	pH 7.00	2(OXY)	11.20	41.0	8.80	12.10	16.40	20.10
		2($NaBH_4$)	0.55	34.5	7.20	6.50	6.60	7.30
NaOBr	pH 5.88	3(OXY)	3.15	13.0	4.90	6.20	7.60	10.00
		3($NaBH_4$)	0.05	4.3	4.00	3.50	3.50	3.70
	pH 9.70	4(OXY)	2.53	27.5	21.60	21.50	23.00	25.10
		4($NaBH_4$)	0.11	25.5	18.50	17.10	17.30	17.50
$KMnO_4$	pH 4.90	5(OXY)	6.75	46.1	17.50	18.10	19.10	21.70
		5($NaBH_4$)	0.50	41.2	13.40	12.90	13.10	13.30
	pH 6.07	6(OXY)	3.42	42.1	20.30	19.70	20.50	21.90
		6($NaBH_4$)	0.26	40.1	14.10	14.20	14.70	15.00
NaOCl/Leuco Cibanone Orange R	pH 7	7(OXY)	3.38	17.5	2.8	3.5	4.5	6.2
		7($NaBH_4$)	0.24	14.3	2.1	1.6	1.8	1.9

NaOCl/Leuco	pH 7	8(OXY)	2.28	14.5	2.2	2.4	3.5	4.6
Calco Yellow 5G		8($NaBH_4$)	0.19	10.4	1.7	1.3	1.4	1.6
$K_2Cr_2O_7$	20 ml 2*N*	9(OXY)	4.10	19.8	1.8	1.7	2.3	4.0
+	$K_2Cr_2O_7$	9($NaBH_4$)	0.01	5.75	1.2	1.1	1.1	1.2
COOH	40 ml 2*N*	10(OXY)	7.13	30.4	2.7	3.5	4.4	7.6
|	$K_2Cr_2O_7$	10($NaBH_4$)	0.01	10.3	1.9	1.8	1.8	1.9
COOH								
$K_2Cr_2O_7$	8 hr	11(OXY)	5.57	34.0	3.5	4.3	6.2	8.7
+ H_2SO_4		11($NaBH_4$)	0.05	13.8	2.4	2.0	2.2	2.5
	24 hr	12(OXY)	12.28	43.4	8.3	10.3	12.3	18.1
		12($NaBH_4$)	0.26	25.9	5.9	5.6	5.8	6.3
NO_2	16 hr	13(OXY)	14.50	41.4	42.5	44.1	47.2	54.6
		13($NaBH_4$)	3.50	33.0	36.0	35.5	36.0	36.6
	48 hr	14(OXY)	19.7	49.9	84.0	82.3	86.0	93.0
		14($NaBH_4$)	4.6	42.0	58.7	58.4	58.8	59.2
KIO_4	4 hr	15(OXY)	4.05	33.5	1.67	6.0	7.1	8.7
		15($NaBH_4$)	0.01	4.3	1.0	0.85	0.85	0.95
	9 hr	16(OXY)	7.21	40.1	2.3	9.9	11.9	14.6
		16($NaBH_4$)	0.01	8.4	1.2	0.95	0.95	1.0

increases pronouncedly in the case of the untreated oxycellulose, less so with chlorous acid-treated sample, but is practically unaffected in the case of borohydride-treated oxycellulose. The alkali sensitivity of the oxycellulose has been ascribed to the presence of reducing groups which are found to be incompletely oxidized by chlorous acid (this reagent did not bring down the copper number to zero), but completely reduced by borohydride treatment (copper number of borohydride-treated sample was practically zero).

Subsequently Nabar, Shenai, and Meghal[24] suggested that the "pseudo-carboxyl groups," which can be reduced by borohydride treatment, might be enediol groups formed at the C_2–C_3 position through enolization of a monoketo derivative and showed that such groups are present in oxycelluloses prepared by oxidizing cotton cellulose with different oxidizing systems.

If one considers the possibility of some of the carboxyl groups of the oxycellulose being bound in the form of lactones, the increase in the alkalimetric carboxyl value with increasing time of contact may apparently be ascribed also to the gradual saponification of the lactones present. But this seems to be hardly the case, since it was shown by Wilson[13] that a treatment with 0.01*N* NaOH for 30 min saponifies the lactones completely and since in the present case the oxycellulose samples are kept in contact with 0.02*N* NaOH for at least 1 hr, the recommended period in the alkalimetric method of Neale and Stringfellow,[3] which was used by Nabar and Shenai.[23] Therefore, when the time of contact with alkali was increased to 4 and 20 hr, the increased carboxyl value does not seem to have arisen from the saponification of lactones. As mentioned earlier, it may be ascribed to the presence of alkali-sensitive reducing groups in the samples. This is demonstrated by the practically constant values obtained in the case of borohydride-treated oxycelluloses, in which the alkali-sensitive reducing groups are absent. Hence the carboxyl value of an oxycellulose determined by the alkali titration method, after subjecting the oxycellulose to borohydride treatment, represents only the free carboxyl groups present in the oxycellulose, as the lactonized groups are reduced to alcoholic groups.

The iodometric method[8] of carboxyl group estimation, on the other hand, determines the total acidity, i.e., free carboxyl groups, enediol groups, and also lactones (which have been shown[15,16] to be cleaved by KI–KIO_3 mixture) present in an oxycellulose. When an oxycellulose containing these groups is subjected to borohydride treatment, enediol groups and lactones are reduced to alcoholic groups, leaving free carboxyl groups unaffected. From this it follows that, irrespective of the type of oxycellulose, both the alkalimetric[3] and iodometric[8] carboxyl values of the oxycellulose should be the same if the estimation is carried out after subjecting the samples to borohydride treatment.

An examination of the carboxyl values of untreated oxycelluloses given in Table I shows that in general the alkali titration method[3] gives higher carboxyl values than the iodometric method.[8] This difference is more pronounced in the case of some oxycelluloses than in others. Further, all the oxycelluloses exhibit alkali sensitivity, as seen from the increase in the

alkalimetric carboxyl values with increasing time of contact with alkali. Oxycelluloses with higher copper number show higher alkali sensitivity.

On treatment of these oxycelluloses with aqueous sodium borohydride solutions, it is seen from the same table that, in every case, the iodometric carboxyl value decreases. As mentioned earlier, this decrease may be ascribed to the reduction of either the enediol groups or the lactones or both if present in the sample.

The fact that the borohydride treatment brings about almost complete removal of alkali sensitivity is seen from the observation that the alkalimetric carboxyl values do not show any increase by prolonging the time of contact of these samples with the alkali solution. It is also seen that borohydride treatment brings down the copper number to a fairly low value. A substantial decrease in the cuprammonium fluidity of the oxycelluloses is also brought about by this treatment. The high fluidity values of the oxycelluloses, therefore, do not indicate the true extent of the rupture of the glucosidic links in the cellulose macromolecule. During the dissolution of an oxycellulose in cuprammonium hydroxide solvent, the high alkalinity of the solvent itself appears to bring about a cleavage of the alkali-sensitive linkages. When such oxycellulose is treated with borohydride, the alkali sensitivity is removed and no further scission of the molecular chains takes place during the dissolution of the sample in cuprammonium hydroxide. The fluidity value of the borohydride-treated oxycellulose may, therefore, be taken as the true measure of the extent of the molecular breakdown which has taken place during the oxidation. It is noteworthy that in oxycelluloses where the copper number is reduced to a very low value, the decrease in fluidity brought about by borohydride treatment is substantial. But where the residual copper number after borohydride treatment is still sizable, the drop in fluidity value is comparatively small (compare $NaBH_4$-treated samples no. 2, 4, 5, 6, 7, 8, 12, 13, and 14). As mentioned earlier, both alkali titration and iodometric methods give the same carboxyl value for the borohydride-treated oxycelluloses, the value representing free carboxyl groups (not lactonized) formed during the oxidation of cellulose.

From the foregoing considerations, it may be concluded that when free carboxyl groups, lactones, enediol groups, and alkali-sensitive reducing groups are present in an oxycellulose, the estimation of carboxyl groups (free as well as lactonized) is rendered difficult by the presence of the other groups. The iodometric method of Nabar and Padmanabhan[8] gives the total acidity, since the treating solution brings about cleavage of lactones, and enediol groups liberate iodine from iodide–iodate mixture. The iodometric or alkalimetric carboxyl values determined after subjecting the oxycellulose to a borohydride treatment represent only the free carboxyl groups, as the other groups are reduced by the borohydride treatment. Both these methods therefore are suitable for the estimation of free carboxylic acid groups in cellulose and oxycelluloses after treatment with sodium borohydride solution. Investigations to evolve methods for the determination

of the three types of acidic groups separately (mentioned above) when present simultaneously in an oxycellulose are in progress and will be reported in due course.

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