

STUDIES ON CARBOXYMETHYLCELLULOSE

Part V.—Carboxymethylation and Properties of the Products

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Carboxymethylation increases the degree of substitution in all the different types of celluloses. While after *four* successive treatments the value for cotton and wood pulp still shows an upward trend, that for jute tends to a limit. Use of wet products in the successive treatments (rather than drying it after each treatment) gives much better results. In *four* treatments with jute and cotton, the degree of substitution (D.S.) of the products were respectively 2.61 and 2.63; but cotton gave a high value of 2.88 after the fifth treatment.

Detergent properties were studied by measuring lowering of surface tension. This and other physical properties are discussed.

Introduction

Commercially, sodium carboxymethylcellulose (Na-CMC) was first used as a detergent aid, but gradually a large number of other important uses were developed. A comprehensive review has recently been published.¹

Since its original study by Jensen,² Chowdhury³ and Hoppler,⁴ the basic steps of the preparation of carboxymethylcellulose have remained unaltered. It is prepared by converting cotton (or good quality pulp) into soda cellulose, which is subsequently etherified by sodium monochloroacetic acid. Usually a partially substituted product is obtained. The maximum degree of substitution is theoretically *three*; but the commercial products have much lower degree of substitution (0.60–0.80).

The main object of this work was to obtain products with higher degree of substitution by using different reaction conditions, and also to study the behaviour of jute cellulose under these reaction conditions and to compare the products with those of cotton and wood pulp. The use of high concentration of alkali in aqueous medium,⁵ carboxymethylation in organic solvents medium,⁶ effect of using impure jute in preference to de-lignified jute⁷ and also that of the application of pressure during alkali treatment had been reported.⁸ These experiments showed that jute cellulose was just as good a starting material as cotton and wood pulp (in fact superior in some cases). The use of ethanol-water as solvent for carboxymethylation gives products having relatively much higher degree of substitution. With impure jute, it has been possible to obtain, in a single stage treatment a product having a D.S. of 1.60.

Complete carboxymethylation of cellulose has not yet been reported even on a laboratory scale and experience in this laboratory on the gradual

improvement of the degree of substitution of the product under different conditions indicated that with increasing D.S., the properties change. Thus the preparation of high D.S. products remains a matter of great interest. The work of Klug and Spurlin,⁹ and Hayakawa and Morita¹⁰ claimed that the multistage treatment gives high substituted product and the D.S. reported by the latter was 1.5 to 2.0, but they did not mention the number of stages of treatment. In the present investigation, D.S. of 2.08, 1.93 and 1.86 respectively from impure jute, cotton and wood pulp were obtained by *four* successive treatments under conditions found more or less optimum in previous work in this laboratory, but without application of pressure. Further, if the products from the different stages were not allowed to dry but used directly (in the wet condition) for the subsequent step, much better results were obtained. In this way through four-stage treatments, products having D.S. of 2.6 could be obtained from cotton or jute.

Carboxymethylation

Mature tossa jute was obtained from the market. After discarding the top and the bottom portions, the fibre was cut into short lengths of 1–2 in. It was then powdered in a shredder, washed several times with distilled water, dried (105°C) and stored in a vacuum desiccator.

Cotton was procured from local market, powdered and refluxed with 2:1 benzene-alcohol solvent in the usual way for dewaxing. The dewaxed cotton was treated with 1% alkali till the alkali-treated solution was colourless. It was then thoroughly washed with distilled water, dried and stored as above.

Wood pulp was obtained through the courtesy of the Karnaphuli Paper Mills Ltd. It was

slightly brown and needed only a mild hypochlorite treatment followed by washing and drying as above.

Procedure.—20 g of stock samples were taken for each experiment and steeped in 17% NaOH in water-ethanol (1:6 by volume) at 28–30°C for 2 hr. To this 80% alcoholic solution of monochloroacetic acid was added dropwise from a burette while the mass was kept stirred. The carboxymethylation was then continued for 6 hr at 40–45°C. The crude Na-CMC was dissolved in water (to make an approximate 2% solution); any residues were filtered off. The solution was concentrated and Na-CMC was precipitated by addition of 80–90% ethanol.

For further carboxymethylation, initially (mentioned hereafter as the first procedure) the precipitated Na-CMC was dried over calcium chloride in a desiccator and weighed. For the subsequent step a finely powdered dried product was taken. It was later found that better results could be obtained if the main bulk of the *undried product* is used for further carboxymethylation. This will be referred to as the second procedure. Results obtained with both these procedures are presented and discussed.

As in previous work, the D.S. was determined by the uranyl gravimetric method.¹¹

Results and Discussion

Carboxymethylation of cellulose is believed to take place through an intermediate formation of alkali cellulose. It is not yet certain whether the sodium hydroxide forms a definite cellulosate or is simply adsorbed. Sodium hydroxide in any case activates cellulose molecule and renders hydroxyl groups more accessible (reactive) to external reagents.

In Table I are recorded the conditions of four successive stages of carboxymethylation of cotton, impure jute and wood pulp and the results obtained therefrom. For comparison of the data obtained, the same amount of each raw material was taken, the experimental conditions remaining the same. For a monosubstituted product (D.S. = 1), the theoretical yield of sodium carboxymethylcellulose should be more than 170% of the weight of cellulose taken. In the case of cotton the yield was (in the first stage and with a D.S. of 1.23) only 108%, much less than the desired value, whereas with wood pulp it was 96%. In the case of jute cellulose, however, the yield was 123% (16 g of product from 20 g of jute containing 65% of cellulose); the D.S. in this case was, of course, somewhat higher (1.41). Careful examination of the procedure would show that there is no other step involved (except of course small handling losses) than the final alcoholic precipi-

TABLE I.—SUCCESSIVE CARBOXYMETHYLATION OF DIFFERENT TYPES OF CELLULOSE IN WATER-ETHANOL MEDIUM (FIRST PROCEDURE).

Type of cellulose used	Number of steps	Amount of fibre or Na-CMC taken (g)	Amount of NaOH used (g)	Amount of monochloroacetic acid used (g)	Amount of Na-CMC obtd (g)	D.S.	Remarks
Cotton	1	20.0	24.0	32.0	21.7	1.23	Soluble in water
	2	15.0	18.0	24.0	17.5	1.61	„
	3	12.0	14.6	19.2	14.8	1.78	Soluble with trace suspension
	4	8.0	9.6	12.8	6.8	1.93	„
Impure jute	1	20.0	24.0	32.0	16.0	1.41	Soluble in water
	2	10.0	12.0	16.0	12.0	1.76	„
	3	8.0	9.6	12.8	10.0	1.97	Soluble with trace suspension
	4	5.0	6.0	8.0	3.6	2.08	„
Wood pulp	1	20.0	24.0	32.0	19.2	1.33	Soluble in water
	2	12.0	14.6	19.2	15.4	1.54	„
	3	10.0	12.0	16.0	11.7	1.67	Soluble with trace suspension
	4	6.0	7.3	9.6	4.1	1.86	„

Steeping conditions: 28–30 C for 2 hr. Concentration of NaOH=17% w/v in water-ethanol (1:6 v/v)
Condition of carboxymethylation: 80% w/v Cl.CH₂. COOH at 40–45°C for 6 hr in water-ethanol, water/cellulose ratio = 1:1(w/w).

TABLE 2.—SUCCESSIVE CARBOXYMETHYLATION OF DIFFERENT TYPES OF CELLULOSE IN WATER-ETHANOL MEDIUM (MODIFIED PROCEDURE).*

Type of cellulose used	Amount of fibre taken (g)	Number of steps	Amount of NaOH used (g)	Amount of monochloro-acetic acid used (g)	D.S.	Remarks
Cotton	2.5g	1	3.0	4.0	1.20	Soluble in water. Insoluble in ethyl alcohol
		2	3.0	4.0	1.99	Soluble in water. Sparingly soluble in ethyl alcohol
		3	3.0	4.0	2.35	Soluble in water. To some extent soluble in ethyl alcohol
		4	3.0	4.0	2.63	Soluble in water. To some extent soluble in ethyl alcohol
Impure Jute	2.5	1	3.0	4.0	1.36	Soluble in water. Insoluble in ethyl alcohol
		2	3.0	4.0	2.21	Soluble in water. Sparingly soluble in ethyl alcohol
		3	3.0	4.0	2.52	Soluble in water. To some extent soluble in ethyl alcohol
		4	3.0	4.0	2.61	Soluble in water. To some extent soluble in ethyl alcohol

*Operating conditions were the same as those mentioned under Table 1.

tation (from 2% aqueous solution of Na-CMC) which may satisfactorily explain the lower yields. It is possible that during the process of carboxymethylation there is some (non-uniform) cleavage of the cellulose chain and the alcohol used is thus unable to precipitate out these fractions from aqueous solution. Alternatively (and this possibility became more obvious when working according to the modified procedure), with increasing average substitution in the chain, the solubility in water increases and the ethanol solvent fails to precipitate out the high D.S. product completely. It is therefore important, at least for commercial production of any high D.S. product, to use a more efficient precipitating method.

In the present study, the application of pressure for conversion to soda-cellulose has been eliminated. For jute cellulose, with application of pressure,⁸ a D.S. of 1.60 was obtained in a single-stage operation; in the present study without pressure treatment, a value of 1.41 has been obtained using 20 g jute. Under similar conditions, using 5 g jute, a D.S. of 1.48 was obtained.³ Considering the number of steps involved and the heterogeneous nature of the reactions, these results (worked out independently) must be considered quite corroborative.

In all the three cases, the D.S. goes on increasing with successive carboxymethylation, indicating that successive treatments with alkali generate 'activated' hydroxyl groups for substitution. As we proceeded through the four stages, the D.S. of cotton and wood pulp continued to increase whereas the D.S. of jute approached a limiting value (Fig. 1). This point has not been fully understood.

Even then under these conditions, jute gave the highest D.S. values—1.41 in the first stage, rising to 1.97 in the third and to 2.08 in the fourth stage. In the case of cotton, a D.S. value of 1.23 was obtained in the first stage; this more or less steadily increased and a value of 1.93 was obtained after the fourth stage. Products from wood pulp had lower D.S. values compared even to cotton, except for the first stage.

With high D.S. product, the crude sodium carboxymethylcellulose formed was highly soluble in water and reprecipitation was difficult. The insolubility of a trace of the higher D.S. product in water might be due to lack of complete homogeneity of substitution or its susceptibility to drying.

Results with Modified Procedure.—In the first procedure (whose results have just been described), the product from each stage was carefully dried and a portion therefrom was taken for subsequent processing. It is possible that due to the drying, the approach of reagents in the intracrystalline and intercrystalline regions was inhibited or slowed down. In the modified procedure, therefore, a small portion of the product was dried to determine the D.S., while the main bulk, still in the wet condition, was carried over for subsequent processing. The surprisingly promising results are presented in Table 2. Experiments in this series were carried out with jute and cotton only.

Giving more or less the same D.S. value in the first stage, (1.36; while 1.41 in the other case),

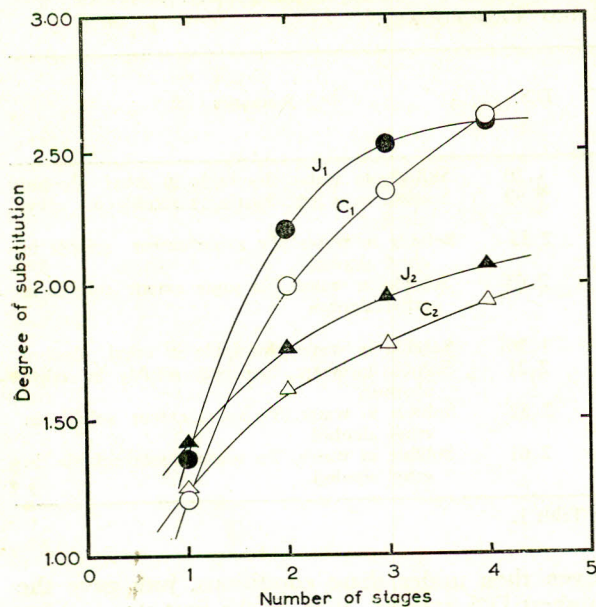


Fig. 1.—Variation of degree of substitution with repetitive carboxymethylation

- C₂ repetitive carboxymethylation of cotton under the first procedure
 C₁ repetitive carboxymethylation of cotton under the modified procedure
 J₂ repetitive carboxymethylation of jute under the first procedure
 J₁ repetitive carboxymethylation of jute under the modified procedure

the modified procedure gave steadily increasing values in the subsequent stages, which reached 2.61 at the end of the fourth stage (Fig. 1). The curve again shows the tendency of approaching a limiting value. On the other hand, with cotton in the modified procedure, a D.S. value of 1.20 was obtained in the first stage (compare 1.23 in Table 1). But it increased more steadily and at the end of the fourth stage gave a value of 2.63 (compared to that of 2.61 for jute). The more important observation was that with successive carboxymethylation cotton maintained increase in the D.S. value. Another carboxymethylation was carried out to obtain a product having a remarkably high D.S. of 2.88. The carboxymethylation depends upon the accessibility of reagent and the availability of the activated hydroxyl group. This also explains why in our earlier work, much longer duration of carboxymethylation than 6 hrs did not produce any better results. Increased substitution by successive treatment with alkali clearly shows secondary activation of the free hydroxyl groups. Increased substitution also gives products that are at least partially soluble in 80% ethyl alcohol.

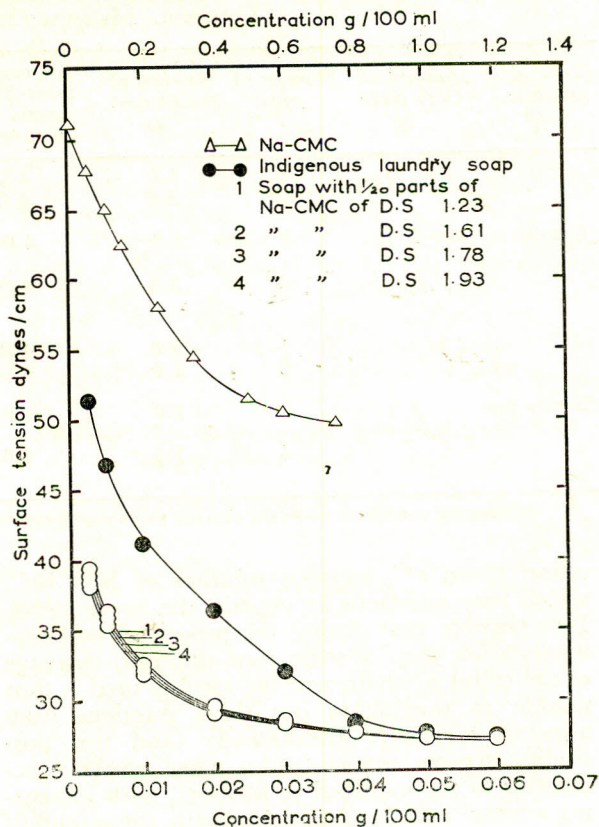


Fig. 2.—Variation of surface tension of aqueous solutions containing different ingredients with concentrations. The scale on top refers to top curve, and that on the bottom of x-axis refers to the five bottom curves.

Water Solubility and Other Physical Properties

Properties of Na-carboxymethylcellulose depend primarily on their water-solubility, which in turn is believed to vary with the degree of substitution and change in the degree of polymerization of the cellulose chain during the preparation. Provided that the experimental conditions are such as would not allow too much degradation of the chain, products having D.S. of 0.40–0.50 are very sparingly soluble; while with a product of D.S. of about 1.00, a clear solution is formed in low concentration, but when the concentration is increased (*ca* 5%), it tends to set as a gel. When the degree of substitution further increases (approaching 2.00), the water-solubility increases considerably. The trace of residue obtained with the products of first procedure should be attributed to too much drying (and probable change) in a very small portion of the product. When the D.S. was above 1.50, and particularly when it was above 2.00, the sodium carboxy-

methylcellulose was probably soluble in alcohol to the extent that it created difficulties in the precipitation of the product from water-ethanol mixtures.

Aqueous solutions of sodium carboxymethylcellulose show a pH slightly above 7.0. The free acid is insoluble in water and its precipitation with 80% ethyl alcohol depends to some extent on the degree of substitution. Thus for a product with a D.S. of 0.7, a pH of about 1-3 is required for precipitation, while products with D.S. of 0.3-0.5 can be precipitated at a pH of 3.0. Sodium carboxymethylcellulose thickens water (without precipitation) over a pH range of 4-12.

Emulsifying Properties of Sodium Carboxymethylcellulose

Morrison and Campbell reported¹² that sodium carboxymethylcellulose has emulsifying properties for paraffin oil-water systems, but failed in the case of vegetable oil-water systems. Later investigation in this laboratory⁵ showed that sodium carboxymethylcellulose preparations from jute having D.S. of 1.05 may be used for vegetable oil-water emulsions. Similar studies were undertaken with Na-CMC having a D.S. of 1.97, prepared through successive carboxymethylation of jute in the present investigation. It was found that satisfactory emulsions could be prepared with high D.S. Na-CMC emulsifies with cod liver oil-water systems also. It was further noted that the stability was best at a pH of 9-10. It was somewhat inferior at pH 7-8, but was rather unsatisfactory above pH of 11.

I.R. Spectrum of Carboxymethylcellulose.—For characterization of the product, the free acid was precipitated and dried at 105°C. The IR spectrum was taken in Nujol in sodium chloride optics with a Beckman Model I.R.4. The following peaks could be recognized:

at 3550 cm^{-1} (for OH-vibration in $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$ groups); at 1700 cm^{-1} (for C=O stretching in $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$ groups) and also at 1375 cm^{-1} (for $\begin{array}{c} \text{O} \\ \parallel \\ \text{O—H} \end{array}$ in plane deformation in secondary alcoholic group).

Detergency Improving Property of Na-CMC.—Na-CMC is not itself a detergent, but it aids the detergency of soap solution, and for this purpose the substance has got the highest tonnage utilization in different countries under different trade names. Products having D.S. of 0.6-0.8 are usually

TABLE 3.—VARIATION OF SURFACE TENSION OF DIFFERENT SOLUTIONS AT 25°C.

Substances used	Concentration of substance g/100 ml	Surface tension of solution dynes/cm
Indigenous laundry soap ..	0.0025	51.5
	0.0050	46.8
	0.0100	41.2
	0.0200	36.3
	0.0300	31.9
	0.0400	28.4
	0.0500	27.7
	0.0600	27.3
Na-CMC (D.S.=1.97) ..	0.00	71.50
	0.05	68.04
	0.10	65.50
	0.15	62.96
	0.25	58.49
	0.35	54.99
	0.50	51.97
	0.60	51.00
Soap with 1/20 parts of Na-CMC of D.S.=1.23 ..	0.0025	39.4
	0.0050	36.3
	0.0100	32.6
	0.0200	29.6
	0.0300	28.6
	0.0400	27.9
	0.0500	27.4
	0.0600	27.1
Soap with 1/20 parts of Na-CMC of D.S.=1.61 ..	0.0025	38.9
	0.0050	35.8
	0.0100	32.1
	0.0200	29.6
	0.0300	28.5
	0.0400	27.9
	0.0500	27.4
	0.0600	27.1
Soap with 1/20 parts of Na-CMC of D.S.=1.78 ..	0.0025	38.7
	0.0050	35.4
	0.0100	32.1
	0.0200	29.4
	0.0300	28.5
	0.0400	27.9
	0.0500	27.4
	0.0600	27.1
Soap with 1/20 parts of Na-CMC of D.S.=1.93 ..	0.0025	38.4
	0.0050	35.4
	0.0100	31.8
	0.0200	29.2
	0.0300	28.5
	0.0400	27.9
	0.0500	27.4
	0.0600	27.1

commercially used for this purpose, but no result has yet been reported on the extent of lowering of surface tension of the solution.

In this study surface tension of (i) solutions of Na-CMC in water, (ii) solutions containing mixture of a laundry soap with Na-CMC of different

D.S. values were measured with the help of a Jung-type torsion balance, applying the bow method. Results are given in Table 3.

The top curve in Fig. 2 indicates the lowering of surface tension of aqueous solutions of Na-CMC with increase in its concentration (given by the top scale of x -axis). It should be pointed out that the order of concentration for this is about twenty times that of soap solution discussed later. Na-CMC did show some lowering of surface tension in aqueous solution, but this was of a low order. In the early stages the decrease in surface tension was sharp (from 71 dynes/cm to 52 dynes/cm). At a concentration of 0.5 g/100 ml, it virtually reached a limiting value. With a sample of laundry soap, the lowering was much sharper, from 71 dynes/cm to 37 dynes/cm, for a concentration of only 0.02 g/100 ml of soap. The surface tension decreased further to about 29 dynes/cm, corresponding to 0.04 g/100 ml, which was found to be the "critical micelle concentration".

Addition of 5% of Na-CMC (by wt) to the soap, decreased the surface tension further (to about 39.0 dynes/cm with a soap concentration of only 0.002 g/100 ml, lowest curves in Fig. 2). With higher concentration also, the lowering of surface tension was more in the presence of the Na-CMC till gradually the critical micelle concentration (0.04 g/100 ml of soap) was reached. At this stage, the curves virtually coincided. This clearly shows that Na-CMC acts as an efficient detergent aid.

At the bottom of Fig. 2, the four curves correspond to four different sets of experiments carried out with soap containing the same proportion of Na-CMC but taken from samples having different D.S. values (from cotton). The curves proved that the acceleration of the lowering of surface tension is independent of the D.S. of the Na-CMC. Similar data obtained from products of varying D.S. derived from jute or wood pulp¹³ also corroborate this observation.

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