

## STUDIES ON CARBOXYMETHYLCELLULOSE

## Part I.—Preparation of a Nontoxic Emulsifying Agent from Jute Cellulose

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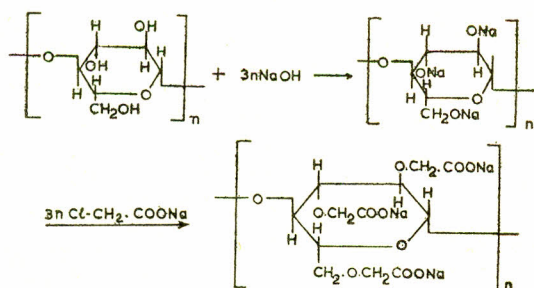
Na-carboxymethylcellulose having a high degree of substitution has been prepared from different cellulosic materials by treatment with a high concentration of NaOH (18-70 percent), followed by reaction with chloroacetic acid. With purified jute cellulose, a better degree of substitution (upto 1.05) was obtained, than either with cotton or bamboo pulp. The process of carboxymethylation was virtually complete in about six hours.

The product was freed from sodium glycolate by three successive extractions with 80 percent (v/v) ethyl alcohol; the purified product was non-toxic. Products having degree of substitution of 1.05 could be used as a stabilizer for emulsion of olive oil in water.

## Introduction

Na-carboxymethylcellulose, a water soluble cellulose derivative, has been known since Jansen discovered it in 1918,<sup>1</sup> and Chowdhury perfected the conditions of preparation<sup>2</sup> in the early twenties. It was first manufactured in Germany in 1924, but its production and use was limited to substituting naturally occurring gums, until detergent-improving properties were discovered in Germany shortly before the World War II. Since then it has been produced on a large scale particularly in Germany and in the U.S.A. Its chief use has since been as an adjunct of synthetic detergents and other important uses are in foods, pharmacy, textiles, paper, paints, drilling muds, and as a soil-improving material. A recent review of the progress in the field and uses of the product is available.<sup>3</sup>

Pure cellulose is necessary for the synthesis of sodium, carboxymethylcellulose. This is first treated with sodium hydroxide solution to obtain soda cellulose, which is subsequently treated with monochloroacetic acid to give carboxymethylcellulose. A portion of monochloroacetic acid may



be hydrolysed to glycollic acid (actually sodium glycolate) which is toxic. As in other etherification processes, three hydroxyl groups per anhydroglucose unit are available for substitution. Con-

ventionally it has been accepted that the complete carboxymethylation should be taken to have a degree of substitution (D.S.) of *three*. So far no commercial product has, however, been prepared with an average (D.S.) of more than 0.6 to 0.8.

Although jute has been known to possess high  $\alpha$ -cellulose content, its use as substitute for cotton or bleached pulp for the production of various cellulose derivatives, has not been given much attention. This is probably due to the difficulty in obtaining jute cellulose in the pure state. The first step in the synthesis of carboxymethylcellulose from jute would obviously be the purification of jute to eliminate the lignin. For the carboxymethylation, in order to appreciate the behaviour of jute cellulose, parallel experiments were also carried out in this investigation with cotton and bleached sulphate pulp. It was noted that carboxymethylation depended upon careful control of the experimental conditions and a high concentration of alkali was necessary to get products having D.S. higher than 0.50. Also a carefully purified jute cellulose was necessary for satisfactory reaction. In the present investigation it was found that the jute cellulose responded well or even better to the reaction, particularly towards the high degree of substitution side, than cotton or bamboo pulp.

Elimination of the sodium glycolate from the product was also thoroughly studied and it was possible to obtain non-toxic carboxymethylcellulose. Finally, the emulsifying capacity of the product for oil-water systems were studied with satisfactory results.

## Experimental

Cotton cellulose was procured from the local market and needed only de-waxing, followed by treatment with 1 percent alkali and careful drying.



The bamboo pulp (sulphate pulp) was obtained through the courtesy of the Karnaphuli Paper Mills. Some samples were already bleached; others were slightly brown and needed only a mild hypochlorite treatment, followed by washing and drying.

Jute or jute waste was first powdered in a grinding machine. The powdered material was thoroughly boiled with sufficient 1 percent sodium hydroxide solution. This was washed and moist powder was treated with gaseous chlorine; this was followed by treatment with alkaline sodium sulphite and drying. A white product was obtained.

*Procedure of Carboxymethylation.*—Purified cellulose was steeped in sodium hydroxide solution of desired concentration, and having a volume varying from 5 to 10 times the weight of the cellulose taken. Steeping was done at 20-25°C. for one to two hours. This converted the raw material into soda cellulose. Excess alkali was then pressed out carefully till the weight dropped down to about five times that of the cellulose taken originally. The pressed mass was thoroughly mixed with chloroacetic acid, for six hours while the temperature was maintained at 35-45°C. It was necessary to prevent the drying of the reacting mass during the process of carboxymethylation, or the reaction would be considerably hampered. This could be best controlled by pressing out the alkali after the process of steeping. After the carboxymethylation was over, the product was carefully washed and dried. Samples were prepared from all the three types of cellulose, namely cotton, bleached bamboo pulp (sulphate), and purified jute cellulose.

These products were tested for their water solubility, viscosity and emulsifying properties. The degree of substitution of the products was determined by the uranyl gravimetric method.<sup>4</sup>

*Determination of Glycollate.*—A quick and satisfactory method had to be set forth for the determination of glycollate. A spectrophotometric method, based on an earlier observation,<sup>5</sup> was developed; this depended on the colour formation between glycollate and 2,7-dihydroxynaphthalene. The reagent was prepared in the laboratory. Naphthalene was sulphonated to give a mixture of 2,6-naphthalene disulphonate and 2,7-naphthalene disulphonate. The latter was separated as the calcium salt and the 2,7-dihydroxynaphthalene was obtained by heating with strong sodium hydroxide solution. This reagent was subsequently purified and dried; it gave an intense colouration with glycollate at 530 m $\mu$ , and it was found to follow Beer's law in the range of 10-80  $\mu$ g. of glycollic acid per ml. of the solution.

## Results and Discussion

First, stress was given to ascertain the volume and the concentration of alkali necessary for satisfactory reaction. As has already been mentioned, the reaction takes place in two stages. In the present case it was found that with 18 percent alkali, the D.S. of the products were relatively low in all cases (approximately 0.30). It increased nearly two-fold by doubling the alkali concentration. It was further noted that provided sufficient volume of alkali was available, further addition had no effect on the degree of substitution. It would be seen from the results in Table 1 that a volume of 5 ml. of NaOH per g. of the cellulose was quite satisfactory. Again, if some of the excess alkali is retained in the soda cellulose by appropriate pressing as described above, chloroacetic acid itself can be used instead of its sodium salt. The more interesting observation from the authors' point of view was that when jute cellulose was satisfactorily purified, it gave a product (Na-carboxymethylcellulose) having a degree of substitution comparable with those obtained from cotton or bamboo pulp. Some experiments were carried out without delignification of the jute powder; these gave unsatisfactory product as expected.

*Effect of Concentration of Alkali on the Degree of Substitution of Na-Carboxymethylcellulose.*—In the earlier section it was noted that even with 36 percent NaOH the degree of substitution obtained in the product was only around 0.50. It was therefore necessary to see if higher alkali concentration would give products having higher D.S. values. Results are presented in Table 2. It was observed that the temperature range of 25-30°C. was unsatisfactory for carboxymethylation. A much higher temperature (say 60°C.) produced a sticky mass, thus disturbing thorough mixing and failed to give a homogeneous product. The temperature range of 35-45°C. was worked out to be the optimum. Usually, experiments were started at the lower temperature and finished at the higher.

9 percent alkali was found rather ineffective to produce carboxymethylcellulose. The D.S. in all cases was of the order of 0.05. This may be due to the failure of the dilute alkali to form soda cellulose. With 18 percent alkali, the D.S. values of the final products were more or less the same for the different raw materials, *viz.*, 0.32-0.33. When the concentration of NaOH was increased to 36 percent the D.S. values of the product from cotton cellulose did not increase as much as those from bamboo or jute cellulose. Thus, under the experimental conditions, cotton cellulose reached the limit towards substitution rather quickly.



TABLE I.—EFFECT OF CONCENTRATION AND VOLUME OF ALKALI USED FOR STEEPING ON CARBOXY-METHYLATION OF CELLULOSE.

Concentration of alkali %	Amount of alkali ml.	Degree of substitution			Water solubility
		Cotton	Bamboo pulp	Jute	
18	50	0.32	0.32	0.33	Turbid dispersion
18	75	0.31	0.35	0.28	"
18	100	0.31	0.31	0.30	"
36	50	0.50	0.62	0.62	Almost clear solution
36	75	0.50	0.55	0.50	"
36	100	0.50	0.50	0.52	"

Cellulose taken for each experiment, 10.0 g.; Chloroacetic acid used for each experiment, 10.0 g.;

Temperature for carboxymethylation, 35°, 45°C.; Time for carboxymethylation, 6 hours.;

TABLE 2.—VARIATION OF DEGREE OF SUBSTITUTION OF NA-CARBOXYMETHYLCELLULOSE WITH CONCENTRATION OF ALKALI USED.

Alkali concentration %	Degree of substitution		
	Cotton	Bamboo pulp	Jute cellulose
9	0.044	0.06	0.04
18	0.32	0.32	0.33
36	0.50	0.62	0.63
50	—	0.72	0.90
70	—	0.91	1.05

Purified cellulose taken for each experiment, 10.0 g.; Amount of alkali used, 50 ml. each.; Alkali cellulose prepared at 25°C. for one hour.; Amount of chloroacetic acid used, 10.0 g.; Time of carboxymethylation, 6 hours at 35°—45°C.

With further increase in the concentration of alkali (50-70 percent), jute cellulose was found more reactive than bamboo pulp.

An observation may be made here regarding the requirement of the chloroacetic acid. For 10 g. of the cellulose taken for each experiment, complete carboxymethylation (tri-substitution) requires 17.5 g. of chloroacetic acid. In actual practice a lesser amount (equal part by weight of cellulose taken) of chloroacetic acid was taken. This could give a maximum D.S. of about 1.70. With jute cellulose, a maximum substitution of 1.05 was obtained. This shows that the requirement of chloroacetic acid, for effective carboxymethylation, would not be much higher than stoichiometric amounts. It is also believed that when large quantities would be handled, carboxymethylation may probably be carried out with only a slight excess of the reagent.

Very little information is available regarding kinetics of carboxymethylation of cellulose. For the set of experiments results of which are presented in Table 2, the period of carboxymethylation was kept at six hours. Several other experiments were carried out for shorter periods under identical conditions, and one experiment was continued for twenty hours. It was noted that the carboxymethylation was rapid in the initial stages upto about three hours, after which it slowed down somewhat. It virtually came to equilibrium in about six hours, and no appreciable substitution took place beyond that period. Thus six-hours carboxymethylation was considered optimum. The water solubility of the product depended directly on its degree of substitution. With a D.S. of about 0.20, the product would give only a fibrous dispersion in water. A one-percent solution of a product with D.S. of about 0.50 would give an almost clear solution. Solubility would increase with higher D.S. values.

*Purification of Na-Carboxymethylcellulose: Removal of Na-glycollate.*—The Na-carboxymethylcellulose that has been prepared by the said method contained (i) some unreacted sodium hydroxide and (or) sodium chloroacetate, (ii) sodium chloride formed during the reaction, and (iii) sodium glycollate, formed by the hydrolysis of chloroacetic acid (or its alkali salt). Food and pharmaceutical preparations should contain a minimum of these impurities. It should be particularly free from glycollic acid or sodium glycollate, which is toxic.

Sodium glycollate cannot be satisfactorily removed by washing the product with water, because of the possibility of the hydrolysis of the carboxymethylcellulose itself to give chloroacetate and subsequently glycollate. A number of organic



solvents were tried and it was found that in acetone or hot 80 percent (v/v) ethyl alcohol the sodium carboxymethylcellulose was insoluble, while the glycollate was soluble. The latter (80 percent ethyl alcohol) was employed for purification of the carboxymethylcellulose (Table 3). The proportion of glycollic acid present in the different samples was found out indirectly by finding the quantity of it extracted in the solvent in three successive extractions. In all cases, three treatments were sufficient to remove virtually all the glycollate. Samples originally contained 7-9 percent of glycollic acid, and in the final product it varied from 0.1 to 0.3 percent (and nil in one sample). This contamination (glycollic acid content of the product) was found below any objectionable limit. Animals were fed in doses of 300 mg. per rat and it was confirmed that the products were absolutely non-toxic and can be used in food and pharmaceuticals. The alkalinity of the samples from jute varied between 0.25-1.50 percent (as  $\text{Na}_2\text{O}$ ).

*Emulsifying Properties of Na-Carboxymethylcellulose from Jute.*—Although some other cellulose ethers have been successfully used as emulsifying agents for various organic liquid/water systems, very little work has been done with carboxymethylcellulose. In the only reference available on this, Morrison and Campbell<sup>6</sup> reported casually,

among other things, that sodium carboxymethylcellulose (prepared from undefined source, but apparently from cotton linters; and no mention was made of the D.S.) is a fairly good emulsifying agent for liquid paraffin, but was unsatisfactory in the case of benzene, toluene, vegetable oils (castor, olive etc.) and cod liver oil. In the case of olive oil, a high viscosity grade material, gave, with a high oil/water ratio of 1:1, an emulsion that was stable for seventeen days.

In the present study the emulsifying properties of the systems involving olive and cod liver oils in water were studied with Na-carboxymethylcellulose derived from jute and having a D.S. of 1.05. These products were soluble up to a concentration of 1.5 percent in water, but were dispersible upto 3.0 percent concentration in water. The viscosity of the solutions was medium, indicating thereby that in these products from jute, the cellulose chain was not probably sufficiently long. The results on the stability of different emulsions are presented in Table 4. The percentage concentration of the active agent (Na-carboxymethylcellulose) is with reference to the aqueous phase only.

In both the cases, it could be said that the stability of the emulsion improved with the concentration of the active material used. This, of course, is expected, but use of much higher con-

TABLE 3.—REMOVAL OF GLYCOLLIC ACID BY SOLVENT EXTRACTION.

Description of the sample	Glycollic acid removed in			Total mg.	Percent glycollic acid
	1st (mg.)	2nd (mg.)	3rd (mg.)		
Bamboo pulp D.S.=0.35	69.0	20.0	2.75	91.75	9.1
Jute sample D.S.=0.32	67.0	12.0	3.0	82.0	8.2
Cotton sample D.S.=0.50	70.0	20.0	3.0	93.0	9.3
Jute sample D.S.=0.62	42.0	30.0	1.0	73.0	7.3
Jute sample D.S.=0.90	54.0	20.0	1.0	75.0	7.5
Jute sample D.S.=0.52	6.4	0.5	0.0	6.9	0.69

80% ethanol used for each extraction, 10.0 ml. Amount of Na-Carboxymethylcellulose used, 1.0 g. each.



TABLE 4.—EMULSIFYING PROPERTIES OF PURIFIED NA-CARBOXYMETHYLCELLULOSE FROM (D.S.=1.05). JUTE.

Amounts of oil and water	Amount of Na-carboxy methylcellulose		Stability in hours	
	g.	% W/V	Olive oil	Codliver oil
10 ml. and 50 ml.	0.8	1.6	2.0	2.0
” ”	1.0	2.0	12.0	24.0
” ”	1.2	2.4	24.0	3 days
” ”	1.5	3.0	3 days	40 days
10 ml. and 40 ml.	0.4	1.0	2.0	2.0
” ”	0.6	1.5	4.0	12.0
” ”	0.8	2.0	18.0	3 days
” ”	1.0	2.5	3 days	7 days
10 ml. and 20 ml.	0.2	1.0	0.5	Unstable
” ”	0.3	1.5	4.0	”
” ”	0.4	2.0	one day	2.0
” ”	0.5	2.5	Stable indefinitely.	4.0

pH of the solution, 10—12 Viscosity of 1% aqueous solution, 14—15 c.p.

centration is limited by the solubility, and probably if products with higher D.S. values could be prepared (without impairing the chain of the cellulose molecule), better results might be expected.

With olive oil, stability increased with increasing oil/water ratio. With ratios (oil-water, v/v) of 1:5 and 1:4, permanent emulsions could not be formed. But when the oil/water ratio was increased to 1:2, a permanent emulsion could be prepared with a Na-carboxymethylcellulose content of 2.5 percent in the aqueous phase. This result was considered quite satisfactory. In the case of cod liver oil, different results were obtained. The emulsions were relatively less stable with higher oil/water ratio. With oil/water ratio of 1:2 or 1:4, emulsions were formed but they were stable for only a few days. With a lower oil-water ratio of 1:5, an emulsion was obtained (with 3 percent concentration of the active material) that was stable for about 40 days.

From the results obtained it is believed that Na-carboxymethylcellulose can be successfully utilized as a stabilizer of emulsions between olive oil and water as satisfactorily as with other commercially available materials from different sources (different chemical compounds).

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