

STUDIES ON CARBOXYMETHYLCELLULOSE

Part II.—Use of Organic Alcohols as Reaction Medium for Carboxymethylation

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Carboxymethylation of purified jute cellulose was carried out in different alcoholic medium containing some water. The effect of the proportion of water (to cellulose) was studied; best result was obtained (D.S.—1.17) with ethyl alcohol, with water/cellulose ratio of 1:1. The product was white, crystalline and soluble in water. Probable reasons for better reaction in alcoholic medium have been discussed.

Introduction

In part I of the paper published in this issue,¹ the authors reported the possibility of preparing sodium carboxymethylcellulose with a high degree of substitution (D.S.)—up to 1.05 in a single treatment. But the concentration of the alkali required (50-70 percent) was rather high. The products were of medium viscosity grade; but these were successfully employed for stabilization of olive oil/water emulsions. Thus a new use for Na-carboxymethylcellulose having a high D.S. was found. A reference to the recent literature on the preparation of sodium carboxymethylcellulose shows a preferential tendency for using some organic solvents as the reaction medium. The information is mostly covered by patents and the influence of the organic medium on the efficiency of reaction or on the properties of the products is not clearly divulged.

Klug and Tinsley² treated cellulose at 25-100°C. for two to six hours in the presence of free alkali with monochloroacetic acid in enough *iso*-propyl alcohol or *tert*-butyl alcohol "to prevent heavy dough formation, and maintain the product in solid form throughout the reaction". They did not mention any other advantage in respect of D.S. or any other properties. They also found methyl alcohol, ethyl alcohol, *n*-butyl alcohol, *iso*- and *sec*-butyl alcohol, acetone, dioxane and hexane as unsatisfactory. Klug and Spurlin³ used a mixture of water and *iso*-propyl alcohol and carried out carboxymethylation by successive treatment of the suspended cellulose with 20 percent sodium hydroxide and chloroacetic acid followed by manganese (as MnSO₄) and hydrogen peroxide as catalyst. Apparently by use of the catalyst they obtained a product with a relatively high D.S., as they claimed that a 2 percent solution of the product was clear and fibre-free. In another patent⁴ increased D.S. was claimed by use of processes basically as above, but using an ester of acrylic acid instead of chloroacetic acid. In a more recent patent⁵, Hercules Powder Company claimed the preparation of carboxyalkyl ethers,

and extended the use of solvents (*n*-propyl alcohol, *iso*- and *sec*-butyl alcohol and dioxane) which had earlier been considered unsatisfactory. Claim was also made in this patent that water/cellulose ratio plays an important part.

Hayakawa and co-workers also published some work on the carboxymethylation of wood pulp cellulose. The first report by Hayakawa, Ogowa and Morita⁶ on the carboxymethylation of purified wood pulp (apparently in the aqueous medium), claimed that the composition and the mechanical treatment of the reacting system affected the properties of the product far more than cellulose sampling, reaction temperature and time. They also claimed that the use of chloroacetic acid up to about 1.5 molar ratio of cellulose resulted in the best D.S. but beyond this side reactions tend to start. In a subsequent work, Hayakawa and Morita⁷ claimed that the multistage treatment was economical for obtaining products having D.S. of 1.50 to 2.00. In a third report,⁸ these workers claimed the use of organic solvents such as acetone, ethyl alcohol, *iso*-propyl alcohol, butyl alcohol, dichloromethane and benzene but did not mention any specific advantage that were derived from this.

Boutlemy⁹ described a procedure for obtaining highly-substituted carboxymethylcellulose. They used a mixture of acetone-dioxane (70:30) and practised the addition of alkali and chloroacetic acid in stages. They separated the product from the reaction medium as the copper salt which was soluble in ammonia. Copper was removed by electrolysis and the ammonium carboxymethylcellulose thus obtained was used for subsequent carboxymethylation. They found that the D.S. increased with decreasing cellulose chain. With cellulose having intrinsic viscosity (2.5 percent in cuprammonium solution) of 29.0, 8.4 and 0.40, respectively, the D.S. of the products were 1.07, 1.18 and 2.20 to 2.30. From the last sample, after four hours of consecutive carboxymethylation, a D.S. of 2.6 was obtained.

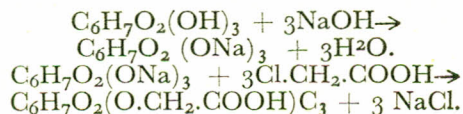
An examination of the above information showed that the use of organic solvents in the different work was random and unsystematic, and although probably a higher degree of substitution might have been obtained, no values have been mentioned except in the work of Boutlemy.⁹ Here also, with a cellulose with a high chain length, the product gave a D.S. of only 1.07, but celluloses having lower chain length (low cuprammonium viscosity) gave higher values.

In highly concentrated aqueous sodium hydroxide medium, the authors obtained a D.S. of 1.05. In the present investigation preference was given to work with purified jute cellulose and use lower aliphatic alcohols. As water is believed to play an important role, the effect of the proportion of water (to cellulose) was also studied. Organic solvents helped not only in increased substitution but also in obtaining non-fibrous, crystalline product.

Experimental

Powdered jute fibre was purified by boiling with sufficient 1 percent sodium hydroxide solution, washing with water, chlorination of the moist powder, followed by boiling with alkaline sodium sulphite solution and final washing. A white cellulose was obtained. This was carefully dried and stored.

The process of preparation of sodium carboxymethylcellulose consisted of two steps represented by the following equations:



The acid thus produced may react with excess alkali to produce the sodium salt. In the earlier experiments the first step was carried out in aqueous medium, by steeping the purified cellulose in aqueous alkali for about an hour after which most of the alkaline solution was squeezed out; this was followed by the treatment of the alkali cellulose with a solution of chloroacetic acid in an organic solvent. Later it was found that as both the chemicals were soluble in (aqueous) alcohols used as solvents, the process could be further simplified as described below. This also gave products having higher degree of substitution and improved properties.

The final process consisted of steeping 10 g. of purified cellulose in 60 c.c. of organic solvent to

which a definite amount of water and sodium hydroxide had been added. After about an hour (when the conversion to the alkali cellulose was believed to have reached an optimum value), 16 g. of chloroacetic acid dissolved in 20 ml. of the solvent was added. Theoretically, 10 g. cellulose required 17.5 g. of chloroacetic acid for complete trisubstitution. The constituents were thoroughly mixed and the temperature maintained at the desired point (in a water bath) for about six hours. After this, the product was well washed with hot 80 percent ethanol and dried. These were then tested for their solubility, degree of substitution and viscosity in dilute aqueous solution. In most of the experiments, some water was added as a part of the reaction solvent; this was mixed with the solvent in the first stage of alkali treatment.

Results and Discussion

All experiments were carried out in alcoholic medium except one in which benzene was used. First the cellulose was treated with alkali and subsequently a concentrated solution of chloroacetic acid was added. The latter treatment was done at 40-45°C. Alcohols used were from methyl to normal butyl and also *iso*-propyl and *iso*-butyl. The solubility of sodium hydroxide in these alcohols are (in g./100 c.c.): methyl, 18.0; ethyl, 9.0; *n*-propyl, 5.0; *n*-butyl, 6.5; *iso*-propyl, 1.0; and *iso*-butyl, 3.0. It was thus decided to use some water in the first set of experiments, so that there may be available sufficient alkali for conversion of the cellulose completely to the soda cellulose and also for neutralization of the excess chloroacetic acid. The water/cellulose ratio was kept constant at 2:1. Other factors were also kept the same throughout the series, so that the effect of the various alcohols could be studied. Results are presented in Table 1; the variation of the degree of substitution with the different alcohols in the homologous series has been presented in Fig. 1.

With most of the solvents, two experiments were carried out; the products were more or less the same, but the degree of substitution varied slightly. This may be due to the fact that the product, or rather the substitution in the cellulose may not be entirely homogeneous and even samples from the same stock (if relatively large) may show slight variation in the degree of substitution. In all these cases both the results have been presented in the Table 1, but the mean value has been plotted in the curve and accepted for discussion. The viscosity data have been obtained by mixing the two products and preparing one solution. The variation of the viscosity of the products with the change of the solvent was not very significant.

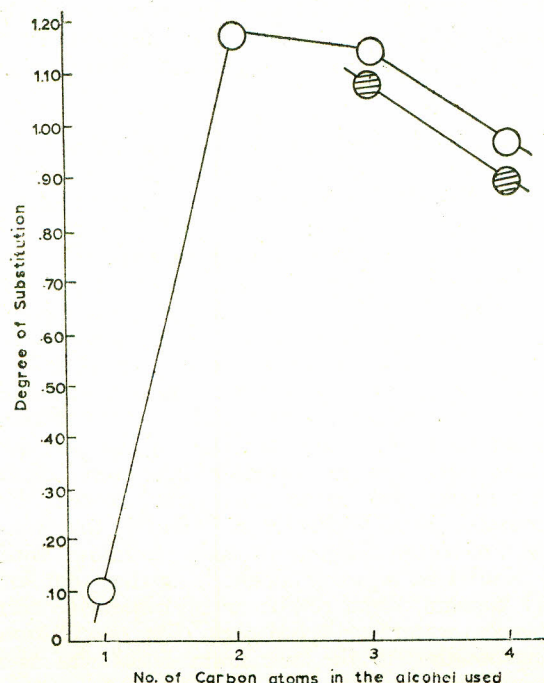


Fig. 1.—Showing carboxymethylation of purified jute cellulose in different alcoholic media (Lower line for *iso*-propyl and *iso*-butyl alcohols).

The variation of the degree of substitution obtained with different alcohols (other conditions remaining the same) can be best seen from Fig. 1.

Surprisingly, a very low substitution was obtained with methyl alcohol; no obvious explanation is available for this. Maximum substitution was obtained with ethyl alcohol (D.S.=1.17), and it again decreased as it went up the homologous series. The slope between ethyl and *n*-butyl alcohol was not high. The ineffectiveness of the higher alcohols (from butyl onwards) should be dependent on the miscibility with water. The *iso*-alcohols, *iso*-propyl and *iso*-butyl, gave lower values than the corresponding normal alcohols; the trend in the decrease was parallel to that of the normal alcohols. The viscosities (of 1 percent aqueous solution) were low and varied between 7.0 and 8.0 cp. except in the case of *n*-butyl alcohol where the viscosity was 10.0 cp.

Experiment with benzene also gave interesting result. Caustic soda treatment was done in the presence of water and benzene, taking care of dispersing them, as far as practicable, with vigorous stirring. The chloroacetic acid was less soluble in benzene, so that it was dissolved in 50 ml. of benzene instead of the usual 20 ml. A.D.S. of 1.02 was obtained.

Effect of Water/Cellulose Ratio.—It has already been mentioned that the conversion of cellulose into soda cellulose was the first step in the present reaction. Weber *et al.*¹⁰ has shown that the conversion of cellulose to soda cellulose in alcoholic NaOH depended not only on the nature of the alcohol but also on the proportion of water. There-

TABLE I.—CARBOXYMETHYLATION OF JUTE CELLULOSE IN DIFFERENT ORGANIC SOLVENTS.

Expt. No.	Organic solvent used	Degree of substitution	Mean D.S.	Viscosity of 1% solution (c.p.)
V 16	Methyl alcohol	.. 0.10	0.10	—
B 18	Ethyl alcohol	.. 1.18	1.17	7.0
V 09		.. 1.16		
B 15	<i>n</i> -propyl alcohol	.. 1.11	1.14	7.5
V 11		.. 1.16		
B 14	<i>iso</i> -propyl alcohol	.. 1.15	1.08	7.0
V 12		.. 1.00		
B 04	<i>n</i> -butyl alcohol	.. 0.90	0.96	10.0
V 03		.. 1.01		
B 03	<i>iso</i> -butyl alcohol	.. 0.88	0.89	7.0
V 13		.. 0.90		
V 01	Benzene	.. 1.02	1.02	8.0

Purified jute cellulose 10.0 g.; NaOH 12g. in 60 c.c. of solvent and 20 c.c. of water; Chloroacetic acid 16 g. in 20 c.c. of solvent; Duration of steeping 1 hr.; Duration of carboxymethylation 6 hrs.

fore in the second series of experiments (Table 2), the effect of varying the proportion of water in the different experiments has been studied. For this, only ethyl and *n*-butyl alcohols were chosen, because in the earlier experiments (Table 1), the former gave the best results and butyl alcohol formed an immiscible layer. Two experiments were carried out in anhydrous alcohols also.

Several points need explanation in respect of results presented in Table 2. For all the experiments the same amount of cellulose (10 g.), alkali (12 g.) and alcohol (both for steeping as well as for dissolving the chloroacetic acid) was used. Only the proportion of water added to alcohol during steeping was varied in the different experiments. 12 g. of NaOH was nearly double the amount required for complete conversion to soda cellulose. But a portion of it must have also been consumed for neutralization of the chloroacetic acid. The concentration of alkali (Column 4, Table 2) has been calculated on the basis of g. NaOH dissolved in total volume of solvent (alcohol plus water) used for steeping. The range of concentration thus available (6—17 percent) was able to give a product in the aqueous medium which had D.S. well below 0.50. In the curves

(Fig. 2) representing the variation of D.S. with the amount of water added, the latter has been expressed in terms of the water/cellulose (v/w) ratio.

It will be noted that with *absolute* ethyl or butyl alcohol, the degree of substitution is low. With addition of 10 ml. of water (for 10 g. of cellulose; water/cellulose ratio 1:1), the product from ethyl alcohol medium has a maximum D.S. of 1.31. With further increase of water/cellulose ratio, the D.S. of the product decreased, more or less linearly with the water/cellulose ratio increase; the slope of the curve is not however very steep. (Fig. 2). With anhydrous ethyl alcohol, a maximum alkali concentration of about 9 percent only was possible. This might explain the low D.S. of the product (0.11); but it seems probable that some other factor might also be in operation. It may be mentioned that Weber *et al.*¹⁰ found, for conversion of cotton cellulose to soda cellulose with (N) NaOH in aqueous alcoholic media, that for ethyl alcohol, best results were obtained with 18 percent water in ethyl alcohol. Our observation (corresponding to the maximum D.S.) was also obtained with a solution which was approximately 17 percent (10 ml. water in 60 ml. ethyl alcohol).

TABLE 2.—CARBOXYMETHYLATION OF JUTE CELLULOSE IN ORGANIC SOLVENTS: EFFECT OF WATER ADDED DURING STEEPING.

Expt. No.	Organic solvent used	Water added (ml.)	Concn. of NaOH, % (w/v)	Degree of substitution (mean)		Viscosity of 1% soln. (c.p.)
V 20	Ethyl alcohol	Nil	9.0*	0.11	0.11	—
B 10	"	10.0	17.0	1.35	1.31	6.5
V 10	"			1.27		
B 18	"	20.0	15.0	1.18	1.17	7.0
V 09	"			1.16		
B 16	"	30.0	13.3	0.92	0.97	9.5
V 08	"			1.01		
B 17	"	40.0	12.0	0.85	0.94	14.0
V 07	"			1.03		
V 18	<i>n</i> -Butyl alcohol	Nil	6.0*	0.14	0.14	—
B 07	"	10.0	17.0	1.10	1.08	7.0
V 14	"			1.05		
B 04	"	20.0	15.0	0.90	0.96	10.0
V 03	"			1.01		
B 11	"	30.0	13.3	0.77	0.82	6.0
V 04	"			0.86		
B 12	"	40.0	12.0	0.70	0.64	7.5
V 05	"			0.57		

Purified jute cellulose 10.0 g.; NaOH taken 12 g. in 60 ml. of solvent and water as shown under each experiment; Chloroacetic acid used 16 g. in 20. ml. of the solvent. Duration of steeping 1 hr.; Duration of carboxymethylation, 6 hrs.

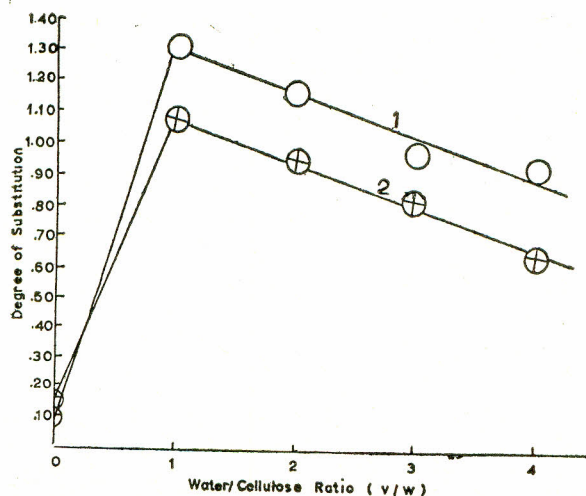


Fig. 2.—Showing carboxymethylation of purified jute cellulose in ethyl and *n*-butyl alcohols. (1, Ethyl alcohol; 2, *n*-Butyl alcohol).

With *n*-butyl alcohol, the carboxymethylation followed more or less the course as that for water-ethyl alcohol system, except that the products had somewhat lower D.S. than the corresponding experiments with ethyl alcohol (Fig. 2). With anhydrous butyl alcohol substitution was insignificant. Highest values were obtained (D.S. = 1.08) with water/cellulose ratio of 1:1; with further increase in the proportion of water, the D.S. values decreased linearly. It is interesting to note that the slopes of the two curves (D.S. versus water/cellulose ratio) for the ethyl and *n*-butyl systems were the same. This suggests that some common factors are probably responsible for the processes.

Since in the solvent medium the sodium carboxymethylcellulose is insoluble, it separated in the

solid form. The medium also facilitates thorough mixing, and maintenance of uniform temperature throughout; this indirectly produces a more uniform product.

Kinetics of Carboxymethylation.—This was studied in ethyl alcohol and butyl alcohol media under optimum conditions. It was found that the carboxymethylation was complete in two to four hours, and after that there was no further significant improvement of the D.S. even when the reaction was continued for twentyfour hours.

Properties of the Products Obtained under Different Conditions.—So far the authors have tried to study the effects of different alcohols and water/cellulose ratio on the carboxylation and degree of substitution of the product. In Table 3 are presented the results of some experiments showing the degree of substitution, general appearance of the products, their solubility in water and viscosity of dilute solution. Study of the data (Table 3) will show that these properties depend mainly on the degree of substitution of the product, and not much on the method by which it has been obtained. Products with low degree of substitution were fibrous and insoluble in water. When the conditions were such as to give higher D.S., the product was floppy (indicating probably that although the degree of substitution was high, the breakdown of the cellulose chain was not much). In other cases (where the D.S. was mostly somewhat still higher) the products were crystalline. The crystalline or floppy products were equally soluble in water. The viscosity (of 1 percent aqueous solution) of the products did not vary very much. In fact it was felt that the viscosity depended on a number of factors, the co-relation of which was not

TABLE 3.—VARIATION OF PHYSICAL PROPERTIES WITH DEGREE OF SUBSTITUTION.

Solvent used	Water/ Cellulose ratio	Degree of substitution	Appearance	Solubility in water	Viscosity of 1% aqueous solution(c.p.)
Ethyl alcohol	0.0	0.11	Fibrous	Very low	—
„	1.0	1.31	Crystalline small lumps	Clear solution	6.5
„	2.0	1.17	Floffy	Do	7.0
<i>n</i> -Butyl alcohol	0.0	0.14	Fibrous	Very low	—
„	0.50	0.52	White floffy	Soluble with dispersed particles.	12.5
„	1.0	1.08	Hard lumps	Clear solution	7.0
„	2.0	0.96	White Crystalline	Clear solution	10.0
„	3.0	0.82	Almost Crystalline	Soluble	6.0

easy and simple. On the whole it could be said that the viscosity varies between 6 and 12.5 cp. And all samples with D.S. higher than 0.80 could be used satisfactorily as stabilizer of emulsion of olive oil in water.

On addition of cellulose to the alkali solution (in alcohol-water mixture) it took up virtually all the liquid and looked like a wetted solid mass. Normally in all experiments the steeping process was continued for an hour; but in some cases it was also observed that a period of ten or fifteen minutes is virtually sufficient for the completion of this reaction. The chloroacetic acid added subsequently in alcoholic solution mixed up thoroughly with the solid, and gradual heating gave a sort of a semi-solid mass. The most difficult problem in the process was to obtain an absolutely homogeneous product. As indicated earlier, this led to products having somewhat different D.S. in different experiments done under similar conditions. The situation could probably be improved by using larger volumes of solvent.

Mechanism of Carboxymethylation in Alcoholic Medium.—In the previous work¹ it was found that in aqueous medium, for satisfactory carboxymethylation, a high concentration of alkali (50-70 percent) was necessary. Even with that a D.S. of 1.05 was obtained. Here, by the use of alcoholic solvent, products with higher D.S. were obtained with relative ease. The D.S. of 1.31 obtained with ethyl alcohol is, as yet, the highest so far reported in single treatment.

During this study two points have become very clear. First, the process depends on the nature of the alcohol used; but anhydrous alcohols were unsatisfactory. Secondly, the D.S. of the product depends greatly on the proportion of water, relative to cellulose, used in the process. No information is available on the mechanism of carboxymethylation in organic solvent media. But if it is presumed that the conversion of cellulose to soda cellulose is the determining factor and the subsequent carboxymethylation is easy and straightforward, some explanation may be offered.

For the first reaction (cellulose to soda cellulose), Weber *et al.*¹⁰ assumed that the interaction between the liquids and the cellulose is governed by a reaction between the hydrogen bonds (in cellulose) and the liquid molecules. Water, alcohols of low molecular weight etc. should not penetrate into the crystal lattice, but react with the weaker hydrogen bonds in the amorphous region. On the basis of this, the reaction should decrease with

increasing molecular weight of the alcohols (as was actually found true in the authors' process also). Presence of water (along with the alcohol) also should have naturally some effect; that is why aqueous alcohols were necessary for satisfactory reaction. Why increasing amounts of water gave steadily decreasing D.S. is not fully understood. It is possible, however, that it might exert some diluting effect on the alkali concentration.

Activation of cellulose appears to be an important step prior to carboxymethylation, or soda cellulose formation. Such activation effects of water, NaOH etc., has been reported by Malm and co-workers¹¹ in connection with the acetylation of cellulose. Activation of cellulose (by other reagents) for synthesis of cellulose ethers has also been observed by Lyubimova and Nikitin¹² to give improved substitution.

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