

Characteristics of the Aqueous Solution of Carboxymethyl Starch Ether

INTRODUCTION

Since its first synthesis in 1924, carboxymethyl starch (CMS) has become one of the most important modified starch products that have been widely applied to textile, petroleum, food, and pharmaceutical industries, etc.¹⁻³ Because CMS is usually used in aqueous form, research about it has focused on its solution properties. Because of a long-term lack of methods to measure the molecular weight of CMS and the distribution of substituents along its chain, research has been limited to its common features, such as the relationship between the viscosity of the CMS solution and the degree of substitution (DS) and concentration, as well as the influences of the electrolyte in the solution and pH value.⁴ Our work deals with the retention of the crystalline structure of the original starch in CMS with a DS of 0.30, the dependence of the viscosity of the CMS solution on the content of low molecular electrolyte and pH value, and the influence of molecular weight on the viscosity of the CMS solution, which made the further study of characteristics of the CMS aqueous solution possible, and which is of great significance in directing and optimizing the application of CMS and in developing new fields of application.⁵

This paper deals with the effects of the degree of substitution (DS), molecular weight (\bar{M}_n), and distribution of substituents ($\Delta 1000/\bar{DP}_n$) on solution viscosity.

EXPERIMENTAL

Preparation of Sample

Sodium hydroxide, water, isopropyl alcohol, and methanol were charged into a four-neck flask with a thermometer and a stirrer, and then 10 g of cornstarch was added at a certain temperature (T_1) for alkalization. Furthermore, monochloroacetic acid dissolved in 40 mL isopropyl alcohol was incorporated, the temperature (T_2) controlled for the etherification reaction, and then the solution of sodium hydroxide titrated. The solvent was removed after the reaction was finished. The product was washed with 80% methanol until Cl^- could not be detected by AgNO_3 . A white powder can be obtained after crushing and drying the mixture in a vacuum dryer. Seventy different samples

were prepared by changing the polarity and concentration of solvents, temperature, and time of reaction, etc.

The Determination of Degree of Substitution

DS is determined according to the method of Zhang and Wu⁶:

Weigh exactly 0.1 g of the CMS sample and dissolve it in a 0.25 M solution of NaOH, then remove it to a volumetric flask of 250 mL to fix its volume. Prepare a series of the standard solution of glycolic acid (with concentration between 15 and 100 $\mu\text{g}/\text{L}$).

Add 1 mL standard solution and 1 mL of the above sample to each of the 25 mL colorimetric tubes by a pipet. To each of these tubes, add 0.5 mL 1% J acid and 5 mL concentrated sulfuric acid, then shake evenly and boil for 1 h. These solutions are brown-yellow. After cooling to room temperature, add 30% NH_4Ac solution to their 25 mL lines and shake them until they turn blue. Measure the values of light absorbance of these solutions at 620 nm in a 721 spectrometer on the basis of a sample comparison. The data are processed with a computer to obtain the glycolic acid equivalent (B) of the CMS sample. The DS value is then calculated as:

$$\text{DS} = 162B / (76 - 58B)$$

Determination of Average Molecular Weight

Weigh exactly 0.2 g CMS and dissolve it in the solution of potassium ferricyanide and boil it for 15 min. After cooled down, neutralize it suitably and titrate the Fe^{2+} with 0.01 N standard solution of sulfuric cerium. The end of titration is determined by an SPM 10 potentiometer.

Determination of the Distribution of Substituents

Dissolve 0.25 g CMS in 25 mL water, then add 1 mL α -amylase solution (900 vitality units/mL) and 1 mL amyloglucosidase (100 vitality units/mL) to the above CMS solution. Transfer the sample to a volumetric flask of 50 mL to fix its volume with water. Put it aside for 74 h and then determine the average molecular weight of the CMS. Calculate the average number of molecular chains per 1000

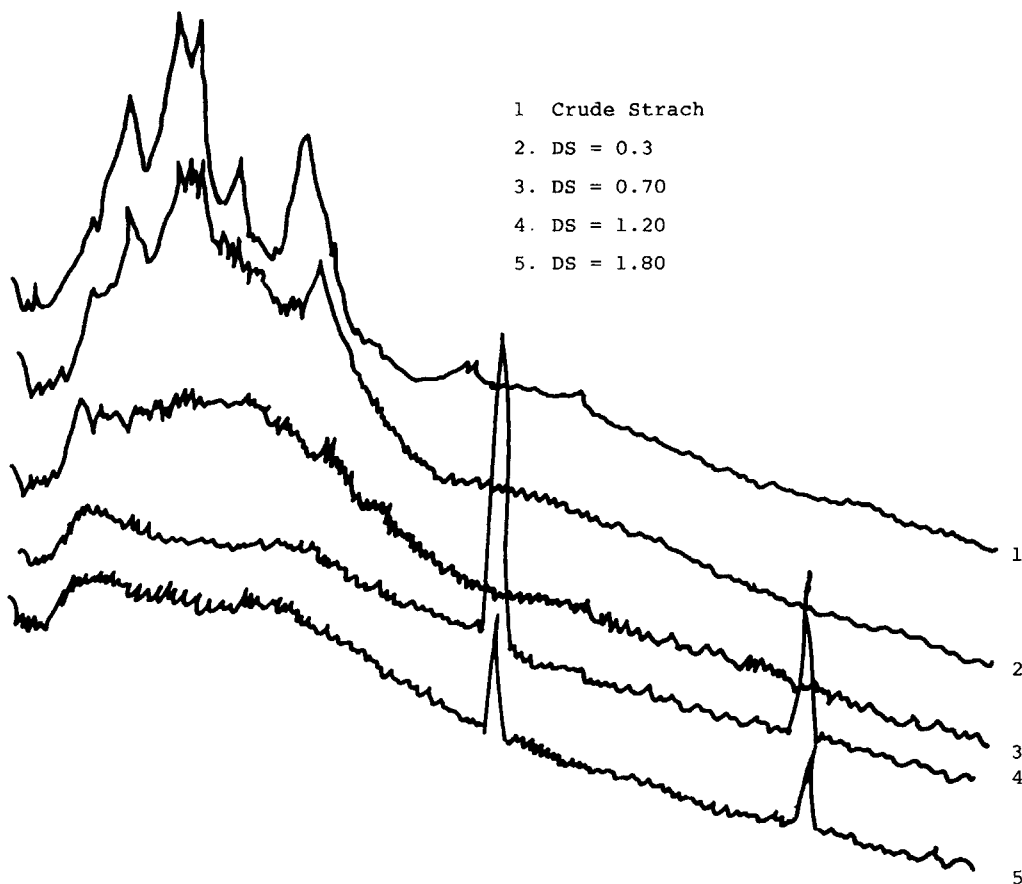


Figure 1 X-diffractions conditions: $\text{CuK}\alpha$, 40 KV, 25 mA, TCL, $1\text{ K} \times 2$.

glucose units; thus, the difference between molecular chain number before and that after degradation is obtained as

$$\Delta 1000/\overline{DP}_n = 1000 \times (162 + 80 \text{ DS})/\overline{M}_{n1} - 1000 \times (162 + 80 \text{ DS})/\overline{M}_{n2}$$

where \overline{M}_{n1} and \overline{M}_{n2} are the number-average molecular weight after and before degradation and 80 is the weight of the substituent $-\text{CH}_2\text{COONa}$ minus 1.

RESULTS AND DISCUSSION

The Relationship between DS and Solubility

The observation of solubilities of CMS with different DS that is dissolved either in deionized water or in 0.2M NaCl solution shows that when DS is in the lower stage the increase of DS favors the dissolution of CMS; when DS reaches about 0.5, it has no apparent influence on the

solubility of CMS in the water medium, whereas DS has an effect on the dissolving behavior of CMS in the salt solution. But when DS is greater than 1.2, the solubility of CMS in the salt solution decreases.

Curve 1 in Figure 1 shows the X-diffraction of starch, and curves 2–5, CMS with DS of 0.3, 0.7, 1.2, and 1.80, respectively. Curve 2 shows that CSM with its DS of 0.3 still partially retains the crystalline structure of the original starch. The carboxymethyl groups only distribute on the surface of starch particles; thus, it has poor solubility.

For CMS with a DS equal to 0.70 (Curve 3), the complete destruction of the crystalline structure of the original starch transforms it into a totally amorphous state; therefore, it has excellent solubility. For CMS with a DS of 1.20 and 1.80, new crystalline structures are formed, replacing the original ones. Moreover, the degree of crystallization of the former is more perfect than that of the latter, which causes the solubility decrease in the 0.2M NaCl solution. That is why CMS of high DS is more difficult to dissolve in the 0.2M NaCl solution than is CMS of intermediate DS. The difference of solubility between CMS in the salt solution and in deionized water is due to the existence of Na^+ ions in the medium and its shielding effects.

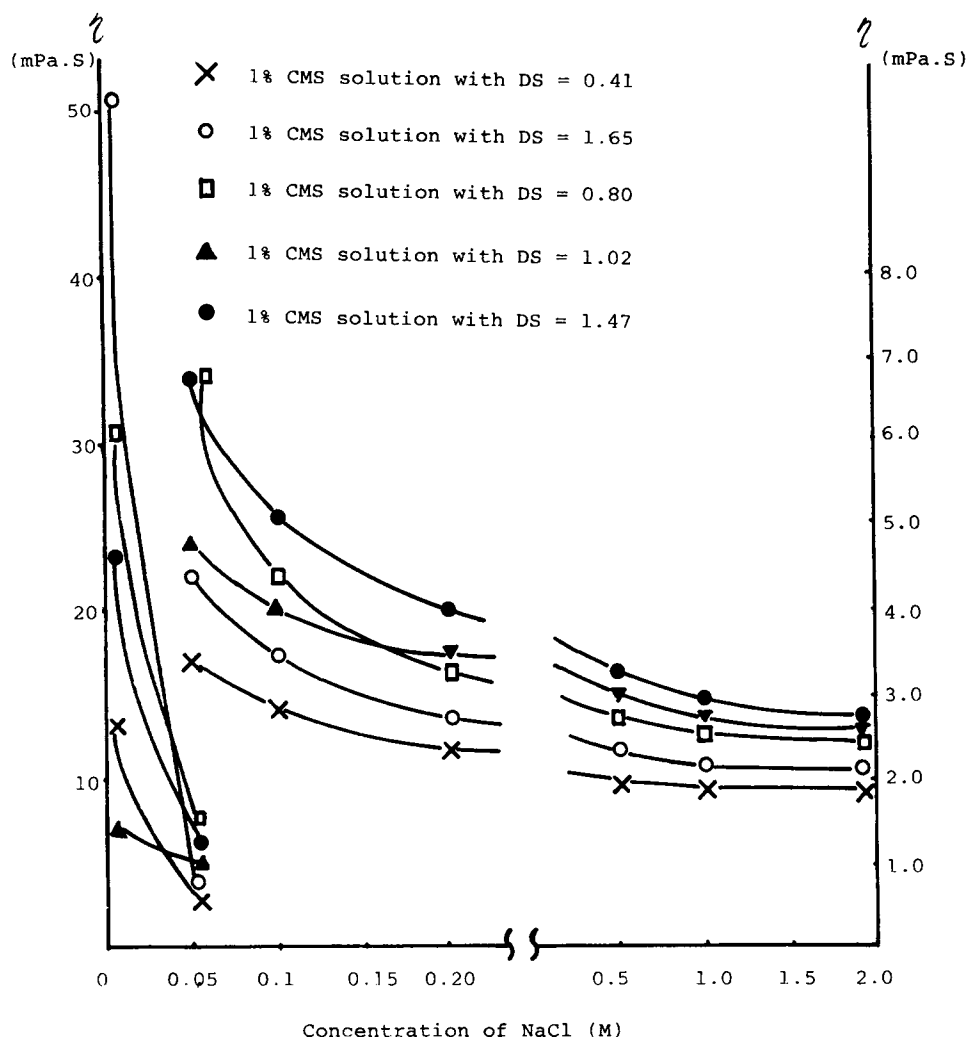


Figure 2 Influence of concentration of NaCl on viscosity of the CMS solution. Viscosities for NaCl concentration less than 0.05 M are on the left scale; the rest are on the right side.

The Influence of Salt Concentration and pH Value on Solution Viscosity

The curves in Figure 2 show that the CMS solution viscosity with different DS varies with salt concentration as well. With the addition of NaCl to a pure water solution of CMS, the viscosity of the system decreases rapidly at lower NaCl concentration, whereas when the NaCl concentration reaches 0.2 M, the influence becomes less apparent. This might be attributed to the presence of Na⁺ in the solution, which causes the ionized anionic groups ($-\text{CH}_2\text{COO}^-$) to be shielded and makes the stretching macromolecular chains into a curl form, thus resulting in a decrease in the viscosity. When NaCl concentration reaches a certain value (about 0.2 M), the solution shows the features of a neutral macromolecular solution, i.e., its viscosity is slightly influenced by NaCl concentration. Figure 3 shows that the dependence of the CMS (DS = 0.7)

solution viscosity on the pH value. It shows that, in case of the water medium, when pH is between 6.0 and 10.0, the viscosity is the highest and the curve of viscosity against pH flattens; while pH is higher than 10.0 or lower than 6.0, the viscosity decreases rapidly. This can be explained in that when pH is lower than 6.0 the electrostatic repulsion between $-\text{CH}_2\text{COO}^-$ groups can be eliminated due to the combination of H⁺ with them, causing polymer chains to be in the curl form and viscosity to reduce accordingly; when pH is greater than 10.0, the viscosity declines because the added alkali also acts as an electrolyte, as mentioned above. In 0.2 M NaCl medium, similar results are obtained for pH less than 10.0; however, for the solution with pH greater than 10.0, the viscosity increases slightly instead of decreasing with pH increasing. This might be due to the incorporation of NaOH that helps to dissolve the insolubles suspended in the solution,⁷ whereas the influence of the electrolyte in the viscosity is less significant.

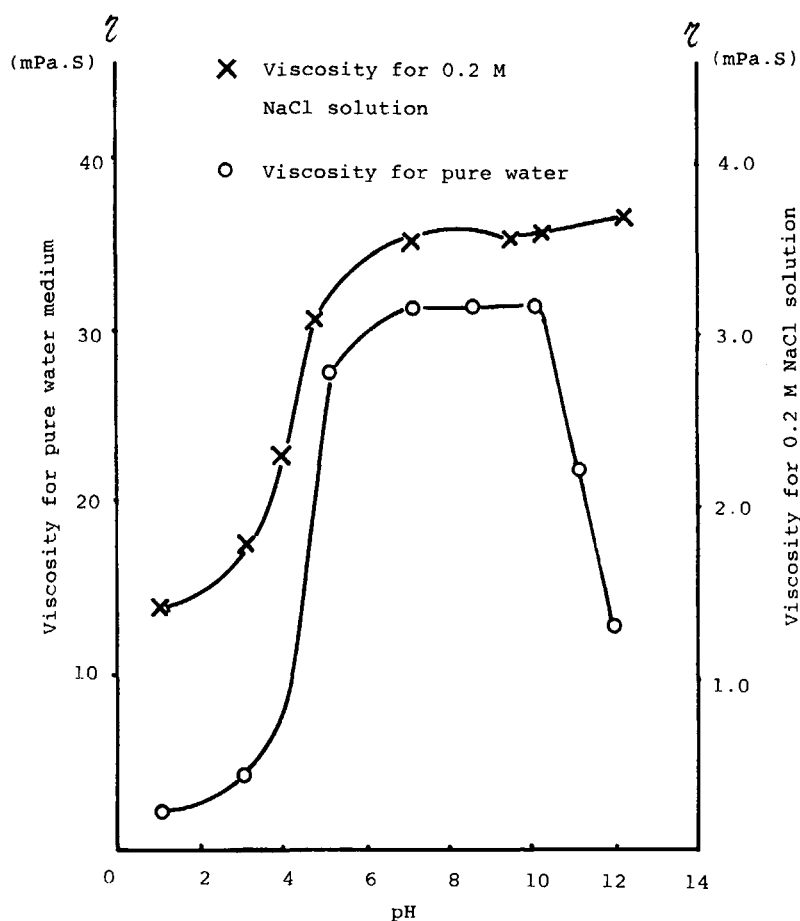


Figure 3 Effect of pH value on viscosity of 1% CMS solution.

From the above, it can be seen that although the CMS samples used have been purified, there still is a certain amount of small molecule electrolyte that affects the viscosity of the CMS solution in the water medium; this obscures the real factors causing the variation of viscosity. If the system is in the 0.2M NaCl medium and the pH value ranges from 7.5 to 9.5, the following discussions are more applicable.

The Relationship between DS and Viscosity

Table I lists the viscosity data for CMS samples that have the same molecular weight, but different DS. Results show

that at lower DS the solution viscosity enhances with the DS; when DS reaches 0.8 or so, the viscosity reaches a maximum value, then it decreases, which agrees with the observations of the CMS solubility mentioned above. The abnormal data found in Table I, e.g., Nos. 5 and 8, may be attributed to the difference between the distribution of substituents. This will be discussed later.

The Relationship between Molecular Weight and Viscosity

Table II shows the relationship of the solution viscosity of CMS, distribution of substituents ($\Delta 1000/\bar{D}P_n$), and

Table I Dependence of Viscosity on DS

	No.								
	1	2	3	4	5	6	7	8	9
\bar{M}_n (10^5)	1.50	1.58	1.54	1.55	1.56	1.58	1.58	1.54	1.49
DS	0.31	0.41	0.48	0.68	0.69	0.81	0.89	1.04	1.61
Viscosity (mPa s)	1.34	2.90	2.97	3.40	8.10	4.53	6.08	3.83	5.85

Table II Relationships of Molecular Weight, Distribution of Substituents, and Viscosity

	No.								
	1	2	3	4	5	6	7	8	9
DS	1.02	1.01	1.05	1.04	1.10	1.06	1.06	1.00	1.00
\bar{M}_n (10^5)	0.57	0.73	0.85	1.54	2.08	2.32	2.90	3.54	2.72
$\Delta 1000/\bar{DP}_n$	8.60			10.93	3.68		7.62	6.06	
Viscosity (mPa s)	3.15	3.25	3.45	3.83	4.23	3.27	3.40	5.50	4.29

molecular weight (\bar{M}_n) at almost the same DS (DS = 1.00). It can be seen that an increase in \bar{M}_n leads only to a little enhancement in the viscosity, e.g., for Nos. 1, 4, and 7, their $\Delta 1000/DP_n$ is 8.60, 10.93, and 7.62, respectively (only a little difference), their molecular weight is 0.57, 1.54, and 2.90×10^5 , respectively (significant difference), and their corresponding viscosity is 3.15, 3.83, and 3.40 mPa s, respectively (also little difference).

On the one hand, number-average molecular weight is sensitive to the proportion by weight of smaller molecules, to which the viscosity is insensitive. On the other hand, starch is composed of amylose and amylopectin; in the cornstarch used for preparing CMS, its amylopectin content is about 70%. As far as the branched polymer is concerned, molecular weight is the sum of all the branched chains, but the clew density corresponds only to the molecular weight of each single branched chain; hence, the decrease in clew density caused by the molecular weight is compensated by the increase of the density of the branched chain. This reduces the dependence of the clew density on the molecular weight, or it even disappears completely. This can be confirmed by the difference of the dependencies of the specific viscosity on the molecular weight between high-pressure branched polyethylene (LDPE) and low-pressure polyethylene (HDPE). Similar phenomenon can be found in branched polysaccharide glycogen and in some proteins. This is one of the major reasons that the molecular weight of CMS cannot be determined by the viscosity method.

The Relationship between Substituents Distribution and Viscosity

After reaching the conclusion that molecular weight has no obvious influence on viscosity, Table III shows that the viscosity of CMS (DS = 0.70) is greatly dependent on its substituent distribution. The more uniformly the substituents distribute, i.e., less $\Delta 1000/DP_n$, the higher its viscosity is. For example, the molecular weights of samples Nos. 4 and 5 are 2.90 and 3.11×10^5 , respectively (on the same level), but their solution viscosities are 3.88 and 7.13 (mPa s), respectively (considerably different).

It is quite reasonable to conclude that the difference in viscosity is caused by different $\Delta 1000/\bar{DP}_n$, of which one is 90.99 and the other is 25.62. The viscosity of sample No. 1 is the lowest (1.98 mPa s) due to the largest $\Delta 1000/\bar{DP}_n$ (127.75), which seems to prove that CMS with uneven distribution contains some segments completely composed of unsubstituted glucose units, or that it even partially retains the crystalline structure on the original starch, leading to the result that part of the chains exist in the curl form. In contrast, CMS with even distribution exists in the fully stretching form in its solution because the substituent groups repulsing each other uniformly distribute along the chain.

Further exploration of Table II reveals that the CMS solution viscosity with high DS (DS = 1.00) is less influenced by the distribution of substituents. This is because it has so many substituent groups that the chains are en-

Table III Relationship of Distribution of Substituents, Molecular Weight, and Viscosity

	No.				
	1	2	3	4	5
DS	0.72	0.72	0.69	0.74	0.72
\bar{M}_n (10^5)	0.76	0.91	1.56	2.90	3.11
$\Delta 1000/\bar{DP}_n$	127.75	37.56	9.9	90.99	25.62
Viscosity (mPa s)	1.98	3.73	8.10	3.88	7.13

abled to stretch as long as possible in the solution, even if the substituents are nonuniformly distributed along its chain. Therefore, this factor becomes less significant compared to intermediate DS CMS.

CONCLUSIONS

1. The crystalline structure of the original starch is partially retained in CMS with a DS of 0.30, but completely destroyed in CMS with a DS of 0.70, and the new one is formed in CMS with DS of 1.2 and 1.8.
2. The viscosity of the CMS solution strongly depends on the content of low molecular electrolyte and pH value. But in the case of CMS dissolving in 0.2M NaCl solution and with pH value ranging from 7.5 to 9.5, the dependencies become very slight.
3. The viscosity of CMS in 0.2M NaCl solution increases with the DS. It is largest when the DS reaches about 0.8; beyond that, it reduces slightly.
4. The influence of molecular weight on the viscosity of the CMS solution is not very remarkable, but the influence of distribution of the substituent group alone is quite significant, especially for CMS with an intermediate DS.

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