Solution Properties of Water-Soluble Polymers.   I. Control of Aggregation of Sodium Carboxymethylcellulose (CMC) by Choice of Solvent and/or Electrolyte*

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INTRODUCTION

The process for manufacture of sodium carboxymethylcellulose (CMC) can be varied in many ways to produce a wide variety of properties. Properties which are varied in practice are degree of substitution (D.S.), degree of polymerization (D.P.), and uniformity of substitution of the carboxymethyl substituent along the cellulose chain. The last property has been shown to give large variations in the behavior of plain water solutions of CMC. The present work shows still wider variations in solution behavior with variations in the dispersing medium.

deButts, Hudy and Elliott[1] have reported their observations on the thixotropic, hysteresis, and gel-forming character of solutions of certain types of CMC. They reported the following observations on nonsmooth CMC dispersions: that their consistencies could be reduced by mechanical means, that they could be mechanically activated to undergo time-dependent gel formation, that a gel fraction could be isolated by strong centrifugation, and that the gel fraction was completely dispersible in 5% sodium hydroxide solution. They explained their observations on the basis of residues of crystalline cellulose which remained in the product after manufacture. When the product was dispersed in water, the crystalline centers acted in the manner of a "mass of hair held together by a burr." The result was a gel center whose structure was schematically represented as in Figure 1. The present work strengthens the original conclusions of deButts, Hudy, and Elliott and adds substantial detail on the nature of CMC in solution.

OBSERVATIONS

The following observations from the current work will be interpreted on the basis of the existence of discrete gel particles or aggregates varying in size and rigidity with variations in solvent environment.

(1) The dispersion of a strongly aggregated, high-viscosity type of CMC in water solutions of simple electrolytes results in systems with abnormally low viscosities. In contrast, systems of identical composition but in which CMC is added to the water and dispersed *before* the electrolyte, are only slightly less viscous than CMC in pure water.
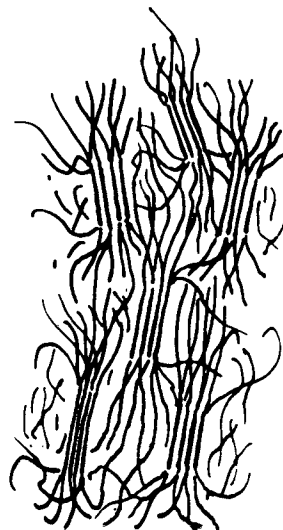
(2) Samples of CMC having no measurable ag-

Fig. 1. Schematic diagram of a gel center of CMC in a dispersion. Clustered parallel lines represent chain segments involved in crystal structures.

gregation tendencies are indifferent to the above order-of-addition phenomenon in simple electrolyte systems. They show only small decreases in viscosity when dissolved in simple salt systems, as compared with their viscosities in pure water. They also disperse completely in solvents poorer than water.

(3) Samples with moderate aggregation strengths show still other effects. For example, in a solvent poorer than pure water the viscosity contributed by CMC may be many times higher than that for CMC in water. If the poor solvent also has a simple salt present at the time the CMC is added, the resulting viscosity may be still higher or may decrease, depending on a wide variety of conditions.

None of the above systems appears to be in a state of three-dimensional gelation, nor is there evidence for any so-called "yield value." Of course, CMC solutions can give true gels when crosslinked by suitable polyvalent ions.

DISCUSSION

Principles of Viscometry of Suspensions and Aggregates

The principle technique for demonstrating degrees of aggregation was viscometric. The ultimate quantitative explanations for viscosities of suspensions and dispersions, other than very dilute ones, are still awaiting development and universal acceptance. The art and science of rheology has, however, developed to a point where some semi-

quantitative comparisons can be made and understood to the satisfaction of most observers. When a solid polymer powder is added to a liquid and equilibrated, the polymer may remain as a suspended powder (state I); it may swell to a point where all solvent is imbibed into the particles (state II); or it may disperse completely into its individual molecules (state III). It may exist also in states Ia, Ib, or IIa between the above three states, or different portions of the polymer powder may, at equilibrium, be in different states. These conditions are roughly depicted in Figure 2 in which the average degree of disaggregation is related to the viscosity of the system. We may briefly outline reasons for validity of this diagram:

State I is roughly represented by Einstein's equation for a dilute suspension of solid spheres

$$\eta_{sp} = k'V \tag{1}$$

where η_{sp} is the specific viscosity, k' is a constant, and V is the volume fraction of solid. For volume fractions of from 1 to 10%, viscosity would be relatively low.

States Ia and Ib are swollen aggregate states which may be roughly represented by the generalized empirical equation[2] for concentrated suspensions of spheres

$$f(\eta) = kV/(1 - S'V) \tag{2}$$

where k is similar to Einstein's k', V is the same as in eq. (1), and S' is another constant equal to about 2. It follows that when the volume fraction of
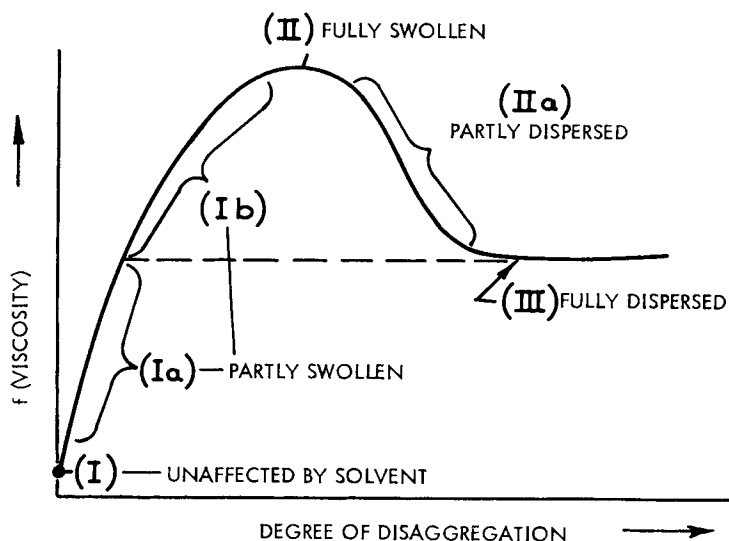

Fig. 2. Degree of disaggregation and the resulting viscosity contribution of a polymer–liquid system.

swollen aggregate approaches about 0.5, the denominator will be small and viscosity should increase quite rapidly and be very large. It would be impossible to apply this treatment directly to our problem for several reasons, among them being that the CMC aggregates are soft and deformable and, on the average, not spherical. We differentiate Ia and Ib as the states of aggregation which give viscosity below or above the viscosity of the molecularly dispersed polymer solution (state III).

State II is the condition of maximum swelling and rigidity of state Ib. It may be regarded as a system of discrete gel particles occupying almost the entire volume of the system and resulting in the "peak" viscosity.

State IIa is the condition where many of the internal associations giving state II are broken. The aggregate, or what is left of it, may be regarded as easily deformable, requiring little stress to deform it and make it conform to the flow pattern.

Finally, state III, the complete molecular dispersion, results in a final viscosity lower than the peak.

The picture described above has been used often to describe the behavior of starch suspensions as they are made to thicken.[3] Such behavior can be seen also in almost any operation where a soluble polymer is put into a solvent and made to dissolve. Whereas in these two cases the states are transitory, more permanent ones can be demonstrated with CMC.

Factors Influencing Degree of Swelling or Dispersion of CMC

All solvents and salt systems employed in the present work would dissolve CMC completely (molecularly) if there were not binding or cross-linking centers prohibiting such dissolution.[1] Many of the forces operating to disperse this hydrophilic polyelectrolyte may be recognized and qualitatively evaluated. We can visualize water associating with the CMC through interactions such as hydrogen bonding, polar associations with different portions of the anhydroglucose unit, and association with the negative charge on the CMC. These forces can be generally lumped into a single descriptive term such as "solvation" or "hydration" forces. They serve to make the CMC desire the environment of the solvent more than itself. In a rough sense, solvent molecules may be looked upon as wedges, coming between association points in the solid (amorphous) polymer and aiding separation and solution. It might be reasonable to invoke other solvent forces acting at one or another stage of swelling or dispersion, such as osmosis.

In addition to the above solvation forces, CMC has ionic forces promoting its dispersion. The solvent, in addition to associating with the negative charges on the polymer, associates with the mobile counterion. This association, plus the effect of the dielectric constant, reduces the energy required to separate the counterion from the vicinity of the polymeric ion. An interesting case can be seen to develop in an aggregate where the concentration of polymeric ion and counterion is high. A number of mobile cations could become displaced a significant distance from certain parts of the aggregate. This should result in areas with negative charges on adjacent polymer chains, without counterions close by to reduce their repelling effect. The resulting force of repulsion is a significant contribution to the rate and extent of separation and dispersion of CMC. If a salt is present in the medium at the time of introduction of CMC, the frequency of occurrence of a counterion in the vicinity of repelling chains is increased. The net result is a reduction of the forces for separation. An analogous picture has been proposed for the behavior of dilute solutions of polyelectrolytes with and without added salts.[4] Added salts may also reduce to some extent the solvation power of the solvent, but this effect will be small in the present case.

Certain types of CMC offer resistance to complete dispersion in water. This has been postulated to be due to internal binding by residual crystalline areas of cellulose.[1] A logical extension of this picture is that the crystal residues in such samples of CMC exist in a broad range of sizes and strengths. It is proposed that when CMC is added to a good solvent a large number of original associations are effectively broken by the solvent system. However, the forces of solvation and mutual ionic repulsion are insufficient to separate all polymer–polymer associations in these types of materials. Had the solvent been poorer, or contained a salt, a significant number of weaker binding associations would have been kept intact. The results would have been dispersions with new and interesting physical properties.

EXPERIMENTAL

The viscometers were essentially the same instruments as were used in the earlier work.[1] They were concentric cylinder viscometers of good geometry, so that shear rates and shear stresses

calculated from their measured dimensions were accurate to within ±10%. The range of shear rates available was 0.3 to 4400 sec.$^{-1}$ The shear stresses available varied from about 10 to 2×10^4 dynes/cm.^{2}. All viscosities were determined at 25°C.

The highly aggregated CMC systems were prepared by dispersing the various components into water in the order indicated. The salts were Baker Analyzed Reagents. A Brookfield counterrotating mixer set at half speed was used for agitation. Solutions with CMC added were agitated under these conditions for 20 min. Measurements were made within one-half hour after preparation. (Data pertinent to this series are summarized in Figures 3 and 4.) Several solutions of this series were picked randomly and observed periodically for over 8 weeks. None of them changed in viscosity by more than 20%, indicating that adequate equilibration was reached at the time the first measurement was made.

Several systems were used to demonstrate solvent effects on a well-dispersed CMC. The first was a water system in which the hydrocolloid was dispersed by Lightnin' Mixer agitation for 20 min. The other systems were sugar–water solutions made up of varying ratios of the two com-

ponents. The CMC was mixed with one to two volumes of sucrose, and the mixture was dispersed in the water. After complete solution of the solids, the rest of the sugar was added and dissolved. Agitation was the same as for the aqueous systems except that it was usually longer. Variations in mixing time were not significant because the particular well-dispersed CMC used in sugar–water systems was quite insensitive to moderate differences in shear history.

Glycerol–water systems were chosen to demonstrate the effect of a poor solvent on moderately aggregated CMC. The CMC was dispersed in the glycerol, and the required amount of water or salt solution was added to the dispersion. This system was then agitated by the Lightnin' Mixer for 3 min. and then allowed to stand overnight before viscometric readings were made. (Results are given in Figures 5 through 8.)

RESULTS

(1) Strongly Aggregated CMC: Variation of Aggregation by Means of Soluble Metal Salts

A high-viscosity type of CMC (D.S. 0.7) was selected which had a very high degree of structure in pure water. A broad spectrum of flow proper-
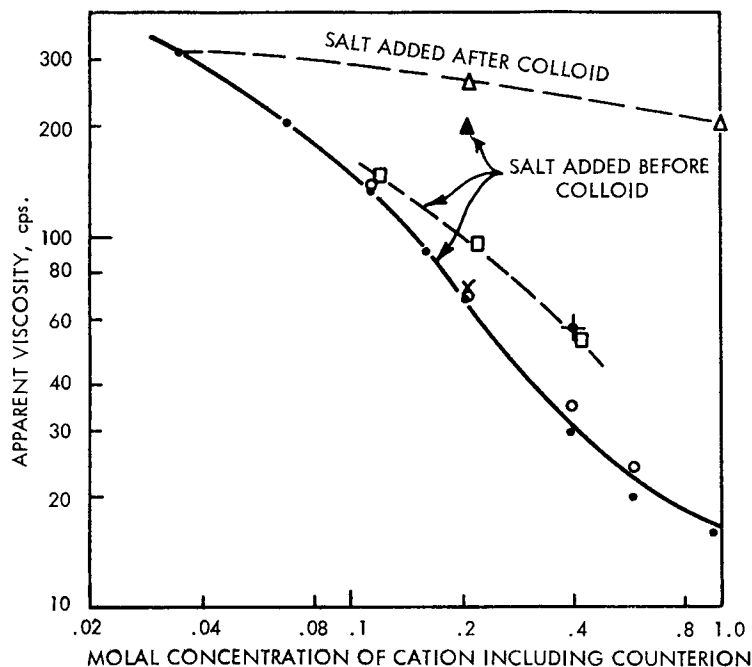

Fig. 3. 30 sec.$^{-1}$ viscosities for 1% highly aggregated CMC (D.S. 0.7) in monovalent salt systems: (▲) CMC dispersed in pure water, precipitated, dried, and then dispersed in NaCl solution; (●, △, ▲) NaCl; (✛) NaCl + NaOH (pH 10.1); (O) Na₂SO₄; (□) Na₄P₂O₇·10H₂O (pH 9.5–9.8); (✕) KCl or LiCl.
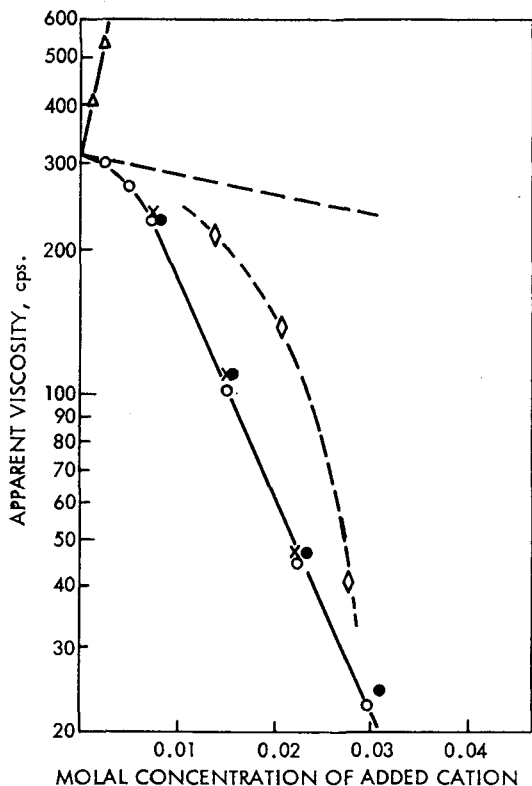
Fig. 4. Viscosities of 30 sec.$^{-1}$ for 1% highly aggregated CMC (D.S. 0.7) in solutions of various salts, in which the salt was dissolved completely before CMC was added: (O) Co(NO$_3$)$_2$·6H$_2$O; (●) CaCl$_2$·2H$_2$O; (×) BaCl$_2$· 2H$_2$O; (◇) HCl; (△) Al$_2$(SO$_4$)$_3$·18H$_2$O; (— —) NaCl curve from Figure 3.

ties was studied on 1% solutions of this material. One of the most useful properties found was the apparent viscosity of the solution determined at the 30 sec.$^{-1}$ shear-rate level. Such data are reproduced in Figures 3 and 4.

It can be seen readily from Figure 3 that the viscosity of a 1% dispersion of this type of CMC in aqueous systems containing monovalent cations is profoundly dependent on the order of addition of the CMC and salt. Thus when a solution of the CMC in water is treated with about 5% sodium chloride (~0.9 molal), the resulting viscosity is still 60% of the original. If the order of addition of the two solids is reversed, however, only about 5% of the viscosity without salt results. The observation on the former CMC solution is typical of the small salt effects usually observed for dispersed CMC's at higher (>0.5%) concentrations.

It is seen in Figure 3 that for systems in which the salt was dissolved first, a continuous drop in apparent viscosity resulted as solvents containing increasing amounts of salts were used. Considering the lack of a "peak" viscosity, it is consistent with the system shown in Figure 2 to conclude that this CMC sample is in the Ia or Ib state of average aggregation when dispersed in pure water. Modification of the medium with simple electrolyte (before the CMC is added) results merely in a more strongly aggregated state approaching state I. It should be noted also that the other simple monovalent cations, potassium and lithium, behave quantitatively similarly to sodium. Thus complexing by a specific cation, such as in the case of potassium–carrageenin interactions,[5] appears ruled out, since some significant differences should have shown up among these three cations.

One other conclusion may be drawn from the experiments shown in Figure 3. We suggest that most of the broken linkages cannot reform. This is borne out by the fact that addition of salt after the CMC does not result in any significant evidence for three-dimensional crosslinking or gelation, as would be expected on re-formation of linkages. Neither does the compact gel structure appear to reform. A more significant experiment was performed in which CMC was dispersed in plain water and then recovered from solution by adding salt and methanol and precipitating. The product was purified and dried (95°C. in vacuo). At this stage the product was highly concentrated and probably in the most favorable state for re-formation of the crystalline linkages that had been broken when the CMC was initially dispersed in water. Yet, when the product was dispersed in 0.2 molal sodium chloride solution, it was almost three times as viscous as the regular example and only about 30% less viscous than the example in which the hydrocolloid was added before the salt. It therefore seems logical to conclude that little if any re-formation of crystal structure can be made to occur in simple dispersions of this type of CMC.

Various anions were tried in an attempt to determine whether an osmotic mechanism of swelling was operating. A two-phase system could be visualized—a swollen gel, the surface of which might be a semipermeable membrane, and the solvent–solute phase. It could be argued that one significant mechanism of salt retardation of swelling could be that salt was prohibiting entry of solvent into the gel by osmotic means. This was open to test by varying the concentration of total ions while maintaining the same cation concentration. It was possible to vary the ratio of particle concentration from eight to five (eight particles of sodium chloride

to five particles of tetrasodium pyrophosphate) and still have the same cation concentration. The significant results are shown in Figure 3 where a sodium pyrophosphate medium is compared with a sodium chloride medium. The pH of the latter medium was adjusted to the range of pH encountered in the former. The two dispersions showed identical viscometric behavior. It may therefore be concluded that salt effects observed on the partially swollen gels dealt with in this work were not osmotic effects. These experiments demonstrate also significant pH effects.

Some experiments on the effect of ions other than simple monovalent are shown in Figure 4. On an equivalence basis, hydrogen ion was the most efficient viscosity-depressing ion examined. This was not surprising because almost every hydrogen ion added was expected to neutralize a negative polymer charge, thereby very efficiently reducing internal repulsion forces.

The divalent cations calcium, barium, and cobalt all behave in an identical manner (Fig. 4). The viscosity-depressing effect of these cations is found to be much greater than that of monovalent cations even when comparison is made on the basis of ionic strength.

The following are the reasons for believing that divalent cation effects shown in this work are primarily, if not entirely, simple electrolyte (ionic strength) effects as discussed earlier, and not coordination complexing or crosslinking effects: (1) A true coordinate crosslinking ion, trivalent aluminum, causes only viscosity increases when present in the system at comparable levels (Fig. 4). (2) There is no significant degree of measurable gel formation or other three-dimensional crosslinking when the CMC is added first and the divalent cation second. (3) CMC samples of equal composition and viscosity grade are known (well-dispersed types) which behave the same no matter which solid (divalent cation or hydrocolloid) is added to the solvent first. (4) If a chelate complex of the type

$$\left[\begin{array}{c} O \\ CH_2 \quad Cell \quad H \\ O=C \qquad O \\ O—M \end{array} \right]^{+}$$
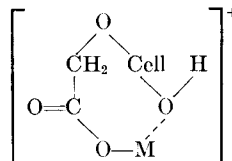
were formed to any extent, it would be amazingly fortuitous if the three cations tested all formed this structure to the same extent at the same concentrations.
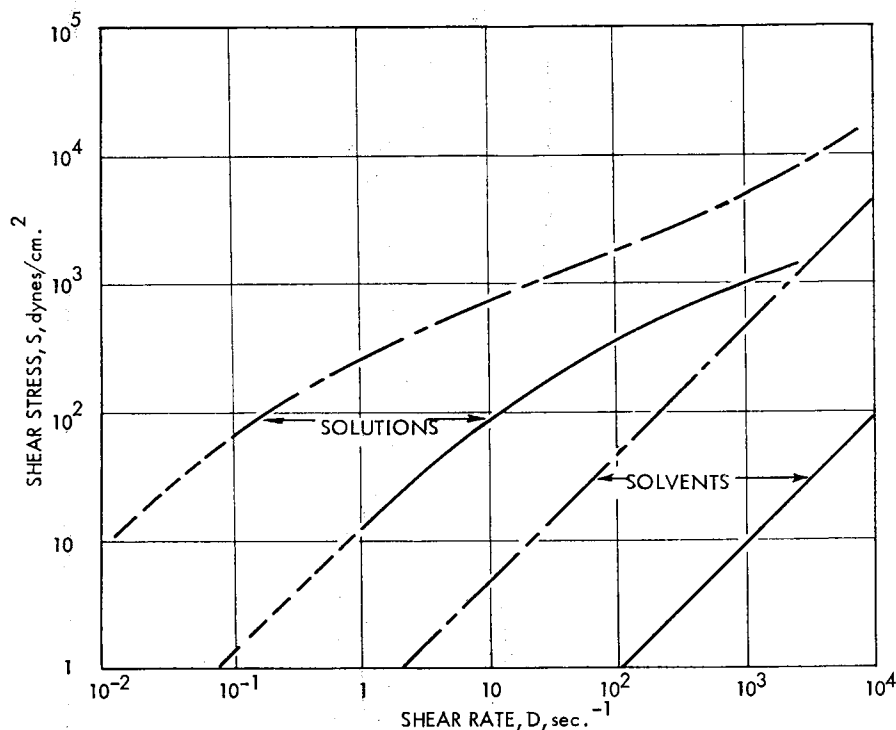

Fig. 5. Flow curves for 1% (w/v) CMC (D.S. 1.2, very high viscosity, well-dispersed) in water and 60:40 sucrose:water solvents: (—) water, (— · —) sucrose—water, (— —) extrapolations.

(2) Well-Dispersed CMC in Salt Solutions and Various Solvents

It was mentioned previously that well-dispersed or smooth types of CMC showed very small (10–40%) viscosity losses when simple salts were added. Also, they were insensitive to the order of addition of salt or hydrocolloid to the water.

The behavior of the well-dispersed types in solvents other than plain water was evaluated. A high-viscosity sample of CMC with D.S. 1.2 was selected for study in various sucrose–water solutions as solvents.

The study consisted of an analysis of the broad viscometric flow properties of these solutions. All solutions were structure-free as determined by smooth solution texture and lack of thixotropy or loss of viscosity with time when subjected to moderately high stress. The viscometric flow curves of two of these solutions are shown in Figure 5. The aqueous CMC solution shows almost Newtonian (slope ~1) behavior at shear stresses below 10 dynes/cm.², and the solution of CMC in aqueous sucrose probably behaves in the same way, as shown by a reasonable extrapolation from existing

data. Both solutions are markedly non-Newtonian in the shear-stress range between about 200 and 5000 dynes/cm.². In addition, the sucrose–water solution was in a transition approaching a high-stress (>10,000 dynes/cm.²) Newtonian region. This flow behavior is not surprising. It has been well characterized by Philippoff and co-workers[6] for many cellulose derivatives and a large number of other polymers. One thing, however, stands out in Figure 5. To a good approximation the sucrose–water solution curve is shifted uniformly down the shear rate axis. The magnitude of this shift is almost exactly the same as the shift of the sucrose–water solvent. In fact, the relative viscosities obtained at the same shear stress are almost (eq. 3)

$$(\eta_{rel})_S = (\eta_{apparent})_S / \eta_{solvent} \qquad (3)$$

identical. The case is further proved in Figure 6 by a plot of relative viscosities versus shear stress for the well-dispersed CMC in several different sucrose–water solvents. In all cases the CMC was present at equal weight-to-volume concentrations. The maximum variation occurs at low shear stresses and amounts to about 40–60% higher relative vis-
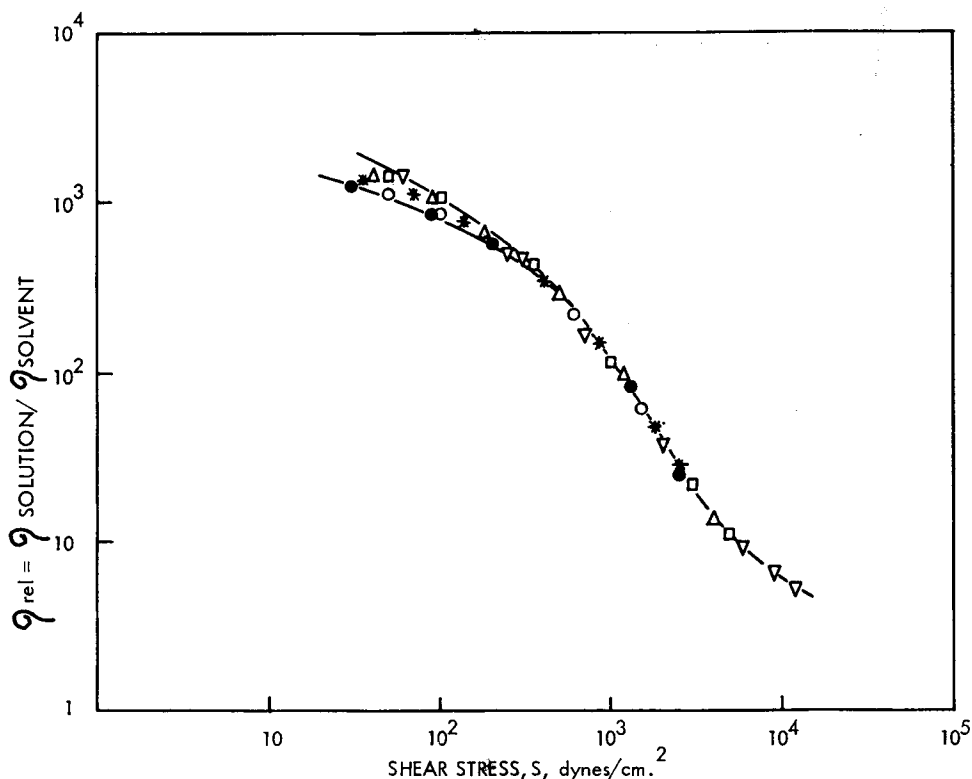

Fig. 6. Relative viscosity versus shear stress for 1% (w/v) CMC (D.S. 1.2, very high viscosity, well-dispersed) in sucrose:water solvents with various amounts of sucrose (w/w): (O) 0%, (●) 20.0%, (*) 30.0%, (△) 40.1%, (□) 50.1%, (▽) 60.0%.

cosity for the solution having the highest sugar content. This is a surprisingly small variation when one considers that the shear rates involved in making the low-stress measurements vary by 4000–5000% between the aqueous and 60% sucrose solutions. Similar effects have been observed for stress variations[7] and for the low-shear Newtonian flow behavior in different solvents.[8] The present example, however, covers a broader range of stresses and viscosities than is usually found in the literature.

A discussion of the significance of these observations with respect to the mechanism of thickening of fluid systems by polymers will be undertaken in a later paper. It is suggested, however, that the CMC molecule was very similar in conformation or spatial arrangement in all of the solvents used. This is in accord with the small effects observed in salt solutions. It should be mentioned also that other water-soluble polyols, e.g., glycerol, when combined with water yield solvents which give the same stress-predictable behavior. Also, CMC (D.S. 0.7) when manufactured to give the most uniform distribution of substituent shows exactly the same correlatable flow properties as the sample in Figure 6.

(3) Moderately Aggregated CMC: Effect of Varying Solvent Power and Electrolyte

The knowledge of the flow behavior of well-dispersed CMC in solvents other than pure water can be used in studying variations of aggregation. A medium-viscosity CMC was selected with D.S. 0.7 to 0.8, made so as to impart only slightly non-uniform substitution. In water at 2% concentration this material was almost completely dissolved (state III). It showed no measurable breakdown when subjected to high shear stresses. Its solution texture was also visually smooth. Its aqueous solution flow curve is shown in Figure 7.

A prediction was made for the flow properties of this CMC in 55:45 glycerol:water solvent assuming the material dispersed to the same extent. Because this solvent was almost ten times as viscous as water, the predicted flow curve would be displaced to the left of the water solution flow curve by a factor of ten (Fig. 7). Upon measuring the actual flow properties of this system, a completely different curve resulted, designated as the "observed" glycerol:water curve in Figure 7. Thus instead of the predicted tenfold increase in viscosity (measured at the same shear-stress), the observed increase was more like one hundredfold, at least at lower shear rates and stresses. At higher stresses a viscosity loss due to shear was observed, further indicating the existence of an aggregated fraction of material in the glycerol–water suspension. Another property of this dispersion was the fact that it, too, reverted to Newtonian flow at low shear stresses. Thus no three-dimensional gel network developed, nor was there evidence for any so-called "yield point."
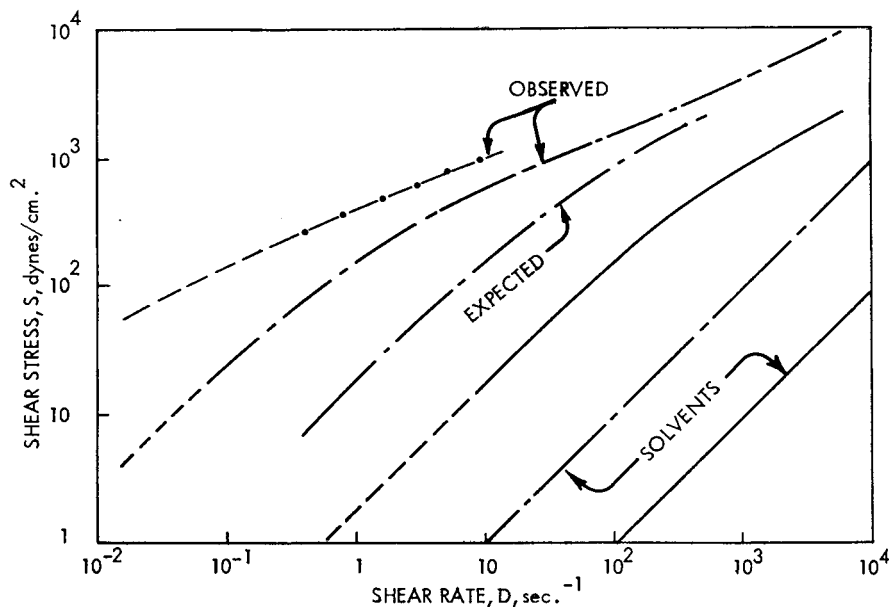

Fig. 7. Flow curves for a moderately aggregated CMC (D.S. 0.7₉ medium viscosity) in various solvents: (—) water, (— - —) 55:45 glycerol:water, (- · -) 55:45 glycerol:water + 1% NaCl, (− −) extrapolations.
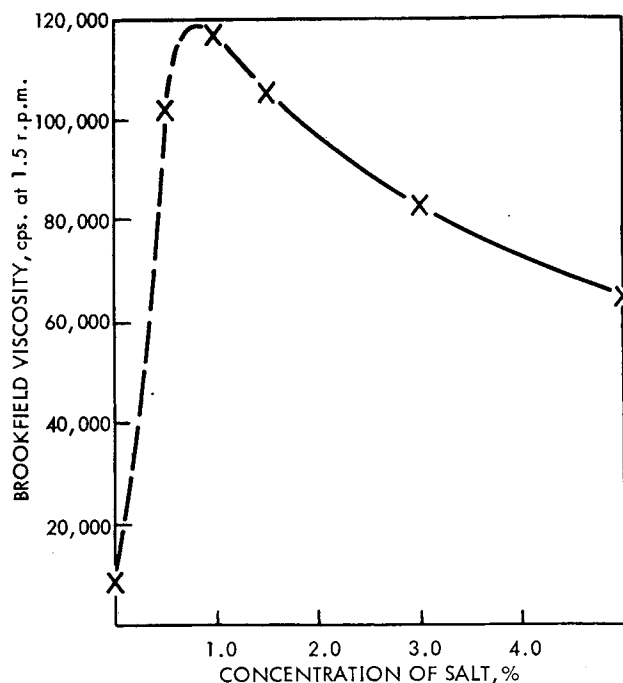
Fig. 8. Brookfield viscosity versus concentration of sodium chloride in 55:45 glycerol:water solvent.

Thus, it was shown that a poor solvent promoted the retention of significant aggregation in this type of CMC. This experiment did not define clearly the precise state of aggregation, however, because states IB through IIa were still possible. The way to answer this question was to add some simple electrolyte to a glycerol–water solvent, disperse the CMC, and observe whether the flow curve of the resulting system showed increased or decreased viscosity. It is seen in Figure 7 that 1% sodium chloride caused a viscosity increase, at least by a factor of three and probably much more at still lower shear-stresses. It can then be seen that the combination of poor solvent and added electrolyte caused a partially aggregated, partially dispersed state IIa material to strengthen its aggregate while still occupying the major proportion of solution volume.

A logical extension of the above results is to propose that further addition of simple salt would shift the average state of aggregation from IIa back to II and then further back to Ib. The test of this idea is shown in Figure 8 where simple Brookfield viscosity values for a CMC in glycerol–water–sodium chloride are plotted against the concentration of added salt. The predicted behavior does indeed hold. Somewhere between 0.5 and 1% sodium chloride concentration, state II is attained

and is at least ten times more viscous, in this example, than the glycerol–water dispersion without added salt. At higher salt concentration, the viscosity is seen to decrease appreciably as state Ib is entered and the aggregate binding forces become strong enough to decrease appreciably the volume occupied by the aggregate.

Conclusions

The work described here is interpreted on the basis that discrete particles or granules of some types of CMC contain internal binding forces. These binding forces cause the particles to retain some degree of identity when contacted with solvent. These forces are believed to residue in crystalline residues of unreacted cellulose which are present in a broad spectrum of strengths and bind many macromolecules together. Weaker residues are destroyed merely by adding the CMC to a good solvent. Fewer residues will be broken if the solvent is poorer or a noncoordinating simple electrolyte is present. Evidence suggests that, once broken, there is little or no tendency for crystal residues to re-form.

It has been demonstrated that the degree to which binding centers may be broken can be controlled. Systems with wide variations in rheological and other physical properties result. In select cases it is possible to reverse usual solvent–electrolyte effects (poor solvent and added electrolyte usually cause viscosity reductions) and predictably produce large viscosity increases.

The stress-dependent flow behavior shown for completely dispersed CMC in solvents of varying viscosity is considered to be very significant, particularly because of the very broad spectrum of stresses and relative viscosities over which it is applicable. Other stress effects have also been characterized and will be discussed in later papers.

References

1. deButts, E. H., J. A. Hudy, and J. H. Elliott, *Ind. Eng. Chem.*, **49,** 94 (1957).

2. Robinson, J. V., *Trans. Soc. Rheology*, **1,** 15 (1957), and references therein.

3. See, for example, E. G. Mazurs, T. J. Schoch, and **F. E.** Kite, *Cereal Chem.*, **34,** 141 (1957).

4. Fuoss, R. M., and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

5. Idson, B., *Chem. Week*, **79**, No. 3, 66 (1956).

6. Brodnyan, J. G., F. H. Gaskins, W. Philippoff, and E. G. Lendrat, *Trans. Soc. Theology*, **2**, 285 (1958); W. Philippoff, *Viskositat der Kolloide*, Steinkopf, Dresden, 1942.

7. Horowitz, H. H., *Ind. Eng. Chem.*, **50**, 1089 (1958).

8. Johnson, M. F., W. W. Evans, I. Jordan, and J. D. Ferry, *J. Colloid Sci.*, **7**, 498 (1952).

Synopsis

Previous investigations on the solution properties of sodium carboxymethylcellulose (CMC) have led to the conclusion that crystalline cellulose regions, remaining after processing act as binding or crosslinking sites for the establishment of a fraction comprised of swollen gels or aggregates in solution. The present paper deals with recent work which has led to a broader characterization of the degree of aggregation of CMC and its control in solution. Stages of disaggregation are defined for CMC when added to a solvent, ranging from a polymer particle unaffected by solvent through various degrees of swelling to a state of complete dispersion. Examples are given of these various disaggregation stages which were attained and controlled by varying the solvation power and/or ionic strength of the solvent. Degrees of disaggregation were characterized by broad variations in rheological behavior. Viscosity differences of several hundredfold as well as other physical changes in the solutions were found. The results are interpreted to mean that the numerous binding centers which cause CMC aggregation have a wide distribution of strengths. The addition of CMC to a good solvent causes the weaker binding forces to be destroyed and the stronger to remain intact, imparting rheological properties commensurate with the resulting degree of aggregation. The use of a poorer solvent or the addition of a simple electrolyte causes fewer binding centers to be destroyed, and a corresponding change in dispersion properties. Little, if any, re-formation of broken binding centers has been detected. Known and proposed forces involved in the dispersion of macromolecules into solvent are discussed and applied to observations from the present work.

Résumé

A partir d'investigations précédentes sur les propriétés de solutions du sel sodique da la carboxy-méthyl cellulose (CMC) il a été conclu que des régions cristallines de cellulose qui restent après traitement, agissent comme des sites de liaisons et de ramification, avec formation de fractions constituées de gel gonflé ou d'aggrégats en solution. Cet article traite d'un travail récent, qui a conduit à une caractérisation plus large du degré d'aggrégation de la CMC et le controle en solution. Des étapes de desaggrégation ont été définies pour la CMC, ajoutée à un solvant, à partir d'une particule polymérique non affectée, par différents degrés de gonflage, jusqu'à l'état de complète dispersion. Des exemples sont donnés de ces étapes de désaggrégation, qui ont été attéintes et controlées en variant la force de solvation, et/ous la force ionique du solvant. Les degrés de désaggrégation ont été caractérisés par de larges variations de comportement rhéologique. Des différences viscométriques de plusieurs centaines de fois aussi bien que d'autres changements physiques en solution ont été notés. Les résultats ont été interpretés da la manière suivante; les centres de pontage qui causent l'aggrégation de la CMC ont une large distribution de forces. L'addition de CMC à un bon solvant occasionne la rupture des forces de liaison les plus faibles, tandis que les plus fortes restent intactes. Les propriétés rhéologiques dépendent alors du degré d'aggrégation. Un solvant pauvre ou l'addition d'un électrolyte simple occasionne la rupture d'une quantité de centres de liaison moins nombreuses, et de là un changement correspondant en propriétés de dispersion. Peu, sinon auoune reformation de centres de liaison n'a été détectée. Des forces connues et d'autres proposées, qui interviennent dans la dispersion de macromolécules, ont été discutées et appliquées aux observations faites dans ce travail.

Zusammenfassung

Frühere Untersuchungen der Eigenschaften von Natriumkarboxylmethylcellulose (CMC) in Lösung haben zu dem Schluss geführt, dass noch vorhandene, kristalline Cellulosebereiche als Bindungs- oder Vernentzungsstellen für den Aufbau einer aus gequollenem Gel oder Aggregat bestehenden Fraktion in der Lösung wirksam sind. In der vorliegenden Arbeit wird über neuere Versuche berichtet, die zu einer umfassenderen Charakterisierung des Aggregationsgrades von CMC und seiner Festlegung in Lösung führten. Bestimmte Disaggregierungsstufen, vom unbeeinflussten Polymerpartikel über eine Reihe von Quellungsgraden bis zum Zustand völliger Dispergierung, werden für CMC beim Einbringen in ein Lösungsmittel angegeben. Beispiele für die verschiedenen Disaggregierungsstufen, die sich durch Variierung der Solvatisierungsfähigkeit und Ionenstärke des Lösungsmittels einstellen lassen, werden angeführt. Der Disaggregierungsgrad wurde durch grosse Veränderung im rheologischen Verhalten charakterisiert. Mehr als hundertfache Viskositätsunterschiede und andere physikalische Veränderungen wurden in den Lösungen gefunden. Die Ergebnisse werden dahingehend interpretiert, dass die zahlreichen Bindungszentren, welche die CMC-Aggregation verursachen, eine breite Verteilung der Bindungsfestigkeit besitzen. In einem guten Lösungsmittel werden die schwächeren Bindungskräfte in CMC aufgehoben und die stärkeren bleiben bestehen; die rheologischen Eigenschaften entsprechen dem resultierenden Aggregationsgrad. Schlechtere Lösungsmittel oder zugesetzte, einfache Elektrolyte führen zur Zerstörung einer geringeren Änzahl von Bindungszentren und einer entsprechenden Änderung der Dispersionseigenschaften. Rückbildung zerstörter Bindungszentren wurde, wenn überhaupt, so nur in geringem Ausmass festgestellt. Eine Diskussion der bei der Dispergierung von Makromolekülen in einem Lösungsmittel wirksamen, bekannten und angenommenen Kräften wird gegeben und diese auf die Ergebnisse der vorliegenden Arbeit angewendet.