Rheology and Water Swelling of Carboxymethyl Starch Gels

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Synopsis

A series of gels differing in ionic content was prepared by derivatizing starch with varying amounts of carboxymethyl add-on. Some derivatives were lightly crosslinked with epichlorohydrin to reduce soluble material and increase the amount of gel. The gel fraction of each batch was isolated, and viscosity $\eta$, shear modulus $G$, and swelling in water and salt solution were then determined. One gel suspension, examined in more detail, was demonstrated to behave as a closely packed gel thickening agent, thereby warranting use of the three reduced functions: reduced concentration $cQ$ ($c$ is weight concentration of polymer, $Q$ is swelling capacity in excess fluid), $\eta/cQ$, and $G/c^{1/3}$. At $cQ$ greater than about 2, $\eta/cQ$, and $G/c^{1/3}$ reach constant plateau values, as is typical of other examples of closely packed gel thickeners. In a comparison among the gel suspensions, plateau values of the reduced viscosity function were nearly proportional to the apparent crosslink density $G/c^{1/3}$, in agreement with other closely packed gel thickeners, but were not affected by ionic content of dry polymer. The water swelling capacities of the different gels ranged from 47 to 450 g/g and were correlated with both ionic contents and apparent crosslink densities, but the effects of these variables were less than suggested by theory.

INTRODUCTION

The carboxymethyl derivative of starch (CMS) is well known and has been extensively examined in the past. With even a modest substituent content, the products are largely water-soluble polyelectrolytes with somewhat viscous dispersions. In this kind of product, for which such a wide variety of reaction conditions are possible, some CMS preparations would likely be essentially insoluble or would contain a significant fraction of insoluble or gel material. Such gels should be additional examples of closely packed thickeners, and some of them might have high water swelling capacities. We have prepared and examined a number of them to compare with other examples of this class. The possibility of varying the carboxymethyl add-on, and hence the ionic content of the polymer, was a further attractive reason for examining CMS. Previously, all closely packed thickeners that we had examined had only a narrow range of ionic content, and this significant variable and its relation to water swelling capacity was not considered.

A theoretical relation for swelling of polyelectrolyte gels has been given by Vermaas and Hermans and by Flory. The swelling weight ratio, $Q$ (g swollen gel/g dry polymer) depends on the ionic strength of the medium, $\mu$, on the ionic content of the polymer, $I$ (meq of Na ion/g dry polymer in salt form), and on the number of moles of crosslinks per g of polymer, $N$:

$$Q^{5/3} = \frac{I^2}{4000\mu N \rho^{2/3}}$$

(1)
Inclusion of the density of dry polymer $\rho$ and the coefficient 4000 converts their equation to our variables, which are on a weight basis. The solvent–polymer interaction term has been omitted because it would be negligible at the relatively high values of $Q$ we observe. Vermaas and Hermans confirmed their equation (including the solvent–polymer interaction term) using cellulose xanthate gels which had lower $Q$ values than ours. The equation is only a guide to the effect of $I, N,$ and $\mu$ on $Q$, because it is based on a dilute solution approximation as well as on a Gaussian approximation to molecular chain arrangements. Our gels are sufficiently dilute, but in water and very dilute salt the chains are probably stretched beyond the lengths for which the Gaussian distribution is applicable. Although not quantitatively applicable, eq. (1) can be used as a suggestive basis in experiments to enhance water swelling power.

In a polyelectrolyte solution, ionic strength is defined as $\phi$

$$\mu = \phi m + M$$  \hspace{1cm} (2)

where $m$ is equivalent concentration of co-ions (COO$^-$ groups) in the swollen gel, $M$ is molarity of added uni-univalent salt, and $\phi$ is the osmotic coefficient, which is lower than unity for polyelectrolyte counterions.$^6,^7$

For a given polyelectrolyte, the value of $\phi$ depends on the linear charge density $\xi$ along the polyelectrolyte chain. Katchalsky’s review$^8$ shows values of $\phi$ at moderate and high values of $\xi$, but not for our lower values. $\phi$ was calculated from Manning’s theory,$^9$ assuming that the distance between adjacent substituents is 6.7 Å for a degree of substitution (D.S.) of 1. The residue length O—O$'$ in α-1,4-linked glucose chains$^{10}$ is 4.3 Å, but the helical chain structure, which may be partly retained in solution, places adjacent C-6 atoms further apart. With this assumption, $\xi$ reaches the critical value, unity, at D.S. = 0.93. In Manning’s theory, if $\xi$ becomes higher than unity, counterions condense on the chain to lower the effective charge density. This condensation is in addition to the Debye–Hückel effect, both of which lead to lower $\phi$. The condensation condition leads to separate equations for $\phi$ above and below $\xi = 1$, which are, in terms of D.S. of CMS,$^{11}$

$$\phi = 1 - 0.535\text{D.S.} \hspace{1cm} \text{D.S.} < 0.93$$ \hspace{1cm} (3)

$$\phi = 1/(2.14\text{D.S.}) \hspace{1cm} \text{D.S.} > 0.93$$ \hspace{1cm} (4)

These equations are somewhat uncertain in view of the assumptions made, but they are adequate for the present study. Manning has reviewed the theory and applications.$^{11}$

In the derivation of eq. (1), the retractive force of the elastic network is balanced at equilibrium by the osmotic pressure in the gel. This osmotic pressure, determined almost entirely by the counterions in $I$, requires the correction factor, $\phi$. The equation for swelling is then

$$Q^{5/3} = I^2\phi^2/4000\mu N \rho^{2/3}$$ \hspace{1cm} (5)

As D.S. is increased toward 1, it is anticipated from eqs. (3), (4), and (5) that further increase in D.S. (or $I$) would be largely ineffective because $\phi$ becomes inversely proportional to D.S.

Experimental relationship between ionic strength and water swelling capacity closely follows eq. (5) at high swelling. We had noted earlier that $Q^{-1}$ was linear with $\mu^{1/2}$, i.e., $Q^2$ rather than $Q^{5/3}$ was inversely proportional to $\mu$, in saponified
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starch–polyacrylonitrile graft copolymers (H-SPAN) with low enough $N$\textsuperscript{12} in Carbopol-941,\textsuperscript{13} and in saponified cellulose–polyacrylonitrile graft copolymer (H-CPAN) at low enough $\mu$.

Now in eq. (5) all variables which influence $Q$ can be measured, except $N$, which is not readily determined. $N$ can be estimated from the shear modulus $G$, which is determined from primary normal force $P_{11} - P_{22}$ and shear stress $\tau$ in a cone-and-plate rheometer\textsuperscript{15}:

$$G = 2\tau^2/(P_{11} - P_{22})$$

An apparent value of $N$ is obtained from the equation relating $G$ to $N$ in a solvent-swollen rubbery network\textsuperscript{16}:

$$N = \frac{G/c^{1/3}}{\rho^{2/3}RT}$$

The function $G/c^{1/3}$, where $c$ is weight concentration (g/g) of polymer in the gel, is the shear modulus corrected for solvent swelling, $R$ is the gas constant, and $T$ is absolute temperature. Substitution in eq. (5) gives an equation for $Q$ in terms of experimentally known variables:

$$Q^{5/3} = \frac{I^2\phi^2RT}{4000\mu(G/c^{1/3})}$$

Again, while not quantitatively applicable to present results, eq. (8) is the best available reference relation for correlating swelling and rheological properties of polyelectrolyte gels.

Other starch gel derivatives containing carboxyl groups have been prepared by Hofreiter et al.\textsuperscript{17} These gels imbibe water, are highly viscous suspensions in water, and appear to behave qualitatively like our carboxymethyl starch ones. The critical structures in both are the fixed ions and the relatively permanent gel structure.

EXPERIMENTAL

Carboxymethyl starch was made by two procedures. The first procedure was that of Sloan, Mehlretter, and Senti,\textsuperscript{18} in which commercial pearl corn starch was suspended in ethanol or water–ethanol, then chloroacetic acid was added, and the suspension was refluxed; NaOH (2.5 moles per mole chloroacetic acid) was added slowly in 90% ethanol. The mixture was nitrogen sparged before and during addition of NaOH. After an additional reaction time with reflux, the product was recovered by filtering and was washed with 80% ethanol.

The second procedure was run similarly, but in a 1-liter Sigma-blade mixer. No nitrogen sparge was used. Solvent was water or water–ethanol. Chloroacetic acid was poured in slowly as a dried powder. Water at a set temperature was circulated through the mixer, and NaOH was added as dry solid in increments over the reaction interval. In some runs, epichlorohydrin was added to increase crosslinking.\textsuperscript{18} In these runs, an additional reaction period was given at the set temperature. Excess alkali from the carboxymethylation reaction was available to permit the epichlorohydrin to react. Details for individual runs are given in Tables I and II and in the results section.

Gel, as opposed to soluble, material was isolated from the crude product by
two successive low-speed centrifugations (2000 rpm, 15 min) in the presence of 1M NaCl. Salt was then washed from the gel by resuspension in 1M HCl and centrifugation. A total of six successive washes with water containing concentrations of HCl diminishing to 0.0005M HCl removed salt and converted the gel to the acid form. This acid-form material was titrated to pH 7.6 with 2M NaOH, to produce each purified gel fraction. A weighed portion of the neutralized gel suspension was dried in an oven at 120°C overnight to determine \( I \). Not all carboxyl groups are titrated to salt form at pH 7.6, but ions contributed by excess base are minimized at this pH.

Both \( \eta \) and \( P_{11} - P_{22} \) were determined in a Rheometrics mechanical spectrometer with cone-and-plate fixtures by methods given earlier. We continue to use a small angle-head centrifuge to determine swelling ratio in excess solvent. Suspensions with the gel fraction occupying about half the total volume are centrifuged at 3600 rpm (1300 \( \times g \)) for 90 min. Gel volume is then measured. Though this method is probably not as accurate as the ultracentrifuge, it is much more convenient and is adequate.

### RESULTS AND DISCUSSION

#### Carboxymethyl Starch Preparations and Gels

A series of CMS batches was prepared, with a wide diversity of properties (Table I). In particular, the amount of add-on was varied, but we noted that the gel was usually present as only a minor component if the amount of carboxyl...
TABLE II
Properties of Gels of Carboxymethylcellulose

| Gel batch | CMS mg/g CMS | Time, hr | Temp., °C | Epichlorohydin recovered, fraction of total | \( I_a \) meq/g | \( Q_{OH} \) | \( Q_{H_2O} \) | \( \phi \) | cQ | \( |\eta_{100}/cQ|_p \) | \( [G_{100}v^{1/2}]_p \) \( \times 10^{-3} \) |
|-----------|-------------|----------|-----------|------------------------------------------|----------------|--------|----------|--------|-----|-----------------|----------------|
| 1         | A           | —        | —         | 0.74                                     | 0.36           | 39     | 47       | 0.97   | 1.90| 5.0             | 3.7             |
| 2         | B           | —        | —         | 0.10                                     | 0.53           | 88     | 168      | 0.95   | 1.82| 10.7            | 33              |
| 3         | C           | —        | —         | 0.16                                     | 0.66           | 125    | 329      | 0.94   | 2.04| 2.8             | 4               |
| 4         | D           | —        | —         | 0.36                                     | 0.70           | 98     | —        | 0.94   | 1.61| 7.0             | 7.9             |
| 5         | E           | —        | —         | 0.20                                     | 0.72           | 152    | 425      | 0.93   | 2.02| 4.0             | 5.9             |
| 6         | F           | 5        | 1         | 62                                        | 0.41           | 1.11   | 89       | 0.89   | 1.48| 103             | 231             |
| 7         | G           | —        | —         | 0.42                                     | 1.65           | 185    | 313      | 0.84   | 2.13| 9.1             | 10.3            |
| 8         | H           | —        | —         | 0.49                                     | 2.05           | 220    | 340      | 0.79   | 2.68| 5.3             | 4.6             |
| 9         | I           | —        | —         | 0.33                                     | 2.54           | 230    | 262      | 0.72   | 2.32| 9.0             | 7.8             |
| 10        | J           | 5        | 1         | 62                                        | 0.47           | 2.60   | 132b     | 0.71   | 1.20| 115             | 123             |
| 11        | K           | 12.5     | 1         | 62                                        | 0.45           | 2.78   | 123b     | 0.69   | 1.62| 53              | 94              |
| 12        | L           | —        | —         | 0.54                                     | 2.82           | 202    | 270      | 0.68   | 2.14| 5.5             | 3.5             |
| 13        | M           | —        | —         | 0.58                                     | 2.92           | 210    | 282      | 0.67   | 2.20| 14.1            | 15.1            |
| 14        | M           | —        | —         | 0.39                                     | 2.94           | 189    | 220      | 0.67   | 3.50| 14.0            | 10              |
| 15        | N           | 5        | 1         | 62                                        | 0.75           | 2.94   | 124b     | 0.67   | 1.38| 87              | 105             |
| 16        | O           | 1.6      | 18        | 27                                        | 0.28           | 4.18   | 228      | 0.46   | 2.18| 23.3            | 31              |
| 17        | O           | 5        | 72        | 27                                        | 0.29           | 4.28   | 211      | 0.44   | 1.79| 38              | 50              |
| 18        | O           | 1.7      | 72        | 27                                        | 0.15           | 4.52   | 278      | 0.41   | 1.96| 9.8             | 17.1            |
| 19        | P           | 7.8      | 66        | 27                                        | 0.28           | 4.72   | 137b     | 0.38   | 1.90| 36              | 45              |
| 20        | P           | 7.8      | 18        | 27                                        | 0.04           | 5.06   | 263      | 0.34   | 1.98| 6.3             | 21.7            |
| 21        | Q           | 34.2     | 18        | 27                                        | 0.12           | 5.10   | 232      | 0.33   | 1.59| 10.1            | 39              |

a Meq NaOH/g of salt-form polymer to titrate to pH 7.6.

b These values determined by extrapolating the experimental curve.
add-on was high. Other experiments were oriented toward increasing gel content or changing other properties. Gelatinized starch was used in a few batches, for example, and was air dried or cooled in the refrigerator in an attempt to increase crosslinking by retrogradation or crystallization. In other experiments, a crosslinking agent, epichlorohydrin, was introduced to increase crosslinking and amount of gel fraction. Since this treatment was effective, other attempts were discontinued.

The carboxyl add-on varied from 0.06 moles per mole anhydroglucose unit (AGU) to 1.4 (Table I). These data were obtained from the gel fractions after isolation. The yields of carboxymethylation on the starch were up to 86% of amount of chloroacetate in the reaction mixtures (batches J and K) but were variable. Individual yields are not given, but yields appeared to depend mostly on concentration of starch and reactants in the suspending solvent. In batches J and K, which were duplicate runs, weight of starch was 88% of weight of water, and no liquid was added. The problem of the relatively large amount of soluble material was not completely solved and deserves further attention. In this report, our emphasis is on the gel material that occurred in the material at hand.

The gel fraction of each CMS batch was isolated and its properties were determined (Table II). The fraction of gel recovered was sometimes low, as noted. The fractionation procedure is adequate because H-SPAN or other material that is mostly gel has a high recovery when processed similarly.

Some CMS material was crosslinked to promote gel formation, either in the mixer (batches F, J, and K) or in separate portions of a CMS batch (batches O and P), to compare the effects of different amounts of crosslinking in a given CMS batch.

Sometimes, differences in properties were observed that were difficult to evaluate. As an example, CMS batches J and N were duplicates, except that J was mixed continuously during the crosslinking reaction and N was not. The properties of their gels, 10 and 15, are similar (Table II); however, they were very different in appearance. Gel 10 was very smooth and easy to measure; 15 was more granular, opaque, and rough on the free surface, even though it had been ground before the gel was isolated. It was difficult to measure because it tended to come out of the rheometer. Both gels had particles of about the same size, but those in N seemed to be more agglomerated or rougher in appearance in excess salt. This difference deserves further study.

Comparison with Closely Packed Gel Thickeners

The gel material in CMS should behave as a polyelectrolyte in swelling and as a closely packed gel thickener in rheology at sufficiently high concentration. Gel 14 (Table II) was checked in detail to compare it with our other examples. Viscosity $\eta$ of the gel suspension in water was shear-rate thinning, like other polymeric material (Fig. 1). The shear modulus $G$ was not constant with shear rate $\dot{\gamma}$, but rose at higher $\dot{\gamma}$. In our earlier studies on H-SPAN gels, $G$ was constant with $\dot{\gamma}$ or nearly so, but $G$ for Carbopol-941 was curved as in Figure 1. All of the CMS gel preparations had curves for $G$ versus $\dot{\gamma}$ similar in shape to that in Figure 1. This slope prevents our making an absolute interpretation of $G$ as an indication of crosslink density; but since all curves were similar, the values
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Fig. 1. Relationship to shear rate $\dot{\gamma}$ of viscosity $\eta$ and shear modulus $G$ for gel 14 in water: (●) $\eta$, (○) $G$.

of $G$ at $\dot{\gamma} = 100$, $G_{100}$, should indicate the relative value of modulus between gels.

In an ideal rubbery network, $G$ defines the number of crosslinked chains, eq. (7). The reduced modulus $G/c^{1/3}$ corrects for varying concentration of polymer in the swollen gel and is nearly constant with $c$ for other gel thickeners when the gel particles are closely packed. The values of $G_{100}/c^{1/3}$ for gel 14 (Fig. 2) are nearly constant on dilution in isoionic solvent, provided $cQ$ is significantly greater than 1. When gel 14 was diluted in water, $G_{100}/c^{1/3}$ rose, as is usual for other closely packed gels (Fig. 2).

The reduced viscosity function $\eta/cQ$ is nearly constant for closely packed thickeners, diluted in either salt solution or water, provided $cQ > 2$. The behavior of gel 14 (Fig. 2) is typical of other members.

Swelling behavior of gel 14 in water and salt solution was essentially linear with $Q^{-1/2}$ (Fig. 3) but is somewhat curved at the high end. For the other CMS gels also, plots were linear up to $Q^{-1}$ in the range of 0.01 to 0.02, and then were curved. The cellulose graft copolymer studied earlier was strongly curved above $Q^{-1} = 0.008$. The value of $\phi$ needed to determine $\mu$ was calculated from Manning’s theory, eqs. (3) and (4), and is given in Table II for each of the gels. In the presence of salt, it is assumed that the additivity law holds true.

Fig. 2. Reduced viscosity function $\eta_{100}/cQ$ and reduced modulus function $G_{100}/c^{1/3}$, plotted against reduced concentration $cQ$ for gel 14: (●) diluted in water; (X) diluted in isoionic NaCl.
Viscosity Correlated with Modulus and Ionic Content

For each gel preparation, the values of $\eta$ and $G$ were measured as functions of $\gamma$, and swelling curves in water and salt solutions were determined. Then the reduced variables $\eta_{100}/cQ$ and $G_{100}/c^{1/3}$ at $\gamma = 100$ were calculated (Table II). The relationship between the plateau values, $[\eta_{100}/cQ]_p$ and $[G_{100}/c^{1/3}]_p$, for all gel suspensions appears in Figure 4. When the value of $cQ$ for the stock gel suspension was lower than 3, the true plateau values were estimated by multiplying by factors representing the change with $cQ$ taken from the water dilution curves in Figure 2. These estimated values were used in Figure 4 and in the statistical analyses. In this series, as for H-SPAN, a greater amount of apparent crosslinking as indicated by $[G_{100}/c^{1/3}]_p$ results in an increase in $\eta$ as well as in $[\eta_{100}/cQ]_p$. Our earlier H-SPAN curve and data are given for comparison.

Multiple regression analysis of $[\eta_{100}/cQ]_p$ on $I$ and $[G_{100}/c^{1/3}]_p$ as independent variables was performed for the CMS gels. Logarithms of all three variables were used to obtain an equation with a power law relationship. The linear (in logs of variables) regression equation was

$$[\eta_{100}/cQ]_p = 7.78 \times 10^{-4}(I^{0.013})[G_{100}/c^{1/3}]_p^{1.06}$$ (9)

Fig. 4. Relationship between the plateau value of the reduced viscosity function, $[\eta_{100}/cQ]_p$, and the plateau value of the reduced modulus function, $[G_{100}/c^{1/3}]_p$, for all CMS gels (●) and for earlier data on H-SPAN (×). Numbers refer to gel preparation in Table II.
The standard error of estimates of $\log [\eta_{100}/cQ]_p$ was 0.223, which corresponds to a 66% mean variation from the regression equation.

The analysis confirms our earlier conjecture that the reduced viscosity of closely packed gel suspensions is determined mainly by the elastic structure that gives rise to the modulus. The exponent for $[G_{100}/c^{1/3}]_p$ is nearly unity.

There was virtually no dependence of $[\eta_{100}/cQ]_p$ on $I$, as indicated by the low experimental exponent for $I$. Correlation with $I$ was not significant. The same information is shown by the lack of drift with number sequence (increasing $I$) in Figure 4. Multiple regression using $I\phi$, as suggested by theory, eq. (5), and $[G_{100}/c^{1/3}]_p$ as independent variables led to the same conclusions. Values of $\eta$ do depend on $I$, but the increased $\eta$ with higher $I$ is compensated in $[\eta_{100}/cQ]_p$ by a higher $Q$.

The line for the earlier H-SPAN series is somewhat displaced from the average position of the CMS data. Lines describing different series of H-SPAN samples are also somewhat displaced from each other, but the slopes are similar. Reasons for this variation among different series are not understood. In the CMS series the variation of $G$ with $\gamma$ makes it difficult to compare quantitatively with other materials, but the common slope value of unity is a valid comparison. The correlation in Figure 4 does have the advantage that both $\eta$ and $G$ are measured at the same $\gamma$, and hence the factors determining $G$ under these conditions would also affect $\eta$, perhaps proportionately.

**Correlation of Swelling Volume with Modulus and Titer**

From the swelling curves of CMS gels as typified by Figure 3, the values of $Q$ in $\mu = 0.01$, $Q_{0.01}$, were interpolated. These values are given with $Q$ in water, $Q_{H_2O}$, in Table II. (For four gels, as indicated in Table II, $\mu$ in water was higher than 0.01. For these gels, plots of $Q^{-1}$ versus $\mu^{1/2}$ were extrapolated to $\mu = 0.01$, a value unattainable in reality.)

Multiple regression analysis of $Q_{0.01}$ on $I\phi$ and $[G_{100}/c^{1/3}]_p$ as independent variables was performed with data on all gels. Logarithms of all three variables were again used to obtain a power law relationship among variables as predicted by eq. (8). The calculated regression equation was

$$Q_{0.01} = 523(I\phi)^{0.78}[G_{100}/c^{1/3}]_p^{-0.15}$$

The standard error of estimate was 0.114 in the logarithm, corresponding to a mean variation of 30% from the regression equation. The theoretical eq. (8) gives

$$Q_{0.01} \sim (I\phi)^{1.2}[G/c^{1/3}]_p^{-0.6}$$

so the experimental exponents are both less in magnitude than the theoretical ones. $I\phi$ and $[G/c^{1/3}]_p$ do have major effects on $Q$, but the functional dependence of $Q$ on these variables is less than predicted by theory for these CMS gels.

Gels no. 16 to 21 have approximately the same $I$ as does H-SPAN. Their $I\phi$ values are somewhat greater, because the ions are placed on the starch chains rather than closer together as on the grafted side chains in H-SPAN. According to the theory, e.g., eq. (12), the greater $I\phi$ values of the CMS gels should allow greater $Q$. Their $Q_{0.01}$ values, though, are only about 40% of those for a H-SPAN
with comparable $G$. This difference is not likely caused by difficulty in measuring $G$ because $[G/c^{1/3}]_p$ for the CMS gels would have to be at least ten times the measured values to give coincidence with H-SPAN data. The lowered $Q$ observed in CMS gels compared to H-SPAN is similar to the lower $Q$ observed in our series of H-SPAN gels with constant $I$ but shorter grafted chains, as compared to the long-chain grafts. Apparently, long grafted chains are necessary for high swelling capacity in starch-based polymers. For H-SPAN, the lower $Q$ of gels with shorter grafted chains was explained partially, but not entirely by their higher values of $[G_{100}/c^{1/3}]_p$. $Q$ for these gels was only about 60% of that for long-chain H-SPAN with similar $[G_{100}/c^{1/3}]_p$. Both this result and our present data on CMS gels suggests that experimental measures $I\phi$ and $[G_{100}/c^{1/3}]_p$ do not carry sufficient information to completely characterize the swelling behavior of closely packed thickeners in general. The experimental measures do correlate well with swelling and viscosity properties and therefore appear to be important though incomplete descriptions of molecular structure in the gels.

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