

# Influence of Formaldehyde on Viscosity Stability of Concentrated Aqueous Amylose Solutions

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**T**HIS STUDY of amylose-formaldehyde-water solutions forms a part of a general investigation into the properties of amylose as a new raw material for the production of films, fibers, coatings, etc., resembling those based on cellulose. Since both cellulose and amylose are polyglucoses, one must expect them to behave similarly.

Whereas cellulose is insoluble in water, amylose is soluble. However, depending on the amylose concentration, such solutions flocculate or solidify to gels after a very short time. The solutions can be stabilized by adding formaldehyde. Although it is possible to make solutions which will be stable for years by choosing appropriate concentrations of amylose and formaldehyde, one can make solutions which at first show practically no change in viscosity, but after standing suddenly begin to increase in viscosity until eventually the whole system gels. This behavior resembles that of viscose, the aqueous alkaline solution of cellulose xanthate, the base solution for the production of viscose rayon and cellophane.

The viscosity increase of viscose solution is important for the regeneration reaction, whereby pure cellulose is formed by acid hydrolysis of the xanthates. To find out whether the viscosity increase of the amylose-formaldehyde system is of equal importance for its behavior in the regeneration step, the more unstable systems were studied in greater detail.

As the chemical aspects of these processes have been published (3), some of the physicochemical features of the amylose-formaldehyde-water system are discussed. Whereas for most viscometric studies of polymer systems very dilute solutions are preferred, this work was done with relatively concentrated systems to get information useful for practical technological purposes.

## EXPERIMENTAL DETAILS

The amylose used was obtained from potato starch by fractionation with magnesium sulfate (4). It is essentially the same product as the Superlose marketed in the United States by Stein, Hall & Co., Inc. According to the manufacturers, this amylose is highly retrograded. This is demonstrated by the solubility of the product. Several recrystallizations with 1-butanol show no substantial increase in the iodine absorption value. Therefore, the amylose was used as is and the laborious recrystallization was left out. In Table I the analyses of the samples are given with the numbers of the figures connected with these samples.

Iodine absorption values were determined with a Philips electrometer according to the method of Bates, French, and Rundle as modified by Wilson, Schoch, and Hudson (13).

Viscosity was measured in a Ubbelohde viscometer at 25° C. The dry amylose was dissolved by stirring for 6 hours in a 1*N* aqueous potassium hydroxide solution at 0° C. in a stream of oxygen-free nitrogen. The degree of polymerization values of amylose were calculated from the intrinsic viscosity by the relation found by Potter and Hassid (7).

$$[\eta] = 0.00166 \overline{D.P.}$$

Aqueous amylose solutions were prepared from a stock solution which contained 10% by weight of amylose. This solution was kept well above the gelation temperature—e.g., 100° C. By diluting the stock solution with water at temperatures between 70° and 90° C., the lower concentrations were made. The higher concentrations were prepared by evaporation of water under normal pressure. The amylose solutions in dilute formaldehyde were made from a stock solution containing 10% by weight of amylose and 10% by weight of formaldehyde. By diluting this solution, followed by distillation under reduced and/or normal pressure, the different concentrations of amylose and formaldehyde were prepared. The precise formaldehyde concentrations were estimated according to the method of Weinberger (11) as modified by Yoe and Reid (14). The stock solutions of amylose-water and amylose-formaldehyde-water were produced continuously in a closed stainless steel apparatus consisting of a gear pump, a heat exchanger operated with steam under a pressure of 90 p.s.i., and a cooling section. The apparatus was designed to produce 10 liters of 10% amylose solution per hour. At this rate there is a residence time of 300 seconds at 160° C. The pH was kept in the range of 5 to 7 by addition of small amounts of sodium hydroxide.

Table I. Characteristics of Amylose Samples Used throughout This Work

Sample	Iodine Abs., Wt. %	Intrinsic Viscosity, $[\eta](1.0N\text{ KOH})$	Figure
A100	19.6	1.10	1, 2
A230	19.3	0.79	3, 4, 5

Measurement of the intrinsic viscosity before and after dissolving the amylose shows the initial *D.P.* value to be decreased by at most 5% of the original value. Viscosity of the concentrated systems was measured with a Brookfield rotation Synchro-lectric viscometer, Model LVF. All systems were kept and measurements were performed at a constant temperature of 23° ± 0.5° C. Amylose was regenerated quantitatively from amylose-formaldehyde-water solutions for analytical purposes as follows:

To 20 ml. of amylose-formaldehyde solution containing approximately 5% of amylose were added 10 ml. of an alcoholic ammonia solution, made by mixing 100 ml. of 25% aqueous ammonia with 900 ml. of 96% ethyl alcohol. After stirring, 70 ml. of 96% ethyl alcohol were added. The precipitated amylose was separated from the mother liquor by centrifugation.

The sediment was suspended in 100 ml. of 96% ethyl alcohol and separated in the centrifuge; this procedure was repeated twice. The hexamethylenetetramine formed by the reaction of formaldehyde with ammonia was no longer present.

The alcohol was displaced by washing the sediment with 100 ml. of dry ether, and the product was dried in an oven for 6 hours at 60° C. and brought to constant weight in a vacuum desiccator over phosphorus pentoxide.

The Phywe supercentrifuge was used to separate the amylose microcrystals. Ultracentrifuge measurements were performed in the Phywe ultracentrifuge.

## EXPERIMENTAL RESULTS

**Amylose-Water System.** Clear molecular disperse solutions of amylose were obtained by heating suspensions of amylose in water for 5 minutes at 160° C. under a pressure of 90 p.s.i. Even retrograded amylose dissolves perfectly under these conditions. After the solutions have been cooled to room temperature, those containing less than 5% of amylose flocculate while solutions of higher concentration rapidly solidify to opaque white gels. Figure 1, an amylose solubility curve, is valid for amylose in the range of  $\bar{M}_w$  values from approximately 500 to 1000. This curve is a part of the normal temperature-composition diagram for this system.

These experiments show that the rate of gelation increases with increasing amylose concentration, representing the normal behavior in gelation reactions of most hydrophilic polymers in solution—e.g., gelatin, agar-agar, etc.

The amylose gels are opaque white brittle bodies, irreversible at normal pressures. Such gels do not show the phenomenon of syneresis to any appreciable extent. Microscopic examination of gel slices having a thickness of about 10 microns reveals that they possess a distinct granular structure. These phenomena point to a crystallization type of insolubilization. In this respect, all amylose solutions in water may be called supersaturated solutions.

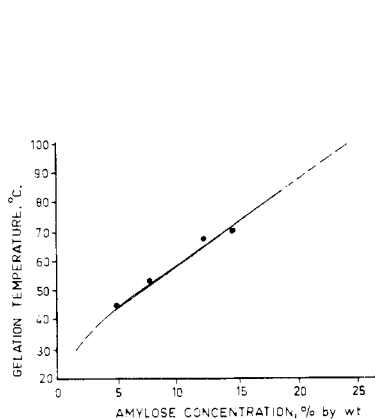


Figure 1. Gelation temperature as a function of amylose concentration

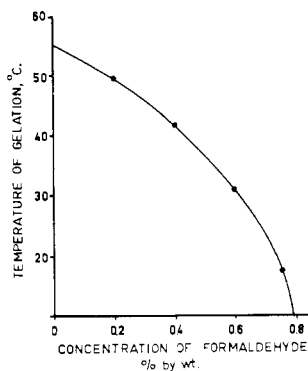


Figure 2. Influence of formaldehyde on gelation temperature of a 10% aqueous amylose solution  
Rate of cooling 2° C./min.

Figure 3. Influence of formaldehyde on rate of change of viscosity of aqueous amylose solutions

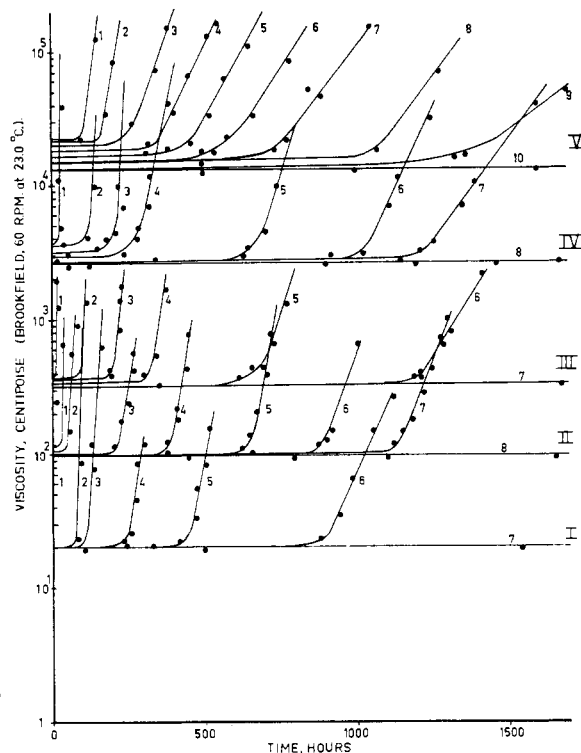


Table II. Compositions of Systems Described in Figure 3

Level Series	Amylose Concn., %	Formaldehyde Concn., Wt. %										pH
		1	2	3	4	5	6	7	8	9	10	
I	6.0	1.00	1.52	1.95	2.44	2.65	3.02	3.49	...	...	...	6.6
II	10.7	1.53	2.00	2.97	3.08	3.98	4.38	4.52	4.88	...	...	6.6
III	14.0	1.59	2.41	3.35	4.01	4.96	5.60	5.97	...	...	...	6.5
IV	20.0	1.75	2.21	2.48	2.67	3.59	5.00	5.34	5.93	...	...	6.6
V	26.0	2.47	2.66	2.90	3.11	3.37	3.59	3.84	4.22	4.56	4.85	6.5

**Influence of Small Quantities of Formaldehyde on Concentrated Aqueous Amylose Solutions.** In 1927 Samec (8) reported that 1% of amylose dissolved in water remained in solution in the presence of 17 to 36% formaldehyde, whereas without formaldehyde such solutions "coagulated to milky liquids" within one day.

Nevertheless, the influence of very low formaldehyde concentrations on concentrated amylose solutions is surprisingly strong (Figure 2). A formaldehyde concentration of only 0.8% by weight is sufficient to decrease the original gelation temperature from 55° to 10° C.

**Influence of Higher Formaldehyde Concentration on Concentrated Aqueous Amylose Solutions.** At increasing formaldehyde concentrations the gelation tendency decreases until it is almost nil. Viscosity measurements of a series of aqueous-formaldehyde systems at varying absolute and relative concentrations of both components over an extended period of time are shown in Figure 3 (compare with Table II).

To describe the regularities which clearly present themselves from these curves, tangents are drawn to them; the distance from the ordinate axis to the point of intersection of both tangents is called the stability of the system as measured in hours. From the slope of the right part of the curve the rate of gelation is calculated as

$$d \log \eta \times 10^2 \text{ hours}^{-1}$$

If the rate of gelation of each curve in Figure 3 is plotted vs. the stability, it can be shown that all systems under investigation demonstrate the same general interdependence

Table III. Precipitation of Amylose from an Unstable Aqueous Amylose-Formaldehyde System in Course of Time

Expt. No.	Time of Aging, Hours	Abs. Viscosity, Poises	Pptd. Amylose, Wt. % of Total Amylose	Intrinsic Viscosity in 1N KOH	Iodine Absorption, Wt. %
AK 0	0	6	0	0.79 <sup>a</sup>	18.7 <sup>a</sup>
AK 1	190	6	4.5	0.65	18.4
AK 2	260	8	6.8	0.66	17.9
AK 3	290	11	8.3	...	...
AK 4	340	54	10.5	0.64	18.7
AK 5	430	1100	50.4	0.69	19.4

<sup>a</sup> Values refer to total amylose dissolved.

(Figure 4). Moreover, the asymptotic character of this curve strongly suggests an ultimate instability of the formaldehyde-amylose systems.

Because of the interdependence of "stability" and "rate of gelation" it is immaterial which quantity is used to describe the influence of the concentrations of formaldehyde and amylose.

In Figure 5 the rate of gelation has been plotted as a function of the molar ratio of formaldehyde to amylose. The curves for the different amylose concentrations show a regular sequence with regard to the values of their absolute polymer concentrations. At constant molar ratio the rate of gelation decreases with increasing polymer concentration. As this is contrary to the general behavior of solutions of most hydrophilic polymers, it is the more surprising in respect to what was found for the amylose-water system.

**Solvent Properties of Aqueous Formaldehyde for Amylose.**

The stabilizing action of aqueous formaldehyde on amylose could simply be the result of physicochemical solvent properties. The solution stability depends on the concentration of both the amylose and the formaldehyde. In the case of a typical solvent action, the amount of solute which can be dissolved does not depend in general upon the solvent composition. Therefore, the stabilizing action of formaldehyde is probably due to the formation of a chemical complex between it and the polymer, rather than the solvent properties of aqueous formaldehyde solutions. However, this is difficult to determine for high solute concentrations in binary solvents like the formaldehyde-water system.

Therefore, the influence of the formaldehyde concentration on dilute solutions of amylose was investigated.

There is a slight increase in the solvent power with increasing formaldehyde concentration, which shows signs of leveling off at 10% formaldehyde concentration. Compared with other solvents—e.g., 1.00N potassium hydroxide—even a 10% formaldehyde solution is a rather poor solvent, as judged by the intrinsic viscosities ( $[\eta] = 2.22$  in 1.0N KOH and  $[\eta] = 1.05$  in 10% formaldehyde).

It is impossible to dissolve dry amylose in cold or boiling dilute or concentrated aqueous formaldehyde solutions. On the other hand, aqueous 1.0N potassium hydroxide dissolves amylose cold as easily as at higher temperatures. Aqueous amylose-formaldehyde solutions must be prepared under pressure to attain the solution temperature.

The initial viscosity values at time = 0 at constant amylose concentration decrease with increasing formaldehyde concentration (Figure 3).

Although the authors advocate a chemical theory to explain the solvent properties of aqueous formaldehyde, this behavior can at least formally be accounted for by the increase in solvent power with increasing amounts of formaldehyde.

**Influence of pH.** The stability of the aqueous amylose-formaldehyde system is markedly dependent on its pH value. This offers an impressive argument for the existence

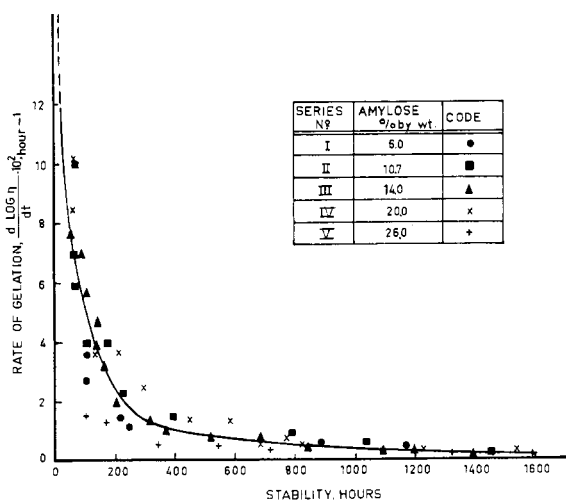


Figure 4. Rate of gelation vs. stability

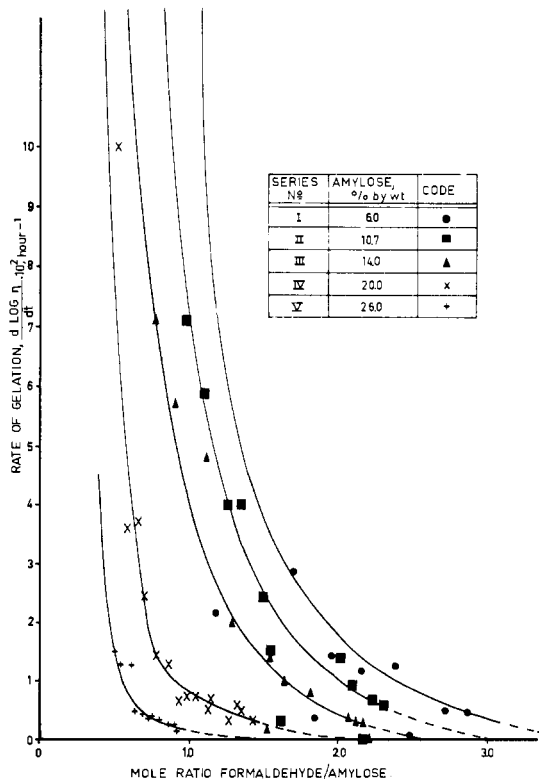


Figure 5. Rate of gelation as function of molar ratio of formaldehyde to amylose

of definite chemical compounds resulting from chemical interaction of the aldehyde with the polymer. There is a strong decrease in stability after the pH is raised above 7. This is in accordance with the findings of Bieber and Trumpler (2). In the course of their studies on the polarographic reduction of formaldehyde in aqueous solution, they reported that addition of 0.5% of starch to an alkaline formaldehyde solution has no influence on the maximum in the potential-current curve. Addition of the same amount of starch to an acid formaldehyde solution lowers this maximum appreciably. They explain this behavior in terms of absorption of the starch to the cathode. However, all the evidence points to the fact that under alkaline conditions there is no chemisorption of formaldehyde on starch and consequently no change in the maximum, whereas at pH values below 7 there is chemisorption of formaldehyde by the starch molecules. Consequently the free formaldehyde concentration diminishes and, therefore, the maximum in the polarographic curve decreases.

**Ultracentrifugal Analysis.** Aqueous alkaline solutions of cellulose xanthate demonstrate a dependence of viscosity on time. The viscosity rise is explained in terms of association of the cellulose molecules to build micellar aggregates (6).

To determine whether this type of mechanism is the cause of the viscosity increase in amylose solutions, the sedimentation behavior of an unstable amylose-formaldehyde solution was investigated at different periods of aging.

It was found that:

The sedimentation rate of the dissolved amylose remains constant over the entire period of time.

Micellar aggregates of two, four, or even 100 molecules are absent.

There is a steady decrease of the amylose concentration in the course of the "ripening" time of the solution.

This must be the result of the formation of macroscopic particles, which therefore rapidly settle in the high gravitational field of force of the ultracentrifuge.

**Characterization of Macroscopic Amylose Aggregates.** As a rule, unstable amylose-formaldehyde systems develop a slight turbidity even before they change their viscosity noticeably. As the viscosity increases, the turbidity also increases. Moreover, there is a general dependence of both stability and turbidity on the molecular weight of the dissolved amylose. Comparison of solutions which differ only with respect to the molecular weight of the dissolved amylose show that after equal times of aging those prepared from the lower molecular weight amylose have the greater rates of increase of viscosity and turbidity. This is in close agreement with the work of Whistler and Johnson (12), who found that the rate of retrogradation of amylose in water solution shows the same dependence on molecular weight. Phase contrast microscopy reveals the presence of minute particles which are in lively Brownian motion. Moreover, a striking difference in morphology exists between the particles precipitated from solutions of low molecular weight amylose and those from the species of higher molecular weight. The former systems contain great numbers of tiny rod-like particles, whereas the latter merely show the presence of point-like particles. Generally, amylose with intrinsic viscosity values of 1.0 or higher in 1N KOH forms only the point-like particles, whereas amylose with  $[\eta] = 0.8$  in 1N KOH or lower always forms the needle-shaped particles. The amylose of lowest molecular weight investigated showed an intrinsic viscosity value of  $[\eta] = 0.4$  in 1N KOH. Figure 6 shows a microphotograph of the anisotropic type of particles. They have a length of 2 to 3 microns and their thickness is 0.2 micron on the average.

Both types of particles were separated with a super-centrifuge and analysis shows them to be identical with the original amyloses, except that the molecular weights, as judged from their intrinsic viscosity values in 1N KOH,

were somewhat lower than those of the starting material (Table III).

The amylose solution contained: 17.5% by weight of an amylose with  $[\eta] = 0.79$  in 1N KOH and 3.4% by weight of formaldehyde. This solution eventually forms the anisotropic type of particles.

The authors consider the needle-shaped retrograded amylose particles as microcrystals of amylose. As far as they are aware, this type of particle has not been reported previously. The retrogradation of amylose from water solutions normally is a very rapid process. Therefore, perfectly shaped crystals are not to be expected, unless the crystallization can be regulated. In this respect formaldehyde may be considered a retarding agent for the crystallization of amylose. Furthermore, these particles show a B-type x-ray diagram, as is normally found for retrograded amylose. Consequently the material is insoluble in both cold and hot water, as well as in aqueous solutions of formaldehyde. The amount of precipitate formed and the viscosity increase with time, together with the constant sedimentation behavior in the ultracentrifuge, lead to the unavoidable conclusion that the rise in viscosity is caused by precipitate formation.

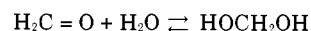
Considering the extremely high viscosity values of these systems, however, one can scarcely believe them to be caused by suspended particles of the dimensions mentioned. Therefore, the presence of other types of association products cannot be excluded. One may postulate the existence of molecular aggregates of amylose possessing a very low degree of association and which remain fully solvated in the solution and so cannot be resolved by the microscope.

## DISCUSSION

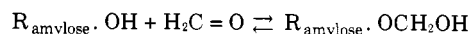
The diversity of the phenomena dealt with above demonstrates the complicated nature of the system investigated. Much additional experimental work is needed. A tentative explanation of some of the more important results is given here.

**Stability Period.** In the amylose-formaldehyde-water system several equilibria may be present, the most prominent being:

Hydration-dehydration of monomeric formaldehyde according to



Hemiacetal formation between amylose-hydroxyl functions and formaldehyde according to



Association of amylose, which essentially is an irreversible crystallization reaction under the prevailing circumstances.

Alcohols and formaldehyde react exothermically to form aldehyde-alcoholates or hemiacetals (10). In an analogous reaction, amylose will be replaced by formaldehyde to form hydroxymethyl groups. According to the degree and homogeneity of this substitution, the molecular symmetry of the amylose chain molecules is more or less disturbed. Consequently, the crystallization (retrogradation) of the amylose molecules is partially or totally prevented. This is the type of reasoning Deuel (5) used to explain analogous phenomena in solutions of pectic substances. Moreover, essentially the same explanation must be given to the phenomena of the water solubility of cellulose ethers of very low degree of substitution—e.g., hydroxyethyl-cellulose.

Since the solutions of amylose are made at temperatures high enough to prevent the crystallization of the polymer effectively, one can easily imagine that when such solutions are cooled, the system will need time to reach equilibrium at this new temperature. If the hemiacetal groupings



Figure 6. Amylose crystals  
Linear magnification 1600 x  
Leitz Ortholux, oil immersion, phase contrast

occupied their places along the amylose chain molecules independent of time, and if the number of substituting groups were high enough, amylose should never crystallize. However, because of the dynamic nature of this type of substitution, places along the amylose chain molecule formerly occupied by formaldehyde become vacant in the course of time. During the small interval of time, once such empty places exist, a second amylose molecule with free hydroxyl function in close proximity to the first one can associate to form a center of crystallinity. As aqueous formaldehyde showed its complete lack of dispersing power as a solvent for amylose, it may be inferred that such bonds, once formed, are never broken. Increase of the formaldehyde concentration naturally increasingly opposes this process. Thus, hydroxymethylation (reversible) has to compete with amylose crystallization (irreversible) and this competitive reaction is the time known as "stability." It is also evident that the stability, which is the reaction time during which these equilibria are established, has to depend on both aldehyde and polymer concentration.

**Decrease in Rate of Gelation with Increasing Polymer Concentration at Constant Molar Ratio of Formaldehyde to Amylose.** If the hydroxymethylation of amylose is accepted as the cause of its solubility in aqueous formaldehyde solution, the problem arises as to how the degree of substitution of the amylose varies with the absolute and relative concentrations of the aldehyde and the polymer. Assuming, as a first approximation, that the degree of substitution of the amylose at constant molar formaldehyde-amylose ratio is independent of the absolute polymer concentration, but is dependent only on the molar ratio of aldehyde to polymer, then the decreasing rate of gelation with increasing polymer concentration at constant molar ratio can be accounted for by an increase in the diffusional resistance caused by the exponential viscosity increase which normally accompanies the increase of the polymer concentration.

In accordance with this explanation, it can be seen that in the region of very high viscosities an especially strong influence exists (in Figure 3, compare curves IV and V with I, II, and III). An alternative explanation might be that the degree of substitution of amylose by formaldehyde is a function of both the molar ratio and the absolute concentrations, so there may be a chance that with increasing formaldehyde concentration the degree of substitution of the polymer increases progressively. In that case the decrease in the rate of gelation is a normal consequence of the higher degree of substitution of the amylose.

**Influence of pH Value on Stability.** Studies of Trumpler and Bieber (1) on the rate of dehydration of methylene glycol showed that this reaction is strongly catalyzed by hydroxyl ions. Though it is generally accepted that aldehyde alcoholates such as hemiacetals are more stable than aldehyde hydrates such as methylene glycol (9), there is no principal difference between the dehydration of methylene glycol and the dissociation of a hemiacetal into alcohol and monomeric aldehyde. Accordingly it would appear that the decrease in stability of amylose-formaldehyde solutions at pH 7 is caused by the dissociation of hydroxymethyl-amylose into formaldehyde and amylose under the influence of hydroxyl ions.

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