

Formation of a Copper-Sorbitol Complex in Copper Sulfate-Sorbitol Systems.

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(Figs. 1-7)

Previous works in our laboratory have been done to obtain some more valuable information on the state of minerals in food materials. From the view point of the importance of minerals in organisms, as ligands such nitrogen and oxygen compounds as amino acids and sugars are of interest because they occur abundantly in organisms. Among these compounds, several amino acids and sugars have been dealt with in the previous papers; the formation of iron-lactose,¹⁾ iron-ascorbic acid,²⁾ copper-glycine,³⁾ zinc-histidine,⁴⁾ zinc-cysteine,⁵⁾ and zinc-methionine⁶⁾ complexes was investigated. Sugar-alcohol, however, has not yet come under examination. Accordingly, in this work, the formation of a copper-sorbitol complex was examined with CuSO_4 -sorbitol solutions as the reaction system.

As for the copper-sorbitol complex, only a few studies have been reported. The formation of the complex is likely to occur in alkaline solutions,⁷⁾ and its composition is estimated to be 3:1⁸⁾ or 2.83:1⁹⁾ in the molar ratio of copper to sorbitol. In general, the complex has a tendency to be formed in rather strongly alkaline solutions.⁷⁾⁻¹⁰⁾ However, such a condition of high pH is not available for considering the formation of this complex during the processing of food materials or in the gastro-intestinal tracts. The pH value of these surrounding media is mostly a weakly acidic or a weakly alkaline one. In this work, therefore, the formation of copper-sorbitol complex under these mild conditions also is examined and the relationship between the solubility and the chemical structure of the complex will be discussed herein.

MATERIALS AND METHODS

1. Reagents

All reagents used were of guaranteed grade, and were dissolved in distilled-deionized water.

2. Reaction systems

Various reaction systems with different molar ratios of copper/sorbitol were prepared by mixing standard CuSO_4 and sorbitol solutions at a given ratio. The pH of the reaction

systems was adjusted to the desired value with 2N-NaOH, 0.1N-NaOH, or 0.1N-HCl. Solutions of 10^{-1} M CuSO_4 and 10^{-2} M sorbitol were used as stock solutions.

3. Identification of the copper-sorbitol complex

The following two methods were applied to ascertain the formation of copper-sorbitol complex in the reaction systems.

(1) Determination of absorption spectra

Absorption spectra of CuSO_4 and sorbitol solutions, and CuSO_4 -sorbitol reaction systems were determined with a Hitachi spectrophotometer Type-124. When a precipitate was formed in the reaction systems, the absorption spectra were determined after removal of the precipitate by centrifugation (3,000 rpm, 30 min).

(2) Potentiometric titration

Potentiometric titration was performed with a Hiranuma potentiometric titration apparatus RAT-Type-101S, using a glass-calomel combination electrode. Titration was carried out with 5×10^{-2} N-NaOH under a stream of N_2 gas. The ionic strength of each reaction system was adjusted to 0.1 with a NaClO_4 solution before titration.

4. Determination of copper and sorbitol in reaction systems

(1) Copper

Copper was determined with a Hitachi atomic absorption spectro-photometer Type-207. When a precipitate was formed in the reaction systems, the determination was carried out on the supernatant which was obtained by centrifuging the reaction system at 3,000 rpm for 30 min.

(2) Sorbitol

A portion of the reaction systems on the above supernatant was acidified with 0.1N-HCl for the purpose of liberating the copper from copper-sorbitol complexes and was then treated with a column of Amberlite IR-120 to remove the copper. On the copper-free effluent, the sorbitol was determined by the periodate-oxidation method.

RESULTS

1. Absorption spectra of CuSO_4 -sorbitol systems

Absorption spectra of the reaction systems with different molar ratios of copper/sorbitol and pH are shown in Fig.1 and Fig.2. In the experiment shown in Fig.1, the reaction systems were of five groups with a molar ratio of 1/1~1/5. The pH of each group was adjusted to the desired value, eleven kinds in all, within a range of 3~13. The absorption spectra of these reaction systems were determined after standing for 30 min at $20 \pm 0.5^\circ\text{C}$. In the cases of the solutions with pH 6~10, the absorption spectra did not illustrate because they were scarcely observed.

As shown in Fig.1, the spectra of the acidic reaction systems were similar to that of the standard CuSO_4 solution alone, while those of the alkaline reaction systems were very different from that of the standard solution in the range of their absorption maxima; their maxima shifted to longer wavelengths.

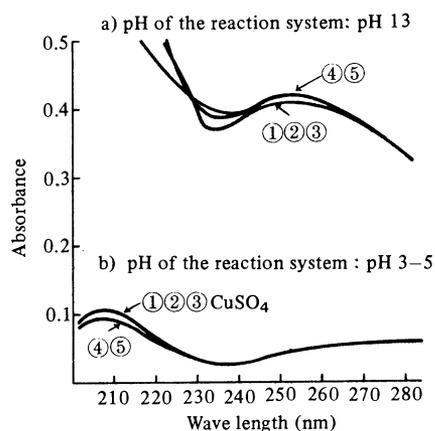


Fig. 1 Absorption curves of five copper-sorbitol systems with different copper/sorbitol ratios of less than 1. Molar ratio of the copper/sorbitol: ①, 1/1; ②, 1/2; ③, 1/3; ④, 1/4; ⑤, 1/5

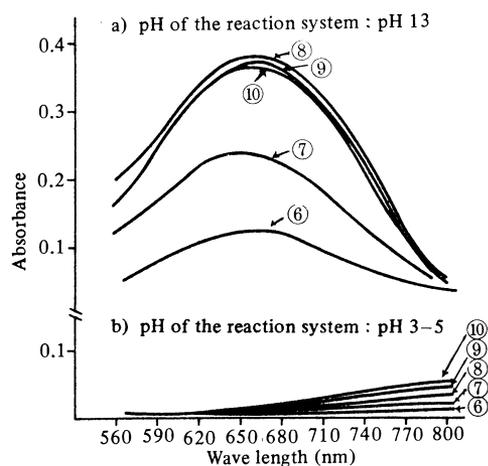


Fig. 2 Absorption curves of five CuSO_4 -sorbitol systems with different copper/sorbitol ratios of more than 1. Molar ratio of the copper/sorbitol: ⑥, 1/1; ⑦, 2/1; ⑧, 3/1; ⑨, 4/1; ⑩, 5/1

Fig.2 shows the visible spectra of the other five groups with copper/sorbitol molar ratios of 1/1~5/1. Other conditions were the same as described in Fig.1. Illustration of the absorption spectra of the reaction systems with pH 6~10 has been omitted for the same reason as described above. The reaction systems in this experiment contained copper in excess compared to the amount of sorbitol. A strong and wide absorption band, which caused by the excess copper ions, appeared in the ultraviolet range, so that the ultraviolet spectrum of the copper-sorbitol complex could not be realized even if they produced to an appreciable amount in the reaction system. Consequently, only the visible spectra were examined on these reaction systems.

The reaction system showed an absorption maximum at 650 nm at the alkaline pH, but not at the acidic pH. The absorbance at 650nm increased with increasing the molar ratio of copper to sorbitol up to 3/1, after that further increase of the copper ratio had no effect on the intensity of the absorption (Fig.2- ⑨, ⑩).

2. Potentiometric titration curves

The formation of copper-sorbitol complex in the reaction systems was ascertained by examination of the potentiometric titration curves. Fig.3 shows the titration curves of five reaction systems with different molar ratio of copper/sorbitol. Lowering of pH was observed at about pH 6.5 on all the CuSO_4 -sorbitol reaction systems.

3. Determinations of copper and sorbitol in reaction system

On the reaction systems of pH 6~10, in which precipitates were formed, removal of the precipitates from the system resulted in an almost total loss of the absorbance due to copper ions or copper-sorbitol complexes. The formation of precipitates is generally observed in the solutions of many kinds of metal especially in the alkaline pH range; this is attributed to the hydrolytic polymerization of free metal ions. In this experiment,

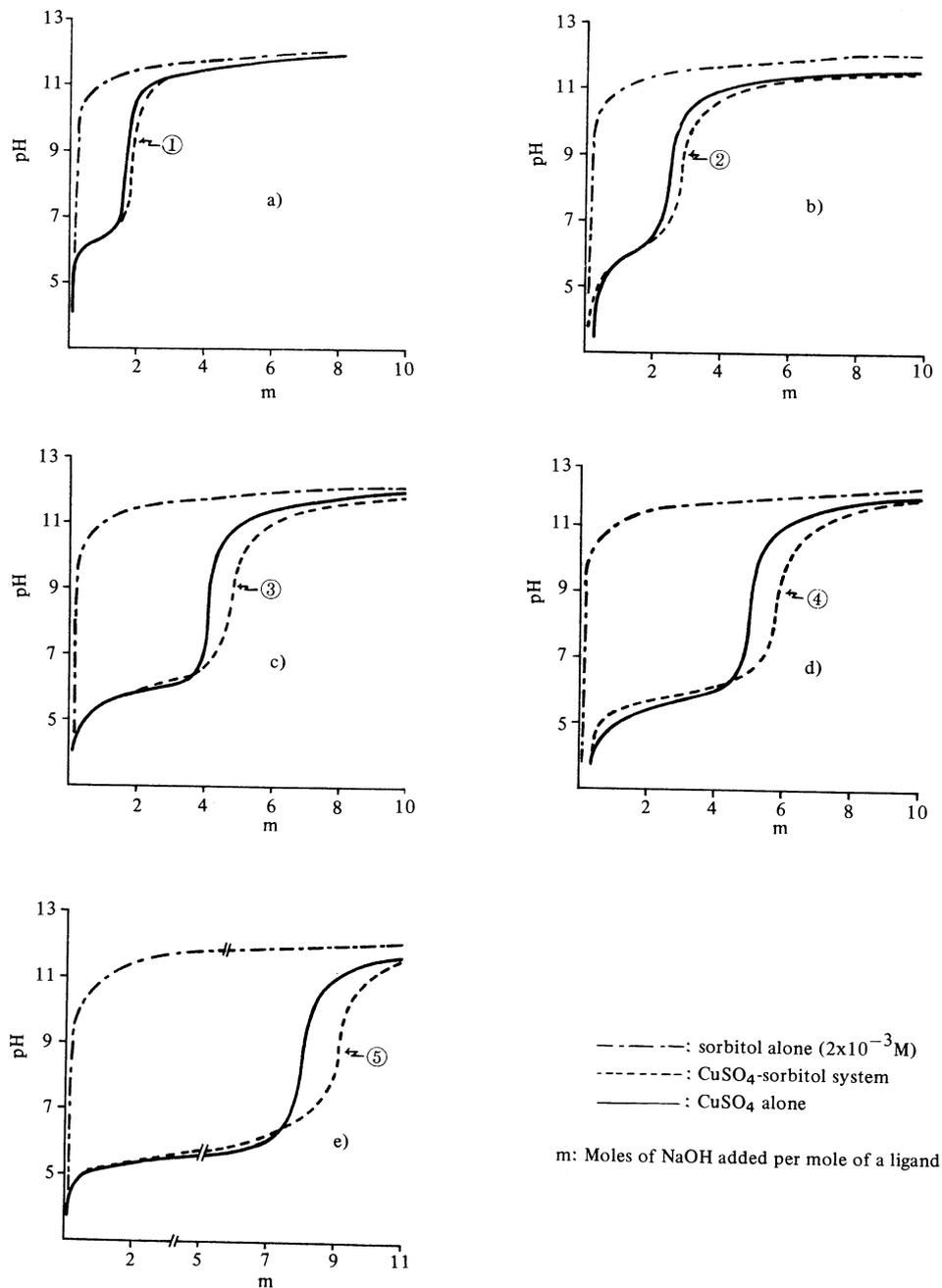


Fig. 3 Potentiometric titration curves of five reaction systems with different copper/sorbitol ratios.

Molar ratio of the copper/sorbitol: ①, 1/1; ②, 2/1; ③, 3/1;
④, 4/1; ⑤, 5/1

such precipitation was examined with the CuSO_4 -sorbitol systems of which the alkalinity and the molar ratio of copper/sorbitol were varied, respectively. Solutions of 32 types in all were prepared as follows, the alkalinity as the concentration of NaOH: 10^{-1} , 5×10^{-2} , 10^{-2} and 5×10^{-3} N; the copper/sorbitol ratio of each alkaline solution: 8 types ranging from 1/1~10/1. Individual reaction system was allowed to stand for 30 min at $20^\circ \pm 0.5^\circ \text{C}$ and the precipitates formed were separated by centrifugation (3,000 rpm, 30 min). The amount of the copper in the supernatant was determined and was regarded as that of the soluble copper. The results obtained are shown in Fig.4.

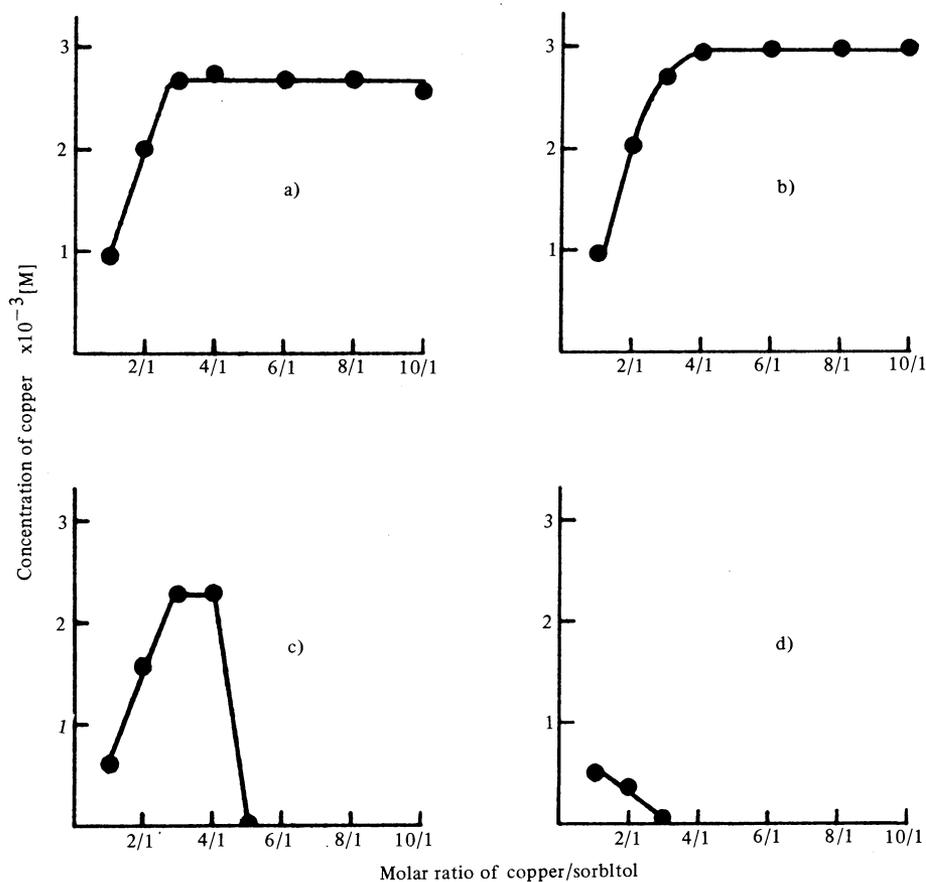


Fig. 4 Effect of alkalinity on the content of soluble copper in various reaction systems.

Concentration of NaOH : a), 10^{-1} N; b), 5×10^{-2} N; c), 10^{-2} N; d), 5×10^{-3} N

The amount of the soluble copper increased with the rise of the copper/sorbitol ratio up to 3/1 (Fig.4-a,b), but the amount remained constant above the molar ratio of 4/1. These results suggest that the copper-sorbitol complex formed is composed of one mole of sorbitol and three moles of copper. Fig.4-a and 4-b show the results obtained with

the two systems having the alkaline concentration of 10^{-1}N and $5 \times 10^{-2}\text{N}$. At the lower alkaline concentrations, 10^{-2} and $5 \times 10^{-3}\text{N}$, the amounts of the soluble copper were small (Fig.4—c,d).

Next we examined the effect of pH on the formation of the copper-sorbitol complex in the reaction systems, of which the molar ratio of copper/sorbitol was restricted to 1/1, 2/1, and 3/1. The pH of each system was adjusted to a given value within the range of pH 7~13.

As will be seen from Fig.5, the amount of the sorbitol in the supernatant decreased markedly with the rise of the pH up to about 10, but it increased sharply at higher alkaline pH values. A critical point appears to exist in the range between pH 9.5 and pH 10.6. On the other hand, the amount of the soluble copper also increased sharply when the pH of the reaction system exceeded 9.5 (Fig.6).

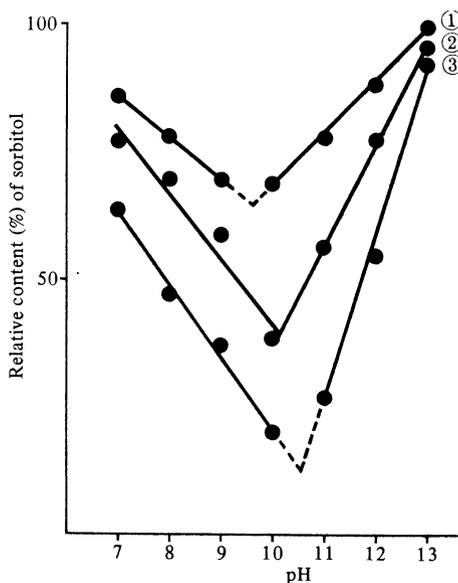


Fig. 5 Changes of the amount of sorbitol in the centrifugal supernatant.
Molar ratio of the copper/sorbitol:
①, 1/1; ②, 2/1; ③, 3/1

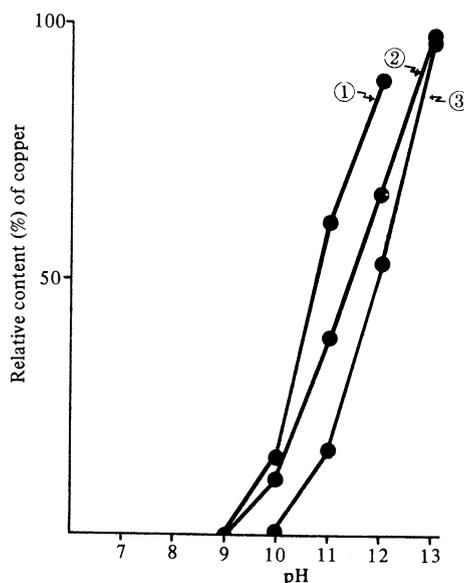


Fig. 6 Changes of the amount of copper in the centrifugal supernatant.
Molar ratio of the copper/sorbitol:
①, 1/1; ②, 2/1; ③, 3/1

DISCUSSION

1. Formation of the copper-sorbitol complex

In most cases, the formation of a certain amount of a metal-chelate in a solution brings about some changes in the absorption spectrum of the solution. Such changes are apparently due to the formation of a certain new chelate ring between the component metal ion and the ligand molecule. In addition, the formation of a metal-chelate probably is accompanied by a decrease of the pH of the solution because one or more protons must be liberated from the ligand. In this experiment, such changes were also

observed. That is, the absorption spectrum of the copper-sorbitol system changed in the pH range of 11~13 (Fig.1 and 2), and the decrease of pH was also ascertained by the potentiometric titration as illustrated in Fig.3. The lowering of pH began at about pH 6.5 and it continued up to pH 11. These results suggest that the copper-sorbitol complex is easily formed in the reaction system at higher alkaline pH values than 6.5.

In Fig.1 and 2, however, the absorption curves of the reaction systems with the pH6~10 were not illustrated because of the fact that a large amount of gel-like precipitates was formed in the solutions and the centrifugal supernatant obtained after removal of the precipitates did scarcely show any distinct absorption spectra. Disappearance of the absorbance due to copper suggests that the copper exists in the gel-like precipitates and not in the supernatant in the pH range of 6~10. Accordingly, the copper-sorbitol complex formed within this pH range is considered to be insoluble. For the consideration of the chemical structure of the insoluble copper-sorbitol complex, those of the iron-sugar¹⁾ and the cobalt-gluconate¹²⁾ complexes provide some valuable information. By reference to them, a structure can be assumed for the insoluble copper-sorbitol complex; namely, it will be similar to the one in which a large number of copper atoms coordinate to one or more sorbitol molecules and each copper atom is polymerized simultaneously by olation into a high molecular weight copper-aquo complex. This assumption is supported by the fact that a considerable amount of sorbitol, which itself is readily soluble, existed in the soluble fraction (Fig.5).

2. The composition of the copper-sorbitol complex in the supernatant

As shown in Fig.2, the absorbance at 650 nm increased in accordance with increase of the copper level in the reaction systems. The increase of the absorbance, however, was observed on the reaction systems with the copper/sorbitol only within 1/1~3/1. On the systems with the copper/sorbitol ratio of more than 4/1, their absorbance showed a constant level similar to that of the CuSO₄-sorbitol system with 3/1 ratio. On the other hand, the soluble copper also increased in proportion to the copper/sorbitol ratio up to 3/1 (Fig.4). These results make the estimate of the composition of the copper-sorbitol complex possible. The complex probably consists of three moles of copper and one mole of sorbitol. This complex is contained in the centrifugal supernatant and is called the soluble copper-sorbitol complex in this paper.

3. The structure and the colloidal appearance of the insoluble copper-sorbitol complex

As shown in Fig.6, the amount of soluble copper was negligible below pH 9.5~10.6 (a critical point) but increased sharply when the pH increased beyond the critical point. A similar result was obtained with the sorbitol content in the centrifugal supernatant (Fig.5). Both components increased steadily till the pH went up to 12, and finally almost all the copper and sorbitol remained in the centrifugal supernatant. This parallelism suggests that the copper-sorbitol complex formed in the alkaline systems above pH 9.5~10.6 is a soluble one.

Such a soluble complex is considered to be formed by either of the following two

manner. In the first manner, the inhibitory effect of sorbitol on the hydrolytic polymerization of copper ions makes it possible to keep the copper-sorbitol complex in soluble state. Similar effects of ligands have been reported for the iron-sugar¹⁾ and iron-scorbic acid²⁾ systems. The results shown in Fig.5 also support this assumption. The appearance of the precipitates formed in the reaction systems was gel-like in the range of pH 7~10 but they changed to suspended particles in strongly alkaline systems with pH 11~13. In the second manner, the electric charges of the copper-sorbitol complex may become a cause that prevents the precipitation of the complex. An interesting consideration was given to the linkages between a metal ion and alcohol groups by KIDA,¹³⁾ who reported that there were two types of these linkages, *i.e.*, R-O-M and R-OH-M. Sorbitol is a polyalcohol with six OH-groups, these groups dissociate to R-O⁻ in a strongly alkaline solution. Although the degree of the dissociation of each OH-group is dependent on the alkalinity of the reaction system, all the groups are likely to dissociate into R-O⁻ at a strong alkalinity, whereas a portion of them is expected to remain undissociated at a weak alkalinity. Accordingly, the state of the linkages of the copper and

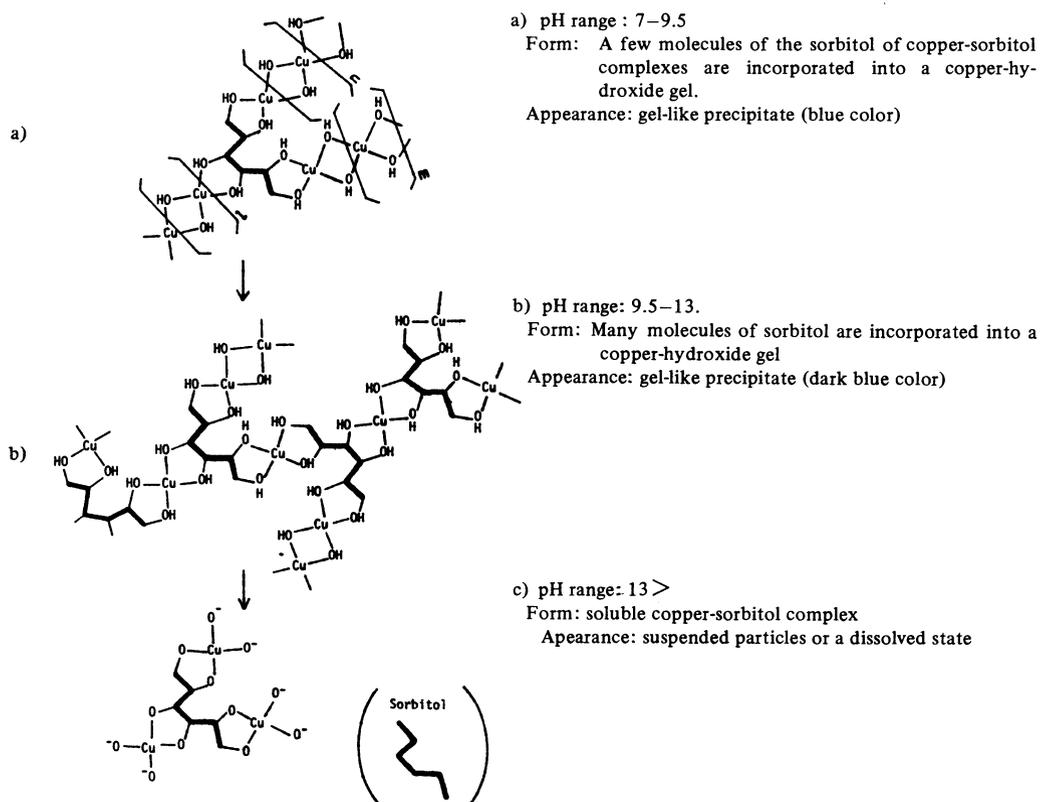


Fig. 7 A model for the transformation of an insoluble copper-sorbitol complex to a soluble one.

the OH-groups in the copper-sorbitol complex are considered to be dependent also on the degree of alkalinity; such a state as $\text{>Cu} \begin{array}{l} \diagup \text{O-C} \\ \diagdown \text{O-C} \end{array}$ (I) or $\text{>Cu} \begin{array}{l} \text{H} \\ \diagup \text{O-C} \\ \diagdown \text{O-C} \\ \text{H} \end{array}$ (II) is expected in a strongly or a weakly alkaline system, respectively. Inversion of the linkage type from II to I must be occurred at the critical point (pH 9.5~10.6). On the basis of these considerations, we propose a model for the transformation of an insoluble copper-sorbitol complex to a soluble one as shown in Fig.7.

SUMMARY

Only a few investigations have been reported on the copper-sorbitol complex, and especially very little is known about the states of this complex in aqueous solutions. Accordingly, the formation of the complex has been investigated spectrophotometrically and potentiometrically with CuSO_4 -sorbitol systems. The copper-sorbitol complex was formed under strongly alkaline conditions above the critical point (pH 9.5~10.6) and it was estimated to have a composition of 3:1 in the molar ratio of copper to sorbitol. Moreover, the complex was ascertained to exist in a state of polymers under pH conditions below the critical point. From the examination of the solubility of the complex, it was found that formation of the soluble copper-sorbitol complex or the insoluble one occurred under pH conditions above or below the critical point, respectively. The relationship between the solubility and the chemical structure of the complex was discussed in this paper, and a model has been proposed.

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硫酸銅—ソルビット系における 銅—ソルビット錯体の生成

今村経明・畑中千歳・堂々隆史

食品のミネラルに関する一連の研究の一部として、今回は銅—ソルビット錯体について研究した結果を報告する。すなわち、 CuSO_4 —ソルビット反応系における銅—ソルビット錯体の生成を、分光光度法と電位差滴定法で確認した。そして、この錯形成に対する、反応系の銅/ソルビット比および pH の影響を調べ、pH 12 以上の強アルカリ条件下で銅 3 : ソルビット 1 の組成比を持つ錯体ができることを確かめた。さらに、この錯形成によって、アルカリ溶液中での銅イオン加水分解重合を阻止すること、およびソルビット 1 モルは銅 3 モル比までこの効果を示すことがわかった。

これらの実験結果に基づいて、銅に結合するソルビットの配位基について若干の考察を加えた。