

# Complexation Mechanism of Dextrin with Metal Hydroxides

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**The complexation of dextrin with metal hydroxides was studied quantitatively by FT-IR and UV-visible reflectance spectroscopic techniques. Though three hydroxyl groups are present in each dextrin molecule, complexation involving only two hydroxyl groups situated at the C-2 and C-3 positions has been studied by many investigators. Involvement of a third hydroxyl group situated at the C-6 position was examined in the present study. Since metal hydroxy sites were found to play a key role in the complexation, precipitates of  $\text{Ca}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$  were separately mixed with dextrin solutions at different ratios. Complexes with a stoichiometry of 2:3 (dextrin:metal ion) were identified, indicating the involvement of a third hydroxyl group. However, the ratio of metal ions to hydroxyl groups of dextrin remained as 1:2. Complexation between dextrin and metal hydroxide via a condensation mechanism is proposed.** © 1998 Academic Press

**Key Words:** dextrin; metal hydroxide; complexation; condensation; FT-IR and UV-visible reflectance spectroscopy.

## INTRODUCTION

Dextrin is commonly used as a dispersing/depressing agent for many mineral beneficiation operations. As a polyhydroxy compound, dextrin is able to participate in a number of chemical reactions characteristic of alcohols. The larger oligo- and polysaccharides with their large numbers of polar hydroxyl groups and conformational flexibility are potential ligands, particularly for metal ions like  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  (1). The role of polysaccharides in different regulatory mechanisms has been investigated by many authors. The highly ionic lipopolysaccharides present in the outer membranes of gram-negative bacteria exhibit significant affinities for metal ions, with the binding not being readily reversible (2). Other derivatives of polysaccharides with additional potential donor sites are Diet and phytic acid. Phytic acid, a phosphate-substituted monosaccharide, which occurs in maize and soybean products, forms highly insoluble complexes with  $\text{Zn}^{2+}$ . Materials with high Diets show gross zinc deficiency due to the formation of insoluble zinc phytates which retard growth and other physiological disorders.

Monosaccharides were also found to form Schiff base complexes whose behavior closely resembles that of amino acids and peptides. Metal-carbohydrate coordination complexes have long been used as mineral supplements because of their greater absorption in the digestive system; e.g., iron-dextrin compositions are used in treating iron deficiency. More recently, metal-pectate compositions have been advocated for their mineral content (3). Pectates, including polygalacturonic acids present in root systems of "Armeria maritima," a copper-tolerant species, were found to act as major binding sites for  $\text{Cu}^{2+}$  ions (4). Thus there are many examples where polysaccharides and their derivatives play important roles in specific biological functions.

Deiana and co-workers (5) have studied the complexation of polygalacturonic acids and suggested an outer-sphere mechanism with nontransition metals and an inner-sphere mechanism with transition metal ions like  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ .

Among the monosaccharides, *cis*-inositol was found to form the strongest complexes, which was attributed to its three synaxial -OH groups (1). The chemical complexation of mono- or disaccharides or their derivatives was studied by some researchers and it was suggested that three adjacent hydroxyl groups in the axial-equatorial-axial position will favor complex formation (1, 6, 7). However, complexes involving only two adjacent hydroxyl groups were also possible. One classical example is complexation between monosaccharides and cuprammonium (8).

There are very few reports on the formation of complexes between dextrin and metal ionic species. Zaidi *et al.* (9) investigated the dextrin-cobalt(III) hydroxide system and confirmed a complexation reaction between them. Similar complexation was noticed with iron (10), chromium, bismuth, and nickel (11, 12). Recently Liu and Laskowski have investigated the interaction of dextrin with various metal hydroxides (13) and observed that dextrin can interact with metal hydroxides, but not with metal cations. A complexation mechanism involving hydroxyl groups situated at the C-2 and C-3 positions was proposed. In fact a primary alcoholic group situated at the C-6 position is more acidic than the secondary alcoholic groups at the C-2 and C-3 positions. There is no reason for the hydroxyl group at the C-6 position not to be involved in complexation.

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In view of the insufficient research on dextrin-metal complexes and the different interaction mechanisms postulated for similar compounds, it was necessary to conduct further research to establish the mechanism of dextrin interaction with metal hydroxides. In the present study complexation of dextrin with calcium and lead ions was investigated by FT-IR and UV-visible reflectance spectroscopic techniques.

## EXPERIMENTAL

### Materials

Dextrin used in the present study is a product of Aldrich Chemical Co., Ltd. Other chemicals like calcium chloride, lead nitrate, and sodium chloride are of Analar grade with a minimum purity of 99.5%. Doubly distilled phenol and  $\text{H}_2\text{SO}_4$  with a purity of 95.5% and a specific gravity of 1.84 were used for the quantitative estimation of dextrin.

### Methods

Dextrin solution was prepared by dissolving a known quantity in deionized water and boiling. The solutions were then cooled to room temperature in a water bath and diluted to the specified volume. Fresh dextrin solutions were prepared each day to minimize the effect of microbiological degradation.

Calcium and lead hydroxides were freshly precipitated from the respective solutions of calcium chloride and lead nitrate by using sodium hydroxide. Dextrin solution was added to these precipitates after the pH was adjusted to be similar to that of the precipitates. Though the lead hydroxide is formed around neutral pH, experiments were conducted at pH 10.50, at which most of the lead will be in the form of  $\text{Pb}(\text{OH})_2$ . The ratio of dextrin monomer to metal ion was varied from 1:1 to 1:4. The mixtures were continuously stirred for 24 h. After that, suspensions were centrifuged at 10,000 rpm for 10 min. The supernatant solutions were analyzed for dextrin to obtain the quantity of dextrin consumed. The spectrophotometric method established by Dubois *et al.* (14) was followed for the estimation of dextrin in aqueous solution. The samples of the reaction products were dried at  $60^\circ\text{C}$  for 24 h and subsequently analyzed by FT-IR diffuse reflectance (DRIFT). Dried samples were found to be crystalline products which are different from the original metal hydroxide precipitates.

Ten milligrams of sample was well dispersed in 200 mg of spectroscopic grade KBr to record DRIFT spectra. Thirty scans were collected on each sample at a resolution of  $4\text{ cm}^{-1}$ . UV-visible spectra of solid samples were recorded using a lab sphere RSA-PE-20 reflectance spectroscopy accessory. The accessory is an optical bench which includes transfer optics and a 50-mm-diameter integrating sphere with special sample-mounting ports for reflectance measure-

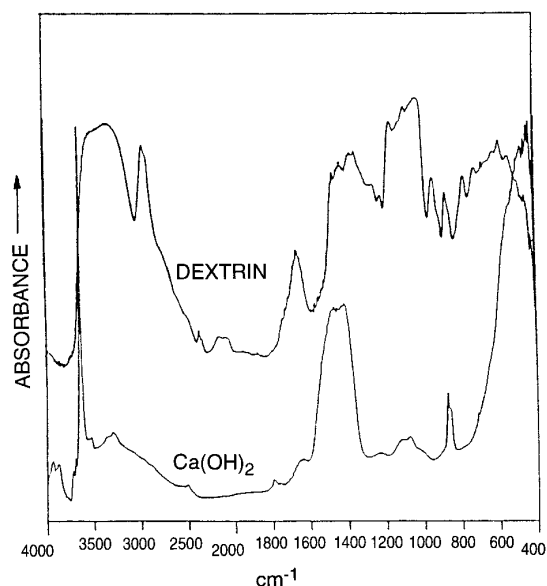


FIG. 1. DRIFT spectra of dextrin and  $\text{Ca}(\text{OH})_2$ .

ments. A white SRS-99 standard reference material, supplied with the instrument, was used for background correction.

## RESULTS AND DISCUSSION

DRIFT spectra of pure dextrin and  $\text{Ca}(\text{OH})_2$  are shown in Fig. 1. Dextrin exhibits a broad band with maximum intensity at about  $3310\text{ cm}^{-1}$  due to the stretching vibration of hydrogen-bonded hydroxyl groups. The band with maximum intensity at  $2929\text{ cm}^{-1}$  and a shoulder at  $2895\text{ cm}^{-1}$  are attributed to C-H stretching vibrations. The frequency region between  $1500$  and  $700\text{ cm}^{-1}$  is rather complicated, arising from  $\text{CH}_2$  and CH deformation modes, C-O-H bending, and C-OH stretching vibrations which are highly coupled (15-17). One of the bands in dextrin that is easily detected and seems to be sensitive to reaction with metal hydroxide appears at  $928\text{ cm}^{-1}$  (pH 10.5). This band is assigned to C-O-H bending (19) overlapping with a skeletal mode involving the  $\alpha(1-4)$  linkage (17, 18).

The spectrum of  $\text{Ca}(\text{OH})_2$  exhibits a sharp and intense band at  $3645\text{ cm}^{-1}$  which is generally attributed to stretching vibrations of free/isolated hydroxyl groups. Other bands at  $1417$  and  $874\text{ cm}^{-1}$  are probably due to  $\text{CO}_3$  groups which might have arisen during precipitation of  $\text{Ca}(\text{OH})_2$ . The strong absorption around  $450\text{ cm}^{-1}$  is characteristic of solid calcium hydroxide.

Spectra of reaction products formed between dextrin and  $\text{Ca}(\text{OH})_2$  and dextrin and  $\text{Pb}(\text{OH})_2$  are shown in Figs. 2 and 3. As mentioned earlier, dextrin and  $\text{Ca}(\text{OH})_2$  were mixed at different mole ratios and were allowed to react.

Many changes could be seen in the spectra of the reaction products with reference to the spectra of pure dextrin and

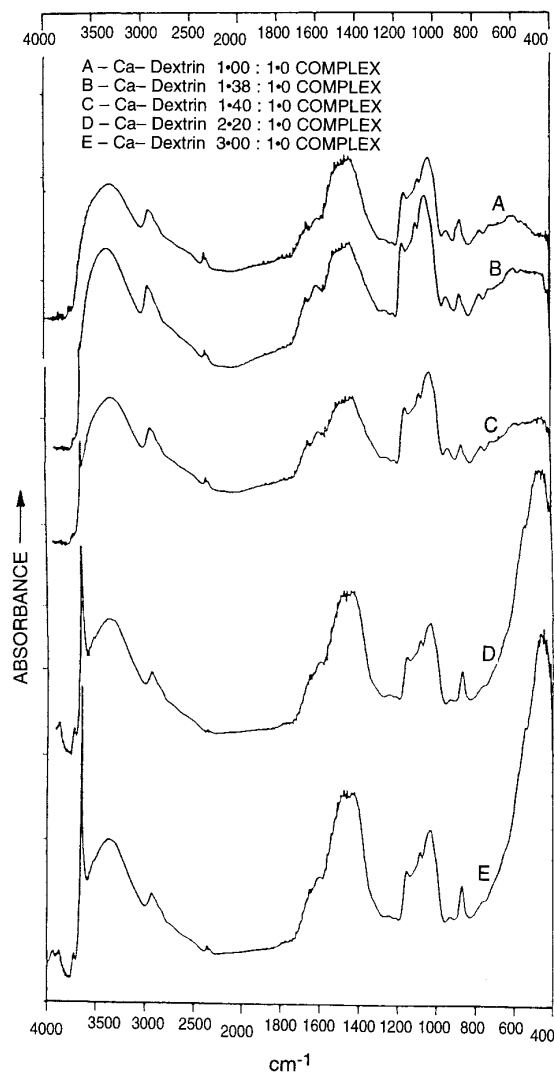


FIG. 2. DRIFT Spectra of Ca-dextrin complexes.

$\text{Ca}(\text{OH})_2$ . The intensity of the band at  $3645\text{ cm}^{-1}$ , which was attributed to the stretching vibrations of OH groups in  $\text{Ca}(\text{OH})_2$ , tended to decrease with increased dextrin content and to disappear when the ratio of  $\text{Ca}(\text{OH})_2$  to dextrin was around 1.38:1.00. Simultaneously the strong absorption band from calcium hydroxide at  $450\text{ cm}^{-1}$  disappeared. Furthermore, the intensity of the band at  $928\text{ cm}^{-1}$  in dextrin was strongly reduced. Based on the above spectral information, it is reasonable to conclude that a chemical complex is formed between dextrin and  $\text{Ca}(\text{OH})_2$ .

Complexation of dextrin with  $\text{Pb}(\text{OH})_2$ , a transition metal hydroxide, was also studied. Lead hydroxide was precipitated at pH 10.50 from lead nitrate solutions and was allowed to react with dextrin at different ratios. The disappearance of the absorption band at  $3645\text{ cm}^{-1}$ , which was attributed to stretching vibrations of free/isolated hydroxy groups of the metal hydroxide, clearly indicates the complexation of dextrin with  $\text{Pb}(\text{OH})_2$ . However, at a  $\text{Pb}(\text{OH})_2$ :dextrin ratio

of 1.38:1.0 the C–O–H deformation at  $938\text{ cm}^{-1}$  is clearly seen in the DRIFT spectrum (Fig. 3, trace B). This implies that unreacted OH functions in dextrin are present in the reaction product, although all of the metal hydroxide has reacted. Accordingly a given amount of dextrin seems to consume more  $\text{Pb}(\text{OH})_2$  than  $\text{Ca}(\text{OH})_2$ , indicating that the type of complex formed between  $\text{Pb}(\text{OH})_2$  and dextrin is different from that formed between  $\text{Ca}(\text{OH})_2$  and dextrin.

Three hydroxyl groups (two at nearby positions, C-2 and C-3, and the other one, a primary alcoholic–OH situated at C-6) are available for complexation from each monomer of dextrin molecule. Liu and Laskowski (13) have projected complex formation involving C-2 and C-3 hydroxyl groups. In fact the primary alcoholic –OH group is more acidic than the secondary alcoholic –OH groups situated on the C-2 and C-3 positions. Assuming that only two hydroxyl groups are involved in the complexation with each calcium atom, the band due to free OH from  $\text{Ca}(\text{OH})_2$  precipitate should appear when the ratio of calcium to dextrin is above 1.0. The absence of the  $3645\text{ cm}^{-1}$  band even at 1.38:1 (Ca:dextrin) clearly indicates the involvement of the third hydroxyl group of dextrin in complexation. By accounting for this third hydroxyl group positioned at C-6, the stoichiometry of Ca–dextrin should stand at 1.5:1.0; i.e., two dextrin monomers are complexed with three calcium atoms.

The results of various workers indicate that the average degree of branching in Canary dextrin used in the present study is approximately 20% (19). It was suggested that two reactions were involved in the dextrinization of starch: (A) hydrolysis of starch molecules to relatively low levels of molecular weight and (B) recombination of these fragments through (1 → 6) linkages to more branched structures (8).

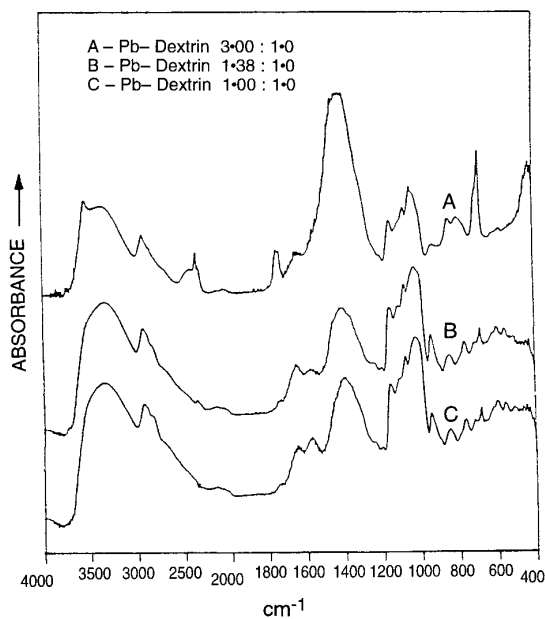


FIG. 3. DRIFT Spectra of Pb-dextrin complexes.

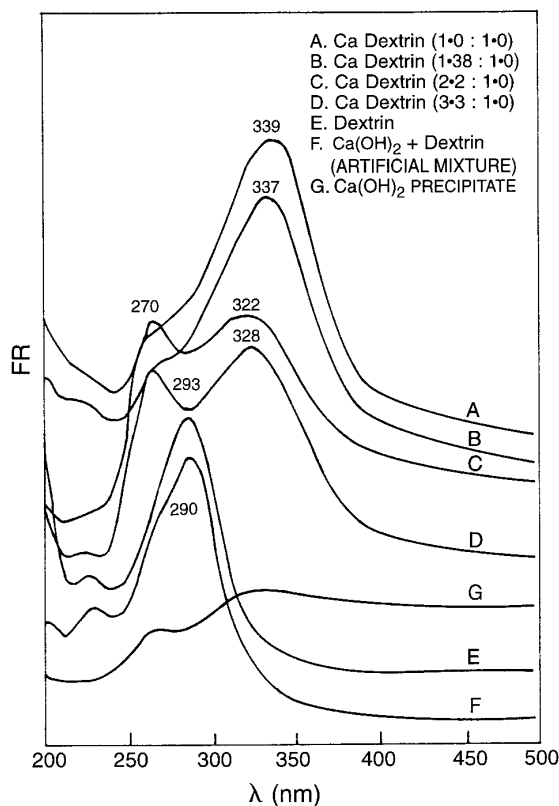


FIG. 4. UV-visible reflectance spectra of Ca-dextrin complexes.

Taking account of this 20% of  $\text{CH}_2\text{OH}$  groups for cross linking, the 1.5:1.0 stoichiometry will remain around 1.38:1.0, which was observed in the present investigation. Above this value, the band at  $3645\text{ cm}^{-1}$  appears to indicate unreacted  $\text{Ca}(\text{OH})_2$  in the reaction product. Thus the above quantitative analysis clearly illustrates the involvement of all three hydroxyl groups of dextrin in the complexation.

From the molecular modeling it is evident that the proximity between two  $-\text{OH}$  groups (C-6 position) from adjacent monomer units of the polymers is close enough to form bonds with metal ions. Because of the helical structure of dextrin, the distance between primary hydroxyl groups of adjacent monomer units will be reduced. Another possibility is that a  $\text{CH}_2\text{OH}$  group from one polymer may be linked to another  $\text{CH}_2\text{OH}$  group of another polymer through a metal ion. In other words, two polymer units are bridged by complexing with a metal ion.

Reaction products formed between dextrin- $\text{Ca}(\text{OH})_2$  and dextrin- $\text{Pb}(\text{OH})_2$  were studied by UV-visible reflectance spectroscopic technique. The spectra of the reaction products along with spectra of pure dextrin,  $\text{Ca}(\text{OH})_2$ , and an artificial mixture of  $\text{Ca}(\text{OH})_2$  and dextrin are presented in Fig. 4. It can be seen that spectra of reaction products are different from those of pure dextrin and  $\text{Ca}(\text{OH})_2$ . The spectrum of dextrin exhibits a characteristic band at 293 nm whereas  $\text{Ca}(\text{OH})_2$  shows a broad and weak band around 270 nm.

Spectra of reaction products above the ratio of 1.38:1.0 (Ca:dextrin) exhibit two bands around 270 and 325 nm, which are typical of those of the binary system. The band at 270 nm exactly coincides with the band of pure  $\text{Ca}(\text{OH})_2$ , whereas the band at 325 nm could be attributed to a calcium-dextrin complex. The artificial mixture of dextrin and  $\text{Ca}(\text{OH})_2$  in a 1:1 ratio also exhibits a band around 290 nm with a small shoulder around 270 nm which corresponds to  $\text{Ca}(\text{OH})_2$ . This clearly illustrates the presence of unreacted  $\text{Ca}(\text{OH})_2$  in the system. On the other hand, spectra of reaction products below a 1.38:1.0 Ca:dextrin ratio exhibit a single band around 338 nm indicating a single compound. In other words, no unreacted  $\text{Ca}(\text{OH})_2$  exists in the system, whereas free and unreacted  $\text{Ca}(\text{OH})_2$  is present when the Ca:dextrin ratio is higher than 1.38:1.0. Thus the UV-visible reflectance spectra clearly indicate complexation between dextrin and calcium hydroxide. UV-visible reflectance spectra of Pb-dextrin complexes,  $\text{Pb}(\text{OH})_2$ , and dextrin are shown in Fig. 5. The UV spectrum of lead hydroxide exhibits a broad band with maximum intensity around 266 nm, whereas spectra of lead dextrin complexes show two resolved absorption bands centered around 253 and 295 nm. The peak position of the latter band nearly coincides with the dominant bond of pure dextrin. However, the sample

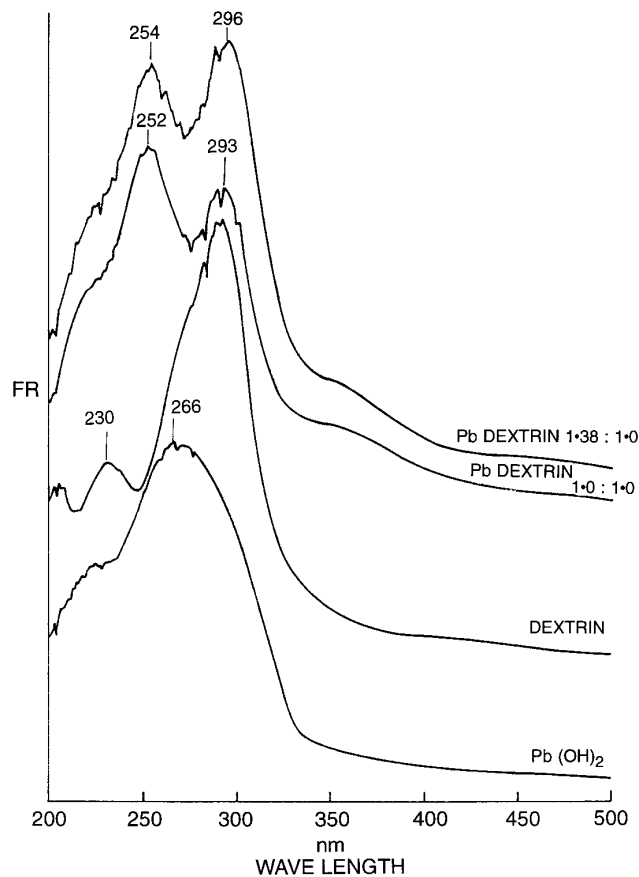


FIG. 5. UV-visible reflectance spectra of Pb-dextrin complexes.

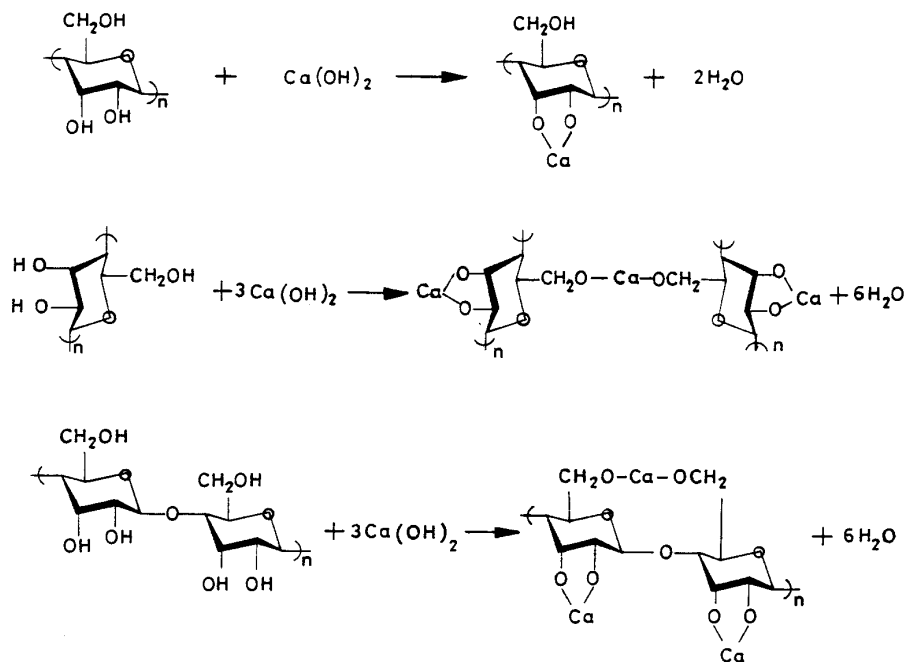


FIG. 6. Model of dextrin complexation with Ca(OH)<sub>2</sub>.

contains no unreacted dextrin, so this band as well as the absorption band at 253 nm must be attributed to Pb–dextrin complexes. It is interesting that the reaction product of lead and dextrin absorbs UV light at 253 and 295 nm whereas the Ca–dextrin complex absorbs at 338 nm. This difference in absorption pattern may indicate that two different types of complexes are formed.

The pH measurements recorded during the complexation reaction indicated no shift in pH. Considering the spectral information and also the pH measurements, a complexation mechanism via condensation as shown in Fig. 6 was proposed. If the complexation of dextrin with metal hydroxide is not obtained by a condensation mechanism, the pH of the suspension should change during complexation. Since there is no change in pH it is reasonable to conclude that the complexation between dextrin and metal hydroxides proceeds invariably through a condensation mechanism. If dextrin is to form complexes with metal ions, protons from hydroxyl groups of dextrin molecules are to be released. Ionization of starch hydroxyls is expected to take place around pH 12.0 (19). However, dextrin was found to interact well below this pH when metal hydroxy sites were available. The metal hydroxide groups are believed to polarize protons of dextrin hydroxyl groups. Furthermore, metal hydroxide sites will act as scavengers, neutralizing protons. In the presence of metal hydroxy sites, hydroxyl groups of dextrin will be easily polarized/ionized, which in turn facilitates attack at electrophilic sites. It was observed that dextrin cannot form complexes with metal cations and metal oxides. The reason dextrin can interact only with metal hydroxides and

not with metal cations could be the above condensation mechanism. In the vicinity of metal hydroxy sites, simultaneous ionization of hydroxyls of dextrin and complexation with metal ions can be visualized.

## CONCLUSIONS

The mechanism of dextrin complexation with hydroxides was studied by FT-IR and UV–visible reflectance spectroscopic methods. Based on the above investigation the following conclusions were drawn:

1. Complexes with definite stoichiometry were identified between dextrin and calcium ions.
2. Complexes with a stoichiometry of two dextrin monomers to three divalent metal ions implying the involvement of a third hydroxyl group of dextrin monomer was established. Though all three hydroxyl groups were involved in the complexation, the ratio of metal ions to hydroxyl groups was found to remain at 1:2.
3. The complexation between dextrin and calcium hydroxides was found to proceed through a condensation mechanism. Metal hydroxy sites were found to play vital roles in the complexation of dextrin with metal ions.

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