An Infrared Investigation of Alkaline- Earth Chelates of N- Hydroxyethylethylenediaminetriacetic Acid and Ethylenediaminetetraacetic Acid

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by
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The author wishes to express sincere appreciation to Dr. Donald L. Wright for his advice, assistance, and patience throughout the course of this investigation.

To My Mother
Sarah G. McDuffie

and

To the Memory of My Father
A.W. McDuffie

Table of Contents

I. INTRODUCTION

II. INFRARED INVESTIGATION

III. RESULTS AND CONCLUSIONS

List of Figures

An Infrared Investigation of Alkaline- Earth Chelates of N-Hydroxyethylethylenediaminetriacetic Acid and Ethylenediaminetetraacetic Acid

by

Sarah McDuffie Bluemel

Infrared investigations of magnesium, calcium, strontium, and barium with both N- Hydroxyethylethylenediaminetriacetic acid and ethylenediaminetetraacetic acid have been conducted in deuterium oxide solutions. The pH of these solutions was varied by adding small amounts of concentrated sodium hydroxide and nitric acid. Infrared spectra were recorded at various pH values for each of the alkaline- earth chelates as well as for HEDTA and EDTA. These spectra were then plotted.

This investigation revealed that protonation of the metal- chelates, HEDTA and EDTA occurred as the solutions were acidified. It further showed that the covalent character of the bonding for both the HEDTA and EDTA chelates is inversely proportional to the ionic radii of the metal ions. There was no evidence established for the bonding of the hydroxyethyl group.

CHAPTER I

INTRODUCTION

An Introduction to Chelation:

Compounds formed by the combination of a central metal ion and coordinating agent that can occupy simultaneously more than a single coordination position are referred to as chelates. Frequently, such chelates contain polydentate ligands which form simultaneously more than one ring. Certain chelating agents which contain both oxygen and nitrogen are particularly effective in forming stable complexes with a wide variety of metal ions. Some of the more important of these chelates are: ethyl ether diaminetetraacetic acid (EEDTA), ethylene glycol bis (β-aminoethyl ether)-N,N' tetraacetic acid (EGTA), diethylenetriaminepentaacetic acid (DTPA), diethylenetriamine (dien), triethylenetetramine (trien), tetraethylenepentamine (tetren), and of particular interest, ethylenediaminetetraacetic acid (EDTA), and N- Hydroxyethylethylenediaminetriacetic acid (HEDTA).

EDTA is known to form stable chelates with many metal ions, but not much is known about the actual structure of its chelates. Some information about the structure of EDTA- chelates has been gained through the studies of Nakamoto, Morimoto, and Martell (5); Sawyer and Paulsen (9,10); Sawyer and Tackett (11);

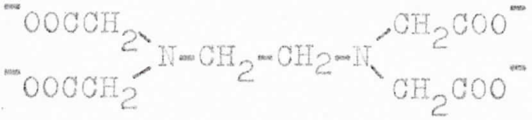
and Sawyer and McKinnie (8). By comparing the structure of EDTA and HEDTA (Figure 1), one can see that the bonding positions are almost identical. The difference is that in HEDTA an hydroxyethyl group has replaced one of the acetate groups. The strength of the metal- chelate bonds is one of the major contributors to the stability. If the hydroxyethyl group forms as strong a bond as the acetate group, then the HEDTA chelates should be as stable as the EDTA chelates.

An Introduction to Infrared Analysis:

Infrared analysis indicates the presence of certain functional groups by recording their absorption bands. Infrared does not destroy the sample or alter the structure in any manner. Once an absorption band has been identified, its "normal position" is recorded. If a given functional group becomes bonded, its absorption band shifts to a different frequency. By studying the spectra of the chelates, one can determine which of the functional groups present are bonded and which are not.

Infrared analysis can be carried out in all of the three physical states. When solutions are used, special care must be taken in choosing the solvent. The solvent should not mask or distort the absorption bands of the species of interest.

EDTA

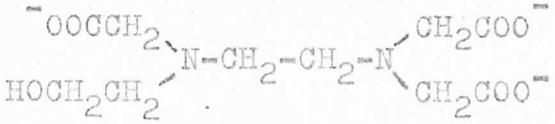


$$\begin{array}{l}{}^{-}OOCCH_2\\{}^{-}OOCCH_2\end{array}\!\!>N-CH_2-CH_2-N<\!\!\begin{array}{l}CH_2COO^{-}\\CH_2COO^{-}\end{array}$$

$pK_1 = 2.0$, $pK_2 = 2.67$, $pK_3 = 6.13$, $pK_4 = 10.26$

$T = 20^\circ$ C $\mu = 0.10$ (1)

HEDTA



$$\begin{array}{l}{}^{-}OOCCH_2\\HOCH_2CH_2\end{array}\!\!>N-CH_2-CH_2-N<\!\!\begin{array}{l}CH_2COO^{-}\\CH_2COO^{-}\end{array}$$

$pK_1 = 2.64$, $pK_2 = 5.33$, $pK_3 = 9.73$

$T = 20^\circ$ C $\mu = 0.10$ (1)

Figure I
A Comparison of the Structure of EDTA and HEDTA

Statement of Problem:

The purpose of this study is to record the infrared spectra of the alkaline- earth chelates of EDTA and HEDTA at various pH values. Solutions were studied because the polyaminocarboxylate chelates are most generally used as titrants. Deuterium oxide was used as the solvent to eliminate the masking effect of water. When water is used as a solvent, the infrared regions from 2900 cm^{-1} to 1800 cm^{-1} and from 1500 cm^{-1} to 1000 cm^{-1} may be ultilized. Water absorbs in the other portions of the spectrum. When deuterium oxide is used as the solvent the infrared regions from 4000 cm^{-1} to 2900 cm^{-1}, from 2000 cm^{-1} to 1300 cm^{-1} and from 1100 cm^{-1} to 900 cm^{-1} may be ultilized. The other portions are not useful because of strong absorption by the deuterium oxide. The main regions of interest in this study were from 1250 cm^{-1} to 600 cm^{-1} which corresponds to the vibration of the $>N-CH_2-CH_2OH$ as a whole (5); and from 1800 cm^{-1} to 1300 cm^{-1} which is the region where the metal- carboxylate bond absorbs(3).

It is further intended that analysis of these spectra should indicate the effect of varying the pH. The coordinating positions for both EDTA and HEDTA are being competed for by both the metal ion and the H_3O^+ ions. The extent of the coordination of the metal ion, therefore, is dependent upon the pH of the solution used. In fairly acidic solutions, partial protonation of the chelating agent may occur. This protonation can be determined by noting the shift of the absorption bands.

Finally, it was hoped that some evidence either for or against the bonding of the hydroxyethyl group could be determined. The hydroxyethyl group is not expected to enter into bonding with the metal ion.

CHAPTER II

INFRARED INVESTIGATION

<u>Materials and Apparatus Used:</u>

Reagent grade chemicals were used throughout this investigation whenever possible. The alkaline-earth ion solutions were prepared in deuterium oxide from the nitrate salts. The deuterium oxide was purchased from the Mathesen Company Inc. and was 99.5% minimum purity. The concentration of the magnesium, calcium, and strontium solutions was 0.600 molar, while the concentration of the barium solution was 0.300 molar.

The HEDTA solution was prepared from the trisodium salt, and the EDTA solution was prepared from the disodium salt, which was reagent grade. The HEDTA was obtained from the J.T. Baker Chemical Company and was assayed at 98% minimum purity. The concentration of both chelate solutions was 0.600 molar in deuterium oxide.

A Beckman Model 72 pH meter equipped with a glass electrode, and a silver chloride reference electrode was used to record the pH of the solutions. No attempt was made to convert the measured pH values to pD values because the difference in the two values was considered to be less than the sensitivity of the instrument.

Because this investigation was carried out on solutions with deuterium oxide as the solvent, silver chloride cells were used in recording the infrared spectra. The silver chloride cells were obtained from the Wilks Scientific Corporation. The silver chloride cell windows contain a 0.025 mm circular depression which enables the cell path length to be changed to a capillary length by placing the flat sides together, to a nominal length of 0.025 mm, or to a maximum length of 0.050 mm. All the spectra used were recorded on a Beckman IR- 7 double beam infrared spectrophotometer. The reference was air.

Procedure:

The metal- chelates were prepared by adding equivalent amounts of the stock metal ion solutions and the stock chelate solutions. Once the chelate had been formed, the pH was varied by adding small amounts of either concentrated sodium hydroxide (50%) or concentrated nitric acid. After the solution was adjusted to a particular pH, a small amount was withdrawn and the spectra was recorded. Although there was a small error of dilution caused by adding acid or base to vary the pH of the solution, the error was negligible and did not effect the results in any noticeable manner. This method did eliminate precipitation noticed in some of the solutions which had been allowed to stand for awhile. The range of the pH variation was from 2.5 to 11.0 in increments of about one pH unit. The solutions were placed in the absorption cells by means of a hypodermic syringe. The amount used was carefully regulated so that the path length would remain constant throughout this investigation.

The spectra were recorded in silver chloride cells at capillary path length. This length was necessary in order that the maximum absorbance intensity of the bands of interest could be recorded. In the study of Nakamoto, Morimoto, and Martell (5) on HEDTA a series of absorption bands caused by the vibration of the $>N-CH_2-CH_2OH$ group as a whole were recorded in the region from 600 cm^{-1} to 1250 cm^{-1}. In order to obtain the greatest possible intensity in this region, the maximum path length of 0.050 mm was used for that part of the spectra. The entire set of infrared spectra for each of the metal chelates was run at one session so that the environmental influence would be minimized. Each run was recorded with a slit width of 1.05 at 1000 cm^{-1}, and the maximum transmittance was adjusted at 2000 cm^{-1}. The scanning speed was 80 cm^{-1} per minute for each spectrum. Slower scanning speeds did not produce any additional resolution of the bands.

CHAPTER III

RESULTS AND CONCLUSIONS

The spectra of the various polyaminocarboxylate chelates, as well as EDTA and HEDTA, are presented in Figures 2 through 11. Because the bands of interest are found in the spectral region from 1800 cm^{-1} to 1300 cm^{-1}, only this section has been included. This region where the metal- carboxylate bond absorbs contains the absorption shifts indicating the change from unprotonated to protonated chelates as the pH is varied. The spectra of each metal- chelate at various pH values are plotted on the same graph in order that the shifts of absorption bands can be easily seen.

The infrared spectra of EDTA obtained at various pH values in deuterium oxide solutions (Figure 2) show only one band at 1595 cm^{-1} when the pH is 10.1. When the pH is lowered to 7.8 two definite bands at 1635 cm^{-1} and 1590 cm^{-1} appear in equal intensity. At a pH of 6.9 there is only a shoulder at 1590 cm^{-1} with the main absorption band at 1635 cm^{-1}. Finally, at a pH of 4.8 only one band at 1635 cm^{-1} is recorded. These spectra are in agreement with those reported by Nakamoto, Morimoto, and Martell (5).

According to Nakamoto, Morimoto, and Martell, three carboxyl stretching bands can be distinguished.

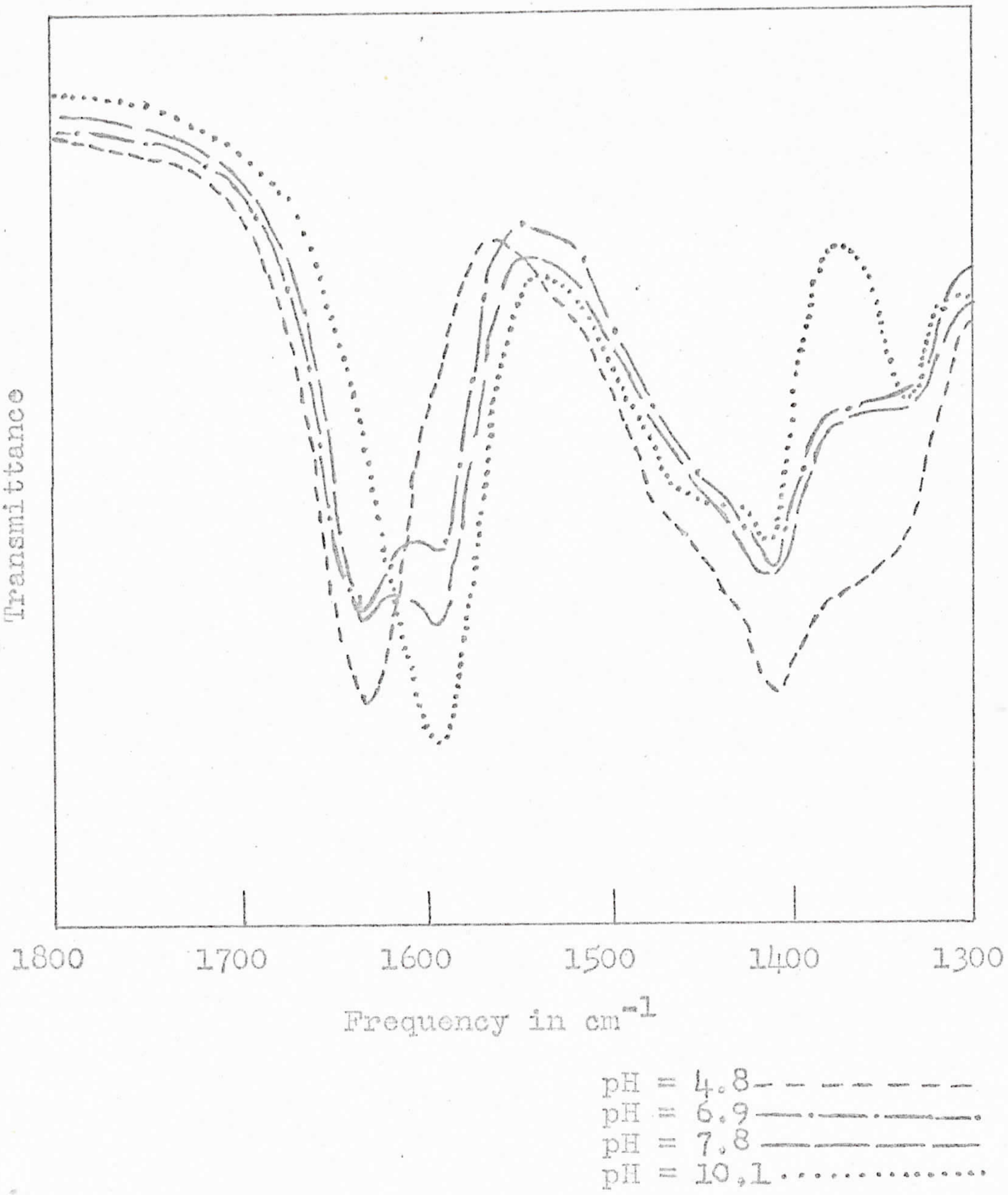


Figure 2

Spectra of EDTA at Various pH Values

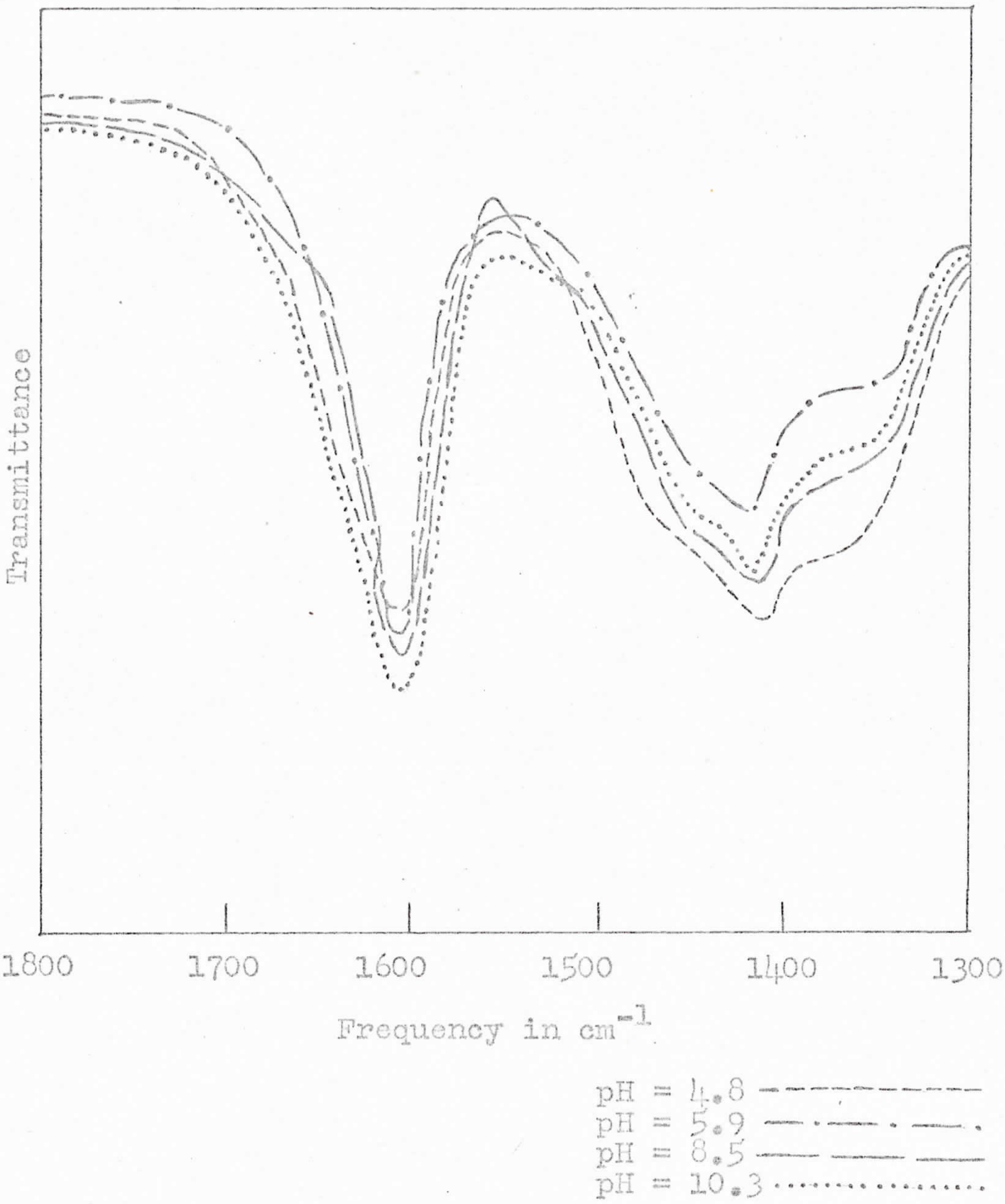


Figure 3

Spectra of Mg-EDTA at Various pH Values

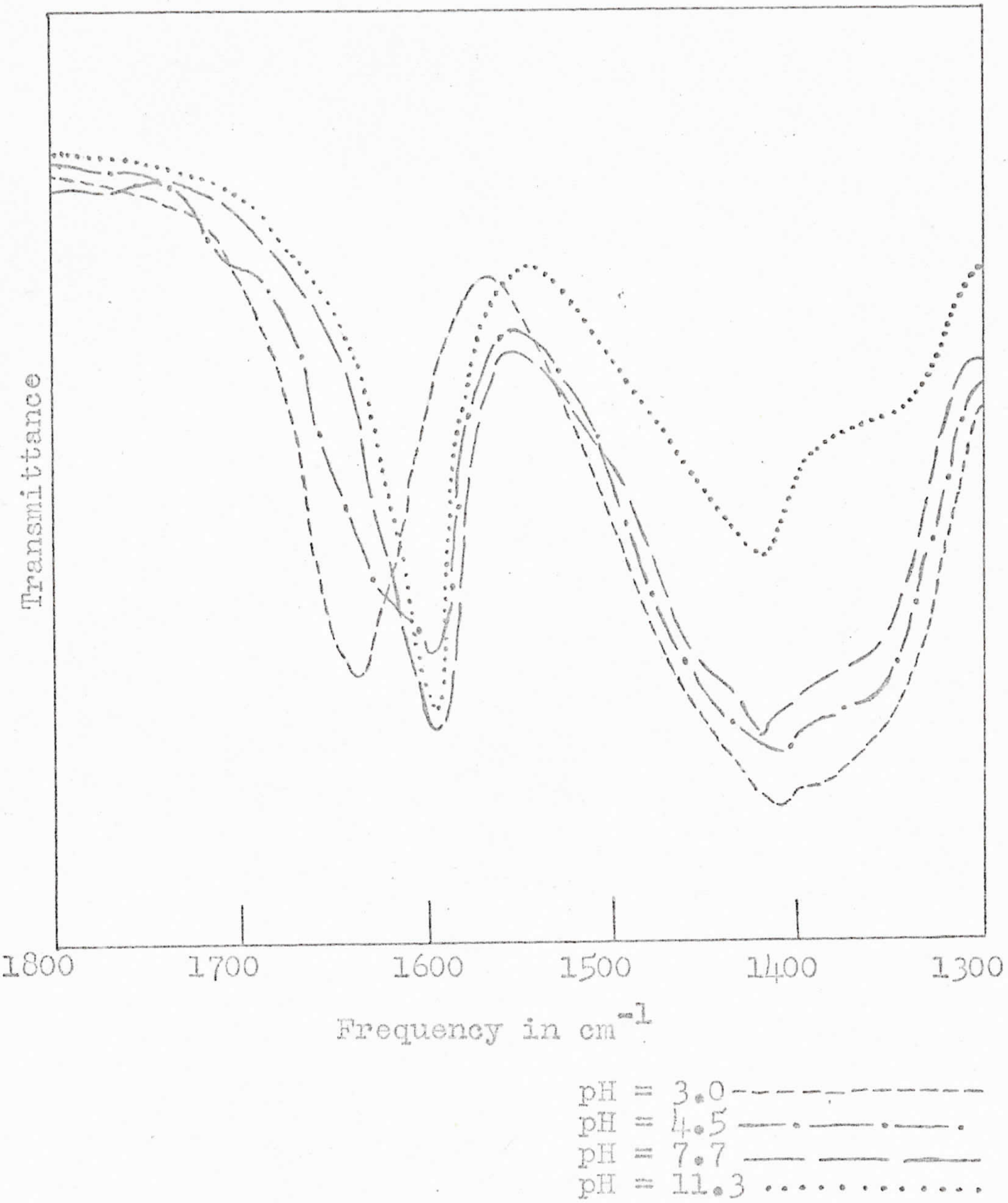


Figure 4

Spectra of Ca- EDTA at Various pH Values

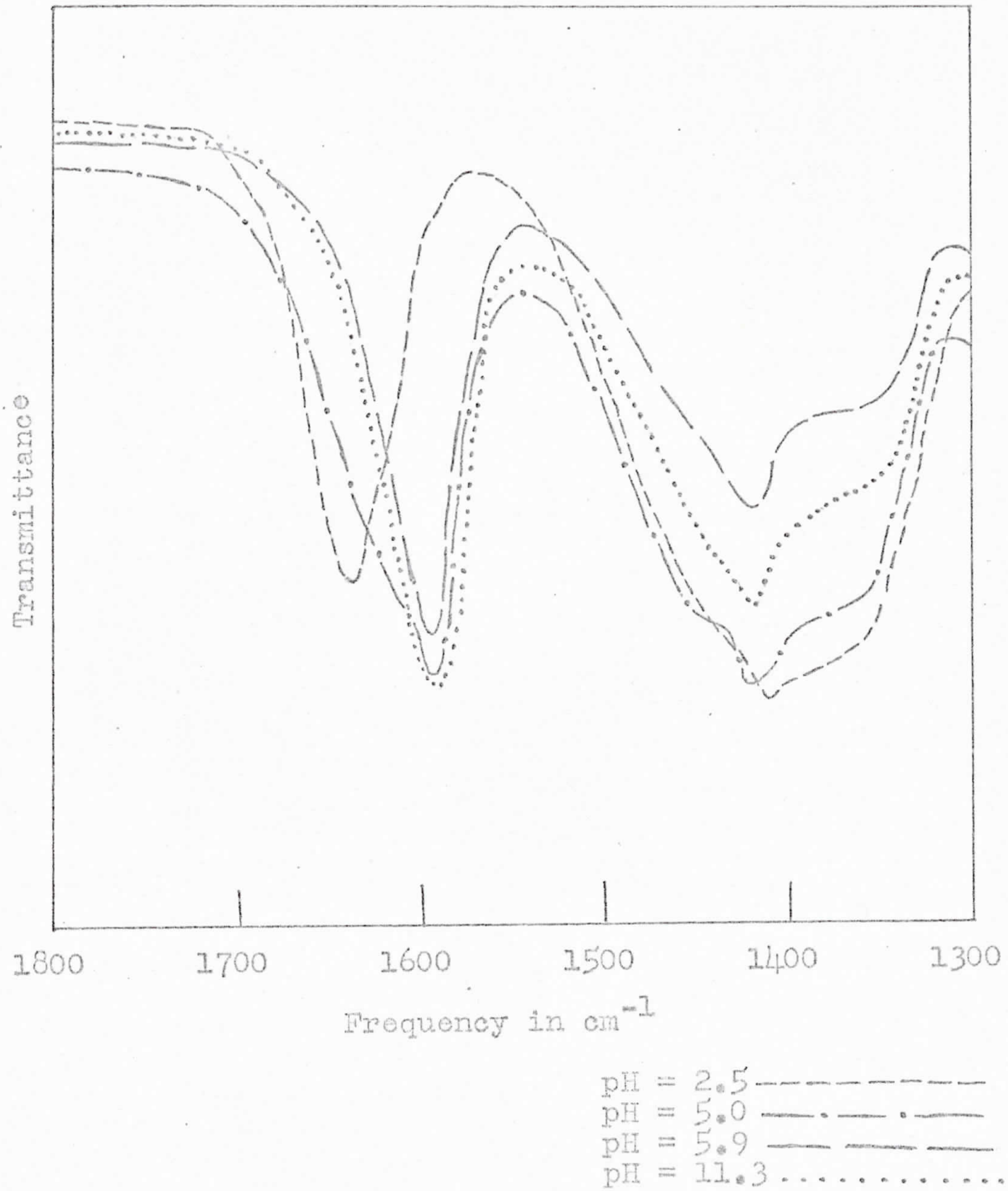


Figure 5

Spectra of Sr- EDTA at Various pH Values

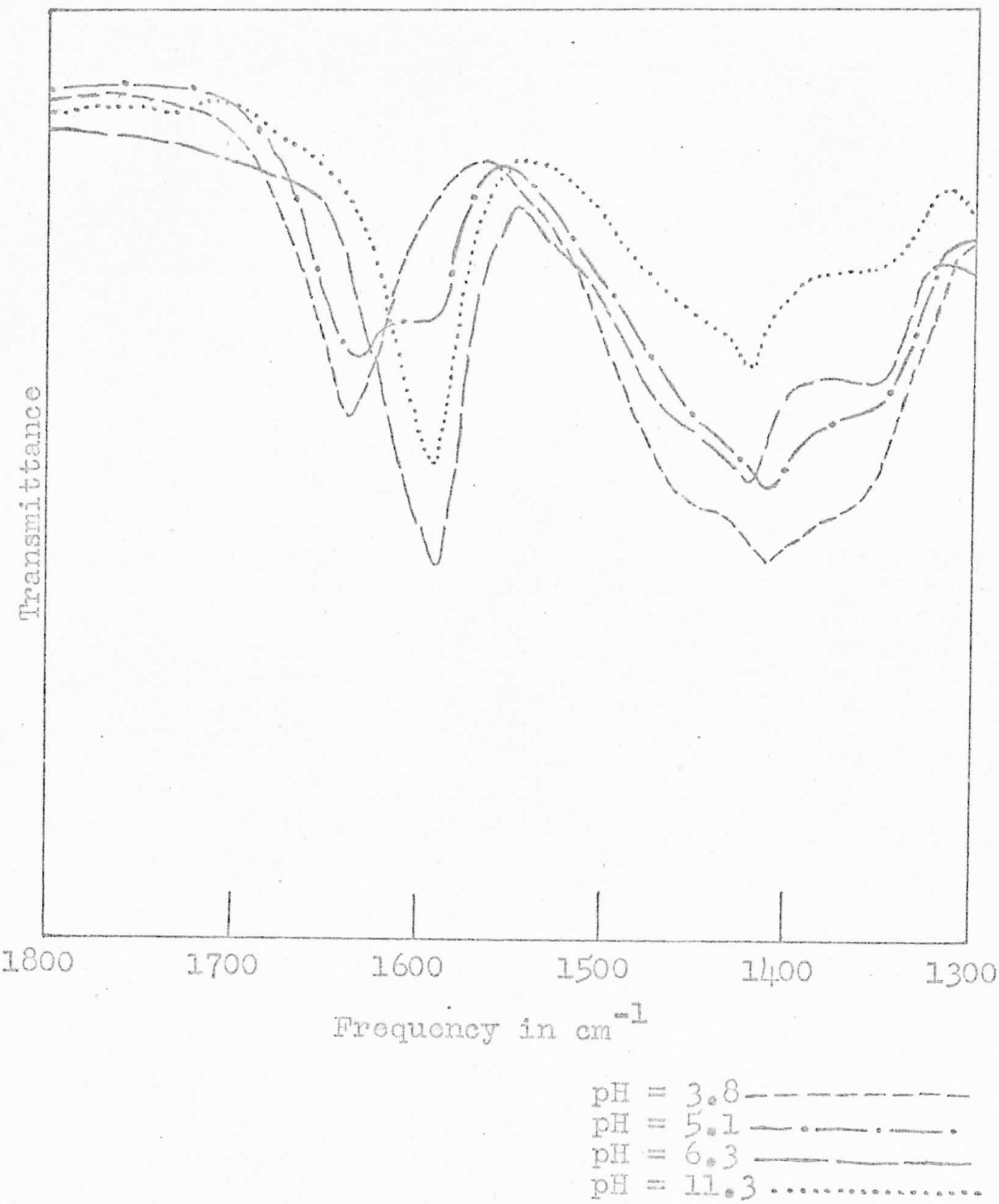


Figure 6

Spectra of Ba- EDTA at Various pH Values

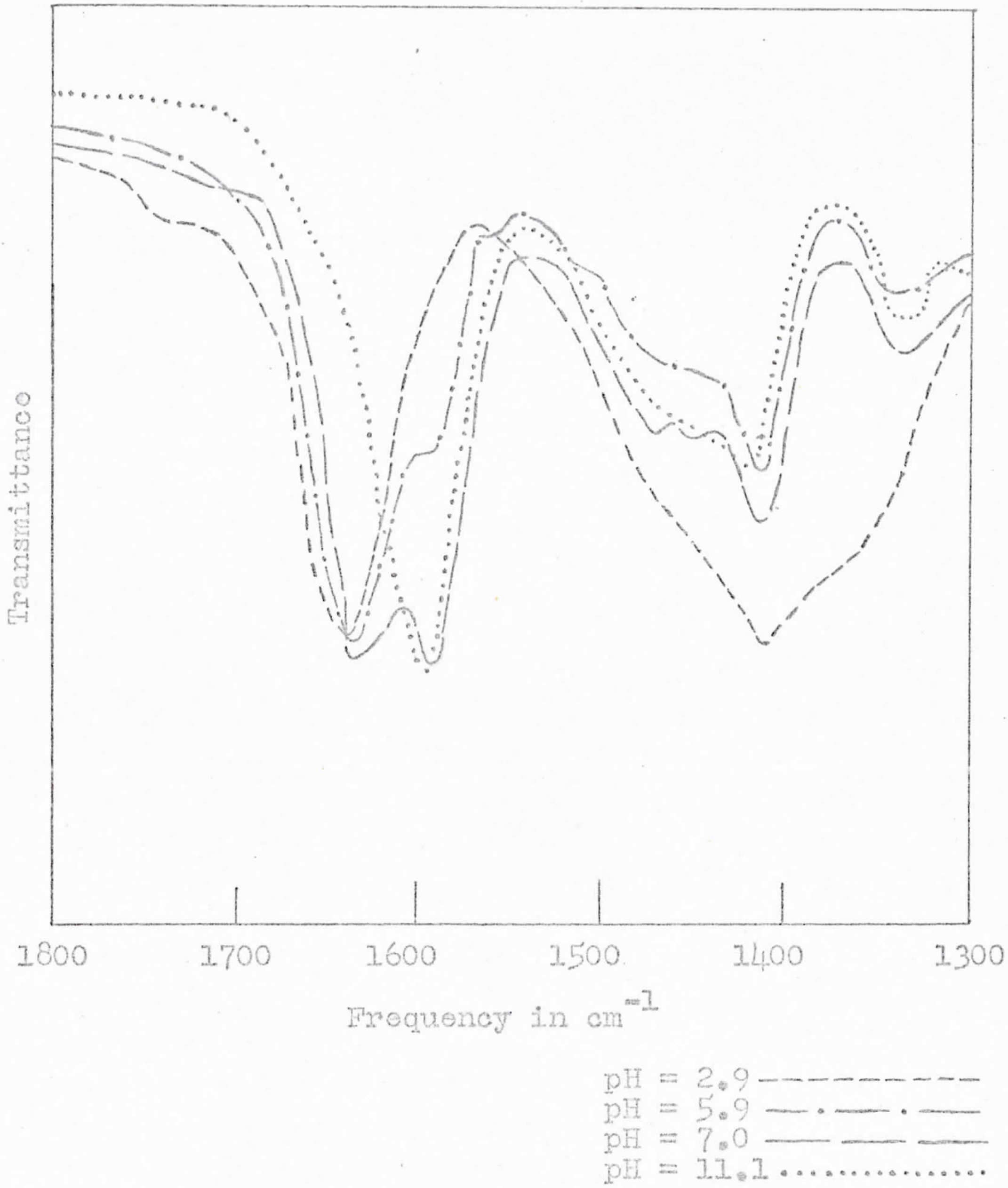


Figure 7

Spectra of HEDTA at Various pH Values

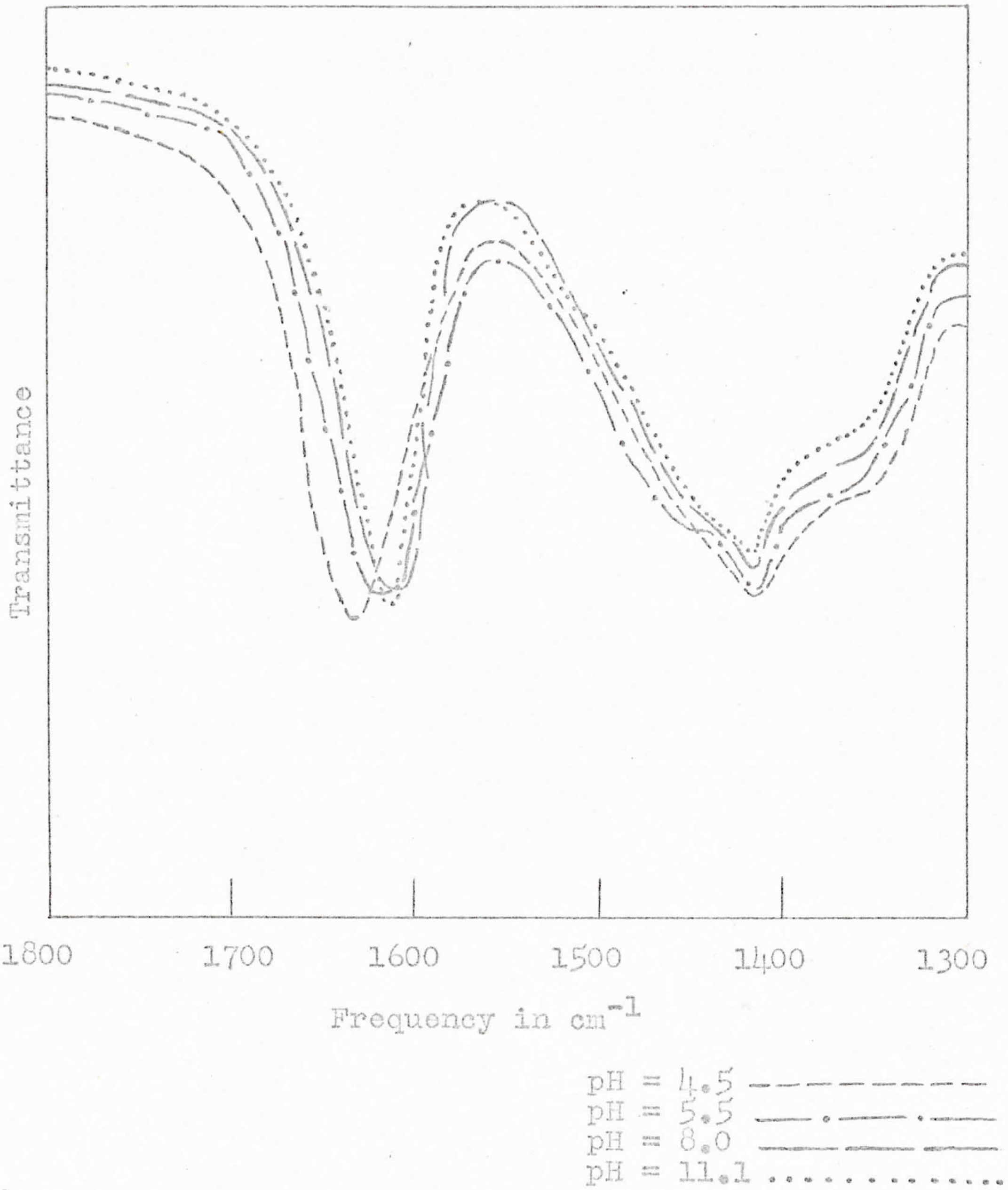


Figure 8

Spectra of Mg- HEDTA at Various pH Values

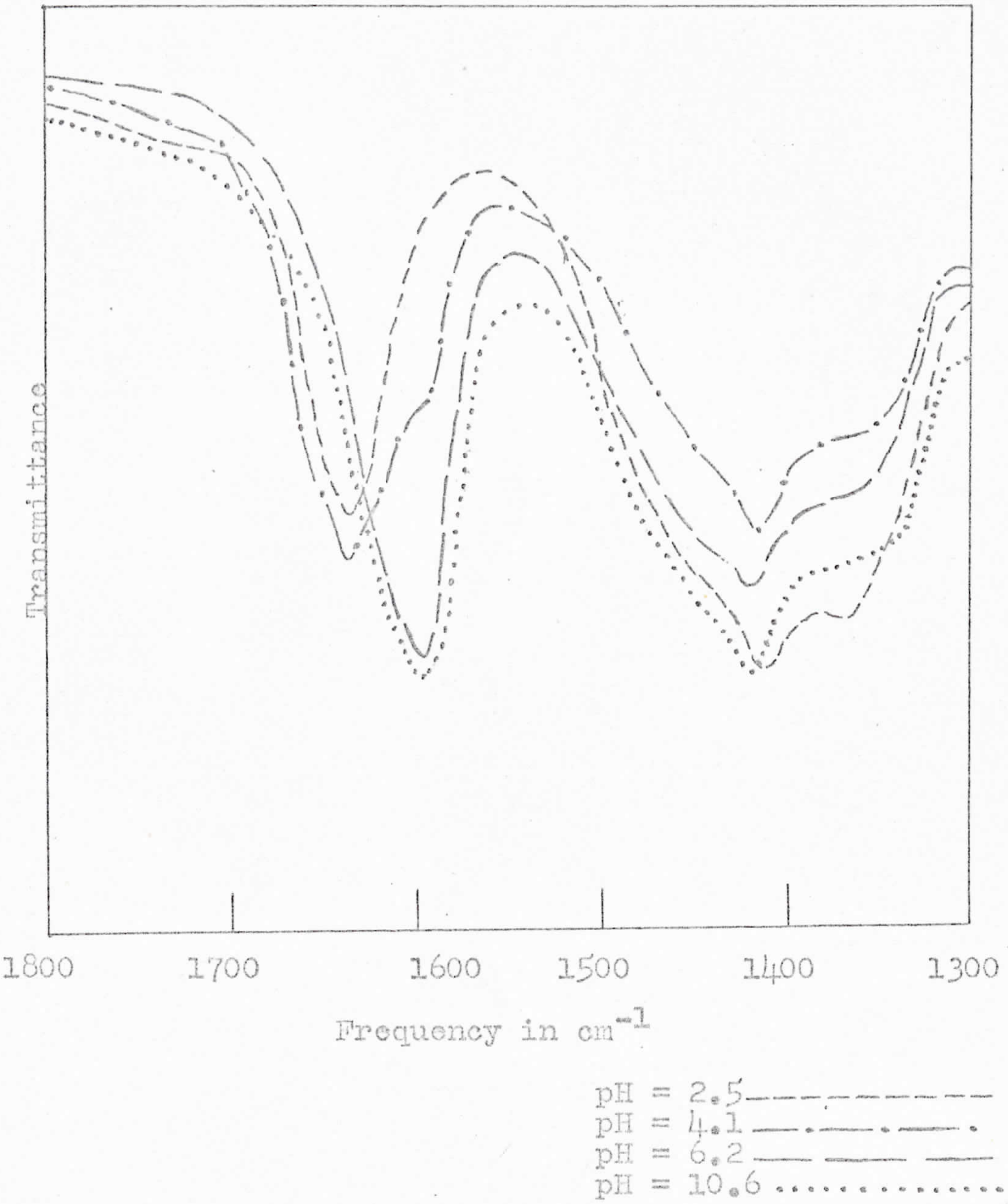


Figure 9

Spectra of Ca- HEDTA at Various pH Values

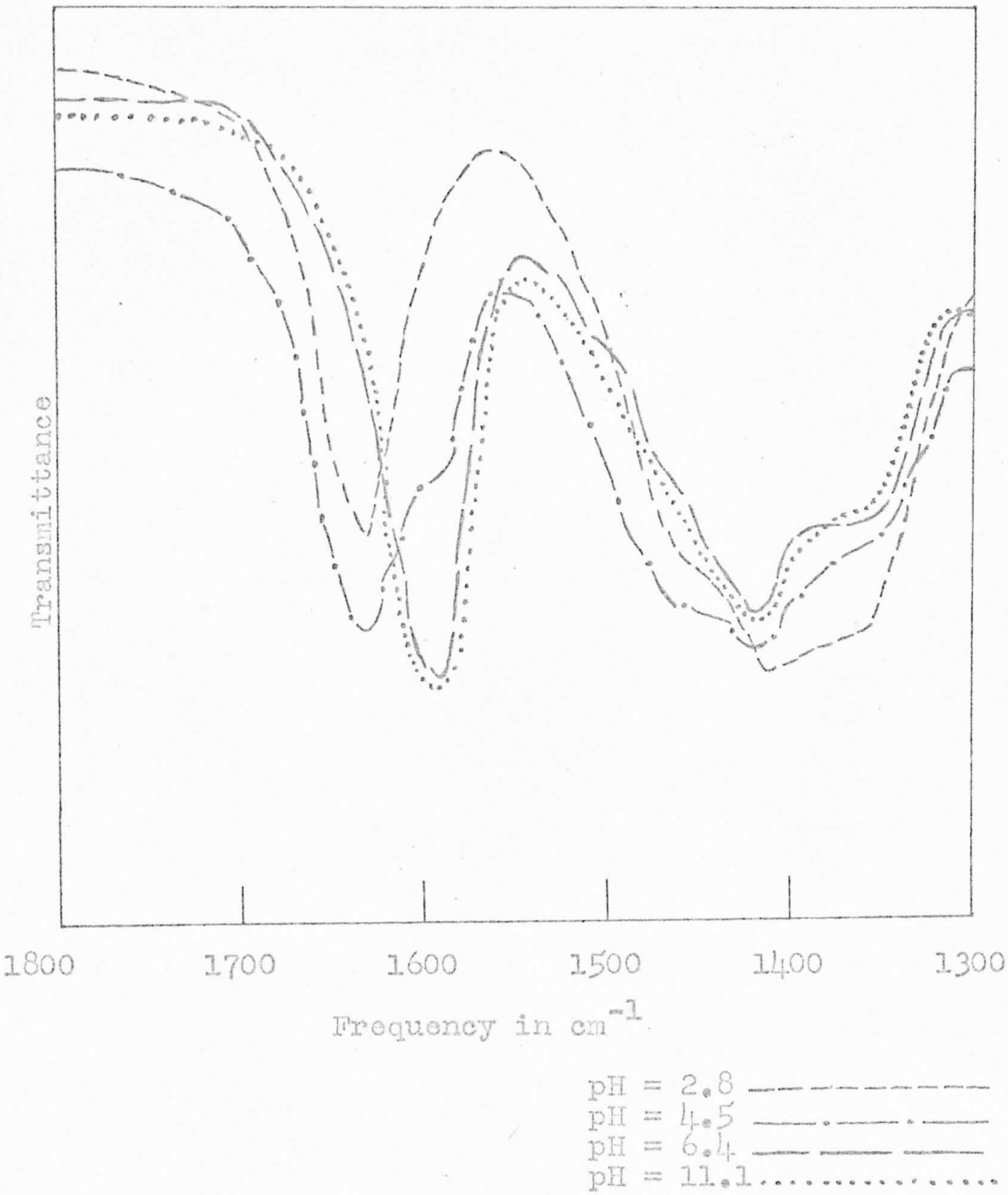


Figure 10

Spectra of Sr- HEDTA at Various pH Values

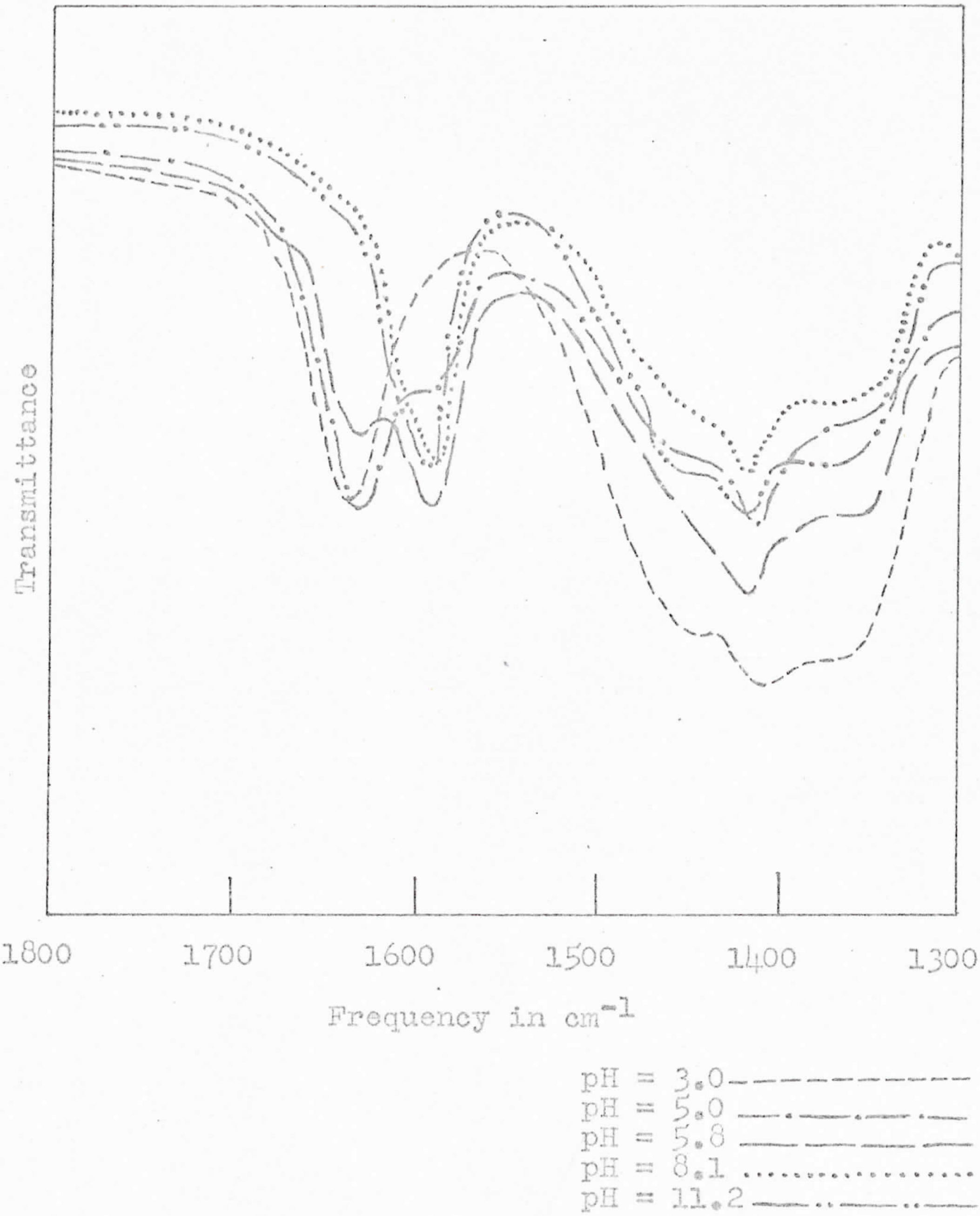


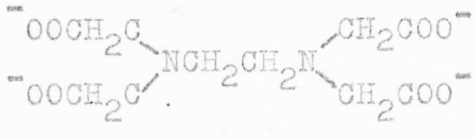
Figure 11

Spectra of Ba- HEDTA at Various pH Values

These bands are referred to throughout this paper in the following manner: type A-- unionized carboxyl (-COOH) band at 1730 - 1700 cm^{-1}, type B--α-ammonium carboxylate ($R_2N^+HCH_2COO^-$) band at 1630 - 1620 cm^{-1}, and type C--α-amine carboxylate ($R_2NCH_2COO^-$) band at 1585 cm^{-1}. The ionization constants of EDTA (H_4Y) for each dissociation step are:

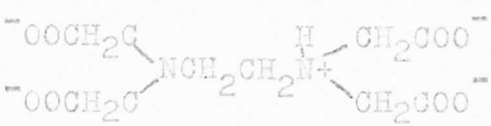
$$\begin{array}{ccccccccc} & pK_1 & & pK_2 & & pK_3 & & pK_4 & \\ H_4Y & \rightleftarrows & H_3Y^- & \rightleftarrows & H_2Y^{2-} & \rightleftarrows & HY^{3-} & \rightleftarrows & Y^{4-} \\ & 2.00 & & 2.67 & & 6.16 & & 10.26 & \\ & & & & I & & II & & III \end{array}$$

Because only one band, type C, appeared at a pH of 9.1 - 10.1 where the tetranegative anion is predominant, Nakamoto <u>et al</u> concluded that the structure of Y^{4-} in aqueous solution must be:



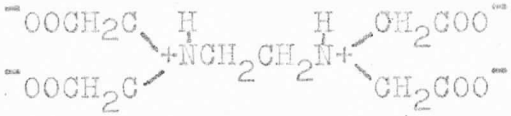
III

Two bands, type B and C appear at a pH from 6.9 to 7.8 where the trinegative anion is predominant. Therefore, according to Nakamoto <u>et al</u> the structure of HY^{3-} in aqueous solution must be:



II

Because only one band, type B, appears at a pH of 4.8, and because the dinegative anion is predominant in this pH range, Nakamoto et al interpreted the structure of H_2Y^{2-} in aqueous solution to be:



I

These conclusions are in agreement with those of Reilley and Sudmeier (7) based on NMR studies.

Similar absorption shifts are noted in the IR spectra of the EDTA chelates of calcium, strontium, and barium reported in this work in Figures 4,5, and 6. The magnesiun chelate (Figure 3) shows no shift in the position of the band as the pH is varied. In fact, the magnesium chelate produces only one band at 1610 cm^{-1} in the pH range from 4.8 to 10.3. This band appears in the same region as the type C band in the unchelated EDTA and is attributed to the coordination of the carboxyl group with the metal ion. This type of bond will be refered to as a type D band. For magnesium the structure would be $R-NCH_2COOMg+$.

There was no indication of the type B band which is expected to appear only when protonation has occurred to a sufficient degree to cause the chelate to partially break apart. Because no type B band appeared, it is concluded that the chelate remained unprotonated down to a pH of 4.8. It is interesting to note that when the pH was lowered past 4.8 precipitation occurred. This precipitant was probably H_4EDTA. The precipitation prevented the infrared spectra from being recorded at low pH values.

The infrared spectra of Ca- EDTA (Figure 4) shows a definite shift in the position of the bands with a variation in pH. A type D band (metal- carboxylate bond) occurs in the pH range from 11.3 to 5.8 at 1600 cm^{-1}. This shoulder suggests that protonation is occurring. At a pH of 3.0 there is only the band at 1635 cm^{-1}, which is type B. This information indicates that Ca- EDTA remains unprotonated from a pH of 11.3 to a pH of approximately 4.5. At a pH of 4.5 a structural change caused by protonation begins to break down the chelate, and at a pH of 3.0 only uncombined calcium and EDTA are in solution.

Variation of the pH also produces shifts in the absorption bands of Sr- EDTA (Figure 5). The change observed is very similar to the change in the Ca- EDTA spectra. A band, type D, is recorded at 1595 cm^{-1} in the pH range from 11.3 to 5.9. The band at 1595 cm^{-1} develops a shoulder at 1635 cm^{-1} at a pH of 5.0. This shoulder suggests that protonation of the chelate is beginning. When the pH is lowered to 4.0 only one band, type B, appears at 1635 cm^{-1}. This information indicates that Sr- EDTA is unprotonated from 11.3 to 5.9. At a pH of 5.0 some of the strontium- carboxylate bonds are being broken by protonation, and at a pH of 4.0 the chelate appears to be completely dissociated.

The infrared spectra of Ba- EDTA (Figure 6) suggests structural changes similar to those observed for Ca- EDTA and Sr- EDTA. A band, type D, is found at 1590 cm^{-1} in the pH range from 11.3 to 6.3. At a pH of 5.1 a shoulder appears at 1590 cm^{-1} on a new band centered at 1630 cm^{-1}. At a pH of 3.8 only one band, type B, at 1630 cm^{-1} is observed. These spectral shifts indicate that Ba- EDTA is unprotonated over the pH range from 11.3 to 6.3. At a pH of 5.1 the Ba- EDTA chelate seems to be largely dissociated, and at a pH of 3.8 no chelated barium remains in solution.

The appearance of the type B band for the various chelates suggests a tendency for the metal- chelate to become protonated at a higher pH value as one goes down the alkaline- earth series. The first indication of the type B band appears for calcium at a pH of 4.5, for strontium at a pH of 5.0, and for barium at a pH of 6.2. No type B band was observed for magnesium. It is assumed that the appearance of the white precipitate indicates that the chelate is protonated at pH values lower than 4.8. This would mean that magnesium is an exception to the observation stated above. According to the apparent ease of protonation of the various chelates, the order of stability is: calcium > magnesium > strontium > barium. The true order of stability is calcium, log K = 10.6 > magnesium, log K = 8.7 > strontium, log K = 8.67 > barium, log K = 7.7 (6).

A comparison of the position of the type D band as a function of the ionic radius can also be made. According to Morris and Busch the coordinated carboxyl group absorbs at a higher frequency as the metal-oxygen bond becomes more covalent (3). The position of the type D band for magnesium is 1610 cm^{-1}, for calcium is 1600 cm^{-1}, for strontium is 1595 cm^{-1}, and for barium is 1590 cm^{-1}. These band positions indicate that the covalent character of the bonding increases in the order barium < strontium < calcium < magnesium. Therefore, for the EDTA chelates the covalent character of the bonds is inversely proportional to the ionic radii of the metal ions.

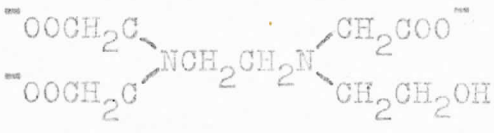
Sawyer and Paulsen (9) studied the alkaline-earth chelates of EDTA in the solid state. They determined the relative covalency of the metal- carboxylate bonds of the various chelates by noting the position of the type D band. From their study, they concluded that the bonds of the magnesium chelate are stronger than those of the calcium chelate in the solid state. They thought that the magnesium chelate was more likely to be partially hydrated in solution and, thus, have weaker bonds than the calcium chelate in solution. However, the results of this study of these chelates in aqueous solution suggest that the Mg- EDTA bonds are stronger than those of Ca- EDTA even in solution.

The infrared spectra of HEDTA (Figure 7) also denotes structural changes when the pH is varied. In the pH range from 11.1 to 9.5, only one band at 1595 cm^{-1} is observed. At a pH of 7.0 two bands at 1635 cm^{-1} and 1590 cm^{-1} appear with approximately the same intensity. When the pH is lowered to 5.9 there is only a shoulder at 1590 cm^{-1} with a strong band at 1635 cm^{-1}. Finally, at a pH of 2.9, a very slight shoulder at 1745 cm^{-1} and a band of high intensity at 1635 cm^{-1} are observed. These spectra are in agreement with the work of Nakamoto et al (5).

Nakamoto et al interpreted their results in the following manner. The ionization constants for HEDTA (H_3X) for each dissociation step are:

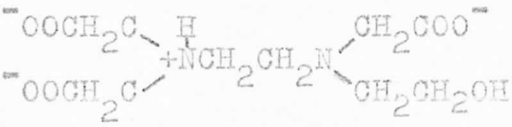
$$\underset{IV}{H_3X} \underset{2.64}{\overset{pK_1}{\rightleftharpoons}} \underset{V}{H_2X^-} \underset{5.33}{\overset{pK_2}{\rightleftharpoons}} \underset{VI}{HX^{2-}} \underset{9.73}{\overset{pK_3}{\rightleftharpoons}} \underset{VII}{X^{3-}}$$

Because the type C band is the only band that appears at a pH of 11.1, and because the trinegative form is predominant, Nakamoto et al concluded that the structure for X^{3-} should be:



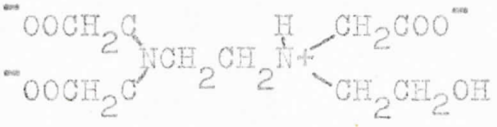
VII

The bands, type B and type C, are of equal intensity at a pH of 7.0. The predominant species present is HX^{2-}. Because the bands are of equal strength Nakamoto et al reasoned that the structure could be either:



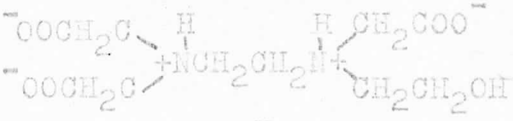
VIa

or



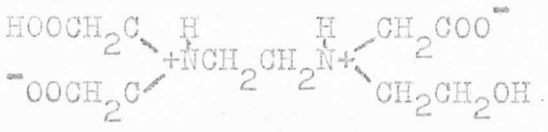
VIb

A strong band, type B, with a shoulder at the position of type C, appears at a pH of 5.9. At this pH value the principal species present is H_2X^-. From this evidence Nakamoto et al concluded that the structure should be:



V

At a pH of 2.9 there is a very slight shoulder at 1745 cm^{-1}, which suggests that a small amount of type A bond is forming. The main band is type B. Because the undissociated form is predominant in this pH range, Nakamoto et al decided that the structure of H_3X in aqueous solution should be:



IV

The NMR studies of Reilley and Sudmeier (7) support the arguments above for the structures given.

Band shifts similar to those observed for the corresponding EDTA chelates are noted in the spectra of the chelates of HEDTA with magnesium, calcium, strontium, and barium. The infrared spectra of Mg- HEDTA (Figure 8) shows a definite shift from a band at 1612 cm^{-1} when the pH is 11.1 to a position of 1635 cm^{-1} when the pH has been lowered to 4.5. The pH at which the chelate becomes protonated is difficult to determine from the spectra. At a pH of 8.0 the band is wide and located at 1615 cm^{-1}. Decreasing the pH to 5.5 broadens the band until it extends from 1610 cm^{-1} to 1630 cm^{-1}. At a pH of 8.0 one would not expect protonation to be important; however, because the band is somewhat broad, one might speculate that protonation is just beginning and a type B band is starting to form. At a pH of 5.5 the very broad band suggests the presence of some type B band absorption. However, at this pH protonation apparently is not sufficient to cause the chelate to break apart. At a pH of 4.5 the band is sharp and positioned at 1635 cm^{-1}, indicating only a type B band. Because of precipitation (probably H_3HEDTA), spectra of Mg- HEDTA could not be determined below a pH of 4.5.

The spectra of Ca- HEDTA (Figure 9) shows structural changes similar to those observed for Mg-HEDTA. In the pH range from 10.6 to 6.2 the band, type D, is located at 1600 cm^{-1}. At a pH of 4.1, the band has shifted to a position of 1635 cm^{-1} with a shoulder at 1600 cm^{-1}. This shoulder indicates that protonation has occurred and is causing the chelate to break apart. At a pH of 2.5 only one band at 1635 cm^{-1} is present suggesting that calcium is no longer chelated.

Sr- HEDTA (Figure 10) shows band shifts similar to those of Ca- HEDTA. In the pH range from 11.1 to 6.4 only one band at 1595 cm^{-1} is observed. When the pH is lowered to 4.5 the band shifts to a position of 1635 cm^{-1} with a definite shoulder at 1595 cm^{-1}, showing that protonation has occurred. It is interesting to note that the shoulder at 1595 cm^{-1} in the case Sr- HEDTA is much more definite than the shoulder at

1600 cm^{-1} is for Ca- HEDTA. When the pH is lowered to 2.8 only one band at 1635 cm^{-1} is present. At this pH the strontium is no longer chelated with HEDTA.

The spectra of Ba- HEDTA (Figure 11) suggest the same structural changes as have been observed for the other alkaline- earth chelates. The band recorded in the pH range from 11.2 to 8.1 occurs at 1590 cm^{-1}. At a pH of 5.8 the band at 1590 cm^{-1} is of the same intensity, but a shoulder has developed at 1630 cm^{-1}. This indicates that the major absorption at this pH was caused by a type D band, but, in addition that some protonation is occurring. However, at a pH of 5.0 the band of major intensity has moved to 1630 cm^{-1}, and only a shoulder remains at 1590 cm^{-1}. At this pH the type B band is responsible for the major portion of the absorption. Therefore, protonation has begun to occur sufficiently to cause some breaking of the barium- carboxylate bonds. At a pH of 3.0 only a band at 1635 cm^{-1} is present; thus barium is no longer chelated.

The pH at which the α-aminocarboxylate band, type B, appears in the metal- HEDTA spectra reveals that the ease of protonation is approximately in the same order as the true stability of the chelates. The first indication of the type B band appears for calcium at a pH of 5.0, for magnesium at 5.5, for strontium at 5.5, and for barium at 5.8, whereas the values of log K for the HEDTA chelates are: calcium, 8.0; magnesium, 7.0; strontium, 6.8; and barium, 6.2 (6). Although the appearance of the type B band occurs at the same pH for magnesium and strontium, it is believed that a more careful study would indicate a difference. However, because the log K values are very close together for these two chelates, it is not surprising that protonation begins at nearly the same pH value.

A comparison of the position of the type D band (metal- carboxylate bond) as a function of the ionic radius is also interesting. The position of the type D band for magnesium is 1612 cm^{-1}, for calcium is 1600 cm^{-1}, for strontium is 1595 cm^{-1}, and for barium is 1590 cm^{-1}. According to Morris and Busch (3) the coordinated carboxyl group absorbs at a higher frequency as the metal- oxygen bond becomes more covalent. Thus, the covalent character of the bonding increases in the order barium $<$ strontium $<$ calcium $<$ magnesium and is inversely proportional to the ionic radii of the metal ions. Similar behavior was noted previously for the EDTA chelates.

In an investigation of HEDTA in aqueous solution by Nakamoto, Morimoto, and Martell (5), some new bands appeared in the 1200 cm^{-1} - 800 cm^{-1} region at high pH values. Two of the bands (at 1140 cm^{-1} and 1040 cm^{-1}) occurred at a pH of 9.0 and above and were ascribed to the $\rangle NCH_2CH_2OH$ group as a whole. Nakamoto et al concluded that the new bands appeared because of the loss of the positive charge of the nitrogen rather than because of the ionization of the hydroxyethyl hydrogen. A careful study of the metal- chelates in the spectral region from 1250 cm^{-1} to 600 cm^{-1} showed no change in the absorption bands as the pH was varied. This region was run at maximum path length to attain the highest intensity possible. Two small bands were present -- one at 1125 cm^{-1} and the other at 1060 cm^{-1} . However, these bands did not change within the pH range from 2.5 to 11.2, suggesting no evidence for the bonding of the hydroxyethyl group.

From their study of the heats and entropies of formation of metal- chelates of HEDTA and EDTA, Wright, Holloway, and Reilley (13) concluded that although the HEDTA reactions are more exthermic by more than 2 Kcal per mole, it seems unlikely that this is because there are stronger bonds between the hydroxyethyl group and the metal ion than between the carboxylate group and the metal ion. A more reasonable explanation for this exothermic effect is the lack of strain in the chelate rings because the hydroxyethyl group is not bonded to the metal ion, allowing the other donor groups to be bonded stronger than in the metal- EDTA chelates. If HEDTA forms only three bonds with the alkaline- earth chelates (the basic nitrogen atoms are not thought to enter into bonding), one would expect the metal- chelates to be easier to break up by protonation than the corresponding EDTA chelates.

An estimate of the ionic character of the alkaline earth- carboxylate bonds can be made by comparing the positions of the absorption bands to that of a covalent metal- carboxylate band. Morris and Busch (3) reported the position of this band for Co- EDTA in the solid state to be 1650 cm^{-1}. The absorption bands are located for Ba- EDTA and Ba- HEDTA at 1590 cm^{-1}, for Sr- EDTA and Sr- HEDTA at 1595 cm^{-1}, for Ca- EDTA and Ca- HEDTA at 1600 cm^{-1}, for Mg- EDTA at 1610 cm^{-1}, and for Mg- HEDTA at 1612 cm^{-1}. Thus, the ionic character for the alkaline- earth chelates of both EDTA and HEDTA seems to be relatively large and increases in the order: magnesium $<$ calcium $<$ strontium $<$ barium.

There are certain limitations inherent in the use of infrared analysis which hinder the detection of the bonding of the hydroxyethyl group. Specifically, infrared absorption depends only on the bond strength and does not directly indicate ring strain and conformations. The structural arrangement of a given chelate contributes greatly to its stability. A method such as nuclear magnetic resonance which depends on the effect of the position of the atoms within the molecule could determine the difference in stability caused by a structural change. Therefore, nuclear magnetic resonance should yield additional information, and when coupled with infrared spectroscopy would lead to a more thorough knowledge of the process of chelation.

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