



Chelation Chemistry

General Concepts of the Chemistry of Chelation



General Concepts

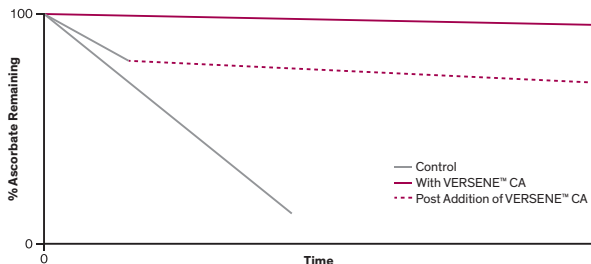
Metal Ions: Why They Behave as They Do

To understand chelation and why chelating agents are useful in the control of metal ions, it is necessary to understand the nature of metal ions and how they behave. When metal-containing compounds are dissolved in water, the metallic component exists as a positively charged, freely moving ion in the solution. These “free” metal ions react to surround themselves with negative ions or polar molecules present in the solution. The number of such molecules or negative ions that coordinate with the metal ion varies, but for most heavy metals (copper, nickel, iron – the common metals of industry) – it is usually 4 or 6. These centers of coordination on the metal ion may be considered “reactive sites.” In general, the reactions caused by free metal ions in solution are due to these reactive sites.

In an aqueous solution containing only a simple metal salt, the reactive sites are occupied by water molecules. When materials are added which interact more strongly or compete more effectively than the water molecule for the reactive site, the sheath of water molecules is displaced and the metal ion requires a new set of properties.

Example: See the reaction of copper ions with ammonia in Figure 1.

Figure 1: Reaction of Aqueous Copper Ions with Ammonia



The water molecules held at the four reactive sites of the copper ion are displaced by ammonia. Because ammonia forms a stronger attachment to the copper ion than does the water, the resultant ammonia copper complex is more stable, and the ammonia can be replaced only by adding to the system some material capable of forming an even more stable complex with copper.

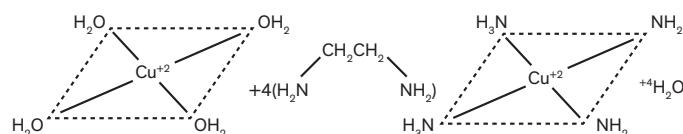
In summary, metal ions possess reactive sites at which the activity of the metal is centered. To inhibit the reaction of a metal ion, it is necessary to introduce a material that forms a stable complex with the metal ion and thus blocks the reactive sites of the metal ion. Further, those materials which form the most stable metal complexes will be most effective in blocking the reactive sites of the metal ion.

Chelation and How it Controls the Metal Ion

The common metal-complexing agents such as ammonia and the cyanide ion can form complexes in which one molecule of the complexing agent coordinates with one reactive site of the metal ion. As in Figure 1, one ammonia molecule fills one reactive

site of the metal ion. When, however, the ammonia is replaced by ethylenediamine (a molecule made up of two amine groups connected by an ethylene bridge), a different type compound results (see Figure 2). The presence of two complexing groups in the ethylenediamine molecule results in the copper being incorporated into a ring-type structure. The copper is said to be “chelated” and ethylenediamine is termed a “chelating agent.”

Figure 2: Reaction of Aqueous Copper Ions with Ethylenediamine



Thus, chelation may be defined as an equilibrium reaction between a metal ion and a complexing agent, characterized by the formation of more than one bond between the metal and a molecule of the complexing agent and resulting in the formation of a ring structure incorporating the metal ion.

Chelating agents control metal ions by blocking the reactive sites of the metal ion and preventing them from entering into their normal (and in many cases undesirable) reactions. Those chelating agents forming the most stable bonds with metal ions will be most effective in preventing metal ion activity.

Properties of EDTA, DTPA, and HEDTA

Structural Properties

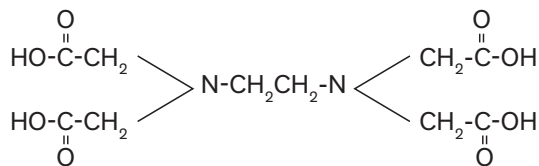
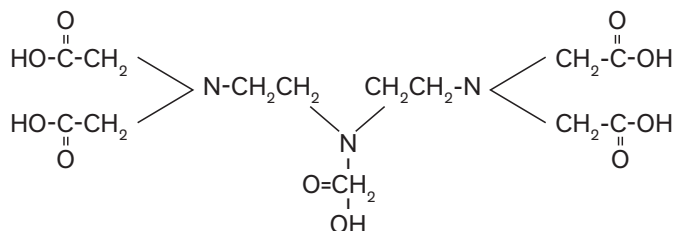
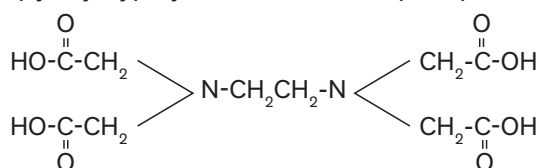
EDTA, DTPA, and HEDTA are among the most widely used metal ion control agents in the industry. An examination of the structure of these materials, as in Figure 3, helps show why this is true. EDTA, DTPA, and HEDTA have six, eight, and six metal-complexing sites respectively, enabling one molecule to interact with all the reactive centers of a metal ion.

The metal-complexing groups include both oxygen and nitrogen atoms, taking advantage of the fact that some metals bond more strongly to nitrogen and others prefer oxygen.

The abundance of metal-complexing groups in EDTA, DTPA, and HEDTA permits a multiple number of metal-enclosing chelate rings to form – a condition promoting stability.

All of the chelate rings which form include the metal in a five-membered ring, a condition that imparts maximum stability.

In general, chelating agents are molecules with metal-complexing groups arranged to produce a number of maximum stability chelate rings.

Ethylenediaminetetraacetic acid (EDTA)

Diethylenetriaminepentaacetic acid (DTPA)

N (Hydroxyethyl) ethylenediaminetriacetic acid (HEDTA)

Figure 3: Structures of EDTA, DTPA and HEDTA

Physical Properties of the Free Acids

The free acids are white, crystalline materials. They are practically insoluble in cold water and in the common organic solvents. The aqueous solubility and the pH of their saturated solutions are presented in Table 1.

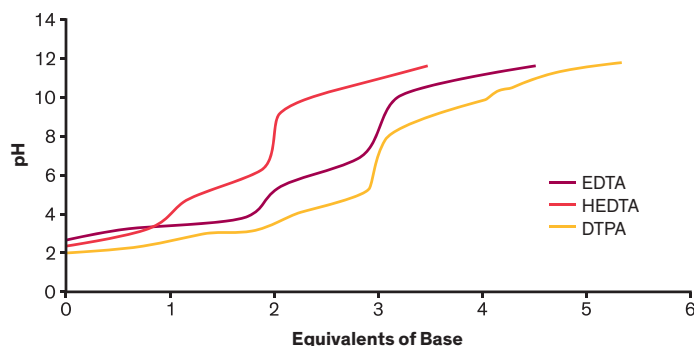
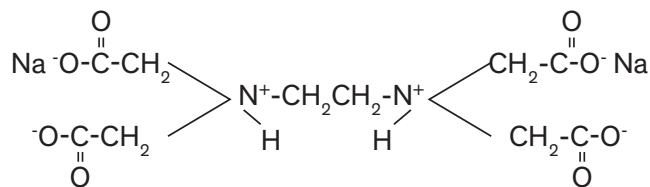
Table 1: Aqueous Solubility and pH of Free Acids

Material	Solubility		pH Saturated Solution, 25°C
EDTA	0.03%	0.42%	2.8
DTPA	0.33%	11%	2.2
HEDTA	6.0%	~70%	2.2

Acid-Base Titration Behavior

As aminopolycarboxylic acids, these chelating agents would be expected to form a series of possible salts upon titration with a strong base. Evidence that such salts actually do exist in solution is provided by the titration curves in Figure 4 for EDTA, DTPA, and HEDTA with standard sodium hydroxide solution.

The curve for EDTA indicates the disodium salt predominating at a pH of 5.0, the trisodium salt at a pH of 8.5, and the tetrasodium salt in the pH region of 11 and upward. The strongly basic nature of the tetravalent species is suggested by the fact that no inflection is seen when the titration is performed in dilute solution. The structure of the disodium dihydrogen ethylenediamine-tetraacetate is that of a “zwitterion,” shown in Figure 5.


Figure 4: Titration Curves for EDTA, DTPA, and HEDTA with NaOH

Figure 5: Structure of Disodium Dihydrogen Ethylenediaminetetraacetate

The structure of the trisodium salt is not unequivocally known. The tetrasodium salt is the most important of this series.

The curve for DTPA in Figure 4 indicates that the titration of the first three hydrogen ions occurs during an overlapping pH region, as is true of the first and second hydrogen ions from EDTA. The curve for HEDTA indicates that the monosodium salt predominates at a pH of 4.0, the disodium salt at a pH of 8.0 and the trisodium salt at a pH of 11.0 and above.

When a solution of a sodium salt of EDTA is titrated with a mineral acid, white crystals of ethylenediaminetetraacetic acid begin to precipitate at a pH of about 2.5. At a pH of 1.8, precipitation is essentially complete. Such precipitation may be used to recover the acid from its alkali metal and alkaline earth solutions. Similar precipitation of DTPA acid is possible, but it is more difficult because of the tendency of solutions to supersaturate.

The acid dissociation constants for EDTA, DTPA, and HEDTA have been measured and are given in Table 2.

Table 2: Acid Dissociation Constants*

Material	Solubility		pH Saturated Solution, 25°C
EDTA	0.03%	0.42%	2.8
DTPA	0.33%	11%	2.2
HEDTA	6.0%	~70%	2.2

From these values it is possible to calculate the relative distribution of each of the species present in an aqueous system as a function of the pH. Plots of this type are presented in Figures 6, 7, and 8.

Solubility of the Various Sodium Salts of EDTA, DTPA, and HEDTA

Because the particular sodium salt in an aqueous system of these chelating agents changes with the pH, and because the various salt forms have different solubilities, solubilities vary with the pH. Therefore, the maximum concentration of chelating agent present in solution is different for each different pH. Consequently, a solution of EDTA at a pH of 11.0 may be quite concentrated but still not saturated; yet if the pH is reduced to 5.0, the solubility of the disodium salt may be exceeded and precipitation of the chelating agent will then occur.

Solubility of the various sodium salt forms of EDTA is shown in Figure 9. The sodium salts of DTPA and HEDTA are, in general, more soluble. Those solubilities have not been accurately determined because of the tendency of the solutions to supersaturate.

Stability, Thermal and Chemical

The wide applicability of VERSENE™ Chelating Agents is due in large measure to their unusual stability. The free acids melt with decomposition at relatively high temperatures: EDTA being stable to 464°F (240°C), and DTPA beginning to decompose at 428°F (240°C). Prolonged heating, however, at temperatures in excess of 212°F (100°C) will cause substantial charring of these acids. The dry alkali metal salts, for example, Na₄ EDTA and Na₅ DTPA, are unaffected by prolonged heating at temperatures up to 392°F (200°C).

Aqueous solutions of the acids and the alkali metal salts are stable indefinitely under any temperature attainable at atmospheric pressure. Temperatures of 400-450°F (204-232°C) may result in decomposition. These solutions are not subject to bacterial or mold breakdown, and are unaffected by high acidity and high alkalinity. They are stable to 10% sulfuric acid and to 20% caustic soda, the limiting factor being solubility in these mediums.

Chemically, EDTA, DTPA, HEDTA, and systems of these chelating agents are extremely stable. VERSENE™ Chelating Agents actually assist in stabilizing solutions of reducing agents. However, in the presence of strong oxidizing agents such as chromic acid, potassium permanganate, and higher concentrations of peroxides, the materials are degraded as evidenced by the loss of chelating activity.

Chelation Reaction

VERSENE™ Chelating Agents are broad-spectrum metal chelating agents. They react with most metals to form stable chelates. These agents do not complex metal atoms in the free metallic state but coordinate only with ionized metals.

The most important and useful property of VERSENE™ Chelating Agents is this ability to form stable metal complexes.

Chelation is an Equilibrium Reaction

The generalizations that deserve equilibrium reaction systems apply to chelation as well.

One consequence is that small amounts of uncomplexed free metal ion and free chelating agent are present in all systems. These concentrations are so small that they are ordinarily of no practical significance.

Also, increasing the relative amount of chelating agent used always serves to decrease the concentration of free metal ions remaining in solution.

The system may be described by an equilibrium constant.

The Stability Constant

The equilibrium constant is a mathematical expression that relates the concentrations of the reactants and reaction products involved in any equilibrium reaction. For chelation reactions this constant is called the “stability constant” and is a measure of the affinity of the complexing agent for a particular metal.

It is apparent that a high value for K means a high ratio of chelated to unchelated metal in the system. This is the practical significance of K.

Practical Significance of Log K

Because a high value of the stability constant for a particular metal reflects a high stability for that chelate, the values of the logarithm of the stability constants for a chelating agent with a series of metals may be used to predict behavior of the chelating agent (Table 3).

If a number of different metal ions are present in a system, the chelating agent will react with the metals in order of decreasing log K values. If, for example, Fe⁺³, Cu⁺², and Ca⁺² are present in a system, any EDTA added will complex the iron first. When the iron is completely tied up, complexing of copper will begin. The calcium will be complexed only if an excess of EDTA above that required for both iron and copper is added.

Log K Values

Log K values for a displacement series when listed in order of decreasing magnitude. In most instances, any metal will displace from its chelate a metal below it in this series. For example, adding a copper ion to a solution of the calcium chelate of EDTA will result in copper replacing calcium in the chelate (see Figure 12). Since metals vary in their affinity for hydroxide (OH) groups, some deviation from the displacement series occurs. In certain instances, depending on the pH, a metal having a lower log K value will be chelated in preference to another metal even though the stability constant of the latter is higher.

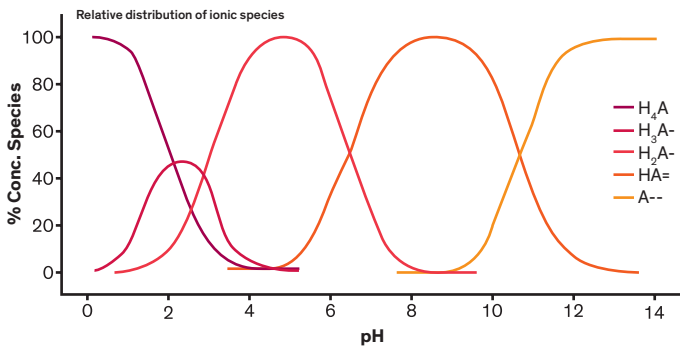


Figure 6: Distribution of Ionic Species in EDTA Solutions vs. pH

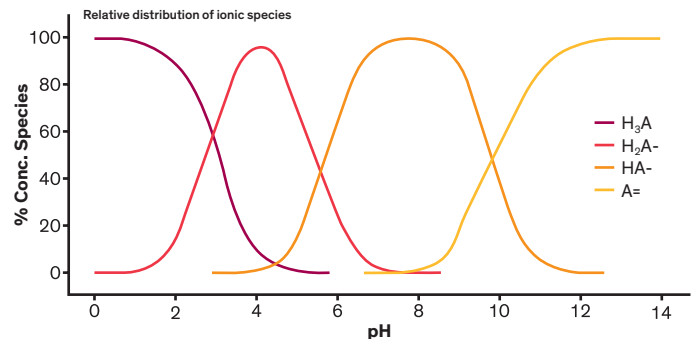


Figure 8: Distribution of Ionic Species in HEDTA Solution vs. pH

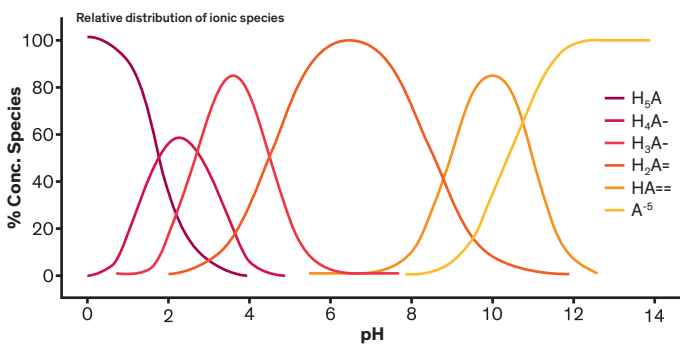


Figure 7: Distribution of Ionic Species in DTPA Solution vs. pH

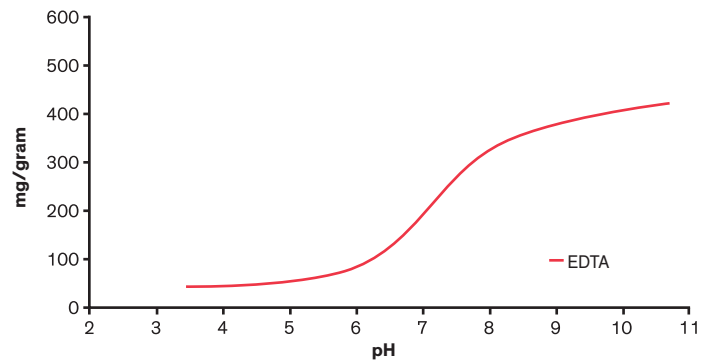


Figure 9: Solubility-pH Relationship for EDTA (25°C)



Figure 10: Reaction between Ferric Iron and EDTA

$$K_s = \frac{(\text{FeEDTA})^{-}}{(\text{Fe}^{+3})(\text{EDTA})^{-4}}$$

Figure 11: Equilibrium Constant for Ferric Ion-EDTA Reaction

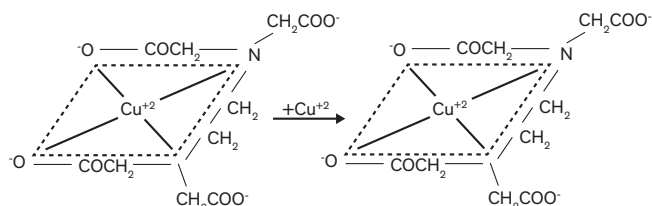


Figure 12: Replacement of Calcium with Copper in EDTA Chelate

Metal Ion-to-Chelating Agent Ratio

Important to understanding the chelation of metal ions with these agents is the fact that, except under exceptional circumstances, one mole of chelating agent reacts to complex one mole of metal. This permits calculating the amount of agent necessary to control any given metal ion.

Rate of the Chelation Reaction

Reactions between free divalent metal ions and these chelating agents in solution are practically instantaneous. With tri-positive ions the rates are relatively slower. Cr^{+3} and Co^{+3} , which exhibit similar behavior in other complex reactions, are exceptionally slow chelate formers.

The rates of reaction between the chelating agents and solid metallic salts are likewise slower. The degree of slowness depends on factors such as the solubility of the metallic salt, the degree of hydration of the solid, the crystalline nature of deposits, and the degree of subdivision of the solid phase. An excellent example of the effect of solubility of the solid on the chelation rate is provided by calcium sulfate and ferric oxide. The iron forms a much more stable chelate than does calcium. However, ferric oxide is so much more insoluble than calcium sulfate that the latter dissolves more quickly in solutions containing a VERSENE™ Chelating Agent.

The Nature of Chelated Metal Ions

Metals chelated with VERSENE Chelating Agents are still present in the system. They are inactivated because their reactive sites are stably blocked so they no longer undergo reaction or cause reaction in the system. This change in the nature of metal ions is reflected by changes in important physical properties.

Oxidation-reduction potential for the metal is changed. In general, for the free metal being oxidized to the ionic state, the potential is increased by the presence of the chelating agent. This increase is promoted by the metal ion being complexed as it forms. For the reaction between two different oxidation states of the same metal, the oxidation potential is increased if the metal in the higher oxidation state forms the more stable complex (see Figure 13). If on the other hand, the log K for the lower oxidation stage is greater, the oxidation potential will be decreased.

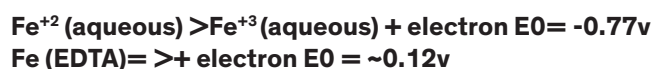


Figure 13: Oxidation Reduction Reaction

Polarographic behavior is also consistent with the decreased availability of the metal ion. Complexing the metal ion increases the half-wave potential. The polarographic behavior of the chelated metal as compared to the unchelated metal has been used as a method for determining the stability constants.

Absorption spectra have been described in the literature for the EDTA complexes of iron, copper, nickel, cobalt, and the rare earths. The alkaline earth complexes are colorless.

Effect of Environment on Chelation

Most industrial chemical systems that benefit by the addition of chelating agents are not simple systems of water and the metal ions. If they were, the selection of the proper agent and the most efficient use concentration would be clear-cut, based on the stability constants. Factors due to other materials in the system profoundly affect the metal-chelation reaction.

Effect of Temperature

In general, increased temperatures result in lower stability constants. However, this effect is usually quite negligible, on the order of only one log unit for each 100°F (38°C) of temperature change.

Effect of Other Metal Ions

Despite the slight effects due to the ionic strength, the only metals that influence the chelation reaction will be those that form stable chelates. Their effects will be relatively easy to predict from the stability constants.

In general, for metals possessing stability constants differing by three log units, the metal forming the most stable chelate will be chelated first, if none of the other environmental factors discussed are operative. If sufficient agent is still present, the lower stability chelate will form next according to the displacement series derived from the stability constants (Table 3).

Effect of Other Anions

The effect of other anions on the chelation reaction is usually nil. That is why EDTA, HEDTA, and DTPA chelating agents are so widely used as metal-control agents. The stability of the metal chelates is great enough so the average anion in the system is unable to displace and react with the chelated metal. For example, EDTA can be used to prevent natural soap from reacting with and precipitating calcium and magnesium hardness ions.

Chelating agents can also extract metal ions from less stable complexes or compounds already formed. The removal of copper oxide films from copper metal, accomplished easily by a Dow chelating agent at a pH of around 5.0, is an example.

However, a few anions exist which, by virtue of forming exceedingly stable metal complexes, can compete effectively with the chelating agents for the metal ions. Such a material is the sulfide anion. Metal sulfides, like the hydroxides, are

Table 3: Log K Values of Metal Chelates of EDTA, DTPA, and HEDTA
 ($\mu=0.1$ M KCl, $T=20^\circ\text{C}$ unless otherwise noted)

Metal	Atomic Weight	EDTA		DTPA		HEDTA	
		Log K	Ref.	Log K	Ref.	Log K	Ref.
V ⁺³	50.95	25.9	1	27.9	19	-	-
Fe ⁺³	55.85	25.1	2.12	28.6	11	19.8	12
In ⁺³	114.76	25.0	3	29.6	20	20.2	20
Th ⁺⁴	232.12	23.2	4	26.6	21	18.5	26
Sc ⁺³	44.96	23.1	4	26.5	22	17.3	27
Hg ⁺²	200.61	21.8	4	26.7	14	20.1	15
Ti ⁺³	47.90	21.3	5	Ti ⁺⁴ 23.4	23	-	-
Ga ⁺³	69.72	20.3	4	25.5-28.1	A, B	16.9	25
Cu ⁺²	63.54	18.8	4	21.1	9	17.4	16
VO ⁺²	(66.95)	(66.95)	18.8	4	-	-	-
Ni ⁺²	58.69	18.6	4	19.6	9	17.0	16
Pd ⁺²	106.7	18.5	6	29.7	24	-	-
Y ⁺³	88.92	18.1	4	22.3	22	-	-
Pb ⁺²	207.21	18.0	4	18.8	14	15.5	15
TiO ⁺²	(63.90)	17.3	5	-	-	-	-
Zn ⁺²	65.38	16.5	4	18.3	9	14.5	15, 16
Cd ⁺²	112.41	16.5	4	18.9	9	13.0	16
Co ⁺²	58.94	16.3	4	18.4	9	14.4	16
Al ⁺³	26.98	16.1	4	18.6	25	14.4	C
Fe ⁺²	55.85	14.3	4	16.5	11	11.6	16
Mn ⁺²	54.93	14.0	4	15.1	9	10.7	16
V ⁺²	50.95	12.7	1	15.1	9	-	-
Ca ⁺²	40.08	10.7	4	10.7	9	8.0	16
Mg ⁺²	24.32	8.7	7	9.0	13	7.0	15
Sr ⁺²	87.63	8.6	7	9.7	13	6.8	15
Ba ⁺²	137.36	7.8	7	8.6	13	6.2	15
Rare Earths	139-175	15.1-20.0	8	20.0-23.5	10	13.2-15.9	17, 18

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extremely insoluble. For this reason, VERSENE™ products are less effective as metal complexing agents when sulfide ions are present.

The insolubility of metal sulfides may be utilized advantageously in regenerating solutions containing VERSENE products. The spent solution is treated with high concentrations of sulfide ion, and soluble chelating agent can be decanted from the precipitate of the heavy metal sulfides formed.

Ionic Strength Effect

Because chelating agent-metal ion systems are in ionic equilibrium, the gross concentration of otherwise inert ions has some effect on chelating efficiency. Thus, high concentrations of sulfates, chlorides, phosphates, sodium ions, potassium ions, and other such materials not entering directly into the chelation reaction tend to lower the stability constant of the metal chelate. However, this effect is negligible in most cases because the stability constants are so great.

Effect of pH

After the stability constant, the most important factor is the pH of the system.

Because chelation is an equilibrium reaction, the entire system is changed by a material that can interact with any of the species present in the system. Hydrogen ions affect the equilibrium because both the metal ion and the chelating agent are sensitive to changes in the pH.

Because EDTA, DTPA, and HEDTA are polycarboxylic acids, the pH determines the particular ionic species which is present in the system (see Figures 6, 7, and 8). The primary chelating species are the tetra-negative EDTA ion, the penta-negative DTPA ion, and the tri-negative HEDTA ion. Increasing the acid concentration (lowering the pH) therefore favors formation of the less highly ionized, weaker chelating species. The competition seen in Figure 14, is between the metal ion (M) and the hydrogen ion for the chelating anions.



Figure 14: Competition of Metal and Hydrogen Ions for Chelating Ions

Since most of the chelates are quite stable, they can withstand a considerable pH drop. When the less strongly chelated alkaline earths are involved, however, the hydrogen ion competes with the metal ion successfully, precipitating the free EDTA acid from the chelates. Increasing the pH stabilizes the completely ionized chelating species, but this advantage is balanced by the tendency of the metal ion to interact with the hydroxide ion. In Figure 15, the competition is between the chelating agent and the hydroxide ions for the metal.



Figure 15: Competition of Chelating Agent and Hydroxide Ions for Metal

Heavy metal hydroxides are quite insoluble materials. When the hydroxide concentration is great enough, a VERSENE Chelating Agent will no longer prevent precipitation of the metal hydroxide. The pH at which such precipitation occurs may be raised by increasing the chelating agent-to-metal ion ratio, but cost is also increased.

The pH range over which a metal is chelated by a 1:1 ratio of agent to metal ion depends greatly on other materials in the system.

Chelation of Calcium

The most significant effect on the chelation of calcium is that of lowering the pH. As the pH drops, hydrogen ions successfully compete with calcium for the chelating agent. If chelation is measured by the standard oxalate titration method, it is seen that the calcium ion is quite completely chelated at a pH of 7.0. However, at a pH of 6.0, the acid begins to interfere with the calcium chelation markedly and at a pH of about 5.5 the calcium is no longer effectively chelated. This successful competition by hydrogen ions makes possible the regeneration of the pure EDTA acid from a system of calcium and a VERSENE Chelating Agent.

The effect of increasing the pH on the chelate is negligible to quite high concentrations of alkali. Optimal chelation of calcium occurs from a pH of 10.0 to 13.0, but the range of effective chelation is broader.

Chelation of Copper

The chelates formed by common divalent heavy metals and VERSENE™ Chelating Agents are stable enough to be relatively unaffected by increasing the hydrogen ion concentration, even down to a pH of 1.0. In fact, it is impossible to precipitate free EDTA acid from its copper chelate, and indications are that such chelates persist until the concentration of acid is high enough to form the amine salts.

The greatest effect pH has on such chelates is found at the higher end of the scale. Since the hydroxides of copper and such common metals are quite insoluble, the addition of hydroxide ions to raise the pH will eventually result in the precipitation of the metal as the hydroxide. In the case of copper, this point is reached at a pH of about 12.0.

Chelation of Iron

The chelation of iron is complicated by the fact that iron exists in both +2 and +3 oxidation states and is very prone to hydrolysis. The ferrous chelate is readily oxidized to the ferric chelate by atmospheric oxygen. Therefore, in most iron chelate systems, the +3 state will predominate.

The ferrous chelate behaves similarly to other divalent heavy metal chelates, remaining stable in the pH range of 2.0-12.0. Relatively weak hydrolysis begins at about a pH of 10.0, but generally this causes no problems.

Stability constants for ferric chelates are appreciably higher than for ferrous chelates. Consequently, the ferric chelate of EDTA is very stable at low pH values. As pH is increased, there

is a tendency for hydroxide complexes of ferric ions to form. Formation begins at a pH of 4.0-5.0, but low concentration of these soluble species usually are of little practical concern. Their control is brought about in part by the formation of basic complexes such as Fe(OH) EDTA in addition to the normal metal chelate.

As the pH of an aqueous solution of ferric EDTA is increased (Figure 16), precipitation of ferric hydroxide begins to occur at a pH of 8.0 and the chelate is completely converted to free EDTA and ferric hydroxide by a pH of 12.0. The ferric-HEDTA chelate is more resistant to hydrolysis and is not completely converted to free HEDTA and ferric hydroxide until a pH of 13.0 is reached. In alkaline solutions, VERSENOL™ 120 Chelating Agent should be used for ferric iron control.

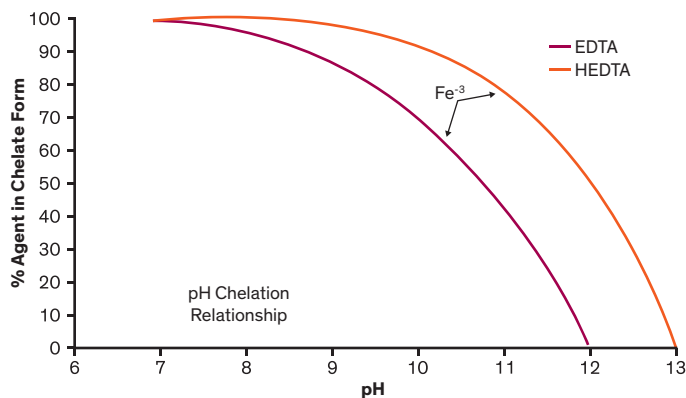


Figure 16: Chelation of Iron vs. pH

Chelation of Zinc

The behavior of the ions of amphoteric metals, such as the zinc ion, is quite similar at lower pH levels to that of other heavy metals. However, their behavior differs in the upper pH levels.

With amphoteric materials, for instance, no hydroxide is precipitated from chelated solutions. Instead, at some point of the pH scale, the chelated metal form gives way to the soluble metal hydroxide species. The transition point for zinc begins at about a pH of 9.0, but is not a major factor until a pH of 12.0 or greater. The soluble zincate results and persists as the pH continues to increase. Such behavior is true for most of the amphoteric materials. The only difference is the exact pH region at which such transformation occurs.

Conditional Stability Constants

The conditional stability constant, $K_{M'L'(ML)'}$, is a more practical expression of chelate strength than is a simple stability constant K_{ML} . It is defined in Figure 17.

$$K_{M'L'(ML)' } = \frac{([ML]')}{(M')(L')}$$

Figure 17: Formula for Conditional Stability Constant

Where (M') is the total concentration of metal in a solution that is not chelated, (L') is the total free chelating agent, and

([ML]') is the total metal chelate concentration. In this equation, the constant has been corrected for metal which is complexed with OH-, the chelating agent for interaction with H+, and the chelate corrected for chelates which include OH or H+. Thus, the conditional constant is not a real constant but depends on the experimental conditions.

Table 4 (on the next page) presents conditional stability constants for the common metal ion species at a pH of 0.0-14.0. To determine the order in which EDTA will react with the metal ions in a particular system, consult the appropriate pH column. The metal ion with the highest constant will be chelated first, then the next highest, and so on.

Table 4 shows the effect of pH on the chelation reaction. With Zn⁺² for example, the constant increases up to a pH of 9.0 as competition by H⁺ for EDTA is decreasing. At a pH of 10.0, however, the strong attraction of Zn⁺² for OH⁻ becomes a factor, and there is an increasing tendency for Zn⁺² to be in solution as an OH complex. Table 4 only considers ions in solution. Thus precipitation of the metal ion with hydroxide may occur when the stability constant is relatively low. Values from that table are illustrated in Figure 18 for some of the representative metals. Conditional stability constants are plotted as a function of pH to give a visual concept of how metal chelation varies in strength.

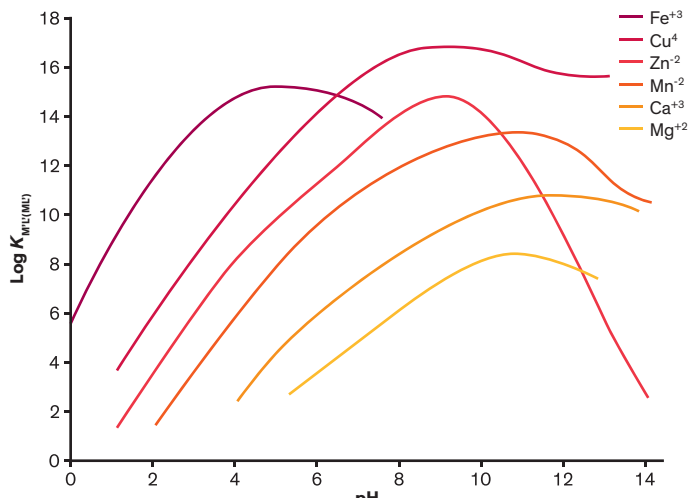


Figure 18: EDTA Conditional Stability Constants vs. pH for Select Metals

Table 4: EDTA, DTPA, and HEDTA Conditional Stability Constants

Log K _{M'L(ML)}																
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	K _{ML}
EDTA																
A1 ⁺³	-	-	2.8	5.2	7.2	8.1	7.2	5.9	3.9	3.4	1.0	-	-	-	-	-
Ba ⁺²	-	-	-	-	-	1.3	3.0	4.4	5.5	6.4	7.3	7.7	7.8	7.7	7.3	7.8
Ca ⁺²	-	-	-	-	2.2	4.1	5.9	7.3	8.4	9.3	10.2	10.6	10.7	10.4	9.7	10.7
Cd ⁺²	-	1.0	3.8	6.0	7.9	9.9	11.7	13.1	14.2	15.0	15.5	14.4	12.0	(8.4)	(4.5)	16.5
Co ⁺²	-	1.0	3.7	5.4	7.8	9.7	11.5	12.9	13.9	14.5	14.7	14.0	12.1	-	-	16.3
Cu ⁺²	-	3.4	6.1	8.3	10.2	12.2	14.0	15.4	16.3	16.6	16.6	16.1	15.7	15.6	(15.6)	18.8
Fe ⁺²	-	-	1.5	3.7	5.7	7.7	9.5	10.9	12.0	12.8	13.2	12.7	11.8	10.8	(9.8)	14.3
Fe ⁺³	5.1	8.2	11.5	13.9	14.7	14.8	14.6	14.1	(13.7)	(13.6)	(14.0)	(14.3)	(14.4)	(14.4)	(14.4)	25.1
Hg ⁺²	3.5	6.5	9.2	11.1	11.3	11.3	11.1	10.5	9.6	8.8	8.4	7.7	6.8	5.8	4.8	21.8
La ⁺²	-	-	1.7	4.6	6.8	8.8	10.6	12.0	13.1	14.0	14.6	14.3	13.5	12.5	11.5	15.4
Mg ⁺²	-	-	-	-	-	2.1	3.9	5.3	6.4	7.3	8.2	8.5	8.2	7.4	-	8.7
Mn ⁺²	-	-	1.4	3.6	5.5	7.4	9.2	10.6	11.7	12.6	13.4	13.4	12.6	11.6	10.6	14.0
Ni ⁺²	-	3.4	6.1	8.2	10.1	12.0	13.8	15.2	16.3	17.1	17.4	16.9	16.0	15.0	11.0	18.6
Pb ⁺²	-	2.4	5.2	7.4	9.4	11.4	13.2	14.5	15.2	15.2	14.8	13.9	10.6	(7.6)	(4.6)	18.0
Sr ⁺²	-	-	-	-	-	2.0	3.8	5.2	6.3	7.2	8.1	8.5	8.6	8.5	8.0	8.6
Zn ⁺²	-	1.1	3.8	6.0	7.9	9.9	11.7	13.1	14.2	14.9	13.6	11.0	8.0	(4.7)	(1.0)	16.5
DTPA																
A1 ⁺³	-	-	-	2.5	4.9	6.5	6.2	5.5	3.0	3.0	-	-	-	-	-	-
Ba ⁺²	-	-	-	-	-	-	1.6	3.5	5.5	7.1	8.1	8.7	8.8	8.7	8.3	8.8
Ca ⁺²	-	-	-	-	1.5	3.0	4.1	5.7	7.6	9.2	10.2	10.8	10.9	10.6	9.9	10.9
Cd ⁺²	-	-	2.1	5.1	7.5	9.7	11.7	13.7	15.7	17.2	17.8	16.9	14.5	10.9	(7.0)	19.0
Co ⁺²	-	-	3.0	5.9	8.1	9.9	11.7	13.7	15.6	16.9	17.2	16.7	14.8	(11.8)	(8.8)	19.0
Cu ⁺²	-	1.6	5.3	8.2	10.3	12.1	13.8	15.8	17.6	18.6	18.7	18.3	17.4	16.4	(15.4)	21.1
Fe ⁺²	2.5	-	0.6	3.5	5.6	7.2	8.8	10.7	12.7	14.5	15.7	16.4	16.5	16.5	16.5	16.0
Fe ⁺³	2.2	6.4	10.1	12.7	14.0	14.5	14.5	14.5	(14.5)	(14.2)	(13.5)	(12.8)	(11.9)	(10.9)	(9.9)	27.5
Hg ⁺²	-	6.1	9.8	12.3	13.4	13.8	13.8	13.8	13.8	13.4	12.4	11.0	9.1	7.1	5.1	27.0
La ⁺²	-	-	0.3	4.2	7.3	9.8	11.8	13.8	15.8	17.4	18.1	18.0	17.2	16.2	15.2	19.1
Mg ⁺²	-	-	-	-	0.4	1.9	3.0	4.3	6.0	7.6	8.6	9.1	8.8	(8.0)	(7.0)	9.3
Mn ⁺²	-	-	-	2.1	4.3	6.3	8.2	12.2	12.2	13.8	14.7	14.9	14.1	13.1	12.1	15.5
Ni ⁺²	-	1.3	5.0	7.9	10.0	11.6	13.0	16.9	16.9	18.4	18.1	18.5	17.6	16.6	15.6	20.2
Pb ⁺²	-	-	2.5	5.4	7.6	9.6	11.5	13.4	15.0	15.7	15.4	14.0	11.4	(8.3)	(5.4)	18.8
Sr ⁺²	-	-	-	-	-	0.9	2.5	4.4	6.4	8.0	9.0	9.6	9.7	9.6	9.1	9.7
Zn ⁺²	-	-	3.2	6.1	8.2	9.8	11.2	13.1	15.1	16.5	15.3	12.9	9.9	(6.6)	(2.3)	18.4
HEDTA																
Ba ⁺²	-	-	-	-	-	0.9	2.3	3.4	4.4	5.3	6.0	6.2	6.2	6.1	5.7	6.2
Ca ⁺²	-	-	-	-	1.2	3.1	4.5	5.6	6.6	7.5	8.2	8.4	8.4	8.1	7.4	8.4
Cd ⁺²	-	-	1.0	3.6	5.8	7.7	9.1	10.2	11.2	12.0	12.3	11.0	8.5	(4.9)	(1.0)	13.0
CO ⁺²	-	-	2.4	5.0	7.2	9.1	10.5	11.6	12.5	13.1	13.1	12.2	10.2	(7.2)	(4.2)	14.4
Cu ⁺²	-	2.4	5.4	8.0	10.2	12.1	13.5	14.6	15.4	15.7	15.5	14.7	(13.7)	(12.7)	(11.7)	17.4
Fe ⁺²	-	-	0.2	2.8	5.0	6.9	8.3	9.4	10.4	11.5	12.4	12.7	12.7	12.7	12.7	12.2
Fe ⁺³	1.9	4.8	7.8	10.1	11.2	11.9	12.3	(12.4)	(12.4)	(12.3)	(12.0)	(11.2)	(10.2)	(9.2)	(8.2)	19.8
Hg ⁺²	2.2	5.1	8.1	10.2	11.0	10.9	10.3	9.4	8.4	7.3	6.0	4.2	2.2	0.2	-	20.1
La ⁺²	-	-	1.4	4.0	6.2	8.1	9.5	10.6	11.6	12.5	12.9	12.4	11.5	10.5	4.5	13.4
Mg ⁺²	-	-	-	-	-	0.5	1.9	3.0	4.0	4.9	5.6	5.7	5.3	(9.5)	(3.5)	5.8
Mn ⁺²	-	-	-	1.3	3.5	5.4	6.8	7.9	8.9	9.8	10.4	10.2	9.3	(8.3)	(7.3)	10.7
Ni ⁺²	-	2.0	5.0	7.6	9.8	11.7	13.1	14.2	15.2	16.0	16.1	15.4	14.4	13.4	12.4	17.0
Pb ⁺²	-	0.5	3.5	6.1	8.3	10.2	11.6	12.6	13.2	13.2	12.6	10.8	(8.1)	(5.1)	(2.1)	15.5
Sr ⁺²	-	-	-	-	-	1.5	2.9	4.0	5.0	5.9	6.6	6.8	6.8	6.7	6.2	6.8
Zn ⁺²	-	-	2.5	5.1	7.3	9.2	10.6	11.7	12.7	13.4	11.9	9.1	(6.0)	(2.7)	-	14.5

Note: Values in parentheses are inclusive of the metal hydroxide ligand complex.

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