Chelates: What They Are and How/Where They Fit

Vatren Jurin Technical Director Brandt Consolidated Inc



Chemistry 101

CHELATION:

Chelation is from <u>Greek</u> χηλή, *chelè*, meaning claw.

These ligands, which are often <u>organic</u> <u>compounds</u>, are called chelants, chelators, chelating agents, or <u>sequestering agent</u>.

The ligand forms a **chelate complex** with the substrate. The term is reserved for complexes in which the metal ion is bound to two or more atoms of the chelating agent.

COMPLEX:

The term **complex** in <u>chemistry</u>, also called a "coordination compound" or "metal complex", a structure consisting of a central atom or molecule connected to surrounding atoms or molecules.

ORIGEN OF THE USE OF CHELATES IN AGRICULTURE



- NATURE
- SYNTHETIC

Tennessee Valley Authority



SOIL AS A SOURCE OF CHELATES AND COMPLEXES



TENESSE VALLEY AUTHORITY

- THE DEVELOPMENT OF LIQUID FERTILIZER
 SOLUTIONS WITH
 PHOSPHATES
- Created an oportunity to deliver Micronutrients
- Strong Chelates were needed
- EDTA'S are introduced from other Industries.

Nutrient Forms



INORGANIC SALTS

- Metal exposed
- Water Solubility
- Not Complexed







Sulfates





Carbonates





Nitrates



Ammonium

Ammonium is often used to complex metals in conjunction with other organic acids such as citric acid. Ammonia (NH4+) is deprotinated to ammonium (NH3) in alkaline conditions so solutions need to be sufficiently alkaline (pH's >9) to allow ammonia to complex metal. Ammoniated Zinc is one of the most common and is used for with Starter NPK's ie 10-34-0



Stepwise Formation Constants

| ion | K _n | log K _n |
|--|----------------|--------------------|
| [Cu(NH ₃)(H ₂ O) ₅] ²⁺ | K ₁ | 4.25 |
| [Cu(NH ₃) ₂ (H ₂ O) ₄] ²⁺ | K ₂ | 3.61 |
| [Cu(NH ₃) ₃ (H ₂ O) ₃] ²⁺ | K ₃ | 2.98 |
| [Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ | K_4 | 2.24 |
| [Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ | К _f | 13.08 |

| Equilibrium Reaction | Log K _f |
|--|--------------------|
| $Cu^{2+} + 4NH_3 \leftarrow \rightarrow [Cu(NH_3)_4]^{2+}$ | 13.0 |
| $Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$ | 8.6 |

Complexes

- Sugar Alcohols
- Organic Acids
- Glucoheptonates
- Lignin Compounds
- Amino acids



- Water Soluble
- Are present in all biological organisms.





Lignin (Courtesy of "Real-World in green chemistry."

Glucoheptonate & Gluconate





Glucoheptonates and Gluconates are biodegradable complexes/chelates that is useful as an alternative for very high pH solutions, especially for Fe⁺³ and Cu⁺²

Stability Constants (Log K Values)¹

[ML]/[M][L]

| | Glucoheptonate | Gluconate |
|-------|----------------|-----------|
| A/+3 | | |
| Ca+2 | 1.25 | 2.2 |
| Cu +2 | 41.2 | 38.9 |
| Fe+2 | 1.1 | 1 |
| Fe+3 | 38.3 | 37.2 |
| Mg+2 | 0.78 | 0.7 |
| Mn+2 | | |
| Zn +2 | 1.82 | 1.7 |

¹ R.M Smith; A.E. Martell, Crtiical Stability Constants, Plenum Press, New York and London, 3rd Edition.

Citrate

Citric acid is natural biodegradable chelator. Because of its carboxyl groups, citric acid chelates / complexes metals in the acidic environment. Often used for formulation stability and foliar applicactions



| | Citrate | |
|-----------------|---------|--------|
| | рКа | Log Kf |
| рК ₃ | 6.1 | 6.1 |
| рК ₂ | 4.6 | 10.7 |
| рK ₁ | 3.1 | 13.8 |



| Stability Constants (Log K Values) ¹ | | | | |
|---|-----------------|-------------|--|--|
| CITRATE | | | | |
| | [MHL]/[M][H][L] | [ML]/[M][L] | | |
| AI +3 | 11.8 | 8.1 | | |
| Ca +2 | 7.6 | 3.4 | | |
| Cu +2 | 9.5 | 6.7 | | |
| Fe +2 | 8.7 | 4.5 | | |
| Fe +3 | 12.4 | 11.2 | | |
| Mg +2 | 7.2 | 3.2 | | |
| Mn +2 | 7.1 | 3.7 | | |
| Zn +2 | 8.7 | 5.0 | | |

¹ R.M Smith; A.E. Martell, Crtical Stability Constants, Plenum Press, New York and London, 3rd Edition.

Synthetic Chelates

- EDTA
- EDDHA
- DTPA
- HEDTA
- NTA

- pH range
- Synthetic
- Metal scavenger
- Carcinogenic



Metal-EDTA complex

EDTA

EDTA forms strong water soluble chelates with polyvalent metal ions over a fairly wide range of pH.

Two concurrent processes are at work here: the deprotonation of EDTA in alkaline media, which is responsible for the chelates' increased stability in alkaline media, and the formation of sparingly soluble metal hydroxides referred to earlier. Iron(III) ions are only chelated in acid media, but iron(II) ions form complexes in both the acid and alkaline pH ranges.



London, 3rd Edition,





London, 3rd Edition.



¹ R.M Smith; A.E. Martell, Critical Stability Constants, Plenum Press, New York and London, 3rd Edition.

WHATS OUR ULTIMATE GOAL



• IN THE LEAF

Britannica

• IN THE SOIL SOLUTION



Soil Applied



Foliar Applied





Thanks