

THE USE OF MOLECULAR MODELING TO TEACH ANALITICAL CHEMISTRY

Carlos Rius-Alonso, Yolanda González-Quezada, Alain Quere Thorent

Universidad Nacional Autónoma de México (MEXICO)

Abstract

Analytical chemistry deals with the use of instrumentation to determine structure or properties of pure compounds or mixtures. The change in the protonation state of an acid that occurs around its pK_a is used in the pH indicators, molecules that change color as a function of their protonation state. This change of color is related to the electronic distribution within the molecule. A small amount of pH indicator added to a solution is often enough for visually observe a change in the pH of that solution during a reaction or titration. In this case the indicator is either protonated or deprotonated during the pH change. Bicolor indicators are used in a wide variety of applications. In this part of the teaching of the analytical course, the change of color is related with the change of the electronic distribution within the molecule. During this part over the course, the relation between the structure and the electronic absorption in the visible region is discussed using Molecular Modeling programs. Some of the common pH indicators are discussed. This is a valuable help for students not only to understand the concept of pH but to correlate the change of color with the change of the structure. Complex formation between metallic ions in aqueous solutions and polydentate ligands like EDTA may be also simulated using molecular modeling programs.

Keywords: analytical chemistry, molecular modeling, pH, acid-base indicators.

1 INTRODUCTION

Analytical chemistry of solution deals with reactions and equilibrium state of solutes in order to find appropriate conditions to characterize or quantify analytes.

Acid-base indicators are used in many procedures of classical analysis, and the color change is the result of electronic changes of the indicator molecules or of its ionized forms, caused by the exchange of protons. The exchange of protons takes place at pH values in the vicinity of pK_a of the molecule indicators.

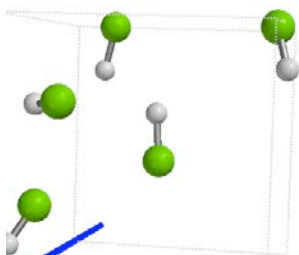
The teaching of how acid-base indicators work may be purely phenomenological, based only on pK_a values and the Henderson-Hasselbalch relation, or it can be visualized through structural changes and its implications on the electronic absorption spectra in the visible region. Most frequently used acid-base indicators are discussed using molecular modeling programs like Odyssey and Spartan. This is a valuable help for students not only to enhance learning about the concept of pH but also to correlate the change of color with the change to the structure of the indicators.

Similarly complex formation between metallic ions in aqueous solutions and polydentate ligands like aminopolycarboxylic acids may be simulated using molecular modeling programs. The process of complex formation between EDTA and a series of metallic cations allows discussion of the effect pH and of the ionic radius of metallic cations and thermodynamic stability of formed complexes.

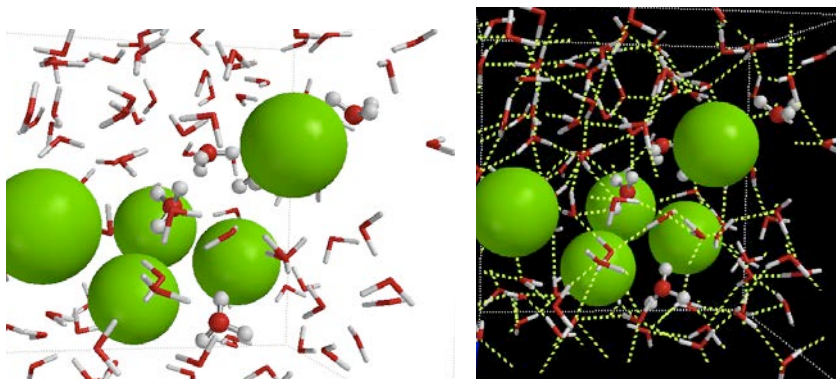
With the aid of 3D structures, the understanding through the process is easier for students.

1.1 Acids and bases

In dilute aqueous solutions, the covalent polar bond of the molecule HCl is ionized because of hydration effects, and the ions formed are almost completely dissociated because of the high dielectric constant of water and of the hydration of the ions. As a result of this processes, HCl in aqueous dilute solutions is considered as a "strong" electrolyte. When HCl is in gas phase, the atoms are held together, but in water, immediately the proton of the HCl is captured by the water.



a) Representation of HCl in the gas phase. Dipole moment of the molecule: 1.08 D.

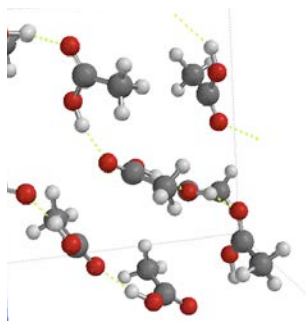


b) HCl in water, hydrogen bonds not visible.
H⁺ ions have been transferred to water molecules.

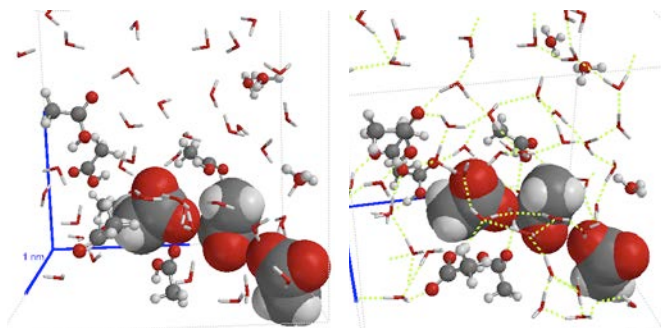
c) HCl in water, hydrogen bonds visible.

Fig 1. HCl.

In a weak acid like acetic acid, only few molecules are ionized, the amount of ionized molecules depends on the strength of the acid and the concentration.



a) Acetic acid in the gas phase. Dipole moment of the molecule: 0.98 D.

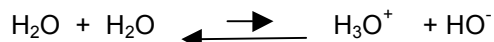


b) Acetic acid in water, hydrogen bonds not visible. c) Acetic acid in water, hydrogen bonds visible.

Fig 2. Acetic acid.

1.1.1 Water and the pH scale

Friedrich Kohlrausch in 1884 published a paper¹ "On the electrical conductivity of water distilled in vacuo" he reported that even after having purified water several times and avoiding any contaminant, (solid liquid or gas). The liquid was still able to conduct a low electrical current, suggesting the presence of ions that can move through the water. This is referred to as self-ionization of water.



The equilibrium constant for self-ionization of water (K_w) is known as *ionization constant for water*. The concentration of $[\text{H}_3\text{O}^+]_{\text{aq}}$ ions and $[\text{OH}^-]_{\text{aq}}$ in pure water must be the same. Using electrical conductivity measurements on pure water indicates that $[\text{H}_3\text{O}^+]_{\text{aq}} = [\text{OH}^-]_{\text{aq}} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$ at 25°C

The law of mass action was developed by Guldberg and Waage in 1867. Ostwald set his dilution law ten years after in 1877². Henderson in 1908 devoted to the study of blood and respiratory functions, published two articles to put forward a simple formula linking $[\text{H}^+]$ and the composition of a buffers solution.^{3,4}

$$[\text{H}^+] = K_a [\text{acid}]/[\text{salt}]$$

One year after Soren Sorensen in 1909.⁵ Introduced the pH concept and the pH scale. In 1916, Hasselbalch merged Henderson's buffer formula with Sorensen's pH scale and wrote an expression now known as the Henderson-Hasselbalch equation⁶.

1.1.2 Acid-Base Indicators

Indicators may be used to measure pH, taking advantage of their color changes when varying pH their color changes with pH. The process is a visual comparison with the color developed in a test solution with a standard color chart for the indicator used.

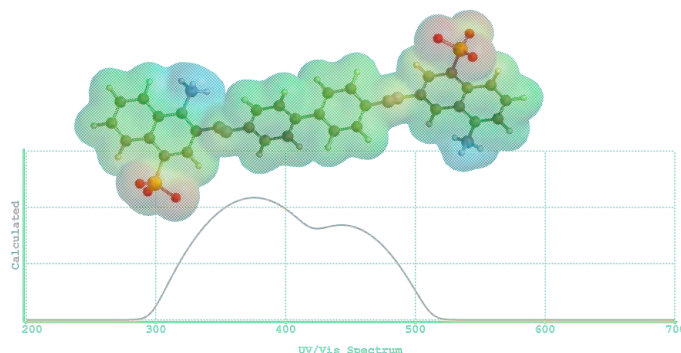
Many bicolor indicators are molecular compounds that usually have a strong conjugation of pi-electrons along the molecules, which allows absorption of light in the visible region of the electromagnetic spectrum. When the electronic configuration changes because of proton transfer, a change in color is observed.

Representations of molecular changes and of the corresponding calculated UV-visible spectra of some bicolor indicators are easily obtained thanks to molecular modeling programs like Spartan and Odyssey, as can be seen afterwards. .

The UV-Vis spectra were calculated using Hartree Fock with 3-21G base, in the vacuum. The spectrums are an approximation of the experimental spectra and are an aid for students to understand the change of absorption with the change of structure. More complex calculation can be done having the computer time for them. Comparing different levels of theory can help students understand the shift in absorption.

1.1.3 Congo Red

Congo red is; disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenyl]phenyl]phenyl]diazenyl-naphthalene-1-sulfonate, is a secondary diazo dye, is soluble in water and alcohol. Change color from blue (at pH below 3) to red (at pH above 5.2).



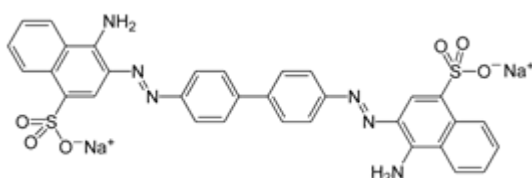
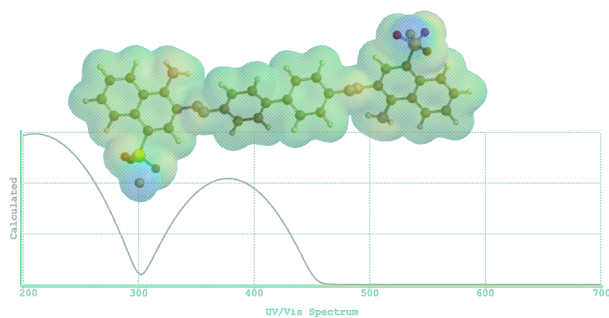
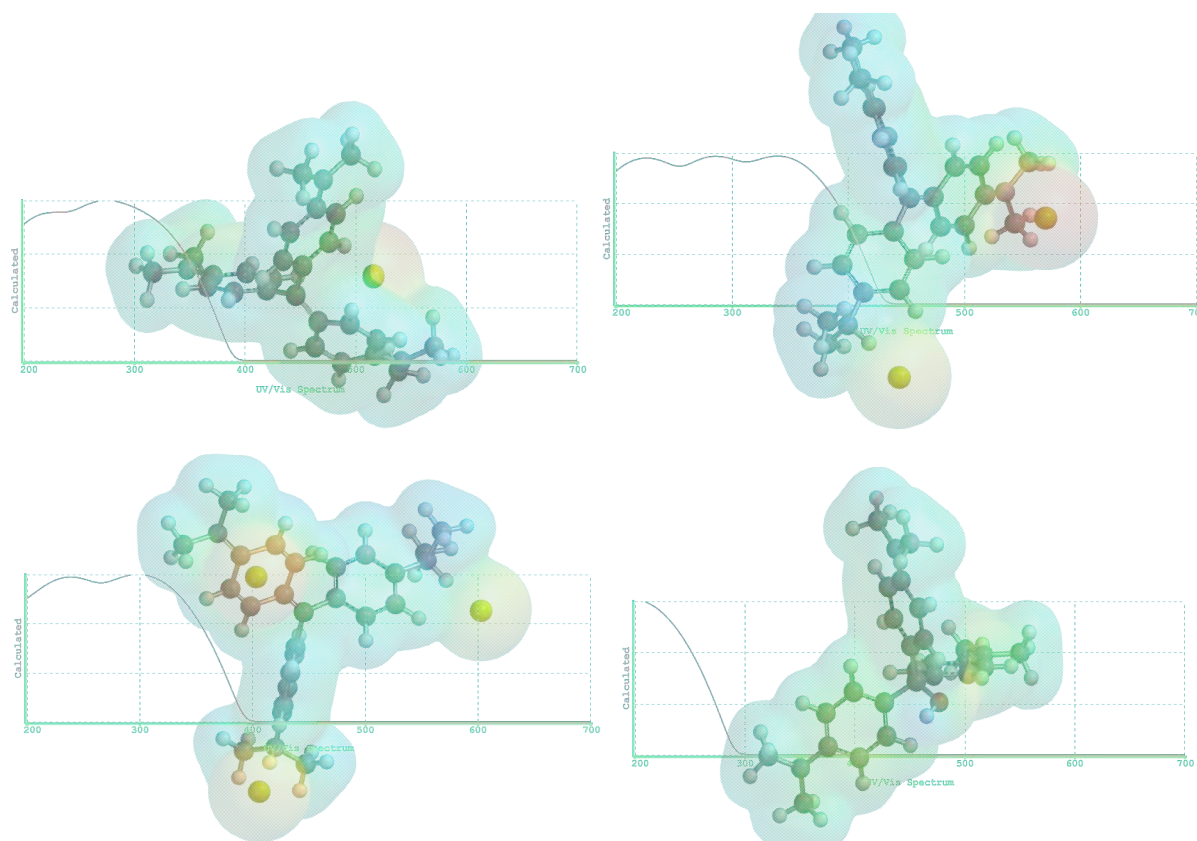


Fig 3. Congo red at different pH. First spectra pH acid, second pH basic.

1.1.4 Crystal Violet

Gentian Violet is a triarylmethane dye also known as “Crystal violet”; it is used as histological stain. It has antibacterial antifungal and anthelmintic properties. Very diluted solutions in water shows a blue-violet color. At pH 1, the color of the solution is green and in concentrated strong acid it is yellow. In strong alkaline solution, the central carbocation is attacked by hydroxyl ions and produces triphenylmethanol, colorless.



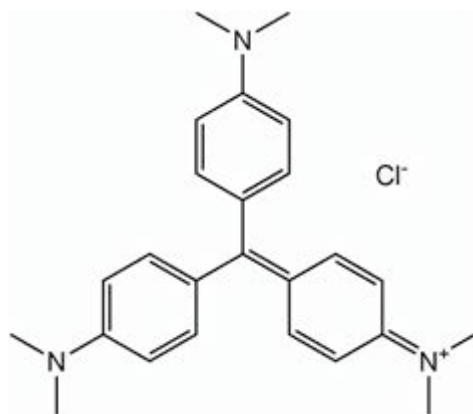


Fig 4. Crystal Violet. At different pH and with their absorption spectra.

1.1.5 Bromophenol blue

It is an acid-base indicator, below pH3.0 is yellow and above pH4.6 is purple. It is used also as dye at neutral pH transmit blue light.

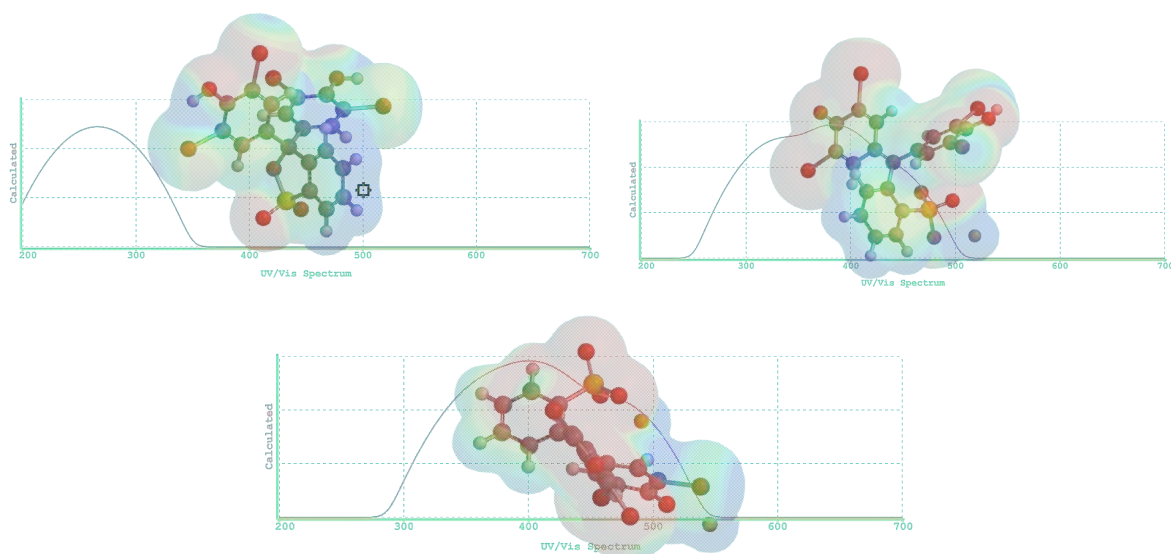
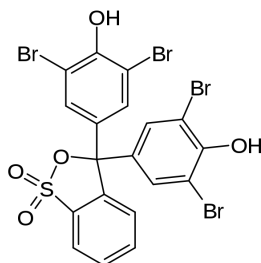


Fig 5 Bromophenol Blue.

2 CHELATING AGENTS

2.1 EDTA

Ethylenediaminetetraacetic acid, is very useful for chelating metals because of its role as hexadentate ligand and sequester metal ions. It usually binds to a metal cation through its two amines and four carboxylates ions. In acidic medium, protonation of EDTA destroys the complexes formed with metal cations. Depending of the size of the metal ion it adopts octahedral geometry with small metals ions, and with large metals ions, the geometry is deformed.

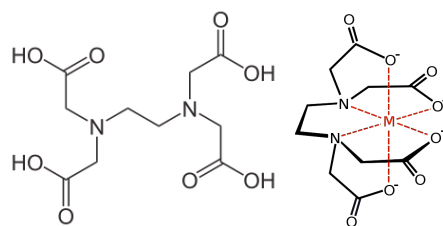


Fig 6 EDTA

2.2 Li+1 Lithium

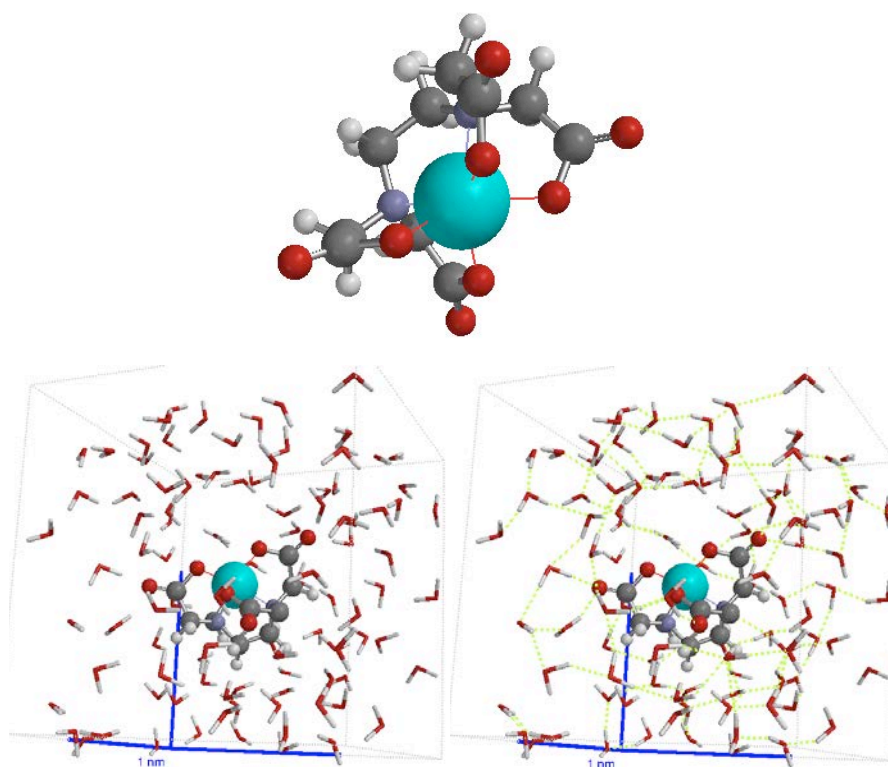
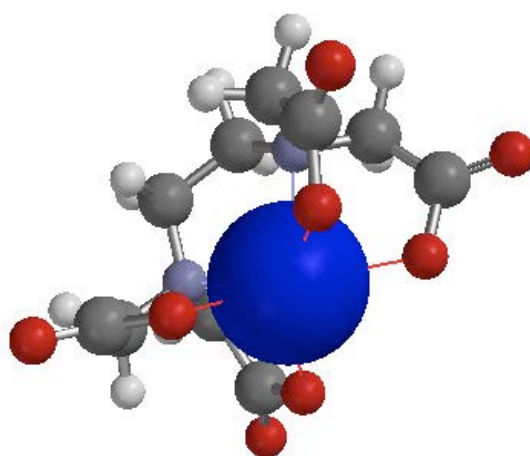


Fig 7 EDTA with Li.

2.3 Na+1 Sodium



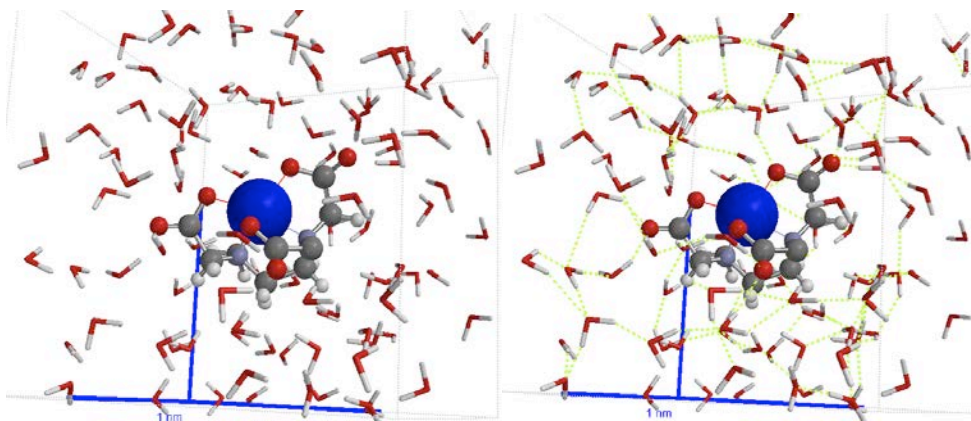


Fig8 EDTA with Na.

2.4 K+1 Potassium

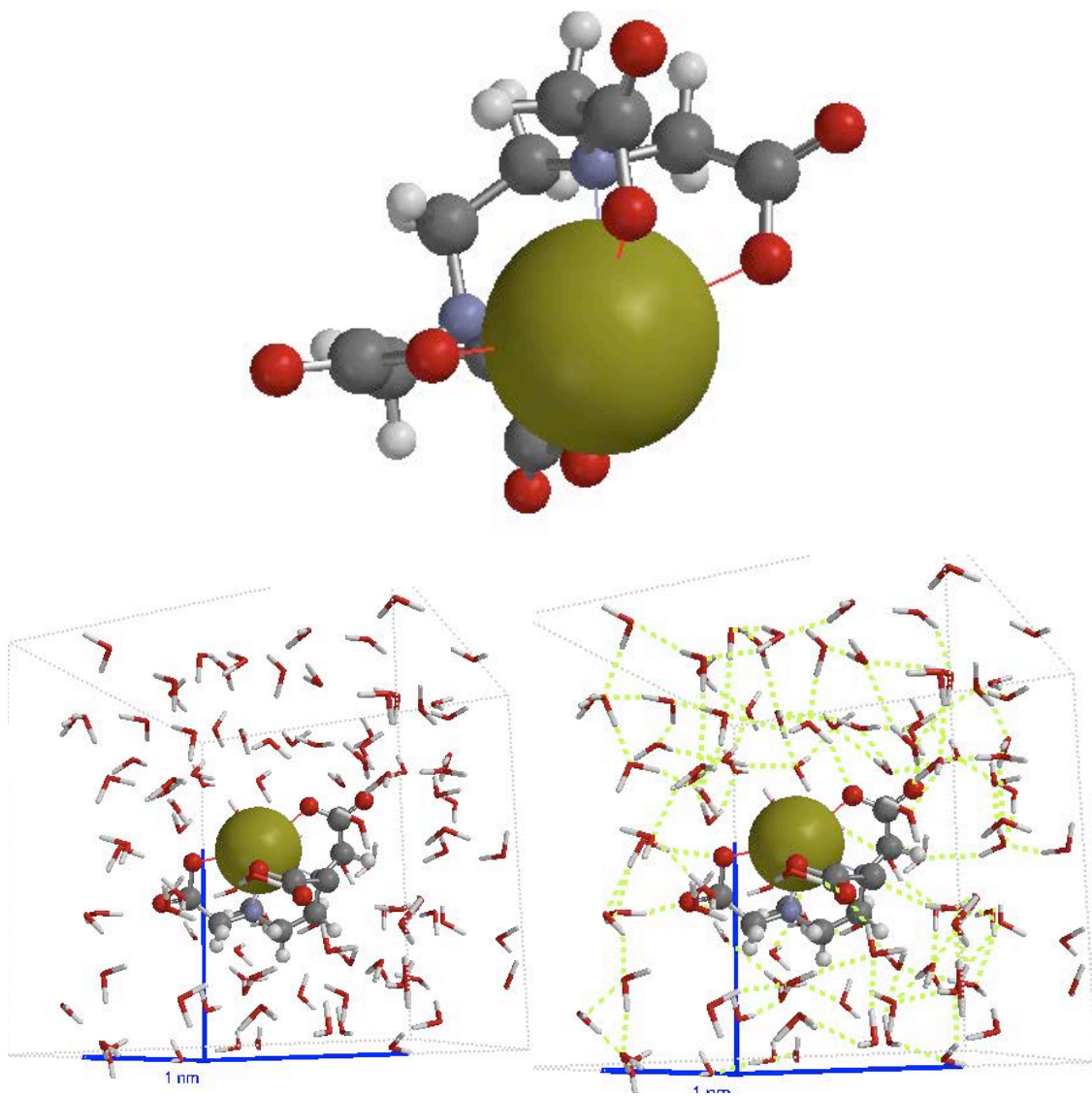


Fig 9. EDTA with K.

2.5 Cs+1 Cesium

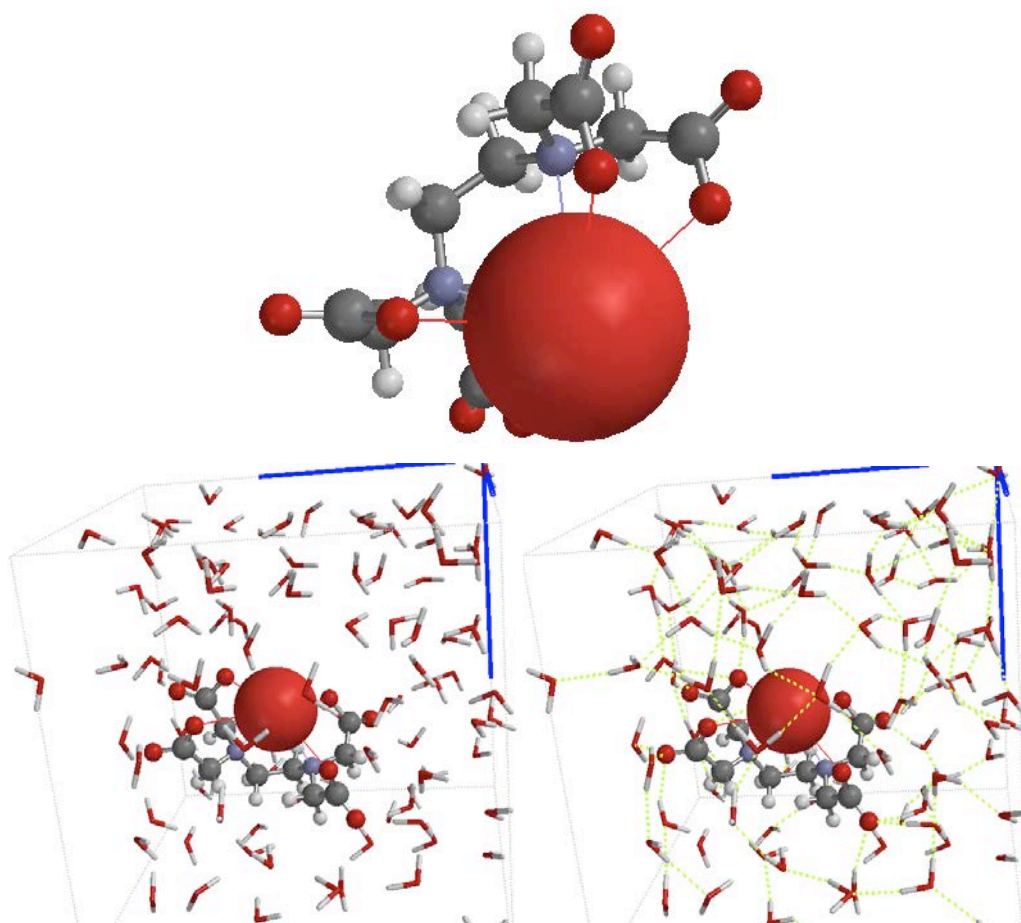
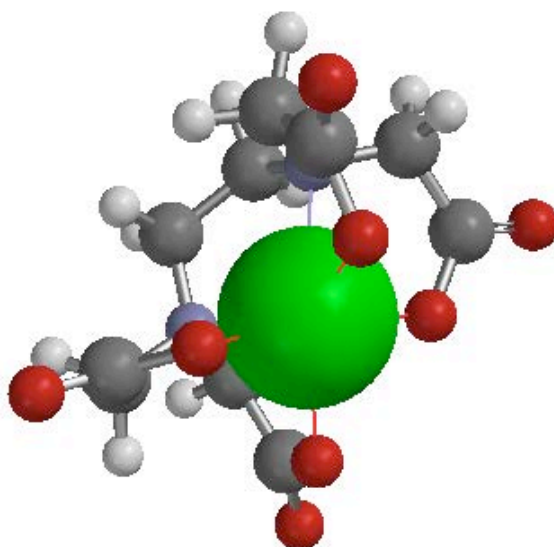


Fig 10. EDTA with Cs.

2.6 Ni+2 Nickel



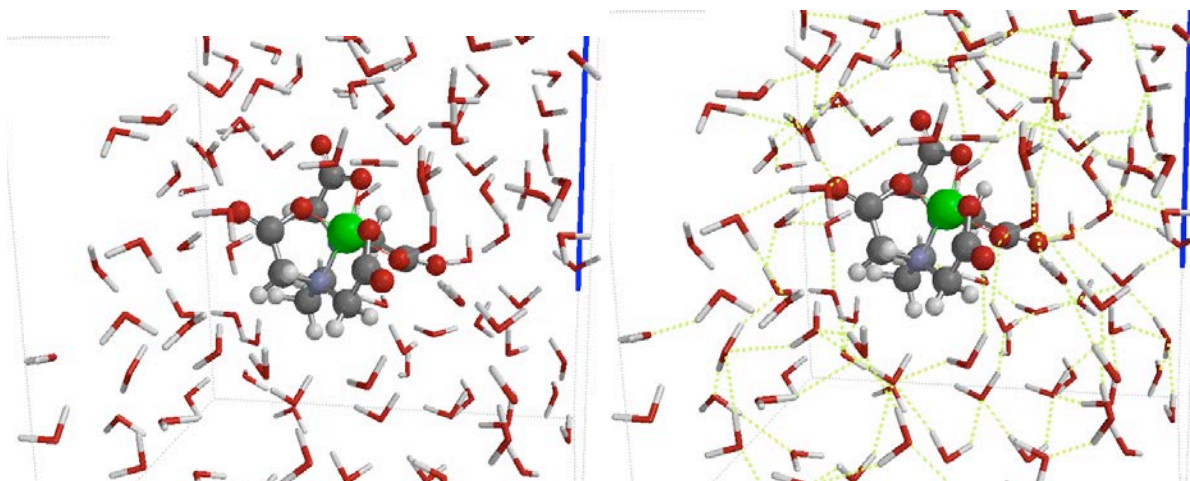
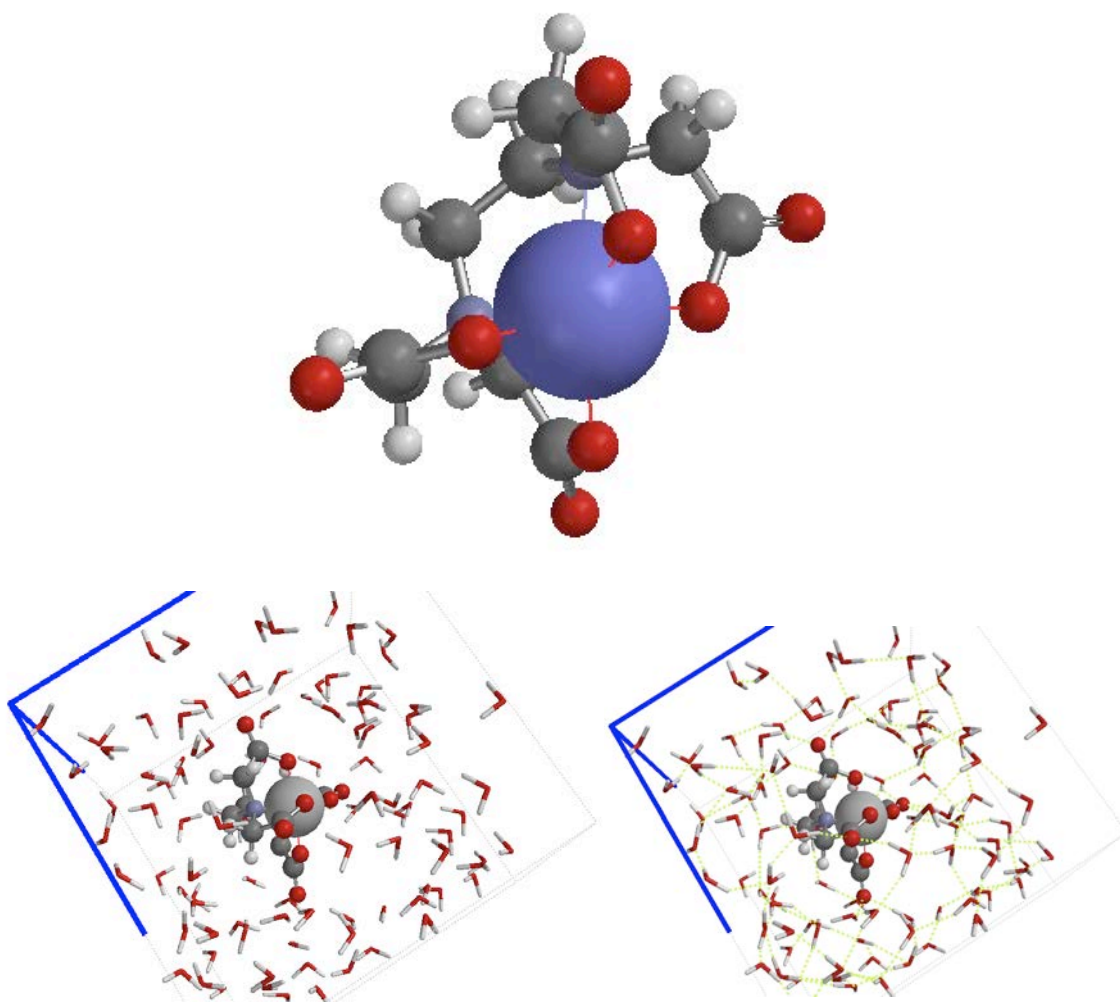


Fig 11. EDTA with Ni.

2.7 Co+2 Cobalt



Flg 12 EDTA with Co.

3 CONCLUSION

This work shows that with the aid of molecular modeling programs like Spartan and Odyssey, it is easy to illustrate some properties of acid-base indicators such as color change and UV-Vis spectra that enhances teaching in that subject. It is also possible to illustrate complex formation between polydentate ligands as aminopolycarboxylic acid and discuss with students the effect of metal ion size on geometry of complex formed.

AKNOWLEDGMENTS

This work was partially supported by a grant from Dirección General de Asuntos del Personal Académico (DGAPA) Universidad Nacional Autónoma de México PE205313.

REFERENCES

- [1] Kohlrausch F. "On the electrical conductivity of water distilled in vacuo", *Philosophical Magazine Series 5*, volume **18**, issue *115*, 1884.
- [2] Po H.N., Senozan, N.M., The Henderson-Hasselbalch Equation: its history and limitations. *J. Chem Educ.* **78**, 11, 1499
- [3] Henderson, L. J. Am. J. Physiol. 1908, 21, 173–179.
- [4] Henderson, L. J. Am. J. Physiol. 1908, 21, 427–448.
- [5] Sørensen, S. P. L. Biochem. Z. 1909, 21, 131–200.
- [6] Hasselbalch, K. A. Biochem. Z. 1916, 78, 112–144.
- [7] All the figure were done using Spartan an Odyssey form Wavefuntion <http://www.wavefun.com/>