Chem Factsheet

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EDTA

Prior Knowledge

To get the most from this Factsheet you should already be familiar with the following terms: *ligand, co-ordinate bond, complex, chelate, ligand exchange* and *co-ordination number*. Factsheet 139 "Ligand Exchange Reactions" will be useful to this end.

After working through this Factsheet you should be able to:

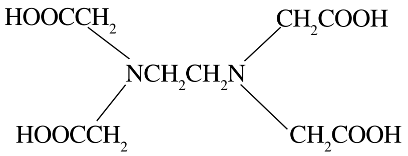
- recall and understand the uses of the complexing agent known as EDTA and its related substances
- do calculations based on the use of EDTA and its related substances
- interpret information about EDTA and its related substances.

Introduction

EDTA is the acronym for the organic compound **e**thylene**d**iamine**t**etra**a**cetic acid. (With some sources quoting 2,2',2'',2'''-(ethane-1,2-diyldinitrilo)tetraacetic acid as the systematic name and others using 2-[2-[bis(carboxymethyl)amino]ethyl-(carboxymethyl)amino]acetic acid it is not surprising that it is commonly referred to as simply "EDTA".) Worldwide over 100,000 metric tonnes are produced annually. Clearly it and related compounds are of great importance. (There is even a song about it sung to the tune of "YMCA" - the January 1979 hit song by the Village People, and a YouTube clip of it!)

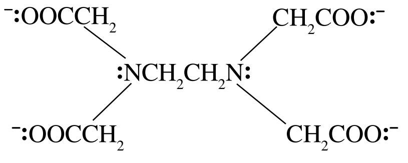
The EDTA molecule is shown below (Fig. 1). When looking at such representations it is useful to remember that all molecules are three dimensional and that rotations can occur around many points in them.

Fig. 1 The EDTA molecule



The anion ($EDTA^{4-}$ shown in Fig. 2) is a very important *ligand* and ***chelating agent*** that is formed by the EDTA molecule losing a proton from each of the carboxylic acid groups (COOH).

Fig. 2 The EDTA anion

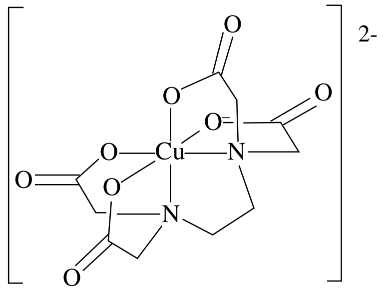


A particle that has more than one site which can act as a ligand towards a metal ion is said to be *polydentate* or *multidentate*. (The word "dentate" is from the Latin for tooth – think of these ligands as being able to "bite" the metal ion more than once.)

The $EDTA^{4-}$ **ion** can form **six** co-ordinate (or "dative co-valent") bonds with a metal ion and so is also known as an ***hexadentate ligand***. (Note the six available lone pairs of electrons - two from nitrogen atoms in the amine groups and four from oxygen atoms in the original carboxylic acid groups – there are other lone pairs but 3D geometry means they are not used.)

Fig. 3 shows the complex formed between $EDTA^{4-}$ and Cu^{2+} (You would not be expected to draw this but might be presented with such a structure. Ensure that you are familiar with what it actually represents. See advice - **)

Fig. 3 The copper(II)-EDTA complex $[Cu(EDTA)]^{2-}$



For this complex the ***co-ordination number*** is six and its shape is ***octahedral.***

The formula of the complex is: $[Cu(EDTA)]^{2-}$
Notice that the overall charge on the complex is worked out as follows:
Charge on complex = (charge on metal ion) + (sum of charges on all ligands involved in complex)
= (charge on metal ion) + (charge on one EDTA ion)
= (2+) + (4-)
= 2-

**ADVICE: It is difficult to visualise and fully appreciate the three dimensional structure of an ion complexed with $EDTA^{4-}$. Use a model kit such as Molymod to make a model of firstly EDTA and then remove the appropriate hydrogens to yield the $EDTA^{4-}$ ion. Link the ion to a sphere having 6 holes so as to represent a complexed metal ion like the one in (figure 3). Handle the model, rotating it and appreciate how "captured" and "trapped" is the metal ion.

Many, many metal ions including Ni^{2+}, Cr^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+} can form such a complex and in them the extensively enveloped metal ions are often unable to behave as they would normally behave in aqueous solution - this is the origin of the main uses of EDTA - and the metal ion is said to be **chelated**. The $EDTA^{4-}$ is the **chelating agent** or **sequester.**

Chelated - Say "key-lated" - from the Greek word meaning "a crab's claw". Imagine that the metal ion is being pinched or nipped by the claws of a crab. The EDTA^{4-} crab has 6 claws so can nip 6 times. *Substituting* (replacing) the six monodentate water ligands in the hexaaqua complex with one hexadentate EDTA^{4-} chelates the metal ion. (The accompanying increase in entropy [2 particles → 7] favours the formation of the chelated complex.)
Sequester – to confiscate or capture and so withdraw from use.

Uses

Generally, the uses of EDTA and related molecules and ions are based around their ability to **sequester** metal ions. One of the common reagents from which "EDTA solutions" are made is the disodium dihydrate salt - $Na_2H_2X.2H_2O$ – where "X" represents the EDTA^{4-} ion. It is frequently listed as an ingredient in shower gels, shampoos etc. If you visit the DOW Chemical website you will find details of their VERSENE™ range of products containing the chelating agents of EDTA, many of which are used in the food industry. The site gives the numerous roles of these additives.

A typical active ingredient is:
calcium disodium **e**thylene**d**iamine**t**etra**a**cetate dihydrate - $CaNa_2X.2H_2O$.

Specific examples of the uses of EDTA and related molecules and ions:

- *Food, textiles, paper and metal industry*: Metal contaminants often end up in food eg copper, iron and nickel that have entered the food from the soil or from machinery during harvesting and processing. The sodium and calcium salts of EDTA are commonly added to foods and drinks because these additives or "sequestering agents" react with the trace metals to form tightly bound complexes (sequestered) so that the metal is no longer able to degrade the food stuffs by catalyzing the oxidation of the fats in the food and make them rancid. The food stays fresh longer. Similarly EDTA is used in the textile industry preventing metal ions from modifying dye colours, the pulp and paper industry inhibiting metal ions from catalysing the decomposition of H_2O_2 that is used in chlorine-free bleaching and in the extraction of some metals from their ores. In agriculture, particularly in Australia and New Zealand, iron chelate baits - specific to snails, slugs and slaters (molluscs and crustacea) – are commonly used.
- *Detergents*: A major use of EDTA has been in detergents. Here it chelates the calcium and magnesium ions that cause water hardness and so prevents scum formation and the blocking of water pipes etc.
- *Medicine*: In medicine, salts of EDTA are used for the treatment of lead poisoning. Intravenous injections of $CaNa_2EDTA$ solution are given over several days. A Pb^{2+} ion replaces a Ca^{2+} ion in each complex and thus the poisonous lead ions are removed and excreted as their stable EDTA complex. Similarly EDTA is used in blood transfusions and surgical operations - to remove calcium ions which could otherwise cause blood clotting - and extensively in blood analysis. EDTA also plays a part in nuclear medicine when it is injected along with a small amount of radioactive material as a tracer so that kidney function can be assessed. (It is believed by some that EDTA chelation therapy is effective for heart disease, clearing clogged arteries and improving blood flow.)
- *Titrations*: EDTA's unusual ability to chelate 1-to-1with metal ions leads to its use to determine the concentration of metal ions in solution by titration with a standard solution of EDTA. Sometimes the use of a metal ion indicator is necessary.

Perhaps this all seems too good to be true? To an extent it is. A problem with EDTA is that it does not readily biodegrade and some countries have banned its use in detergents. This has led to work being done on a structural isomer of EDTA, known as EDDS. The latter may become a suitable alternative chelating agent offering more acceptable biodegradability.

Extension Work

Explore EDDS, its isomers and synthesis.

Calculation work involving EDTA

Useful to remember: Calculations based on EDTA titration results are straight forward. As EDTA reacts with all metal ions in a 1:1 ratio the number of moles of metal ions is exactly the same as the number of moles of EDTA used.

(1) A Complexometric Titration – Worked Example

When 25.00 cm^3 of a nickel(II) sulfate solution were titrated with 0.100 mol dm^{-3} EDTA, 23.50 cm^3 of EDTA were required. The aqueous nickel(II) ions formed a 1:1 complex with the hexadentate EDTA^{4-} ions.

(a) Using EDTA^{4-} to represent the ligands, write a balanced equation for this ligand substitution reaction. (Hint: look back at the box that shows how the overall charge on the complex is worked out.)

(b) Calculate the concentration of the nickel(II) sulfate solution.

Answers

(a) $[Ni(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Ni(EDTA)]^{2-} + 6H_2O$

(b) PLAN:
(1) Find the number of moles of EDTA^{4-} used.
(2) As the ratio metal ions: EDTA^{4-} is 1:1 the answer to (1) is also the number of aqueous $Ni^{2+}(aq)$ moles in the sample.
(3) Knowing the number of moles $Ni^{2+}(aq)$ in the 25.00 cm^3 sample, work out the concentration in the **accepted units of mol dm^{-3}**.

Number of moles of EDTA^{4-} used

$$= \frac{\text{volume (cm}^3) \times \text{concentration (mol dm}^{-3})}{1000}$$

$$= \frac{23.50\ cm^3 \times 0.100}{1000} = 2.35 \times 10^{-3}$$

Number of aqueous Ni^{2+} (aq) moles in the 25.00 cm^3 sample $= 2.35 \times 10^{-3}$

$$\text{Concentration of } Ni^{2+}\text{ (aq)} = \frac{\text{number of moles} \times 1000}{\text{volume (cm}^3)}$$

$$= \frac{2.35 \times 10^{-3} \times 1000}{25.00} = 0.0940 \text{ mol dm}^{-3}.$$

COMMENT: Notice that the numerical values used in the calculation are exactly as given in the question. You should only round to an appropriate number of figures in your final answer. Here the ***lowest*** number of sig. figs. given in the data is 3 – the concentration of the EDTA solution - and so the final answer is also given to 3 sig. figs.

Practice Questions

1. When 20.00 cm^3 of a copper(II) sulfate solution were titrated with 0.200 mol dm^{-3} EDTA, 13.60 cm^3 of EDTA were required. The hexaaqua copper(II) ions formed a 1:1 complex with the hexadentate $EDTA^{4-}$ ions.
   (a) Using $EDTA^{4-}$ to represent the ligands write a balanced equation for this ligand substitution reaction.
   (b) Calculate the concentration of the copper(II) sulfate solution.

2. Write a balanced equation for the formation of the new complex when a solution containing $EDTA^{4-}$ ions is added to an aqueous solution of a chromium(III) salt.

3. EDTA is used to titrate against calcium salts in blood analysis. The EDTA reacts in a 1:1 ratio with Ca^{2+}. Concentrations in the range of 7 to 13 mg of calcium per 100 cm^3 of blood serum are normal.
   1.00 cm^3 of blood serum taken from a patient required 2.65 cm^3 of 0.00150 mol dm^{-3} EDTA solution for titration.
   (a) Calculate the concentration of calcium in the patient's blood serum in mg per 100 cm^3 of blood. (Relative Atomic Mass of Ca = A_r(Ca) = 40.1)
   (b) Is the concentration of calcium in the patient's blood normal? Explain your answer.
   (c) What assumption(s) have you made in your calculation?

4. Read the following description of how the formula of a metal-EDTA complex can be determined:
   When a few drops of sodium 2-hydroxybenzoate were added to 20.00 cm^3 of an 0.125 mol dm^{-3} aqueous solution of iron(III) sulfate a deep purple solution formed.(1)
   On adding an aqueous solution containing $EDTA^{4-}$ ions from a burette with swirling the purple colour slowly faded to a pale yellow solution at the endpoint. (2)
   A total of 25.00 cm^3 of 0.100 mol dm^{-3} of the EDTA solution was needed to reach the endpoint.

   (a) Explain the observations (1) and (2).
   (b) How many moles of Fe^{3+} were in the flask?
   (c) How many moles of $EDTA^{4-}$ ions reacted with the Fe^{3+}?
   (d) From these results what is the formula of the iron(III)-EDTA complex? Is this what you would have "predicted"? Explain your answer.

Answers

1. (a) $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$
   (b) 0.136 mol dm^{-3}.

2. $[Cr(H_2O)_6]^{3+} + EDTA^{4-} \rightarrow [Cr(EDTA)]^{-} + 6H_2O$

   (In aqueous solution some of the hexaaqua chromium(III) ions will have undergone hydrolysis to $[Cr(OH)(H_2O)_5]^{2+}$ etc. Full marks will usually be gained if one of these products of hydrolysis is used instead.)

3. (a) 15.9 mg per 100 cm^3 of blood. (Remember: 1mg = 0.001g or 1×10^{-3} g)
   (b) The concentration of calcium in the patient's blood is **not normal / is higher than normal** as **it falls outside the range of 7 to 13 mg** of calcium per 100 cm^3 of blood.
   (c) It has been assumed that the **only metal ion present / reacting with the EDTA is Ca^{2+}** and that **all of the Ca^{2+} ions present in the blood sample reacted with the EDTA**.

4. (a) (1) - This is a *ligand substitution reaction* in which the 2-hydroxybenzoate ions replace the water molecules as ligands around the iron(III) ions. The purple colour is the iron(III)-2-hydroxybenzoate complex.
   (2) – This is another *ligand substitution reaction*. This time, as the $EDTA^{4-}$ ions were added, they replaced the 2-hydroxybenzoate ligands.
   (b) Number of moles of Fe^{3+} in the flask: 2.50×10^{-3}
   (c) Number of moles of $EDTA^{4-}$ ions reacted with the Fe^{3+}: 2.50×10^{-3}
   (d) Formula of the iron(III)-EDTA complex: $[Fe(EDTA)]^{-}$
   Yes, the formula is as predicted.
   The ratio Fe^{3+}:$EDTA^{4-}$ was 1:1. This is (almost always) the ratio for the reaction between a metal ion and $EDTA^{4-}$.

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