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Metal Complexes and the Environment: Microscale Experiments with Iron–EDTA Chelates

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Abstract: The presence of ligands in natural and artificial environments is increasing. Science majors need exposure to experiments that deal with ligands and complexes in the environment. Two such experiments are presented here: The dissolution of a nonsoluble polluting gas (NO) by complex formation with [Iron(II)EDTA] and the decomposition of [Iron(III)EDTA] by exposure to light. The experiments involve the preparation of Iron–EDTA complexes, which are then used to demonstrate the positive and negative effects of ligands in the environment. These experiments are appropriate for applied inorganic chemistry or environmental chemistry laboratories. The first one takes approximately three hours to complete, and the second takes less than two hours.

Introduction

Ligands are present in many natural environments. They enter the environment from a myriad of industrial and other human activities. Some naturally occurring ligands are citrate ions (found in natural waters as a consequence of biological activity), humic acids (normally found in soils), amino acids, and other natural organic matter (NOM). Artificial ligands include the aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), and their ions; phosphates; and crown ethers [1–3].

Complex formation of metal ions with ligands can change many properties of the metal ions, for example, their charge, solubility, color, standard potential, and stability. In addition, metal mobility, bioavailability, bioaccumulation, toxicity, and persistence in the environment are frequently dependent on the chemical form of the metal ion. For example, there is normally a significant difference in the adsorption behavior of a free metal ion as compared to its anionic complexes with mineral oxides. In addition, the speciation of ligands may drastically affect the nature of their complexes. For example, EDTA, one of the most commonly used artificial chelating agents, can be present as five different chemical species depending on the pH of the medium: H_4EDTA, H_3EDTA^-, H_2EDTA^{2-}, $HEDTA^{3-}$, and $EDTA^{4-}$; thus, its complexes can be anionic, cationic or neutral. This can have dramatic effects in their properties and behavior. A case in point is the EDTA complexation of Fe^{3+}, in which the neutral complex formed with $HEDTA^{3-}$ is more than 20 orders of magnitude less stable than the corresponding anionic complex with $EDTA^{4-}$ [2]. (For ligand speciation calculations the chemical-species distribution algorithm can be used [4]).

There are many other examples of environmental phenomena and applications involving metal complexes. Several are listed below.

Metal-complex and ligand adsorption onto natural oxides [1–3, 5, 6]
Dissolution of natural oxides [3]
Dissolution of metal scales [7, 8]
Metal ion removal and uptake by biological systems [9–11]
Interactions of metal complexes with bacteria [12, 13]
Heavy-metal extraction from soils [2, 14, 15]
Radioactive decontamination [12, 16]
Metal extraction from liquids [17]
Recovery of metals [2, 18, 19]
Treatment of gaseous pollutants [20, 21]
Metal separation by polymeric ligand exchange (PLE) [22–24]

In the experiments presented here, iron–EDTA complexes will be prepared and used to demonstrate the positive and negative environmental roles that ligands play. These experiments are: (1) the dissolution of a nonsoluble polluting gas (NO) by complex formation with [Fe(II)EDTA], and (2) the decomposition of [Fe(III)EDTA] upon exposure to light.

EDTA has been selected for these experiments because it has a great number of applications in pharmaceutical, health care, and cleaning products; photography; textile and paper manufacturing; water softening; and agriculture. It is present in sewage effluents, fresh water, and groundwater [1]. Significant concentrations (up to approximately 0.02 mM) have been found in effluents from wastewater treatment plants. It is a strong complexing agent for many metal ions and a persistent pollutant due to its high stability and low biodegradability. It is also resistant to decomposition by ionizing radiation and thermally stable [25]. Some of its complexes are light sensitive (typically [Fe(III)EDTA], which can undergo total photolysis in a sunny day within several hours), while others are only slightly affected (e.g., [Mn(II)EDTA], [Co(III)EDTA]), and others are not affected by light at all.

Removal of Nitric Oxide by Complex Formation with [Fe(II)EDTA]

Background. The emission of nitrogen oxides is continuously the focus of new environmental rules [26]. Such oxides, mainly NO and NO_2, commonly designated as NO_x, are problematic for several reasons, including [26–28]: (a) their ability to combine with volatile organic compounds on sunny days to produce ozone, which is the cause of several health

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problems; (b) the contribution of nitric oxide to ozone depletion in the ionosphere ($NO + O_3 \rightarrow NO_2 + O_2$); (c) the contribution of nitric oxide to the production of smog in the troposphere; (d) the attachment of nitric oxide to hemoglobin, thereby preventing normal oxygen transport.

The large majority of nitrogen oxides entering the atmosphere from anthropogenic sources are produced by the combustion of fossil fuels [27]. Some 95% of this oxide production is comprised by colorless, odorless, toxic, nonflammable nitric oxide (NO), which is produced in large amounts by the high-temperature reaction

$$N_2 + O_2 \rightarrow 2\ NO \qquad (1)$$

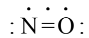
As soon as NO comes in contact with oxygen, it is oxidized to nitrogen dioxide, a brown acidic gas [29, 30].

Many processes have been proposed and used for NO removal from combustion gases. Dry processes include selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) [31–35] with NH_3 and N_2H_4. The latter suffers from catalyst poisoning when the waste gases are heavily loaded with additional pollutants or dust [36]. Some of the wet processes are aimed at the simultaneous removal [37] of SO_2 and NO; however, due to the low solubility of NO in water (1.25×10^{-3} M atm^{-1} at 50 °C) [38], chemical reactions, either in the gas phase or in aqueous media, are needed to enhance its solubility.

Practically all of the aqueous scrubbing reactions can be grouped as follows (note that several of these can also be used for the simultaneous removal of SO_2).

1. Absorption–oxidation with MnO_2, Mn_2O_3, Mn_3O_4, H_2O_2, $HClO_3$, CrO_3, $KMnO_4$/NaOH, $NaClO_2$/NaOH [36, 39–41].
2. Absorption–reduction with SO_3^{2-} [36].
3. Absorption–complexation with thiochelates, ferrous salts, aminopolycarboxylate chelates [36, 42].

The last set of reactions can be understood in the light of the structure of NO, adequately described by the nonpaired structure proposed by Linnet [43]:



$$:\dot{N}\overset{\cdot}{=}\dot{O}:$$

The last electron in the NO electronic structure ($2\pi^1$) enters an antibonding π orbital, which explains the observed paramagnetism. This structure enables the relatively easy formation of the NO^+ ion, which has a shorter and stronger bond than NO itself [43]. Because both the N and O atoms have lone pairs, NO and NO^+ can, in principle, form complexes with metal cations. It has been shown by ab initio calculations that the ground states of $M(NO)^+$ (where M = Cr, Mn, Fe, Co, Ni) are linearly bound at the nitrogen [28]. This complex-formation property is the key for the process that is addressed in the present experiment, as discussed below.

Several iron chelates are effective for the removal of NO [35, 42, 44, 45]. Even though iron aminopolycarboxylate chelates (EDTA, NTA, IDA) are not as effective as, for example, some thiochelates (2,3-dimercapto-1-propanesulfonate, dimercaptosuccinate, dithioloxalate, aminoethanethiol, cysteine, penicillamine), EDTA will be used here due to its wider availability and low cost. Reported removal of NO is as high as 70–80% with enhancement factors for NO absorption being typically in the range 100–500 [46, 48]. Interestingly enough, [Fe(II)EDTA] can form the corresponding (mono)nitrosyl complex [Fe(II)NO(EDTA)], whereas the Fe(III) chelate is inactive in this regard [37, 45]. On the other hand, the opposite is true for the scrubbing of H_2S with Fe–EDTA because the Fe(III) chelate is the active form, whereas the Fe(II) moiety is inactive [47]. For this reason, a practical NO scrubbing system must include the Fe(III) to Fe(II) reduction step. Reducing agents include: SO_3^{2-} and HSO_3^{-} ions formed by the dissolution of accompanying SO_2, externally added $S_2O_4^{2-}$ or S^{2-} ions, ascorbic acid, iron metal, glyoxal, and electrochemical reduction [37, 44, 46, 48–50].

The NO reduction products depend on the reduction method and include NH_4^+, NH_3, N_2, N_2O, $NH_2(SO_3H)$, and $HON(SO_3)_2^{2-}$ [35, 42, 49, 51].

In the following experiment, students will prepare NO gas, a solution of [Fe(II)EDTA], and the corresponding nitrosyl complex by bubbling NO in the chelate solution. Then, the nitrosyl ligand will be chemically reduced to regenerate the chelate. This makes the experiment even more interesting from an environmental perspective. Finally, other test reactions for NO will be performed.

Experimental and Discussion. *Preparation of NO.* NO can be prepared by several methods. We have used the first method described below (we place 50–80 mg of KNO_2 in a 5-mL vial and add with a syringe 0.2 mL of 1 M H_2SO_4), but the others are also suitable [30, 43, 52].

1. $6\ NaNO_2(s) + 3\ H_2SO_4(aq) \rightarrow 4\ NO(g) + 2\ H_2O(l) + 3\ Na_2SO_4(aq) + 2\ HNO_3(aq)$

2. Reaction of moderately concentrated nitric acid with copper (using more concentrated nitric acid produces NO_2).

$$8\ HNO_3(aq) + 3\ Cu(s) \rightarrow 3\ Cu(NO_3)_2(aq) + 4\ H_2O(l) + 2\ NO(g)$$

3. $2\ KNO_2(aq) + 2\ KI(aq) + 2\ H_2SO_4(aq) \rightarrow 2\ NO(g) + 2\ K_2SO_4(aq) + I_2(aq) + 2\ H_2O(l)$

4. $KNO_2(aq) + K_4Fe(CN)_6(aq) + 2\ CH_3COOH(aq) \rightarrow NO(g) + K_3Fe(CN)_6(aq) + 2\ CH_3COOK(aq) + H_2O(l)$

5. $3\ KNO_2(s) + KNO_3(s) + Cr_2O_3(s) \rightarrow 4\ NO(g) + 2\ K_2CrO_4(s)$

Because NO reacts with any oxygen present in the system to form brown fumes of acidic NO_2, a basic trap needs to be inserted between the preparation chamber and the scrubbing vessel to prevent it from interfering in this experiment (see Figure 1). Nitrogen gas (or any other inert gas) is used as a carrier gas. **Note: Do not start producing NO gas until the entire set-up is ready, the iron chelate has been produced (see below), and nitrogen gas has been bubbling for 5 minutes.**

Caution: NO gas may be irritating to the eyes, throat, and nose, and it is known to have other biological effects including increased vasodilatation. It is strongly recommended that the experiment be performed under a fume hood in a well-ventilated area.

Preparation of the Basic Trap. A KOH trap is prepared by placing 10–15 mL of 1 M KOH in a 25-mL filter flask. Connect its side arm to the scrubbing vessel with a rubber hose (see Figure 1). Insert a piece of glass tubing through a one-hole

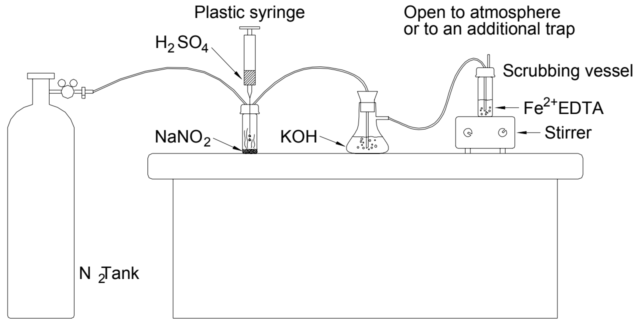


Figure 1. Experimental set-up for the formation of the nitrosyl complex.

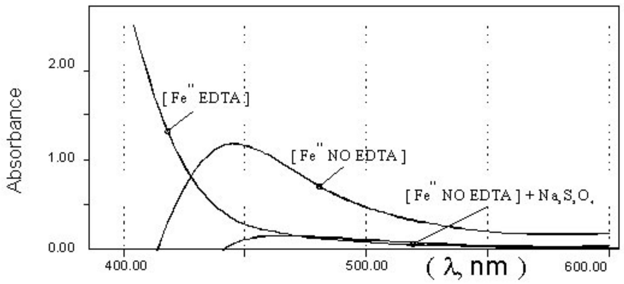


Figure 2. Absorption spectra of [Fe(II)EDTA] with and without NO.

rubber stopper. Connect this tube with a rubber hose to the exit stream of the NO preparation chamber. The filter flask will receive the NO gas carried by the nitrogen.

Preparation of the [Fe(II)EDTA] Chelate. Place 3 mL of water in a 5-mL vial (herein called the s*crubbing vessel*) equipped with a two-hole rubber stopper and two pieces of glass tubing. Make sure that the entire system is connected and ready. Initiate gentle nitrogen bubbling to remove any oxygen present in the water and in the system (make sure that there is enough solution in both vessels to observe bubbles). In the meantime, calculate and weigh the necessary amount of Fe(II) salt (for example, $FeSO_4•7H_2O$) to form a 0.5–1 M Fe^{2+} solution in the scrubbing vessel. After a few minutes of bubbling nitrogen through the water in this vessel, add the iron salt with stirring. Then, calculate, weigh, and add EDTA (for example, its disodium salt) to form the 1:1 chelate and stir. Excess EDTA can be used if desired to promote chelate formation. Transfer 1–2 mL of the freshly formed chelate solution to a spectrophotometric cell and obtain a scan in the visible region with a UV–vis spectrophotometer (see Figure 2). Then, return the solution to the scrubbing vessel and allow nitrogen to bubble through it for 2–3 minutes. Now, initiate the NO preparation as described earlier.

Formation of [Fe(II)(EDTA)NO]. After a few minutes of bubbling the carrier gas containing NO through the scrubbing solution, a color change (from pale yellow to olive green) due to the formation of [Fe(II)NO(EDTA)] will be observed. At this point, the production of NO can be stopped by opening the preparation flask and flushing it with running water. The small amount of residual nitrite can be flushed down the drain. Transfer 1–2 mL of the green solution (containing the nitrosyl complex) to a spectrophotometric cell and take its visible absorption spectrum as described earlier (see Figure 2).

Regeneration of the [Fe(II)EDTA] Complex. In order to reduce the NO in the nitrosyl complex, add a few milligrams of dithionite (sodium hydrosulfite, $Na_2S_2O_4$) to the scrubbing vessel and stir. In a few minutes, a color change back to the original pale-yellow is observed, signaling the destruction of the NO complex and regeneration of the [Fe(II)EDTA] chelate. Sodium sulfite can also be used for the reduction step (although the color change will be somewhat less spectacular).

Use 1–2 mL of the reduced solution to obtain its visible spectrum. The three spectra (before chelation, after chelation, and after reduction) can be now compared. See Figure 2. An intense absorption band is observed in the second spectrum, but is absent in the other two. This demonstrates the formation and destruction of the NO complex.

Additional Tests. Additional tests and reactions of NO can be performed to demonstrate the following.

1. NO is known to form a brownish nitrosoiron(II) sulfate with aqueous iron(II) sulfate solutions.

2. Roussin´s black salt results from the action of NO upon an iron(II) sulfate/potassium thiosulfate solution [43]. To prepare this solution, dissolve 5 g of $K_2S_2O_3$ in 5 mL of distilled water. Then, add 77 mg of $FeSO_4•7H_2O$ and bubble NO (prepared as described above) through it. After drying the precipitate that forms, blackish-brown crystals can be observed under a microscope. This is a tetrahedral complex. Generally, tetrahedral complexes tend to have more intense absorption bands than the corresponding octahedral ones.

Photolysis of [Fe(III)EDTA]

Background. Natural light can induce many processes of environmental importance either directly (when light is absorbed by the species of interest) or indirectly (when the species of interest reacts with an intermediate called *mediator*, previously excited or produced by light). Environmentally important processes include photosynthesis, photodissociation (e.g., the rupture of organic and inorganic molecules), photoproduction of highly reactive radicals, photodissolution of minerals, and photoredox reactions [54].

The photochemistry of metal complexes is rather interesting, because there are several pathways for reaction upon excitation. For example, in a given transition metal complex that has d electrons, there are several d→d transitions allowed. Likewise, there can be charge-transfer transitions in which the excited state involves the transfer of electronic charge from an occupied orbital in the ligand to an unoccupied orbital in the central metal ion, reducing it to a lower oxidation state (*ligand to metal charge transfer, LMCT*) [55]. The final products depend on whether the irradiation energy is aimed at the d–d bands ($h\nu_1$) or at the charge-transfer band ($h\nu_2$), as respectively exemplified in the generalized scheme below. Here, M is a metal ion in the (n + 1) oxidation state, L is a neutral ligand, and L´ is a negatively charged ligand.

Ligand exchange:

$$[M^{(n+1)+}(L)_5L']^{n+} + H_2O + h\nu_1 \rightarrow [M^{(n+1)+}(L)_4(H_2O)L']^{n+} + L$$

Photoredox reaction:

$$[M^{(n+1)+}(L)_5L']^{n+} + H_2O + h\nu_2 \rightarrow [M^{n+}(L)_5]^{n+} + (L')^0 + H_2O$$

A typical example of this last reaction is the photolysis of iron carboxylato complexes (i.e., complexes with oxalate, aminopolycarboxylates, citrate, humic and fulvic acids), which can occur with high quantum yields. A simplified reaction mechanism (using oxalate as the ligand) is [55, 56]

$$[\mathrm{Fe(III)(C_2O_4)_3}]^{3-} + h\nu \rightarrow \mathrm{Fe(II)} + 2\,\mathrm{C_2O_4}^{2-} + \mathrm{C_2O_4}^{-}$$

$$\mathrm{C_2O_4}^{-}\bullet \rightarrow \mathrm{CO_2}^{-}\bullet + \mathrm{CO_2}$$

$$\mathrm{CO_2}^{\cdot -} + \mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)} + \mathrm{CO_2}$$

Cobalt oxalato complexes behave similarly [57]. The Fe(II) produced in the reaction is capable (in the presence of H_2O_2) of generating OH radicals, which are known to be potent oxidizing agents. This is called the *Fenton reaction*, and when the Fe(II) is produced by the photolytic reduction of Fe(III), it is called a *photo-Fenton reaction*. This reaction pathway can degrade highly persistent compounds (e.g., herbicides) in the presence of Fe(III) reducing agents like oxalate (and very likely, humic and fulvic acids, present in soils) [58]. Interestingly, the Fe(II) photoproduced has also been found to reduce toxic Cr(VI) to the much less problematic Cr(III) species in organic-containing media [59]. Unfortunately, in the absence of important concentrations of dissolved organics (e.g., in atmospheric waters) the OH radicals and other oxidizing species are capable of re-oxidizing Cr(III) to Cr(VI) [60].

As was mentioned earlier, [Fe(III)EDTA] complexes can undergo total photolysis in a sunny day within several hours [25], while other metal ion complexes are only slightly affected (e.g., [Mn(II)EDTA], [Co(III)EDTA]), and others are not affected by light at all. The ability of [Fe(III)EDTA] to undergo photolysis is very fortunate because EDTA is a refractory compound, and thus the natural photolytic pathway provides a means for its destruction. From these cases it can also be deduced that some samples to be analyzed for environmental purposes must be isolated from light immediately after their collection.

In the following experiment, an [Fe(III)EDTA] complex will be exposed to light (either natural or artificial) and decomposed to produce Fe(II), which reacts with an indicator, yielding a highly colored solution.

Experimental and Discussion. Prepare 10 mL of an Fe(III) solution by adding 0.8 g of $FeCl_3{\bullet}6H_2O$ to 8 mL of H_2O in a volumetric flask. Stir and dilute to the 10-mL mark. In a similar fashion, in a separate 10-mL flask dissolve 1 g of $K_3[Fe(CN)_6]$ and dilute to the mark. Finally, add 1 g Na_2EDTA to 5–6 mL of H_2O in a third 10-mL flask, and add approximately 1 mL of 6M NaOH to facilitate dissolution of the EDTA species. Then, dilute to the mark. These procedures yield three solutions (approximately 0.3 M each) that should be more than enough for a large class because only one drop of each is needed.

Now, place approximately 1 mL of distilled water, one drop of the $FeCl_3$ solution, and one drop of the $K_3[Fe(CN)_6]$ solution in a 5-cm-long test tube. Do this in duplicate (*blank* test tube). Add one drop of the EDTA solution to each tube and stir. Wrap the blank test tube with aluminum foil to maintain it away from light. Expose the other test tube to the sunlight or to the light of an overhead projector (or of a slide projector). In a few minutes, a dramatic color change is observed. The blank test tube is then unwrapped, and the difference between both is recorded. Students can now discuss the reason for the occurrence of such a color change in one tube and not in the other. In our experience, students enjoy this experiment and are challenged by the need to understand the chemistry involved. If desired, they can be encouraged to design and perform experiments with other ligands (e.g., citrate, oxalate, some non-carboxylated organics, etc.) and other iron (II/III) indicators (e.g., *o*-phenanthroline, $K_4[Fe(CN)_6]$, SCN^-).

As discussed earlier, the Fe(III) complex undergoes photolysis whereby the Fe(III) species is reduced to Fe(II) by a photoinduced electron transfer from the ligand (in this case, EDTA) that contains a carboxylic group. This ligand becomes oxidized (even all the way to CO_2) with a heterolytic C–C bond breaking.

Another point for discussion with the students is the importance of pH. For example, what would happen if a pH of 2 were used? A pH of 4?, etc. A high pH is recommended because at lower pH values the EDTA forms the tetraprotonated, insoluble form or else the positively-charged complexes, $[Fe(H_3EDTA)]^{2+}$ or $[Fe(H_2EDTA)]^{+}$. Such complexes do not seem to be as photoreactive as the neutral [Fe(HEDTA)] formed in the pH range used here (8–9). This EDTA speciation can be explained by the equilibria described in the introductory section. The appearance of a strong blue color upon exposure to light is due to the reaction between the photoproduced Fe(II) and the $[Fe(CN)_6]^{3-}$ ion, which forms Prussian blue [61]. Because there is no Fe(II) in the blank test solution, this color does not appear there.

Conclusions

Metal complexes are increasingly important in environmental studies, phenomena, and applications. A simple experiment has been developed to show the removal of NO from a gas mixture by complexation with [Fe(II)EDTA] forming the [Fe(II)NO(EDTA)] complex. The original [Fe(II)EDTA] complex is then regenerated by the reductive removal of NO to be reused. The concentrations used throughout this paper work well, although there is probably room for further reduction. Likewise, the photolytic decomposition of [Fe(III)EDTA] by natural or artificial light has been demonstrated.

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