

## EXPERIMENTAL E-pH DIAGRAMS OF Fe(III)/Fe(II) SYSTEM IN PRESENCE OF VARIABLE CONCENTRATION OF DIFFERENT LIGANDS

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### ABSTRACT

The experimental E-pH diagrams of Fe(III)/Fe(II) in the presence of variable concentrations of ligand like EDTA, acetate, citrate, oxalate, cyanide, salicylate and ortho-phenanthroline (o-phen) are plotted and interpreted. The experimental curves fit well with the theoretical ones except for cyanide and o-phen. The conditional standard potential of the Fe(III)/Fe(II) system was calculated. The formula of the complex Fe(II)-ligand was determined for some ligands by redox titration of Fe(II) in the presence of variable concentrations of a ligand against a suitable oxidant.

**Keywords:** E- pH diagram, Fe(III)/Fe(II) system, Ligands, complex formula, conditional standard potential.

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### INTRODUCTION

The E-pH diagram for ox/red systems such as Fe(III)/Fe(II), Cu (II)/Cu, ... found in the literature [1-3] are plotted in the absence of a ligand (L). In these diagrams, only the hydroxide complexes or the oxides were taken into account. Most references in the literature contain simplified theoretical E-pL diagrams, at constant pH, like the Fe(III)/Fe(II) system in the presence of SCN<sup>-</sup>, EDTA, F<sup>-</sup> or Cu(II)/Cu(I) system in the presence of NH<sub>3</sub> [3-6]. These references do not take into account the formation of the precipitates M(OH)<sub>n</sub> due to the pH range considered. In fact, the problem is more complicated, and we must consider the effect of pH on the stability of the complex, because the ligand (L) and the metal ions M<sup>n+</sup> frequently have acid-base properties and the stabilities of ML<sub>n</sub> complexes are strongly affected by the formation of hydroxides. There is competition between OH<sup>-</sup> and L to react with the metal ion. Specialised electrochemistry books [5,7],

contain a theoretical E-pH diagrams for some redox systems (Ag<sup>+</sup>/Ag and Fe(III)/Fe(II)) in the presence of excess ligand (such as NH<sub>3</sub>, EDTA, F<sup>-</sup>, or o-phen). In these curves, the formation of the complex of superior order ML<sub>n</sub> and the hydroxides complexes were only taken into account, however the situation is not so simple, because the solution could contain combined complexes such as M(H<sub>i</sub>L) and /or M(OH<sub>j</sub>)L<sub>i</sub> [5]. In [8] we found The E-pH diagram of Fe (III)/Fe(II) in presence of high concentration of different ligands obtained by redox titration of Fe (II) with an appropriate oxidant at different pH.

It is possible to draw the E-pH diagram theoretically, further information is required, such as the formation constant of ML<sub>n</sub> and of M(OH)<sub>i</sub>, and the predominance domains of the complexes, etc. However, the published values of the formation constant of M(OH)<sub>i</sub> are sometimes controversial [7]. We can overcome these difficulties by drawing these diagrams experimentally and then interpreting the results become easier. Useful

information can be obtained from the experimental diagram: pH range in which the complex is stable,  $E^\circ$  of the new system ox-(L)/red-(L) and prediction of whether successive complexes are being formed compared to only one complex. This diagram can also be used to find the best conditions for the determination of the formula of the complex by potentiometric redox titration in the presence of variable concentrations of a ligand [9].

In this study, we choose the Fe(III)/Fe(II) system, for various reasons:

i) Fe(III) and Fe(II) are stable in water, in comparison to Co(III)/Co(II) system where Co(III) is not stable [1, 4]; ii) Fe(III) and Fe(II) do not precipitate at low pH like Ce(IV)/Ce(III) system where the Ce(IV) precipitates at very low pH [1]; iii) The Fe(III)/Fe(II) system is a typical model for this study, since Fe(III) and Fe(II) form stable complexes with most ligands [2, 9].

The reason to select the ligands (listed below) is that the literature is rich in information about them (nature of the complex, value of the formation constant, theoretical E-pH diagram ...), so the experimental results can be compared to the theoretical ones.

## EXPERIMENTAL

The measurements of pH and  $\Delta E$  ( $E_{Pt} - E_{Ag/AgCl}$ ) were carried out using a Toledo 220 M pH-meter and a voltmeter (reading  $\pm 0.1$  mV or pH units). The reference electrodes in the two combined indicator electrodes (glass and Pt) were Ag/AgCl electrode (3 M KCl). The glass electrode was calibrated using two standards buffers solutions 4.0 and 7.0. The response of the platinum electrode and its slope was verified with Fe(III)/Fe(II) in 1.0 M  $H_2SO_4$ . All the reagents used were purchased from BDH products. The 0.05 M Fe(III) and Fe(II) mixture solution was prepared from hydrated Fe(III) sulphate and Mohr salt ( $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ) respectively in 0.5 M  $H_2SO_4$  for the study of E-pH diagram. The 0.1 M Fe(II) solution was prepared in 0.1 M  $H_2SO_4$  for the determination of the complex formula. Different ligand solutions (citrate, oxalate, acetic acid, fluoride, cyanide, *o*-phen, EDTA and salicylic acid) were also prepared for this study.

## POTENTIOMETRIC PROCEDURE

**Study of E-pH diagram:** 5 ml of an acidic mixture of 0.05 M Fe(III) and Fe(II) was diluted to 40.0

mL with deionized water, then titrated with NaOH in the absence and presence of variable volume of fixed concentration of a ligand, or in presence of variable mass of the ligand. The pH and the potential were measured after each addition of NaOH. Before beginning the experiment, the pH of the solution is lowered to approximately 1.3 by adding concentrated sulphuric acid.

**Determination of the formula of  $[Fe^II L_n]^{2-n}$ :** 10 ml of 0.1 M Fe(II) was diluted to 40.0 mL with deionized water, then titrated with an appropriate oxidant ( $MnO_4^-$ , Ce(IV) or  $Cr_2O_7^{2-}$ ) in the absence and presence of variable volumes of fixed concentration of ligand. From the shift in the equivalent point, the formula of  $[Fe^II L_n]^{2-n}$  complex can sometimes be deduced.

## THEORY

The variation of the conditional standard potential ( $E^\circ$ ) of Fe(III)/Fe(II) as a function of pH in the presence of a ligand is very complicated. This variation is a function of different parameters: pH, and the presence of ligand which may complex with Fe(III) and Fe(II). Different cases can be encountered:

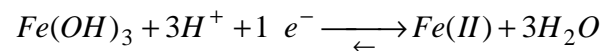
### a) E of the Fe(III) /Fe(II) system as a function of pH in the absence of ligand

For metals ions having acid-base properties, like Fe(III)/Fe(II), the relation between the potential (E) of an inert electrode and the concentrations of Fe(III) and Fe(II) in very acidic medium at 25°C is given by:

$$E = E^\circ + 0.06 \log \frac{[Fe(III)]}{[Fe(II)]} \approx E^\circ \text{ (if } [Fe(III)] = [Fe(II)] \text{)}$$

$E^\circ$  : standard potential of Fe(III)/ Fe(II) system (function of the nature of the acid)

When  $Fe(OH)_3$  precipitates, the redox system will be:



E varies in function of pH [5]:

$$E = E^\circ + 0.18 \times pH_o(Fe(OH)_3) - 0.06 \times \log[Fe(II)] - 0.18 \times pH = cte - 0.18 \times pH$$

$pH_o$  : pH at the beginning of precipitation of Fe(III).

At higher pH, Fe(OH)<sub>2</sub> precipitates and the redox system will be Fe(OH)<sub>3</sub> / Fe(OH)<sub>2</sub> and the potential (E) varies in function of pH [5]:

$$E = E^o + 0.18 \times pH_o(Fe(OH)_3) - 0.12 \times pH_o(Fe(OH)_2) - 0.06 pH = cte' - 0.06 \times pH$$

**b) E of the Fe(III) /Fe(II) system as a function of pH in the presence of ligand.**

The pH at the beginning of precipitation of Fe(III) and Fe(II) is a function of the stabilities of the complexes [Fe<sup>III</sup>L<sub>n</sub>]<sup>3-n</sup> and [Fe<sup>II</sup>L<sub>n</sub>]<sup>2-n</sup>, the acid-base property of the ligand, and the concentration of the ligand [2]. These factors will modify the E-pH diagram. The relation between E and the ratio [Fe(III)]/[Fe(II)] will be [5, 7]:

$$E = E^o + 0.06 \log \frac{[Fe(III)]}{[Fe(II)]} = E^o + 0.06 \log \frac{[Fe(III)]_t}{[Fe(II)]_t}$$

$$[Fe(III)]_t = [Fe(III)] \times \alpha_{Fe(III)(L,OH)}$$

$$\text{and } [Fe(II)]_t = [Fe(II)] \times \alpha_{Fe(II)(L,OH)}$$

$\alpha_{Fe(II)(L,OH)}$  and  $\alpha_{Fe(III)(L,OH)}$ : complexing coefficient of Fe(II) and Fe(III) with the ligand (L) and OH<sup>-</sup>. By comparison to the above equations we can write [7]:

$$E^o = E^o + 0.06 (\log \alpha_{Fe(II)(L,OH)} - \log \alpha_{Fe(III)(L,OH)})$$

E<sup>o</sup>: conditional standard potential of Fe(III)/Fe(II) in presence of (L), it is lower than E<sup>o</sup>, because the complex formation of Fe(III) with a determined ligand is often stronger than that with Fe(II), in other words  $\log \alpha_{Fe(III)(L,OH)} > \log \alpha_{Fe(II)(L,OH)}$ . However E<sup>o</sup> can be larger than E<sup>o</sup>, as in the case of o-phen where  $\log \alpha_{Fe(III)(L,OH)} < \log \alpha_{Fe(II)(L,OH)}$  [5].

$\alpha_{Fe(II)(L,OH)}$  and  $\alpha_{Fe(III)(L,OH)}$  can be expressed as reported in [7]:

$$\alpha_{Fe(III)(L,OH)} = \alpha_{Fe(III)(OH)} + \alpha_{Fe(III)(L)} - 1$$

$$\alpha_{Fe(II)(L,OH)} = \alpha_{Fe(II)(OH)} + \alpha_{Fe(II)(L)} - 1 \approx$$

$$\approx \alpha_{Fe(II)(L)} - 1 \quad (\text{until } pH \sim 8)$$

$$\alpha_{Fe(III)(L)} = 1 + \sum_{i=1}^{i=n} \beta_{iFe(III)L_i} \times \frac{[L]_t^i}{\alpha(L)^i}$$

$$\text{and } \alpha_{Fe(II)(L)} = 1 + \sum_{i=1}^{i=n'} \beta_{iFe(II)L_i} \times \frac{[L]_t^i}{\alpha(L)^i}$$

$\beta_{iFe(III)L_i}$ : overall formation constant for Fe(III)L<sub>i</sub> complex.

$\beta_{iFe(II)L_i}$ : overall formation constant for Fe(II)L<sub>i</sub> complex.

[L]<sub>t</sub><sup>i</sup>: total concentration of the ligand L at power i, [L]<sub>t</sub> = [L] × α(L)

As reported in [7]

$$\alpha_{Fe(III)(OH)} = 1 + 10^{11} \times [OH^-] + 10^{21.7} \times [OH^-]^2 + 10^{21.7} \times [OH^-]^2 + 10^{32} \times [OH^-]^3$$

$\alpha_{Fe(III)(L)}$  in the case of fluoride (monobasic), will be [7]:

$$\alpha_{Fe(III)(F^-)} = 1 + \frac{\beta_1 [F^-]_t}{(1 + [H^+] / Ka)} + \frac{\beta_2 [F^-]_t^2}{(1 + [H^+] / Ka)^2} + \frac{\beta_3 [F^-]_t^3}{(1 + [H^+] / Ka)^3}$$

α(L) is function of [H<sup>+</sup>], so α<sub>Fe(III)(L)</sub> and α<sub>Fe(II)(L)</sub> are also function of [H<sup>+</sup>] (or pH). In the case of EDTA (polybasic), α(L) will be [7, 9]:

$$\alpha(Y) = 1 + \frac{[H^+]}{Ka_1} + \frac{[H^+]^2}{Ka_1 Ka_2} + \frac{[H^+]^3}{Ka_1 Ka_2 Ka_3} + \frac{[H^+]^4}{Ka_1 Ka_2 Ka_3 Ka_4}$$

$$\alpha(Y) = 1 + 10^{10.3} [H^+] + 10^{16.5} [H^+]^2 + 10^{19.2} [H^+]^3 + 10^{21.2} [H^+]^4$$

For the stable complexes [Fe<sup>III</sup>L<sub>n</sub>]<sup>3-n</sup> and [Fe<sup>II</sup>L<sub>n</sub>]<sup>2-n</sup>, and before the precipitation of Fe(OH)<sub>3</sub>, we can neglect α<sub>Fe(III)(OH)</sub> with respect to α<sub>Fe(III)(L)</sub>, and E<sup>o</sup> will be independent of the concentration of the ligand and of pH. In this case, E<sup>o</sup> is given by the well known equation [2, 9]:

$$E^o = E^o + 0.06 \times (\log \beta_n Fe^{II} - \log \beta_n Fe^{III})$$

**c) Determination of the complex formula**

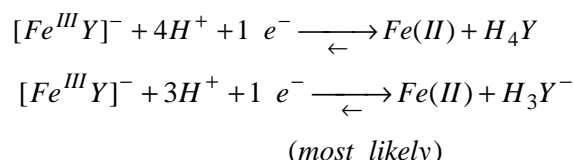
The comparison of the redox titration curves of Fe(II) with an appropriate oxidant in absence and in presence of (L) often shows a new equivalence point, which corresponds to the titration of Fe(II) in presence of (L). Knowing the number of moles of (L) added and the volume at the new equivalent point, it can be possible to determine the complex formula.

## RESULTS AND DISCUSSION

### E – pH diagram of Fe(III)/Fe(II) system in presence of EDTA

The experimental E-pH diagram of Fe(III)/Fe(II) in the absence of ligand other than OH<sup>-</sup> fits well with the theoretical one (Fig.1). The potential of Fe(III)/Fe(II) in sulphuric acid is equal to 460 mV vs. Ag/AgCl electrode, due to the formation of [Fe<sup>III</sup>SO<sub>4</sub>]<sup>+</sup> and [Fe<sup>II</sup>SO<sub>4</sub>]<sup>-</sup> [9]. The E-pH diagram in the presence of low concentration of EDTA with respect to the total concentration of Fe(III) and Fe(II) is similar to that in its absence, only the plateau is observed at lower potential. The decrease in the position of the plateau by ~ 80 mV is explained by the following: EDTA is totally complexed with Fe(III) at low pH, due to the high stability of [Fe<sup>III</sup>Y]<sup>-</sup> ( $\beta = 10^{25}$ ).

The Pt electrode will measure the “mixte potential” of the two systems [Fe<sup>III</sup>Y]<sup>-</sup> / [Fe<sup>II</sup>Y]<sup>2-</sup> and Fe(III)/Fe(II), which is a function of pH and of the total concentration of EDTA [2]. The curve (ABCD) represents the E-pH diagram in the presence of EDTA at concentrations equal to or higher than that of the total concentration of Fe(III) and Fe(II). At the beginning, (point A) the potential of the solution is also lower than the potential of the same solution in the presence of low concentration of EDTA. In the linear part (AB), as was mentioned, Fe(III) is in the FeY<sup>-</sup> form, but Fe(II) is not complexed yet with EDTA. In this pH range, EDTA exists in solution as H<sub>4</sub>Y and H<sub>3</sub>Y<sup>-</sup>, so the redox system in solution is:

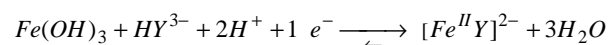


The slope of the linear part (AB) is 0.18 V (3x 0.06) and the equation of E as a function of pH corresponds to  $E = cte - 0.18 \times pH$ . In part (BC) we have a plateau (at ~ -80 mV) which means that Fe(III) and Fe(II) are both complexed with EDTA since the potential does not vary with pH. The redox system in solution is [Fe<sup>III</sup>Y]<sup>-</sup> / [Fe<sup>II</sup>Y]<sup>2-</sup>, it's E° is independent of pH, and of [Y<sup>4-</sup>]:

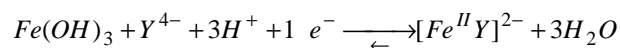
$$E^{\circ} = 0.77 + 0.06 \times \log \frac{\beta([Fe^{II}Y]^{2-})}{\beta([Fe^{III}Y]^{-})}$$

Experimentally, E° vs. SHE is equal to: - 80 + 210 = 130 mV. This value is in accordance with the theoretical value [2].

For a concentration of EDTA equal or higher than that of the total concentrations of Fe(III) and Fe(II), the curves are superimposed, and are thus independent of the concentration of EDTA in the solution (Fig.1). In part (CD), the curve becomes linear again due to the destruction of [Fe<sup>III</sup>Y]<sup>-</sup> and the formation of Fe(OH)<sub>3</sub> which begins at point C. The redox system in this pH range becomes:



or



The potential of this system is once again a function of pH. From this experiment we deduce that, the best range of pH for the determination of the complex's formula Fe<sup>II</sup>-EDTA by potentiometric titration is between 4 and 6 (Fig. 1).

The titration curves of Fe(II) with KMnO<sub>4</sub> in acetic buffer in the presence of variable concentrations of EDTA, show two equivalent points, the new one (the first) occurs at lower potential corresponding to the oxidation of [Fe<sup>II</sup>Y]<sup>2-</sup>, that shifts to the right, proportionally to the concentration of EDTA in solution (Fig. 2). The titration curve of Fe(II) alone in acetic buffer (pH ~ 4) shows a plateau at ~ 200 mV vs. Ag/AgCl electrode. This is due to the [Fe<sup>III</sup>(acetate)<sub>2</sub>]<sup>+</sup> / Fe(II) system, however in the presence of EDTA, the titration curve shows a plateau at ~ -80 mV corresponding to the system [11]. The average ratio of the number of moles of EDTA to the number of moles of Fe(II) titrated until the first equivalence point is equal to 1.1.

### E - pH diagram of Fe(III)/Fe(II) in the presence of oxalate

In literature three complexes of Fe(III) with oxalate were found [2, 11]:  $\beta_1 = 10^{9.4}$ ,  $\beta_2 = 10^{16}$  and  $\beta_3 = 10^{20}$  and two complexes with Fe(II) :  $\beta_1 = 10^{4.5}$  and  $\beta_2 = 10^{5.2}$ , thus the redox system of Fe(III)/Fe(II) in the presence of variable concentration of oxalate is very complicated. The acid dissociation constants of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> are 10<sup>-1.2</sup> and 10<sup>-3.9</sup> [2].

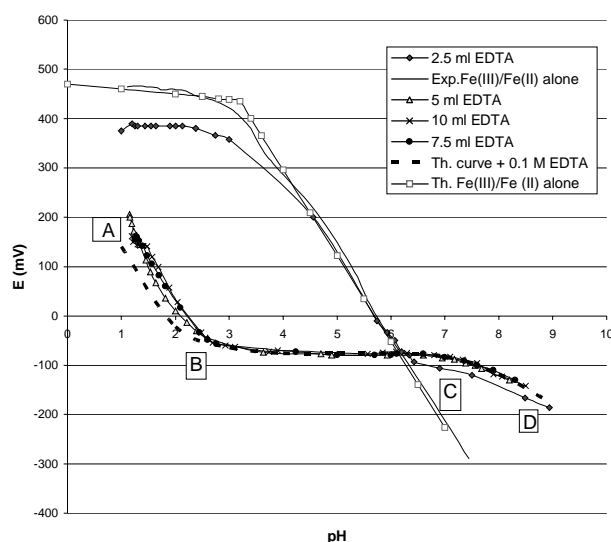


Fig. 1. E-pH diagrams of Fe(III)/Fe(II) in presence of variable volume of 0.1 M EDTA.

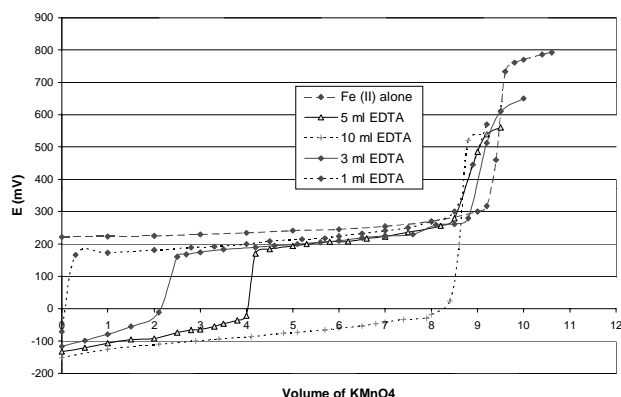
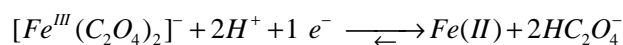


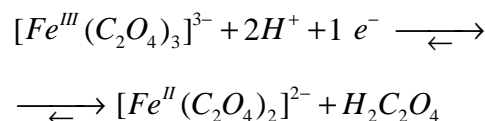
Fig. 2. Titration curves of 10 ml of 0.1 M of Fe(II) with KMnO<sub>4</sub> in presence of variable volume of 0.1 M of EDTA.

The E-pH diagrams of Fe (III)/Fe(II) in the presence of variable concentrations of oxalate are similar to those obtained in the presence of EDTA (Fig. 3): For low concentrations of oxalate (dash curve), the complex formed between Fe(III) and oxalate is  $[Fe^{III}(C_2O_4)]^+$  or  $[Fe^{III}(C_2O_4)_2]^-$  and the potential measured corresponds to the “mixte potential” of  $[Fe^{III}(C_2O_4)]^+$  and Fe(II) or  $[Fe^{III}(C_2O_4)_2]^-$  and Fe(II).

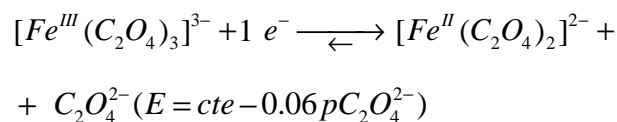
For moderate concentrations of oxalate (curve ABC) (Fig. 3) the potential at point A is lower than that in the absence of oxalate, we can say that the  $[Fe^{III}(C_2O_4)_3]^{3-}$  or  $[Fe^{III}(C_2O_4)_2]^-$  complexes are stable at low pH [12]. The redox system in (AB) will be:



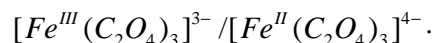
or with less probability:



The slope in this part is 0.12 (2x0.06) and the relation between E and pH can be written as follows  $E = cte - 0.12 \times pH$ . Then the curve (ABC) exhibits a plateau at (BC), between pH 3.5 and 7. Its position and width, varies with the concentration of oxalate in solution (~ -100 mV). The redox system in this case will be:



The potential and the conditional standard potential at (BC) are independent of pH, they are a function of  $[C_2O_4^{2-}]$  in solution (Fig. 3). This result is in accordance with that cited in [13], obtained by voltammetry. The experimental curve obtained in this study is similar to the theoretical one. For higher concentrations of oxalate, the redox system at the plateau (BC) will be:



The titration curves of 10 ml of 0.1 M Fe(II) with  $K_2Cr_2O_7$  in the presence of variable concentrations of oxalate, at pH ~ 3.5 shifts down as the concentration of oxalate in solution increases. These curves show one equivalent point at the same volume of dichromate;

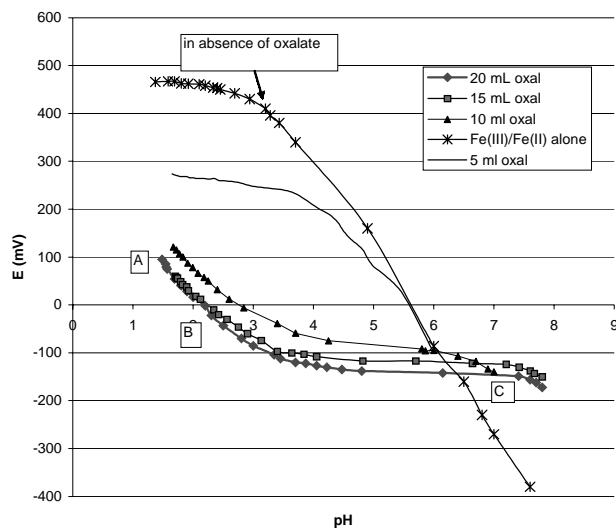


Fig. 3. E-pH diagrams of Fe(III)/Fe(II) in presence of variable volume of 0.125 M oxalate.

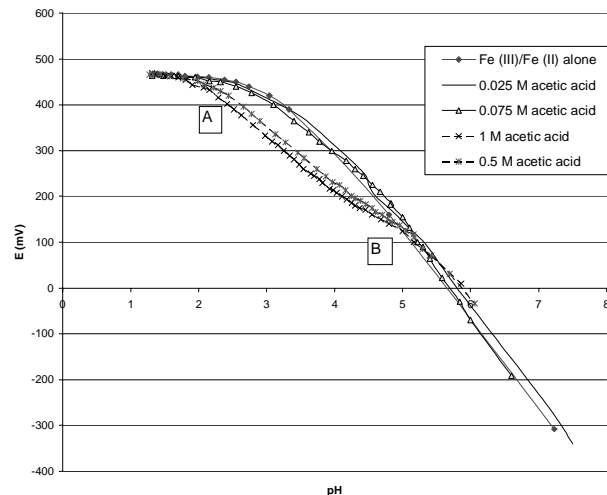
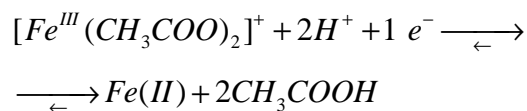


Fig. 4. E-pH diagrams of Fe(III)/Fe(II) in presence of variable volume of 0.1 M acetic acid.

however its potential varies strongly with the concentration of oxalate in the medium. It is not possible to deduce the formula of this complex as in the case of EDTA. For high concentrations of oxalate, the titration curve remains the same because we have the same redox system as mentioned above. Its  $E^{\circ}$  at pH  $\sim 3.5$  is equal to  $-80$  mV vs. Ag/AgCl electrode.

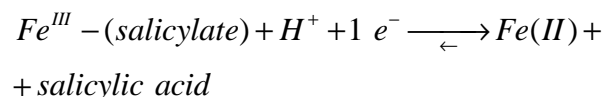
#### E - pH diagram in presence of acetic acid

The E-pH diagrams of the Fe(III)/Fe(II) in the presence of variable concentrations of acetic acid show that for low concentrations, the Fe(III)-acetate or Fe(II)-acetate complexes are not stable, because the corresponding E-pH diagrams are overlaid with the E-pH diagram in the absence of acetate (Fig. 4). The  $\text{Fe(OH)}_3$  dissociates  $[\text{Fe}^{\text{III}}(\text{CH}_3\text{COO})_2]^+$  in a wide pH range [7]. It was not possible to deduce the formula of this complex Fe(II) acetate using the suggested method. However at very high concentrations of acetic acid, the curve E-pH deviates slightly lower for the range of pH between 2 and 5, due to the formation of  $[\text{Fe}^{\text{III}}(\text{CH}_3\text{COO})_2]^+$ . The slope of the linear part (AB) is equal to 0.12 ( $2 \times 0.06$ ) (Fig. 4), so the relation between E and pH will be:  $E = \text{cte} - 0.12 \times \text{pH}$  and the redox system will be:



#### E- pH diagram of Fe(III)/Fe(II) in presence of salicylic acid

In the literature, it was found that only Fe(III) forms a violet complex with salicylic acid ( $\text{pK}_a = 3$ ) [2]. The E-pH diagrams of Fe(III)/Fe(II) in the presence of variable concentrations of salicylic acid are similar to those found in the presence of acetate. For  $\text{pH} < 4$ , the E-pH diagram is slightly under Fe(III)/Fe(II) curve alone. For  $\text{pH} \geq 4$ , the curve rejoins that of Fe(III)/Fe(II) alone, due to the precipitation of  $\text{Fe(OH)}_3$ . From the E-pH diagram, it can be deduced that the formation constant of Fe(III) with salicylate is less than the formation constant of Fe(III) with acetate. However, the formula of the complex Fe<sup>II</sup>-salicylate can not be determined by the suggested method, due to the small decrease in potential in the presence of salicylate. The slope of the linear part of the graph ( $\text{pH} < 4$ ) is 0.072, so the possible redox system of Fe(III)/Fe(II) in presence of salicylic acid will be:

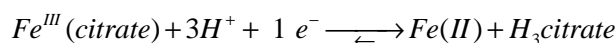


#### E - pH diagram of Fe(III)/Fe(II) in presence of citrate

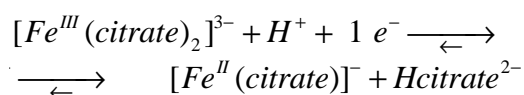
In literature, it was found that Fe(III) can form several complexes with citrate, three complexes with citrate as  $\text{Fe}^{\text{III}}-(\text{citrate})_n$ , with  $1 \leq n \leq 3$  and two as  $\text{Fe(III)}(\text{H}_i\text{citrate})$  with  $i = 1$  or  $2$  [14]. However Fe(II) forms only one complex with citrate (1 to 1). The E-pH diagram of Fe(III)/Fe(II) in the presence of citrate is similar to that in the presence of acetate. The E-pH diagrams deviates downward with respect to that of acetate, because the complexes of Fe(III) and Fe(II) with citrate are more stable than with acetate. As the curve moves down with increasing concentration of citrate, it can be said we are facing the formation successive complexes between Fe(III) and citrate.

For high concentrations of citrate, the E-pH diagrams are overlaid. We do not observe any plateau, so the number of ligands attached to Fe(III) and Fe(II) are different at any given pH. As the E-pH curves in the presence of citrate are under that of Fe(III)/Fe(II) alone, that means the formation constants of  $\text{Fe(III)}(\text{citrate})_n$  is larger than that of  $\text{Fe(II)}(\text{citrate})_n$ .

The E-pH diagram in the presence of high of citrate concentration, can be divided into two linear parts: The slope of the linear part of the curve, between pH 2 and pH 4 is equal to 0.18 ( $3 \times 0.06$ ) and as  $\log \alpha \text{Fe(II)}(\text{cit}, \text{OH}^-)$  in this pH zone is  $\sim 0$  [5], the convenient redox system will be:



In the second linear part, from pH 4 to pH 8, the slope is equal to  $\sim 0.06$ , hence the redox system in accordance with the pKa value of citric acid is:

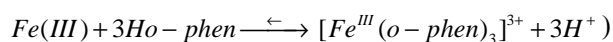


The theoretical curve fits well with the experimental one.

The titration curves of Fe(II) with dichromate at constant pH (3.2), in the presence of variable concentrations of citrate show two equivalent points (Fig. 5). The first occurs at a low potential and shifted to the right, proportionally to the concentration of citrate in the solution. It was found that the average  $n'$  is 1.27, so the complex Fe(III) with citrate at this pH is 1 to 1.

#### E - pH diagram of Fe(III)/Fe(II) in presence of ortho-phenanthroline (*o*-phen)

Fe(III) forms a pale blue complex with *o*-phen ( $\beta [\text{Fe}^{\text{III}}(\text{o-phen})_3]^{3+} : 10^{14}$ ,  $\lambda_{\text{max}} : 590 \text{ nm}$ ). Fe(II) also forms a stable red complex with *o*-phen ( $\beta [\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+} : 10^{21}$ ,  $\lambda_{\text{max}} : 510 \text{ nm}$ ) [2]. *O*-phen is a weak base (pKa = 5) [2]. The E-pH diagram of Fe(III)/Fe(II) in the presence of a stoichiometric concentration of *o*-phen with respect to that of Fe(III) and Fe(II) is located above that of Fe(III)/Fe(II) alone. (Fig. 6) However, the theoretical standard potential must be more than the experimental value [2, 3]. The experimental curve is different to the theoretical one [5] which increase with pH to reach a plateau at pH  $\sim 3$  (Fig. 6). A spectroscopic study of a mixture of Fe(III) and *o*-phen as a function of pH does not show the formation of  $[\text{Fe}^{\text{III}}(\text{o-phen})_3]^{3+}$  at any pH. This may be due to the value of the equilibrium constant of the reaction ( $\sim 0.1$ ):



However the  $[\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+}$  complex is very stable at any pH.

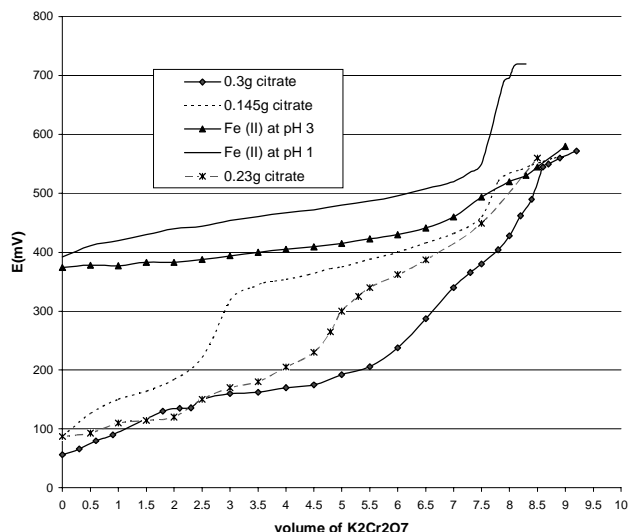


Fig. 5. Titration curves of 10 ml of 0.1 M Fe(II) at pH 3.2 in presence of variable mass of tri sodium citrate.

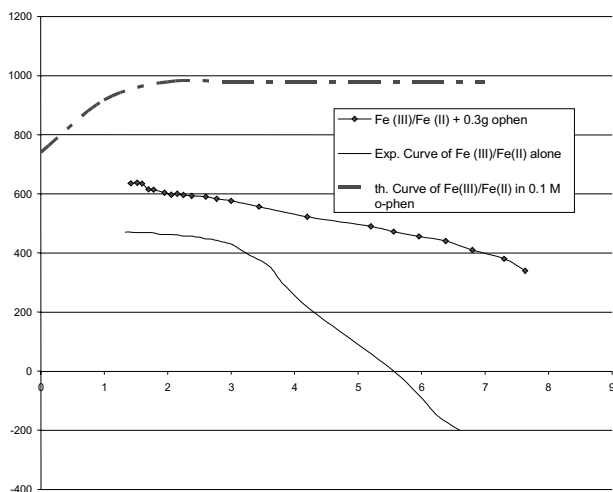


Fig. 6. E-pH diagrams of Fe(III)/Fe(II) in presence of *o*-phen.

The slope of the experimental linear part is equal  $\sim -0.044$ , which is not compatible with the Fe(III), *Ho*-phen/ $[\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+}$  system. Repetitive experiments with lower concentrations of the metal ions and *o*-phen gave the same result. Further studies with other techniques could be helpful in understanding the behaviour of the iron system in the presence of *o*-phen.

According to the experimental E-pH diagram, it was noticed that, the best pH range to find the formula for  $\text{Fe}^{\text{II}}(\text{o-phen})_n$  complex by potentiometry is less than 3. The titration curves of an acidic 10 ml of  $10^{-2}$  M Fe(II) solution with  $10^{-2}$  M Ce(IV) in the presence of variable

concentrations of *o*-phen, shift to the left, proportionally to the concentration of *o*-phen in solution in accordance to the results published by J. Mesplede [9]. These curves are located above the titration curve of Fe(II) alone in contrast to the titration curves of Fe(II) in presence of EDTA. It was found that the ratio (number of mole of *o*-phen /number of mole of Fe(II) engaged in the complex) varies between 3.1 and 3.3. It was also found from the potential at the equivalent point, that  $E^\circ$  of  $[\text{Fe}^{\text{III}}(\text{o-phen})_3]^{3+}/[\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+}$  system is  $\sim 1\text{V}$  vs.  $\text{Ag}/\text{AgCl}$ . It was not noticed a second equivalent point corresponding to the titration of  $[\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+}$ . This is because of the change in  $\Delta E$  at  $\pm 1\%$  of the second equivalent point is only 30 mV [14]. The complex  $[\text{Fe}^{\text{III}}(\text{o-phen})_3]^{3+}$  is not stable with time, it returns to  $[\text{Fe}^{\text{II}}(\text{o-phen})_3]^{2+}$ .

#### E - pH diagram of Fe(III)/Fe(II) in presence of cyanide

The E-pH diagrams of Fe(III)/Fe(II) in the presence of variable concentrations of KCN, showed an unexpected results (Fig. 7). Theoretically the conditional standard potential of  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  system is equal to 0.36 V which is less than the normal standard potential (0.77 V)[2], so theoretically the E-pH diagram of Fe(III)/Fe(II) in the presence of KCN must be independent of pH and located under the E-pH diagram of Fe(III)/Fe(II) alone. Experimentally, it was observed that the potential varies with pH and (Fig. 7). The experimental E-pH diagram shifts up proportionally to the concentration of KCN. In fact the Fe(III)/Fe(II) system in the presence of  $\text{CN}^-$  is a very complicated system, since free Fe(II) or free Fe(III) in the presence of  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  or  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  solutions both give specified precipitates [15]. In this situation a redox system other than the  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  system exists. To explain the unexpected result, it can be said that, the theoretical E-pH diagram found in the literature may be obtained from the  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  and  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  solution mixture. The determination of the complex formula by the suggested method is impossible. It was noted that there is no interaction between Fe(III) or Fe(II) and  $\text{CN}^-$  at  $\text{pH} < 3.5$ , because the curves in the presence and absence of  $\text{CN}^-$  are superposed in this pH zone.

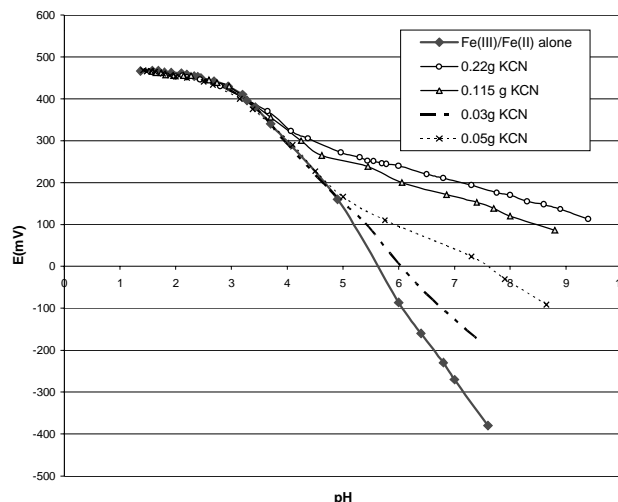
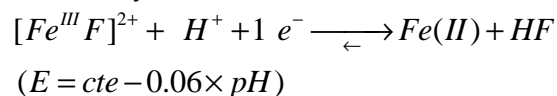


Fig. 7. E- pH diagrams of Fe(III)/Fe(II) in presence of variable mass of KCN.

#### E - pH diagram of Fe(III)/Fe(II) in presence of fluoride

The E-pH diagram of Fe(III)/Fe(II) in the presence of  $\text{F}^-$  is a good example for the detection of successive complexes between  $\text{M}^{n+}$  and the ligand. Most references describe three uncoloured complexes between Fe(III) and  $\text{F}^-$ :  $\beta_1 10^{5.1}$ ,  $\beta_2: 10^{9.1}$ ,  $\beta_3: 10^{12.2}$  [3, 4]. The predominance domain of each complex is a function of the concentration of  $\text{F}^-$  and indirectly a function of pH. For high concentrations of  $\text{F}^-$ , at low pH the complex  $[\text{Fe}^{\text{III}}\text{F}]^{2+}$  is present, then with increasing pH, it successively passes to  $[\text{Fe}^{\text{III}}\text{F}_2]^+$ , then to  $\text{Fe}^{\text{III}}\text{F}_3$  [3, 11], such that at the beginning of Fe(III) precipitation, the only complex present is  $\text{Fe}^{\text{III}}\text{F}_3$ . Whatever the concentration of  $\text{F}^-$  at the beginning, the potential of the solution is lower than that of the Fe(III)/Fe(II) solution alone (Fig. 8). It can deduced that at low pH, there is complex formation between Fe(III) and  $\text{F}^-$ . The E-pH diagram moves downward as  $[\text{F}^-]$  increases. Each curve presents a narrow plateau whose potential is also a function of  $[\text{F}^-]$ . The pH at the beginning precipitation increases with the increase of  $[\text{F}^-]$ . The theoretical E-pH diagrams are similar to those obtained in our studies.

For low concentrations of  $\text{F}^-$ , the slope of the linear part (AB') ( $\text{pH} < 4$ ) is equal to 0.044 which means the redox system is:



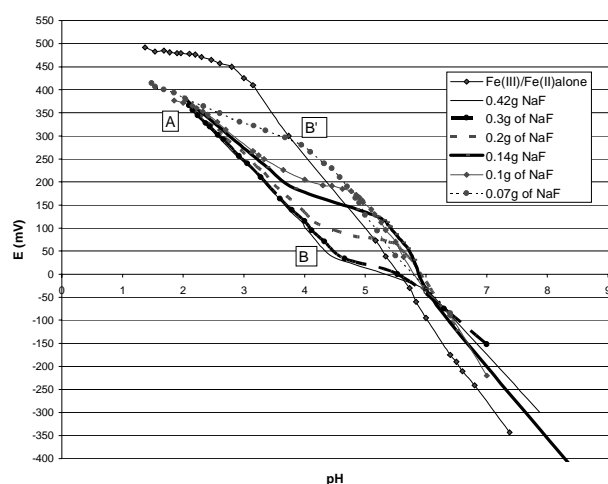
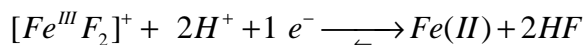


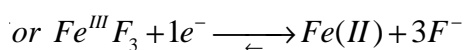
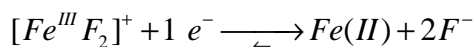
Fig. 8. E- pH diagrams of Fe(III)/Fe(II) in presence of variable mass of NaF.

For high concentrations of  $F^-$ , the slope of the linear part (AB) ( $pH < 4.5$ ) are equal to 0.13 ( $0.06 \times 2$ ) which means the redox system is:



$$(E = cte - 0.12 \times pH)$$

For pH between 4.5 and 5.5, the E-pH diagram shows a narrow plateau and the redox system becomes (in accordance with the  $pK_a$  value of HF):



## CONCLUSIONS

The experimental E-pH diagrams of the Fe(III)/Fe(II) system in the presence of variable concentrations of a ligand fit well with the theoretical diagrams for almost all ligands. The experimental E-pH diagram is an appropriate method to obtain information about the system being studied.

The iron system in the presence of cyanide could not be studied due to the precipitation of Fe(III) and Fe(II) in the presence of  $[Fe^{II}(CN)_6]^{4-}$  and  $[Fe^{III}(CN)_6]^{3-}$ . The E-pH diagram in the presence of *o*-phen is totally different to the theoretical diagram, due probably to the instability of  $[Fe^{III}(o\text{-phen})_3]^{3+}$  in front of  $[Fe^{III}(OH)]^{3+}$ .

A convincing interpretation of E-pH diagram is not possible without having enough information about the redox system studied, especially when dealing with successive complexes. In this case the voltammetry method is better adapted for this type of study, because it yields useful information [5], thus the E-pH diagram is a complementary method in this case. In addition, the E-pH diagram does not allow the estimation of the formation constant of the complex. The determination of the complex formula by redox titration is possible when we only have the formation of one complex between the metal ion and the ligand as in the case of Fe(II) with *o*-phen and EDTA.

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