



**Research/Technical Note**

# Laboratory Synthesis and Titrations of IronIIchloride- $\text{FeCl}_2$ and IronII Ethoxide- $\text{Fe}(\text{OEt})_2$ Using Ethanol-90° - Hexane and Sodium Ethoxide- $\text{Na}(\text{OEt})$

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**Abstract:** Laboratory synthesis of IronIIchloride- $\text{FeCl}_2$  at approximately 200[°C] to 250[°C] using hydrochloric acid-HCl-(33%) and fine iron filament (purity>99%) was done with respecting the reaction stoichiometric. A titration procedure with NaOH-0.05N was established and allowed to titrate the  $\text{FeCl}_2$  synthesized in solution. Thus, the mass yield against raw materials (Iron and HCl) was 67.22[%]. Then, this synthesized  $\text{FeCl}_2$  solution suffered an evaporation-crystallization-drying thermic treatment procedure which efficiency evaluated with NaOH-0.05N titration was up to 98[%]. Secondly, laboratory synthesis procedure of IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  or  $\text{FeO}_2\text{C}_4\text{H}_{10}$  by reflux during 150[mm] at approximately 90[°C] to 115[°C] (maximally) using the previous synthesized  $\text{FeCl}_2$ , sodium ethoxide- $\text{Na}(\text{OEt})$  and ethanol with pure hexane as solvent was carried out. The molar ratios (Iron/Ethanol) and (Ethanol/Hexane/ $\text{Na}(\text{OEt})$ /Iron) were respectively (0.4775/1) and (1/2.5/0.96/0.4775) and permitted to acquire a heterogeneous phases which extraction with a washing-extracting mixed solvent; composed with Ethanol 90°-Pure Hexane-Toluene and another solvent composed only with Ethanol90°-Pure Hexane without ethanol such as the molar ratios of (Ethanol/Hexane), (Hexane/Toluene), (Ethanol/Toluene) and (Ethanol/Hexane)/ $\text{Na}(\text{OEt})$  were respectively 1.27, 20.19, 26.55 and 14.02; followed by a crystallization procedure permitted to obtain pure IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  liquid phases on top and solid grey graphite fine powders with eventually the  $\text{FeCl}_2$  representative-by-product on the bottom solution which concentrations were quantified and evaluated by a titration procedure using NaOH-0.05N and hexane as additive in titrated solution. It was noticed that the concentration of pure IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  in liquid phases increased from the top to the bottom between respectively 1.458E-2 [mol/L] to 1.667E-1 [mol/L]. Then, an evaporation-crystallization procedure to concentrate the previous heterogeneous phases was established and carried out in order to crystallize a large part of the IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  to the solid grey graphite fine powders, the mass yield quantified by the previous titration was up to 97[%]. The grey graphite fine powders was filtered and washed with a washing procedure using water and pure hexane such as ( $\text{H}_2\text{O}/\text{FeCl}_2$ ) and (Hexane/ $\text{H}_2\text{O}$ ) molar ratios were respectively 221 and 14 which efficacy to retain alkenes-ethylene and to extract  $\text{FeCl}_2$  was very high respectively 99.15[%] and 97.07[%] as molars rates with 86.08[%] retention rate of  $\text{Fe}(\text{OEt})_2$ . Finally, the washed grey graphite fine powders suffered a thermic treatment which permitted to increase its purity 99.75[%] with 75[%] as porosity evaluated with acetone.

**Keywords:** Ethanol-90°, Hydrochloric Acid-HCl, Hexane, IronIIchloride- $\text{FeCl}_2$ , IronIIEthoxide- $\text{Fe}(\text{OEt})_2$ , Titrations, Evaporation, Crystallization

## 1. Introduction

First of all, IronIIchloride-FeCl<sub>2</sub> [1, 2] solution synthesis was carried out and a titration procedure using NaOH-0.05N was established to deduce its FeCl<sub>2</sub> yield and the purity of its crystals obtained after an evaporation-crystallization and drying-thermic treatment procedure. Then, this solution was used to synthesize the IronIIethoxide Fe(OEt)<sub>2</sub> [3, 4] and also a titration procedure using NaOH-0.05N and hexane as additive in titrated solution was established to quantify not only the IronIIethoxide-Fe(OEt)<sub>2</sub> in solution but also its crystals obtained after an evaporation-crystallization and drying-thermic treatment procedure. Some laboratory equipment and chemical products were used to realize these synthesis and titrations such as graduated beaker 500[ml], graduated beaker 250[ml], pH-meter, magnetic stirrer-fischer scientific, magnetic stir bar, glass rod, precision balance KERN, hot plate, flask 250[ml], hot-flask 250[ml], laboratory glass filter, filter paper, refrigerator, thermometer, oven, desiccator, crystallizer, hydrochloric acid (purity-33%), fine iron filament (purity >99%), hydrofluoric acid HF-0.0026N, sodium hydroxide NaOH-0.05N, pure toluene, IronIIchloride-FeCl<sub>2</sub>, sodium ethoxide-Na(OEt), test tube 250[ml], burette 50[ml], pipette-10[ml], pear laboratory, ethanol (90% purity), pure hexane, acetone, color indicators - Thymol blue and phenolphthalein.

## 2. IronIIChloride-FeCl<sub>2</sub> Synthesis

Synthesis in laboratory of IronIIChloride-FeCl<sub>2</sub> [1, 2] was carried out using fine iron filament more than 99% purity and hydrochloric acid 33% purity respecting its reaction stoichiometric in the following equation (1). Fine iron filament was cutted down and its synthesis experimental conditions was shown in the following table 1 seeing that its global reaction equation (1) was:

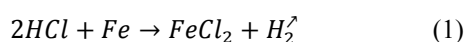


Table 1. Experimental conditions of IronIIChloride-FeCl<sub>2</sub> synthesis.

IronIIChloride-FeCl <sub>2</sub> Synthesis Experimental Conditions	
Iron weight [g]	8.8124
HCl (33%) volume [ml]	30
Iron concentration [mol/L]	0.789
Initial distilled water volume [ml]	170
Initial pH-calculated	2.80
Initial pH recorded	0.45 to 1.27
pKa (HCl) [4, 5]	[-6.3; -7]
Temperature [°C]	[200°C – 250°C]

### 2.1. IronIIchloride-FeCl<sub>2</sub> Solution Synthesis Procedure

Put the 170[ml] distilled water into the graduated beaker 500[ml] containing a magnetic stir bar, then add the 30[ml] of hydrochloric acid (33%) and just now insert into the obtained solution all 8.8124[g] cutted fine iron filament raw material using a glass rod. After, put the beaker 500[ml] on the hot plate and stir vigorously its content all the time using the glass rod, the magnetic stir bar when solution was in ebullition to

discharge efficiently the hydrogen and activate the reaction in the direction of FeCl<sub>2</sub> formation. Noticed that the solution volume decreased and during the synthesis its volume wasn't below 150[ml] and all the time fall to 200[ml] if necessary by adding approximatively 50[ml] of distilled water and all the time the recorded pH was in the vicinity of 4.75. After few hours of synthesis, the iron filament became fine-grained dispersed easily stirred and the solution became greyish. After approximatively 7 hours of synthesis, it was noticed that the iron fine grained unreacted effectively even if the solution was stirred efficiently so the synthesis was stopped after 8 hours. So, the reaction was stopped and the solution volume was fallen to 350[ml] by adding distilled water. Decant the obtained solution during 14[hours], the iron fine grained leftovers agglomerated with eventually FeCl<sub>2</sub> and very few hydrochloric acid leftovers at the bottom; the solution at the top became green. Recover the green FeCl<sub>2</sub> solution [1, 2] and filter to be finally refrigerated. Then, weight the dry iron fine grained leftovers.

### 2.2. IronIIChloride-FeCl<sub>2</sub> Solution Synthesized Yield and Its Titration with NaOH-0.05N Procedure

#### 2.2.1. IronIIChloride-FeCl<sub>2</sub> Solution Synthesized Yield

The results of this laboratory IronIIChloride-FeCl<sub>2</sub> synthesized solution are presented in the following table 2.

Table 2. IronIIChloride-FeCl<sub>2</sub> synthesis results.

Laboratory IronIIChloride-FeCl <sub>2</sub> solution synthesized results	
Total volume of IronIIChloride-FeCl <sub>2</sub> green solution recovered [ml]	360
Initial Iron weight [g]	8.8124
Leftovers dry iron fine grained weight [g]	3.7547
Mass yield against initial iron weight [%]	57.39
Initial HCl (33%) volume [ml]	30
HCl density [g/ml]	1.17
Initial HCl weight [g]	11.583E-3
HCl boiling point-38% [°C] [7-9] (33%-volume fraction = 38.6%-mass fraction)	48
H <sub>2</sub> O-HCl constant-boiling azeotrope [°C] [7-9] at (20.2%-mass fraction = 17.26%-volume fraction)	108.6
Mass yield against initial iron and HCl weight [%]	57.32

#### 2.2.2. IronIIchloride-FeCl<sub>2</sub> Solution Titration with NaOH-0.05N Procedure

Noticed that the mass yield against initial iron and HCl weights (57.32%) was relatively low, so the titration of the obtained IronIIChloride-FeCl<sub>2</sub> green solution was carried out with NaOH-0.05N by taking approximatively 0.1[ml] to 0.2[ml] (V<sub>s</sub>) as sample volume dissolved in 15[ml] of distilled water and Thymol blue or phenolphthalein as indicator dye according to the reaction



At the equivalent point V<sub>e</sub>[ml], the titrated solution which was initially uncolored (phenolphthalein) or yellow (thymol blue) turned into violet (phenolphthalein) or blue (thymol blue).

So, the total moles of IronIIChloride-FeCl<sub>2</sub> in the sample was equal to

$$n_{FeCl_2} = \frac{(0.05N \times V_e \times 0.001)}{2} \quad (3)$$

and its concentration was equal to

$$[FeCl_2] = \frac{n_{FeCl_2}}{V_s} \quad (4)$$

Thus, the obtained IronIIChloride-FeCl<sub>2</sub> green solution concentration was equal to 0.13[mol/L] (Table 3).

**Table 3.** Characteristics of the IronIIChloride-FeCl<sub>2</sub> synthesized solution.

Laboratory IronIIChloride-FeCl <sub>2</sub> solution Synthesized characteristics	
Color	green
Total volume of IronIIChloride-FeCl <sub>2</sub> green solution recovered [ml]	360
[FeCl <sub>2</sub> ] [mol/L]	0.13
Total moles of FeCl <sub>2</sub> [moles]	4.68E-2
FeCl <sub>2</sub> Molar Mass [g/mol]	126.745
Total mass of FeCl <sub>2</sub> deduced by titration [g]	5.9317
Initial moles of Iron [moles]	0.1578
Molar yield [%]	29.64
Initial HCl weight [g]	11.583E-3
Mass yield deduced by titration [%]	67.22

### 2.3. Evaporation, Crystallization and Drying Processes of the FeCl<sub>2</sub> Solution Synthesized into Crystals and Its Titration with NaOH-0.05N Procedure

#### 2.3.1. Evaporation, Crystallization and Drying Procedure of the Synthesized IronIIChloride-FeCl<sub>2</sub> Solution into Crystals

This step consisted of increasing the IronIIChloride-FeCl<sub>2</sub> concentration by removing gradually the water with evaporation process [10-11]. So, transfer the IronIIChloride-FeCl<sub>2</sub> solution in a beaker-500[ml] and put it on a dry sand container which was heated with a hot plate; the temperature increased in the vicinity of 473.15[°K] and the beaker-500[ml] must be stirred during the evaporation process

for its efficiency and in fine to acquire brown to white precipitates indicating the presence of water molecules inside the FeCl<sub>2</sub> crystals. Then, take up with drying process by transferring the precipitates into an oven programmed at 344.15[°K]-5[°C/mn] during 3 hours. A dry brown IronIIChloride-FeCl<sub>2</sub> crystals was acquired which were conserved hermetically in a container inside the desiccator during 12 hours. Finally, IronIIChloride-FeCl<sub>2</sub> crystals with green chartreuse colors which weighted 26.0329[g] was obtained and titrated with NaOH-0.05N to evaluate its purity and the efficacy of the evaporation, crystallization and drying procedure described previously.

#### 2.3.2. IronIIChloride-FeCl<sub>2</sub> Crystals or Solution Titration with NaOH-0.05N Procedure

So, take approximately M<sub>s</sub>=0.0590[g] (or 0.6[ml]) of the IronIIChloride-FeCl<sub>2</sub> crystals (or solution) and dilute with 15[ml] of distilled water. Add few drops of Thymol blue or phenolphthalein as indicator dye according to the reaction (2). At the equivalent point V<sub>e</sub>[ml], the titrated solution which was initially uncolored (phenolphthalein) or yellow (thymol blue) turned into violet (phenolphthalein) or blue (thymol blue).

So, the total moles of IronIIChloride-FeCl<sub>2</sub> in the sample was equal to

$$n_{FeCl_2} = \frac{(0.05N \times V_e \times 0.001)}{2} \quad (5)$$

and its mass concentration was equal to

$$[FeCl_2] = \frac{n_{FeCl_2}}{M_s} \quad (6)$$

Thus, the obtained IronIIChloride-FeCl<sub>2</sub> crystals mass concentration was equal to 1.7797E-3[mol/g] and the efficacy of the evaporation, crystallization and drying procedure was 98.9973% (Table 4).

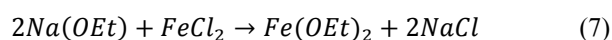
**Table 4.** IronIIChloride-FeCl<sub>2</sub> synthesized crystals – titration with NaOH-0.05N results.

Laboratory IronIIChloride-FeCl <sub>2</sub> crystals synthesis and titration results	
Color	Green chartreuse
Total weight of IronIIChloride-FeCl <sub>2</sub> crystals [g]	26.0329
[FeCl <sub>2</sub> ] [mol/g]	1.7797E-3
Total moles of FeCl <sub>2</sub> [moles]	4.633E-2
Total moles of FeCl <sub>2</sub> in solution (Table 3) [moles]	4.68E-2
Evaporation-crystallization-drying procedure efficacy [%]	98.9973

## 3. IronIIEthoxide-Fe(OEt)<sub>2</sub> or FeO<sub>2</sub>C<sub>4</sub>H<sub>10</sub> Synthesis and Titration

Synthesis in laboratory of IronIIEthoxide-Fe(OEt)<sub>2</sub> or FeO<sub>2</sub>C<sub>4</sub>H<sub>10</sub> by reflux was carried out using the previous synthesized FeCl<sub>2</sub> (§2.) with the sodium ethoxide Na(OEt) concentrated solution synthesized by NaOH and Ethanol-90° [12] respecting the reaction stoichiometric (7) and the typical

synthetic procedure [13-15].



Its synthesis experimental conditions was shown in the following table 5. Noticed that this experimental molar ratio Iron/Ethanol-0.4775 (Table 5) was in the vicinity of the typical synthetic procedure [13-15] approximately equal to 0.4668 and pure hexane was used as additional solvent.

**Table 5.** Experimental conditions of IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  synthesis.

IronIIEthoxide- $\text{Fe}(\text{OEt})_2$ Synthesis Experimental Conditions	
$\text{FeCl}_2$ [moles]	0.0463
$\text{FeCl}_2$ weight [g]	5.8724
$[\text{FeCl}_2]$ [mol/L]	0.6436
$\text{Na}(\text{OEt})$ concentration [mol/L]	2.6192 [12]
$\text{Na}(\text{OEt})$ volume [ml]	34.5907
$\text{Na}(\text{OEt})$ [moles]	0.0906
$\text{Na}(\text{OEt})$ weight [g]	6.1653
Ethanol-90° volume [ml]	6.15
Ethanol pure volume [ml]	5.5
Ethanol [moles]	0.0949
Iron/Ethanol [molar ratio]	0.4775
Hexane [ml]	31.2
Ethanol/Hexane/ $\text{Na}(\text{OEt})$ [volume ratio]	1/5.6/6.3
Ethanol/Hexane/ $\text{Na}(\text{OEt})/\text{Fe}$ [molar ratio]	1/2.5/0.96/0.4775
Temperature [°C]	[90°C-115°C]
Reaction duration [mn]	150

### 3.1. Laboratory IronIIEthoxide- $\text{Fe}(\text{OEt})_2$ Synthesis Procedure

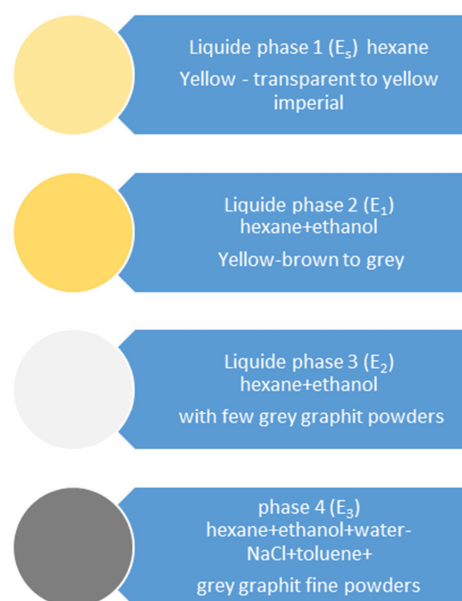
As described on the bibliographies [14], the typical synthesis was done by reflux. Firstly, mix the solvents ethanol-90° and hexane. Put the sufficient quantity of  $\text{FeCl}_2$  salts previously synthesized (§.2.) inside the flask 250[ml] and add the mixed solvents ethanol 90°-hexane. Finally, put all at once the  $\text{Na}(\text{OEt})$ -sodium ethoxide solution inside the flask 250[ml], install the reflux assembly and begin to heat with paying attention in such a way the hot-flask temperature was all the time between 90[°C] and 115[°C] during the synthesis. When the reaction time was elapsed remove the hot-flask with maintaining the reflux assembly functional until there were any drops of solvent-reflux. At the end, a heterogeneous solution was obtained composed with the solvents and the fine powder of the desired product- $\text{Fe}(\text{OEt})_2$  and eventually the by-product salt- $\text{NaCl}$ . Then, Transfer all product inside a glass container using a mix-solvent composed mainly in molar with ethanol-90° mixed with hexane and toluene such as the molar ratio between initial  $\text{Na}(\text{OEt})$  moles and ethanol-90° moles was 0.0326. Its characteristics was shown in the following table 6.

**Table 6.** Characteristics of the washing-extracting mixed solvent.

Ethanol-90° - Hexane and Toluene washing-extracting mixed solvent	
$\text{Na}(\text{OEt})/\text{Ethanol}$ -moles [ratio]	0.0363
Hexane/Ethanol-90° volume [ratio]	1.59
Hexane/Toluène volume [ratio]	25.28
Ethanol-90°/Toluene volume [ratio]	16.22
Ethanol/Hexane moles [ratio]	1.27
Hexane/Toluene moles [ratio]	20.19
Ethanol/Toluene moles [ratio]	26.55
(Ethanol/Hexane)/ $\text{Na}(\text{OEt})$ [ratio]	14.02

When all product were recovered, the hermetic glass container was putted into the refrigerator during two days and 12[hours] to improve crystallization with dissolution of the products inside the mixed-solvents. Thus, three netted liquid phases and grey graphite fine powders mainly composed with IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  were obtained (Figure 1). Noticed that all liquid phases were recovered by seringue from the top to the bottom but the lower phase 4 ( $E_3$ ) was composed mainly

with solid grey graphite fine powders.

**Figure 1.** Liquid and solid phases of IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  synthesized.

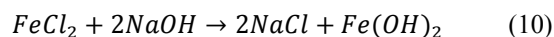
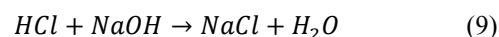
### 3.2. Quantifications of IronIIEthoxide- $\text{Fe}(\text{OEt})_2$ Synthesized by Titration with $\text{NaOH}$ -0.05N Using Hexane as Solvent

#### 3.2.1. IronIIEthoxide- $\text{Fe}(\text{OEt})_2$ Titration With $\text{NaOH}$ -0.05N Using Hexane as Solvent Procedure

To quantify the synthesized IronIIEthoxide- $\text{Fe}(\text{OEt})_2$  in the phases their titration was necessary. Thus, take approximately 0.0200[g] ( $M_s$ ) or 0.6[ml] ( $V_s$ ) as sample. Dilute with 30[ml] of distilled water in a beaker 250[ml] then add 5[ml] of hexane and two or three drops of thymol blue, agitate the obtained solution carefully which turned to light yellow-brown. Begin the titration with the titrant solution  $\text{NaOH}$ -0.05N and noticed that generally after few milliliters aqueous phase of the titrated solution turned to dark brown indicating the presence and titration of unreacted  $\text{FeCl}_2$  or  $\text{HCl}$  obtained by hydrolyze of  $\text{FeCl}_2$  according to the reaction



Indeed, it was noticed that during the grey graphite titration, samples conglomerated with the stir bar thus the firstly titrated chemical compound were probably  $\text{FeCl}_2$  or  $\text{HCl}$  according to the reactions:



Thus, the volume of  $\text{NaOH}$ -0.05N ( $V_{e1}$ ) corresponding to this first changing of color was taken to be used to titrate mainly the unreacted  $\text{FeCl}_2$  assuming that it was the most chemical compound as by product (unreacted reactant) and source of by-product due to water molecules according to the equation (8); and it was normally completely hydrolyzed during the titration. Thus, the total moles of  $\text{FeCl}_2$  in the sample like the equation (5) was equal to

$$n_{FeCl_2} = \frac{(0.05N \times V_{e1} \times 0.001)}{2} \quad (11)$$

and its concentration was equal to

$$[FeCl_2]_{e1} = \frac{n_{FeCl_2}}{V_s} \quad (12)$$

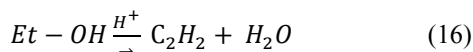
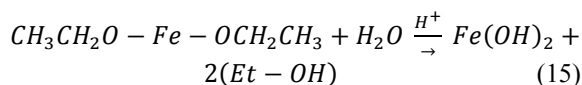
(volume concentration) or

$$[FeCl_2]_{e1} = \frac{n_{FeCl_2}}{M_s} \quad (13)$$

(mass concentration). Also, especially for the grey graphite sample titration it was noticed a back and forth of color between dark and light brown which corresponded and indicated the beginning of the titration of the packed  $Fe(OEt)_2$  conglomerated with the stir bar according to the reaction



where the  $Fe(OH)_2$  went to the aqueous phase and the  $NaOEt$  join the organic phase hexane thus during the titration the  $Fe(OEt)_2$  could stay conglomerated with the stir bar. Noticed that during synthesis, ethylene  $2HC=CH_2$  could be formed according to the hydration reaction catalyzed by protonic  $H^+$ -HCl (15) followed by ethanol dehydration catalyzed by  $H^+$ -HCl to give the ethylene (16) which could reacted by Friedel-Crafts mechanism to give benzene and polynuclear aromatics [16-17].



Thus, if existent the liberation of these ethylene molecules during titration and joining the hexane solvent with the  $Na(OEt)$  molecules were responsible of the basic coloration of it to dark brown. When light blue coloration appeared clearly and lather decreased relatively it indicated that alkenes and all

$Na(OEt)$  produced by the titration reaction (14) have joined the hexane solvent and indicated the equivalent point of the titration with the equivalent volume  $V_{e2}$ . Thus, the total moles of  $Fe(OEt)_2$  in the sample was equal to

$$n_{Fe(OEt)_2} = \frac{[0.05N \times (V_{e2} - V_{e1}) \times 0.001]}{2} \quad (17)$$

and its concentration was equal to

$$[Fe(OEt)_2]_{e2} = \frac{n_{Fe(OEt)_2}}{V_s} \quad (18)$$

(volume concentration)

or

$$[Fe(OEt)_2]_{e2} = \frac{n_{Fe(OEt)_2}}{M_s} \quad (19)$$

(mass concentration).

Pay attention to this previous equivalent point coloration because if not the regeneration of the  $Fe(OEt)_2$  according to the inverse reaction on equation (14) could take place and temptation to continue the titration could take place with certainly overestimation of the results.

### 3.2.2. Quantifications of the Pure IronIIethoxide- $Fe(OEt)_2$ Synthesized in Each Phases $E_s$ , $E_1$ and $E_2$ - §3.1 - Figure 1

Seeing that the IronIIethoxide- $Fe(OEt)_2$  and eventually ethylene was soluble in hexane and ethanol [3, 18, 19] and certainly the  $NaCl$ , water and other by-products like  $FeCl_2$  stayed on the bottom after these two days and 12[hours] which improved crystallization with dissolution of the products inside the mixed-solvents, the quantifications of the pure IronIIethoxide- $Fe(OEt)_2$  synthesized according to the previous procedure titration by  $NaOH$ -0.05N with hexane and the results were shown in the following table 7. Noticed that a non-negligible mass yield of pure  $Fe(OEt)_2$  40.72[%] was obtained not counting the grey graphite fine powders on the phase 4- $E_3$  (figure 1). Thus, an evaporation-crystallization of the total phases was carried out.

Table 7. Quantifications results of the pure IronIIethoxide- $Fe(OEt)_2$  after decantation and crystallization in each phases.

	Phase- $E_s$	Phase- $E_1$	Phase- $E_2$
[ $Fe(OEt)_2$ ]-concentration [mol/L]	1.458E-2	1.042E-1	1.667E-1
Total $Fe(OEt)_2$ -moles [moles]	1.2979E-3	1.855E-2	1.373E-2
Total $Fe(OEt)_2$ -weight [g]	1.8945E-1	2.7074	2.0044
Initial raw materials- $FeCl_2$ and $Na(OEt)$ weight-Table 5 [g]		12.0377	
Mass yield of pure $Fe(OEt)_2$ [%]		40.72	

## 4. IronIIethoxide- $Fe(OEt)_2$ - $FeO_2C_4H_{10}$ Evaporation-Crystallization and Titrations

### 4.1. Thermic Evaporation-Crystallization of IronIIethoxide- $Fe(OEt)_2$ Obtained Heterogeneous Solution

All phases in figure 1 were putted into a beaker 500[ml] and Evaporation, crystallization and drying procedure as described

on paragraph §2.3.1. was carried out until the solution volume decreased approximately 80.47[%] and the solution was colored grey graphite by the fine powders composing the solution. Evaporation was stopped, the obtained solution was decanted during 12[hours] and finally four phases like described on paragraph §3.1. (figure 1) appeared which were titrated with  $NaOH$ -0.05N and as solvent hexane (§3.2.1.). But, noticed that the phase 4 was bathed in hexane during 12[hours] and filtered carefully to recover not only the hexane with extracted  $Fe(OEt)_2$  but also the 19.8797[g] of grey graphite powders which were all titrated. Results of these titrations were in the following table 8. Noticed that the mass

yield of pure Fe(OEt)<sub>2</sub> increased from 40.72[%] to 97.67[%] confirming the efficiency of the evaporation-crystallization procedure described on paragraph §2.3.1. even if there was

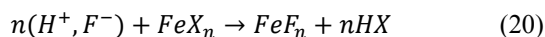
2.33[%] of impurity and over products like alkenes which allowed us to estimate their quantities by titration with HF-0.0026N [20] (Table 8).

**Table 8.** Quantifications results of the pure IronIIethoxide-Fe(OEt)<sub>2</sub> and alkenes after evaporation- crystallization in each phase.

	Phase1-E <sub>s</sub>	Phase2-E <sub>1</sub>	Phase3-E <sub>2</sub>	Phase4-E <sub>3</sub> hexane	Grey graphite
[Fe(OEt) <sub>2</sub> ]-concentration [mol/L]	4.125E-1	4.708E-1	8.33E-3	5.417E-2	3.2334E-3*
Total Fe(OEt) <sub>2</sub> [moles]	1.2788E-2	2.825E-4	2E-4	2.9792E-3	6.43E-2
Total Fe(OEt) <sub>2</sub> -weight [g]	1.8667	0.0412	0.0292	0.4349	9.3858
Initial raw materials- FeCl <sub>2</sub> and Na(OEt) weight-Table 5 [g]	12.0377				
Mass yield of pure Fe(OEt) <sub>2</sub> [%]	97.67				
[C <sup>-</sup> ] alkenes concentration [mol/L]		2.1667E-4			5.3E-3*
Estimated alkenes as C <sub>2</sub> H <sub>4</sub> weight [g]		7.2931E-5			< 0.2
[FeCl <sub>2</sub> ] concentration [mol/L]	-	-	-	-	5.0223E-4

\* mass concentration [mol/g].

Noticed that if the estimated alkenes molecules was only ethylene molecules the total mass of products was slightly more than initial total raw materials weight. This result allowed us to interpret that during their titrations with HF-0.0026N of grey graphite not only alkenes samples were titrated but also FeX<sub>n</sub> according to the reaction (20) and their values could be overestimated. Thus, the estimated weight of aromatics' alkenes functions and other basic by-products molecules FeCl<sub>2</sub> were inferior to 0.28[g] with evaluated-calculated mass concentration inferior to the inflate 3.5866E-4 considering that salt-NaCl formed during synthesis were eluted and evaporated with ethanol-water. That is why a washing procedure was done to the grey graphite and described in the following paragraph 4.2.



#### 4.2. Grey Graphite Washing Procedure

Raw materials used during this washing procedure were water and pure hexane such as their quantities and ratio depending to the titrated value of FeCl<sub>2</sub> were showed in the following table 9.

**Table 9.** Grey graphite washing raw materials composition and quantities.

Washing raw materials composition and quantities	
Sample to be washed weight [g]	3
[FeCl <sub>2</sub> ] on grey graphite [mol/g]	5.0223E-4
FeCl <sub>2</sub> on sample [moles]	1.5067E-3
H <sub>2</sub> O/ FeCl <sub>2</sub> [molar ratio]	221
H <sub>2</sub> O – volume [ml]	6
Hexane/ FeCl <sub>2</sub> [molar ratio]	14
Hexane – volume [ml]	3

Firstly, take a simple laboratory glass filter and place a filter paper with the sample to be washed on. Then, inject first of all the distilled water followed by the pure hexane when water was completely adsorbed in the sample. Leave in the open air under atmospheric pressure and recover the extract in beaker 250[ml]. Normally, the pure hexane molecules overhang the water molecules because of its density and insolubility with them and after some minutes

of filtration 2.7[ml] of water was recovered which represented approximately 25 twice the estimated minimum water volume to wash all sample- FeCl<sub>2</sub>. To evaluate this washing efficiency, the FeCl<sub>2</sub> in the extract solution was titrated with NaOH-0.05N using hexane as solvent and it was established that its efficiency attained 97.07[%] as shown in the following table 10.

**Table 10.** Grey graphite washing procedure results.

Washing procedure results	
Sample to be washed weight [g]	3
[FeCl <sub>2</sub> ] on grey graphite [mol/g]	5.0223E-4
FeCl <sub>2</sub> on sample [moles]	1.5067E-3
Total FeCl <sub>2</sub> on extract [moles]	1.4626E-3
Washing yield-efficiency [%]	97.07
Grey graphite density [g/ml]	0.9588
Initial [Fe(OEt) <sub>2</sub> ]- [mol/g]	3.2334E-3
Initial [Fe(OEt) <sub>2</sub> ]- [mol/L]	3.1002
Initial moles Fe(OEt) <sub>2</sub> [moles]	9.7E-3
Extract moles Fe(OEt) <sub>2</sub> [moles]	1.35E-3
Retention rate of Fe(OEt) <sub>2</sub> [%]	86.08
Initial alkenes [moles]	1.0760E-3*
Extract alkenes [moles]	9.1E-6
Retention rate of alkenes [%]	99.15

\* Initial alkenes deduced by the inflate value of FeCl<sub>2</sub> mass concentration §4.1.

In brief, this washing procedure using water and hexane in such proportion and under atmospheric pressure was efficiency not only at 97.07[%] but also to retain grey graphite Fe(OEt)<sub>2</sub> and alkenes molecules (Table 10). Then, a part of the grey graphite washed sample was treated thermally under the oven.

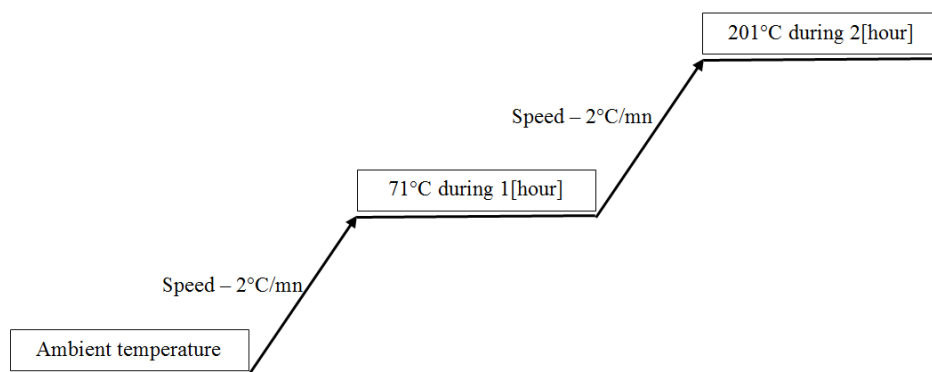
#### 4.3. Washed Grey Graphite IronIIethoxide-Fe(OEt)<sub>2</sub> Thermic Treatment

2.1377[g] of washed grey graphite IronIIethoxide-Fe(OEt)<sub>2</sub> was subject to oven thermic treatment according to the following oven program on the figure 2. At the end, a fine grey graphite powder was obtained with 75% of porosity evaluated with acetone according to a procedure described in bibliography [21, 22]. Also, its IronIIethoxide-Fe(OEt)<sub>2</sub> purity was evaluated with NaOH-0.05N with hexane as



solvent titration (cf. §3.2.1.) and results were shown in the following table 11. Noticed that the thermic treatment

increased its purity by 2.68 points.



**Figure 2.** Oven program of washed grey graphite IronII Ethoxide-Fe(OEt)<sub>2</sub> thermic treatment.

**Table 11.** Washed Grey graphite IronII Ethoxide-Fe(OEt)<sub>2</sub> thermic treatment results.

Thermic treatment results	
Sample to be treated weight [g]	2.1377
Treated sample weight [g]	1.1541
Mass loss rate [%]	46.01
Porosity[%]	75
Purity [%]	99.75

Evaporation-Crystallization of the Solution Extract Phase 3-E<sub>2</sub>

Also, evaporation-crystallization of the solution extract-E<sub>3</sub> (figure 1) was carried out such as transvase the solution in a beaker 250[ml] and heat in a hot-flask with paying attention that the temperature didn't exceed 70[°C]. When the solution turn in ebullition, remove it from the hot-flask and agitated carefully the solution using a magnetic stirrer until its temperature decreased approximately at 25[°C]. Then, replace the beaker 250[ml] under the hot-flask with paying attention again that the temperature didn't exceed 70[°C]. Again, when the solution turn in ebullition, remove it from the hot-flask and agitated carefully the solution using a magnetic stirrer until its temperature decreased approximately at 25[°C]. In fine, remake the same procedure until all solvent and water were removed. In this case, brown fine crystals of IronII Ethoxide-Fe(OEt)<sub>2</sub> were obtained [3].

## 5. Conclusion

Firstly, laboratory synthesis procedure of IronII chloride-FeCl<sub>2</sub> at approximately 200[°C] to 250[°C] using hydrochloric acid-HCl-(33%) and fine iron filament (purity>99%) with respecting the reaction stoichiometric was successful. The mass yield against raw materials (Iron and HCl) deduced by mass balance was 57.32 [%] but to control and to refine this result, the established titration procedure with NaOH-0.05N to titrate the synthesized FeCl<sub>2</sub>-solution was a success and gave a mass yield equal to 67.22[%]. Also, it was showed the efficiency of the evaporation-crystallization-drying thermic treatment procedure, to acquire IronII chloride-FeCl<sub>2</sub> crystals colored

with green chartreuse, which efficacy was evaluated with NaOH-0.05N titration procedure was 98.9973[%]. Secondly, not only, laboratory synthesis procedure of IronII Ethoxide-Fe(OEt)<sub>2</sub> or FeO<sub>2</sub>C<sub>4</sub>H<sub>10</sub> by reflux during 150[mn] at approximately 90[°C] to 115[°C] (maximally) using the previous synthesized FeCl<sub>2</sub>, sodium ethoxide-Na(OEt) [12] and ethanol with pure hexane as solvent such as the molar ratios (Iron/Ethanol) and (Ethanol/Hexane/Na(OEt)/Iron) were respectively (0.4775/1) and (1/2.5/0.96/0.4775) was a success; but also the washing-extracting mixed solvent; composed with Ethanol90°-Pure Hexane-Toluene and another solvent composed only with Ethanol90°-Pure Hexane without ethanol such as the molar ratios of (Ethanol/Hexane), (Hexane/Toluene), (Ethanol/Toluene) and (Ethanol/Hexane)/Na(OEt) were respectively 1.27, 20.19, 26.55 and 14.02; were very efficiency to wash the reactor flask-250[ml] and over used laboratory glassware to extract all synthesized product. Once recovered, the established crystallization procedure permitted to obtain heterogeneous phases composed with pure IronII Ethoxide-Fe(OEt)<sub>2</sub> liquid phases on top and solid grey graphite fine powders on the bottom solution. The established titration procedure using NaOH-0.05N and hexane as additive in titrated solution permitted not only to quantify the concentration of pure IronII Ethoxide-Fe(OEt)<sub>2</sub> in liquid phases which increased from the top to the bottom as respectively 1.458E-2 [mol/L] to 1.667E-1 [mol/L] but also to evaluate the FeCl<sub>2</sub> representative-by-product at the bottom phase approximately 5.0223E-4 [mol/L]. Also, the mass yield of pure IronII Ethoxide-Fe(OEt)<sub>2</sub> in liquid phases was 40.72[%]. Thirdly, also the established evaporation-crystallization procedure to concentrate the previous heterogeneous phases in order to crystalize the IronII Ethoxide-Fe(OEt)<sub>2</sub> was efficacy to increase the extracted IronII Ethoxide-Fe(OEt)<sub>2</sub> mass yield to 97.67[%]. Fourthly, the grey graphite was filtered and washed to remove the eventual ethylene and FeCl<sub>2</sub> by-products according an established procedure using a simple laboratory glass filter, a filter paper and water with hexane as washing product such as (H<sub>2</sub>O/FeCl<sub>2</sub>) and (Hexane/H<sub>2</sub>O) molar ratios were respectively 221 and 14. This procedure efficacy to retain

alkenes-ethylene and to extract FeCl<sub>2</sub> was very high respectively 99.15[%] and 97.07[%] as molar rates with 86.08[%] retention rate of Fe(OEt)<sub>2</sub>. Once washed, the efficacy of the thermic treatment procedure which suffered the grey graphite Iron(II)ethoxide-Fe(OEt)<sub>2</sub> allowed to increase its purity 99.75[%] with 75[%] as porosity evaluated with acetone. Finally, to confirm the efficacy of the evaporation-crystallization procedure, it was used to crystallize the pure Iron(II)ethoxide-Fe(OEt)<sub>2</sub> solution at maximally 70[°C] until to acquire fine brown crystals of Iron(II)ethoxide-Fe(OEt)<sub>2</sub>.

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