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Quantification of Fe (II) Ions in the Synthesis of Polypyrrole by Spectrophotometric Detection

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Abstract: ***This paper presents the study of synthesis of Polypyrrole nanocomposite from pyrrole monomer incorporating anhydrous Iron (III) Chloride as an oxidant using chemical oxidative polymerization method. The experiment was conducted over a period of 4 hours at a temperature of 5^0C with varied concentrations of $FeCl_3$, oxidant to monomer ratio were ranging from 0.5 to 2.0. The reaction of polypyrrole with 1, 10-phenanthroline forms a complex, Spectrophotometer (EQ 820D) was used to investigate the maximum wavelength (λ_{max}) and to quantify the Ferrous Fe (II) ion content in polypyrrole solution using a colorimetric technique. Series of standard Fe solutions were formulated to establish the relationship between optical absorbance and Fe concentration. The presence of Fe(II) ions validated the process that led to the production of polypyrrole from its monomer. The current paper focuses on a simple and exact approach for estimating the Iron (II) content in polypyrrole.***

Keywords: Polypyrrole, 1,10-phenanthroline, spectrophotometer (EQ 820 D), Fe(II)

1. Introduction

Nanomaterials are one of the most popular scientific and technological research topics due to their size-dependent characteristics, which are advantageous in a variety of applications such as medicine, the environment, energy, and multiple sectors [1-2]. Polypyrrole (PPy), one of the most extensively researched conducting polymers, has prospective uses in a various domain due to its environmental resilience and excellent electrical conductivity [2]. Pyrrole can be electrochemically or chemically oxidized to produce PPy. PPy can be electrochemically polymerized in order to produce a polymer. Although this method is not appropriate for mass production., the chemical technique is simple, inexpensive, and scaleable [3-4]. Many oxidants have been employed in conventional chemical oxidative polymerization to produce PPy; However, in this study, we incorporated $FeCl_3$ as an oxidant. Ppy solutions had been made for four different $FeCl_3$ concentrations, for the oxidant to monomer ratio from 0.5 to 2.0 range [2-3].

In the formation of PPy, the pyrrole monomer is reacted with ferric Fe(III) ion and gets converted into ferrous Fe(II) ion[17]. Consequently, the primary goal of this work was to determine the concentration of Fe (II) in the PPy solution. This implies that the reaction of synthesis of PPy through pyrrole has been completed. We used a colorimetric approach to determine the Fe (II) content. Based on how a solution's colour changes with changes in concentration, colorimetric analysis is used [19].

The most basic kind of absorption analysis uses colorimetric techniques. For this, we worked with a spectrophotometer (EQ 820D) that operates in the visible range from 350 nm to 650 nm [19-20]. Both the wavelength selection along with the readings was carried out digitally. Based on the reaction shown below, involving the formation of a complex species that absorbs in the visible region, spectrophotometry provides a practical method to quantify the concentration of Fe (II), which can be treated to form a coloured solution, in which the colour intensity is proportional to the amount of the Fe(II)[21]. In the determination of iron (II) in aqueous solutions,1, 10-phenanthroline ($C_{12}H_8N_2$) is used as the ligand that reacts with Fe(II) to form strongly coloured complexes. With ferrous ions (Fe^{2+}), it reacts in a ratio of 1:3 to form an orange red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$ in aqueous medium as per the following equation [19].

$$Fe^{2+} + 3\ Phen \longrightarrow Fe(Phen)_3^{2+}$$

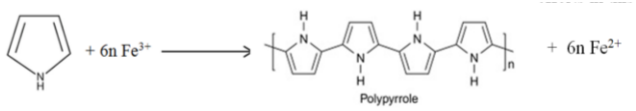
After the colour change, we noted the absorbance of the coloured solution at the relevant wavelength (λ_{max}), which we acquired by monitoring absorbance at different wavelengths of standardized solution. Finally, using the measurements of the absorbance of standard solutions of known concentrations, we plotted a calibration curve and estimated the concentration of the unknown sample corresponding to the absorbance value obtained through spectrometer [14].

In this paper, we present a simple interface for fabrication of PPy via chemical oxidative polymerization with $FeCl_3$ as an oxidizing agent [21]. This research provides a convenient method for evaluation of concentration of Fe(II) ion which can be treated to form a coloured solution, where colour intensity is proportional to the concentration of the substance [20-22].

2. Theoretical Background

In mid-19th century, researchers first began exploring into the characteristics of natural polymers including cellulose, silk, and rubber [2]. The study of polymers is still active topic today, with researchers developing novel forms of polymers. Shirakawa Hideki, a Japanese chemist, discovered in 1963 that some organic polymers, such as PPy, may conduct electricity when doped with specific compounds [3].

In the 1970s, Researchers like Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa persisted in their investigation of the electrical characteristics of PPy and other conductive polymers [4]. In 1977, MacDiarmid and Shirakawa were awarded the Nobel Prize in Chemistry for their work in this area. During the polymerization process, pyrrole reacted with iron(III) from $FeCl_3$ forming iron(II) ions. In 1977, MacDiarmid and Shirakawa were awarded the Nobel Prize in Chemistry for their efforts in this field [3-5].



The PPy solution should contain Iron(II) ions once this reaction is finished. The key objective of our research is to estimate the Fe(II) composition of PPy.

Blau reported the initial discovery of 1,10-phenanthroline complex formation with iron(II) [11]. The complex served as an internal indicator for the oxidimetric titration of iron with the ceric ion by Walden, Hammett, and Chapman. Fortune and Mellon created a method for spectrophotometrically measuring iron that is reliant on the synthesis of the iron(II), 1,10-phenanthroline complex[14]. The concentration of Fe^{2+} has been measured using a variety of techniques. The spectrophotometric approach has developed into a significant option for the detection of Fe^{2+} due to its benefits like simplicity, high speed, and sensitivity [16–17].

Spectrophotometer is based on the principle of photometric techniques [14]. According to it, a beam of incident light with an intensity of I_0 travels through a solution and is partially reflected, partially absorbed, and partially transmitted. If I_r, I_a, and I_t are the portions of the light that were reflected, absorbed, and transmitted, respectively. Then we can write,

$$\mathbf{I_0 = I_r + I_a + I_t} \text{ ----------(i)}$$

In the spectrophotometer, I_r is eliminated because the measurement of I_t and I_0 is sufficient for the measurement of I_a. So, I_r is kept constant. Beer-Lambart law can be used to determine the relationship between the amount of light absorbed and the concentration of substance [19], the law can be expressed as:

$$\mathbf{A = \varepsilon c l} \text{ ----------(iI)}$$

where A is the absorbance, ε is the molar absorptivity or extinction coefficient, c is the concentration of the absorbing species, and *l* is the path length of the light through the solution. The law is widely used in analytical chemistry to quantify the concentration of substances in a solution[21].

3. Experimental Work/Research Methodology

3.1 Materials

3.1.1. Chemicals

i) Pyrrole (C_4H_5N) monomer of reagent grade purchased from Loba Chemie Pvt. Ltd. Its stored in dark at 0°C. Iron(III) chloride hexahydrate (analytical grade) was used as oxidant. To remove any possible impurities, Pyrrole was distilled under reduced pressure before use. The solutions of Pyrrole (monomer) and $FeCl_3.6H_2O$ (oxidant) were synthesized in deionized water.
ii) 1,10-phenanthroline
iii) Potassium Hydrogen Phthalate
iv) Sulphuric acid (H_2SO_4)

3.1.2. Instruments:

Digital Spectrophotometer (EQ 820D): the optical system consists of lamp, grating monochromator, Photodiode, Lens system and cuvette holder.

3.2. Experimental procedure:

3.2.1. Synthesis of Polypyrrole:

PPy was synthesized via a modified chemical oxidative polymerization method [1-4]. Briefly, 1 mL of aqueous Pyrrole solution (1 M) was taken and 10 mL of $FeCl_3$ added dropwise in it. The mixture was continuously stirred for 4 hour at 5^0C with a magnetic stirrer. After the completion of the reaction, a black precipitate of PPy was obtained. The precipitate obtained was filtered by vacuum filtration and washed several times with deionized water. The filtrate obtained through this was used for further analysis. Same procedure followed for four different concentrations of $FeCl_3$ [3-5]. The oxidant to monomer ratios were as 0.5, 1.0, 1.5, 2.0. These four samples are named as S1, S2, S3, S4.

3.2.2. Analysis of Fe(II) ions:

Firstly, 100 ppm of Fe(II) solution was prepared by using Ferrous Ammonium Sulphate (FAS) [0.176 g of FAS + few mL of concentrated H_2SO_4 dissolved and diluted to 250 mL]. Pipetted out 0, 0.5, 1.0, 1.5, 2.0, 2.5 cm^3 of 100 ppm Fe(II) solution in 50 cm^3 of standard measuring flask labelled from 1 to 6. To each flask, we added 5 cm^3 of 0.5 M Potassium Hydrogen Phthalate (KHP) and 5 cm^3 of 0.25% 1,10-phenanthroline. Each of this flask diluted up to the mark by distilled water. The reaction of Fe(II) is shown in figure 1. The PPy filtrate obtained previously, which contains high iron percent was diluted to the suitable quantity and treated in a same manner as other solutions. Then, we used flask no. 1 as a blank and flask no. 4 solution for λ_{max} determination using spectrophotometer. Set the wavelength at λ_{max} value and measure the absorbance of each solution using flask no. 1 as blank solution. The schematic diagram of this process is shown in figure 2 below.

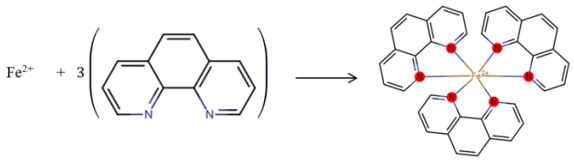


Figure 1: Reaction of formation of $Fe^{2+}(Phen)_3$ complex

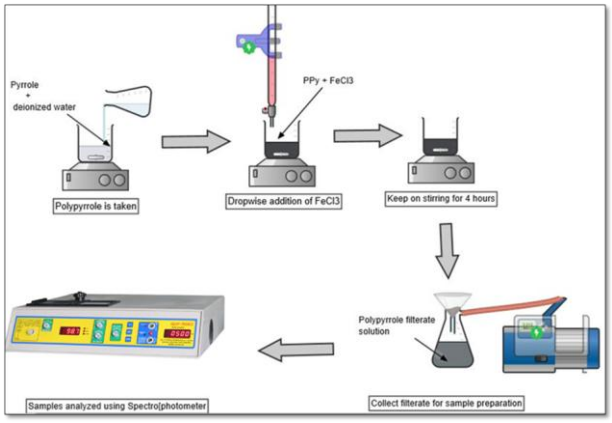


Figure 2: Schematic diagram of the synthesis, filtration and sampling process

4. Result and Discussion:

4.1. Recording the visible spectrum of the iron-phen complex:

Table 1: Absorbance of the iron-phen complex obtained from 3 ppm standard solution of Iron(II)

Sr. No.	Wavelength (nm)	Absorbance
1.	410	0.07
2.	425	0.08
3.	440	0.12
4.	455	0.13
5.	470	0.14
6.	485	0.18
7.	500	0.22
8.	515	0.24
9.	530	0.22
10.	545	0.16
11.	560	0.09
12.	575	0.05
13.	590	0.02
14.	605	0.01
15.	620	0

4.2. Graph between wavelength and absorbance for the standard solution (from Table 1).

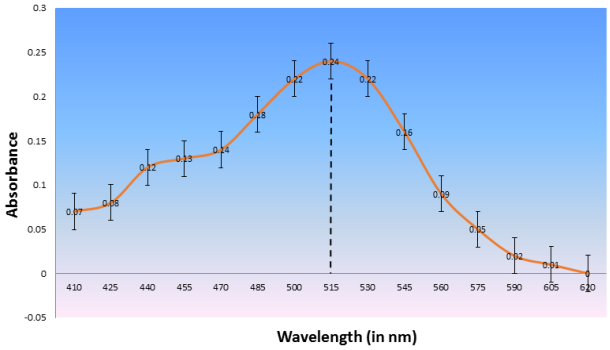


Figure 3: Visible spectrum of the Iron-phen complex

As per the spectrum obtained above, the wavelength of maximum absorption, λ_{max} is found to be **515 nm**.

4.3. Collecting absorbance data for the Beer-Lambart Plot:

Table 2: Absorbance values of the phen-complexes of standard and sample solutions of Fe(II) ions

Sample No.	Concentration of Fe(II) in PPM	Absorbance at λ_{max}
1	0.5	0.12
2	1.0	0.17
3	1.5	0.23
4	2.0	0.24
5	2.5	0.36
S1	Unknown (M.R. = 0.5)	0.05
S2	Unknown (M.R. = 1.0)	0.08
S3	Unknown (M.R. = 1.5)	0.10
S4	Unknown (M.R. = 2.0)	0.22

4.4. Plotting the calibration curve

Graph between the absorbance and the concentration of ferrous ion in the standard solution

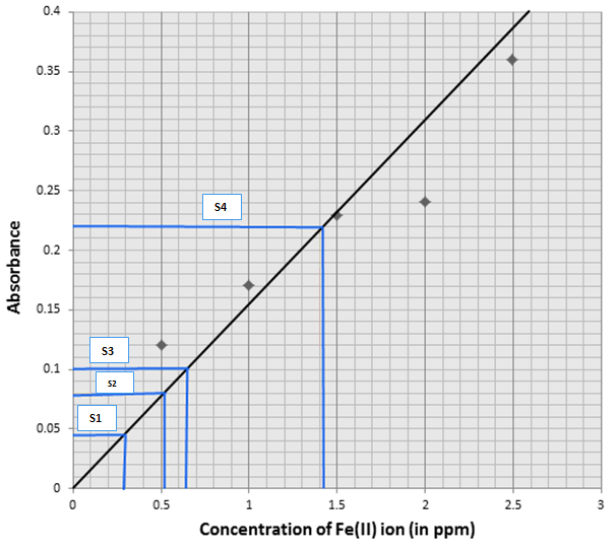


Figure 4: Calibration plot of absorption vs. Concentration

4.5. Determining the concentration of the ferrous ions in the sample from calibration curve:

We plotted the value of absorbance of the sample solution on the calibration curve and determined the corresponding concentration value (in ppm).

The concentration of ferrous (Fe^{2+}) ions in the given sample = (Value obtained from the calibration curve) X (10000) ppm

The factor of 10000 comes from the fact that we took 1 cm^3 of the sample solution and first diluted to 100 cm^3. From this diluted solution, we have taken 0.5 cm^3 and finally diluted it to 100 cm^3.

The result obtained by using above formula is shown in the table as:

Table 3: Concentration of Fe(II) ions for different M.R.

Sample No.	Molar Ratio of Oxidant to Monomer (M.R.)	Concentration Values obtained from the graph	Concentration of Fe^{2+} ions (in g/L)
S1	0.5	0.3	3
S2	1.0	0.505	5.05
S3	1.5	0.515	5.15
S4	2.0	1.405	14.05

This implies that the concentration of Fe(II) ion in the PPy sample depends on the amount of $FeCl_3$ added to it.

5. Conclusion

In this study, PPy nanocomposites were successfully synthesized in the aqueous medium by a modified simple chemical oxidative polymerization method. The wavelength of maximum absorption for the iron-phenanthroline complex had been determined to be 515 nm. For this wavelength we have plotted the calibration curve, which estimated the Iron(II) content from the PPy solution, implies that the reaction of synthesis of PPy is completed. The result obtained indicates that as $FeCl_3$ is added to the reaction of PPy synthesis, the quantity of Iron(II) content increases.

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