

Spectrophotometric determination of iron (III) catalyst in organic compound chlorinations

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Abstract. In the science or industrial practice of chemical processes, iron (III) is sometimes used as a catalyst in organic compound chlorinations due to its effectiveness and low cost. Thus, a fast and easy method of determination in the system is useful especially when metallic iron is used as a precursor which is readily converted into iron (III) chloride by the gaseous chlorine used in the chlorination reactor. In the latter case, the determination of the produced catalytically effective iron (III) is a prerequisite for controlling the kinetic progress of chlorination. In this work, a method for the spectrophotometric determination of iron (III) chloride in organic media after complexation with methyl ethyl ketone is investigated. The formation of a strong σ -complex of iron (III) with methyl ethyl ketone allows direct determination of iron at 360 nm. Beer's law is valid up to absorbance 2.42, where the iron (III) concentration is $20.7 \text{ mg}\cdot\text{L}^{-1}$, with molar absorptivity (ϵ) equal to $6.532 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and Sandell's sensitivity $8.5 \times 10^{-3} \text{ }\mu\text{g}\cdot\text{cm}^{-2}$. Standing time for color development is of the order of a few seconds and stability of color measurements exceeds 12 months. The method may be used among other applications in organic compounds chlorinations catalyzed by iron. These systems are complicated due to the coexistence of various complexes. Nevertheless, the method proposed being simple, fast, and not depending on the composition of the chlorination mixture and the amount of methyl ethyl ketone added was found to be suitable.

Keywords. iron-catalyzed chlorinations, iron complexation, iron determination, organic compounds chlorinations.

1 INTRODUCTION

1.1 Aim of the investigation

In chlorinations of organic substances, metallic iron powder is sometimes used as a catalyst. In these cases, the catalytic action of iron is due to its previous transformation to iron (III) chloride by the reactant chlorine and the byproduct hydrogen chloride. Thus, methods for the determination of iron (III) chloride in organic media are needed for investigating its catalytic action. In the majority of such determinations, aqueous solutions of iron are utilized finally, even if the iron has been previously extracted by an organic solvent, such as chloroform, ethyl, or isopropyl ether and isobutyl methyl ketone. In these cases, determinations are time-consuming and the errors increase by the error of separation of iron from its solutions in inorganic and organic solvents [1]. Thus, from the viewpoint of simplicity and accuracy, the direct determination of iron in organic media is preferable.

This could be accomplished by the investigation of possible complexes of iron with various organic compounds. Complexes of iron (III) with compounds, such as pyridine [2], calixarenes [3], and lignin model compounds [4] have been mainly utilized as oxidation catalysts. Fatiadi [5] has reviewed chemical and stereochemical applications of organo-iron complexes. Some iron (III) complexes with organic compounds have been investigated with e.g., flumequine [6], yet only for iron (III) determinations in aqueous solutions.

Numerous other papers deal with the determination of iron (II) and iron (III) in aqueous media especially for foods or environmental samples [7-14]. However, none of them aims at determining iron directly in hydrophobic organic media during chlorinations.

To the best of our knowledge, no direct (without previous extraction) determination of iron (III) in organic media after complexation has been investigated yet. The present work is directed to study the iron (III) - methyl ethyl ketone complex for the determination of iron in hydrophobic organic solvents during chlorinations of organic compounds. The reaction model considered is the chlorination of p-xylene by chlorine gas.

1.2 Description of the model system

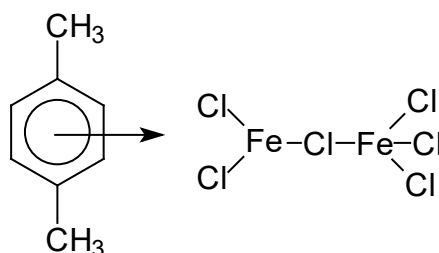
In a system of substitution chlorination of organic compounds by gas chlorine in the presence of iron as a catalyst (Friedel-Crafts system), various complexes are formed which influence the reaction kinetics. In these systems the following possibilities of formation of complexes with the catalyst may occur:

- Catalyst - co-catalyst
- Catalyst - substrate
- Catalyst - reactant
- Catalyst - product
- Catalyst - solvent

The catalyst, in this case, is iron (III) chloride, co-catalyst is the byproduct hydrogen chloride, the substrate is the organic compound being chlorinated, the reactant is chlorine, the product is the chlorinated compound and solvent could be the same compound being chlorinated. As a model chlorination system has been selected the chlorination of p-xylene without a solvent.

By analogy to aluminum halides which have been extensively investigated it is concluded that the above systems include carbonium ion complexes of the form $\text{ArH}_2^+\text{FeCl}_4^-$ or generally $[\text{ArH}_2 \cdot n\text{ArH}]^+[\text{FeCl}_4 \cdot m\text{FeCl}_3]^-$. These complexes may be separated as solids or oils from fairly strong solutions, provided that their polar nature results in low solubility in hydrocarbons. They may be considered as salts of supposed acid HFeCl_4 , whose proton is attached with a σ -bond to a carbon atom of the aromatic nucleus. In contrast to π -complexes of a Lewis acid with an aromatic hydrocarbon, which are covalent non-conductive compounds of relatively low stability, the ionic σ -complexes are more stable and they are considered as catalytically inactive.

In the model system the complexes of iron (III) chloride with p-xylene and its chlorinated products it is expected by analogy to aluminum halides to have the form:



The degree of substitution of the aromatic nucleus significantly influences the basicity and consequently its reactivity to form complexes. Thus, it has been found [1] that π -basicity of hexamethylbenzene is about 4 to 15 times greater than that of p-xylene, whereas σ -basicity of hexamethylbenzene differs from that of p-xylene by a factor of the order of 10^5 . In addition to the above complexes, there is also the possibility of the formation of complexes between the aromatic nucleus and the halogen used. These complexes are in general 1:1 complexes [15].

The complexes under investigation of iron (III) chloride with ketones in proportion to aluminum halides are expected to be 1:1 complexes ($\text{FeCl}_3 \cdot \text{RCOR}'$) with a high enthalpy of formation of the order of 20 kcal/mol. The aliphatic ketone selected as a complexation agent of iron (III) chloride

is methyl ethyl ketone, mainly because of its lower vapor pressure compared to dimethyl ketone which has also proved effective in iron determinations.

A further complication of the system is the possibility of ketones to form relatively stable complexes with chlorine and hydrogen halides ($\text{RCOR}'\cdot\text{Cl}_2$, $\text{RCOR}'\cdot\text{HCl}$). Yet, these complexes are stable only at very low temperatures. Finally, aromatic compounds form also weak complexes with halogens.

2 EXPERIMENTAL

2.1 Materials

Stock solutions of iron (III) chloride in p-xylene, 2-chloro-p-xylene, and methyl ethyl ketone (MEK) were prepared in a dry box using analytical reagent chemicals.

2.2 Apparatus

A PerkinElmer Coleman 124 Double Beam spectrophotometer with 10 mm fused silica cells was used for absorbance measurements.

2.3 Procedure

To about 1 mL of iron (III) chloride solution in an organic solvent, such as p-xylene or 2-chloro-p-xylene, a few mL of MEK is added and the absorbance is measured at 360 nm against a blank of pure MEK. If absorbance exceeds 2.42 the sample is diluted with MEK so that absorbance is in the linear range 0 up to 2.42. If chlorine and hydrogen chloride are present in the samples, due to a chlorination procedure in progress, a nitrogen gas stream is passed through the samples to remove these gases.

3 RESULTS AND DISCUSSION

3.1 Selection of conditions

Solutions of anhydrous FeCl_3 in p-xylene and its first chlorination product (2-chloro-p-xylene) were obtained after mild heating. These solutions resulted in a sharp peak absorbance at 292 nm and a sharp peak absorbance at 295 nm, respectively (Figure 1). After cooling, separation of an insoluble solid started which continued for days. Thus, the attempt to investigate a method of direct determination of iron (III) by complexation with the existing aromatic compounds (reactant and product) failed, due to the low solubility of the resultant complexes.

The use of methyl ethyl ketone as a complexation agent requires decomposition of the aromatic nucleus - iron (III) chloride complexes existing in the system with the formation of the more stable and soluble methyl ethyl ketone - aromatic nucleus complex. Indeed, after the addition of MEK in the system, no precipitation, but instead a redissolution of the eventually separated iron (III) chloride - aromatic compounds complexes was observed.

Solutions of known concentration in FeCl_3 were prepared then, both in pure MEK and in mixtures of MEK with p-xylene. Absorption spectra of these solutions against blanks made of pure p-xylene, 2-chloro-p-xylene, MEK, and their mixtures resulted in two absorption peaks at 325 and 360 nm. The absorption maximum at 325 nm depends on the composition of the solution, whereas that at 360 does not (Figure 2). The peaks at 292 and 295 nm did not appear in the presence of p-xylene and 2-chloro-p-xylene, respectively. This shows clearly that the complex of FeCl_3 with the aromatic nucleus is indeed decomposed and the more stable complex with MEK predominates.

The variation in height of the maximum at 325 nm supports the hypothesis of considerable difference in absorption spectra of MEK and p-xylene and interference due to the formation of the complex MEK - p-xylene. To clarify this situation the absorbance of MEK was measured against blanks made of p-xylene and 2-chloro-p-xylene at the region of above peaks in the presence and absence of MEK in the reference solutions.

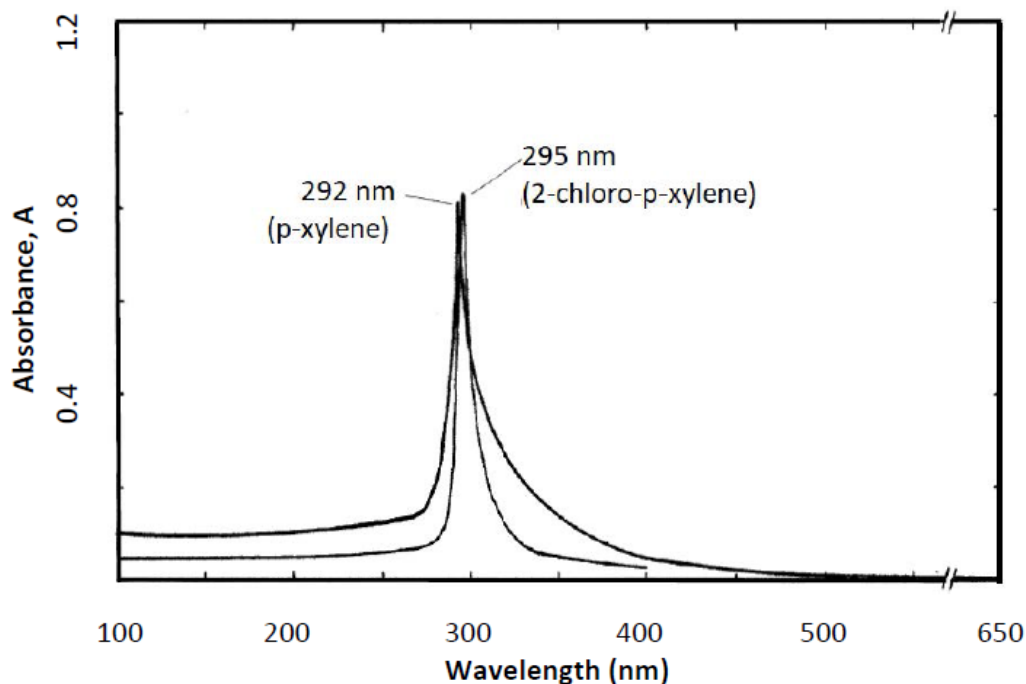


Figure 1. Absorption spectra of the FeCl₃ / p-xylene and FeCl₃ / 2-chloro-p-xylene complexes with p-xylene as reference solution.

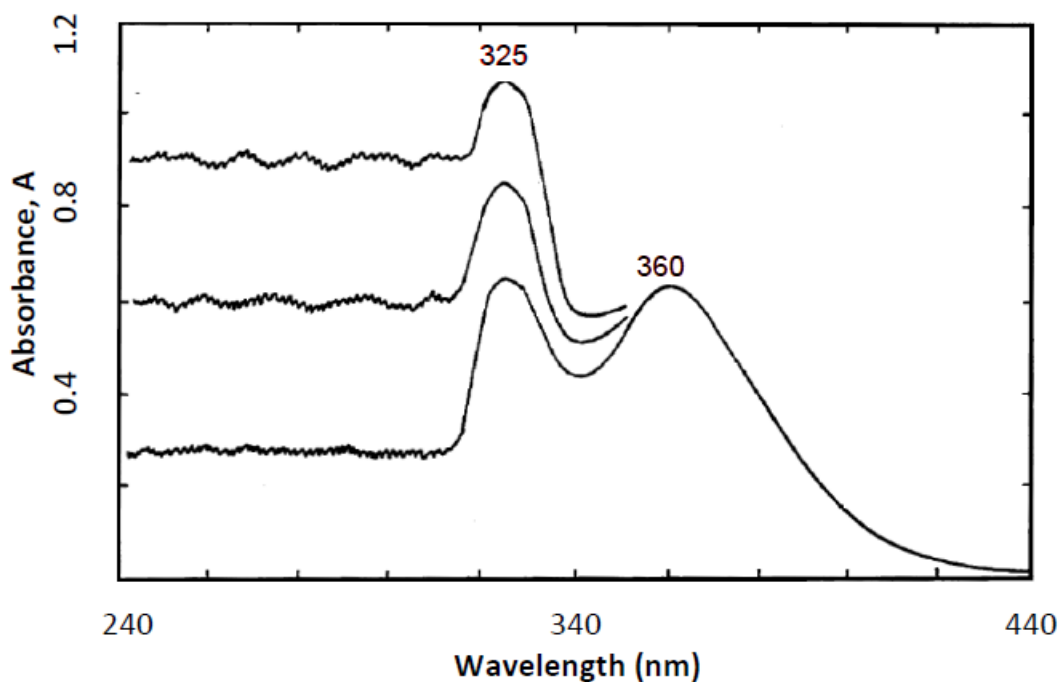


Figure 2. Absorption spectra of the FeCl₃ / methyl ethyl ketone complex of varying composition (p-xylene and methyl ethyl ketone) and methyl ethyl ketone as a reference solution.

Absorption spectra were identical for the two blanks used and gave no absorbance at 360 nm, yet a strong maximum at 325 nm depending on the presence or not of MEK in the blank (Figure 3). This confirms the initial hypothesis and excludes the maximum at 325 nm for the quantitative determination of FeCl_3 . Moreover, the use of 2-chloro-p-xylene instead of p-xylene as a blank did not affect the absorbance at 360 nm.

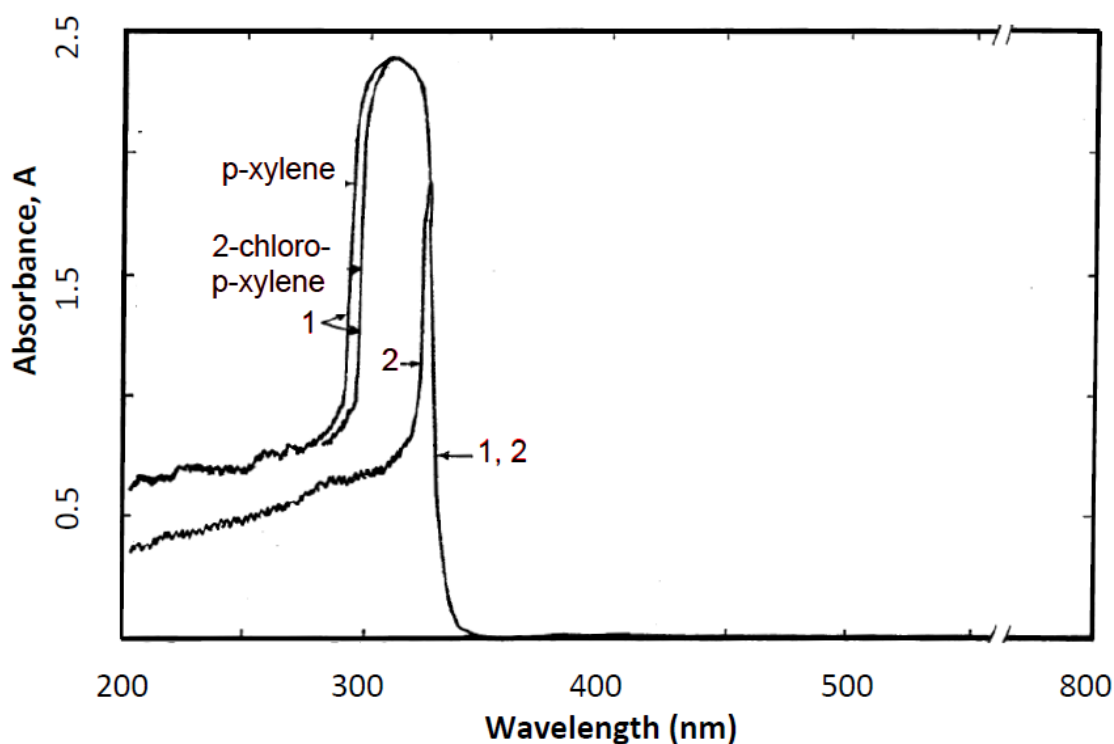


Figure 3. Absorption spectra of methyl ethyl ketone with reference solutions p-xylene and 2-chloro-p-xylene, in the absence (1) and presence (2) of methyl ethyl ketone in the reference solutions.

The stability of absorbance of the FeCl_3 -MEK complexes with time is remarkable. After 12 months of preservation at room temperature, measurements were still unchanged. The standing time for color development was found to be of the order of a few seconds.

Thus, measurements of absorbance at 360 nm of solutions of FeCl_3 in chlorinations of aromatic hydrocarbons after addition of MEK for the formation of a complex, showed that all aims set are accomplished:

- The complex formed first between the aromatic nucleus and FeCl_3 , which separates on cooling, re-dissolves after the addition of MEK.
- This complex decomposes by the action of MEK and the more stable MEK- FeCl_3 complex is formed.
- Absorbance at 360 nm does not depend either on time or on the composition of the solution.

3.2 Interferences

Selectivity against other metals has not been investigated since no other metals are normally encountered in organic compounds chlorination.

The above selection of conditions is valid, only when solutions are prepared with analytical quality reagents for the complexation of FeCl_3 with MEK and subsequent spectrophotometric

measurements. Nevertheless, in real chlorination conditions, the samples contain also dissolved or complexated chlorine and hydrogen chloride gases. These gases which may interfere with the determination of iron can be removed using an inert gas stream to move the equilibrium reactions to the left and decompose the complexes with the gases. Thus, the absorption spectra of real samples taken from chlorination reactors and treated with a nitrogen gas stream were compared to samples without dissolved gases. No significant differences were observed in these two spectra, indicating that interference from chlorine and HCl is insignificant and the treatment with the nitrogen gas is sufficient.

3.3 Calibration and molar absorptivity

A calibration curve was prepared for the conditions described in the procedure in a cuvette with a light path 10 mm (Figure 4). A linear absorbance-concentration relationship was obtained with $R^2 = 0.992$ for iron (III) concentrations up to absorbance 2.42, where the FeCl_3 concentration is 0.37×10^{-3} M (or $60 \text{ mg} \cdot \text{L}^{-1}$ FeCl_3 or $20.70 \text{ mg} \cdot \text{L}^{-1}$ iron (III)). This corresponds to an absorbance limit value equal to 2.42.

The molar absorptivity (ϵ) of the iron (III) chloride - MEK complex, as calculated in the linear region of the calibration curve, is at 360 nm:

$$\epsilon = 6.532 \times 10^3 \text{ L mol}^{-1} \cdot \text{cm}^{-1}$$

Then, the concentration of FeCl_3 is given by the relationship:

$$C = 1.531 \times 10^{-4} \times \text{Abs} \text{ mol} \cdot \text{L}^{-1}$$

or expressed as Fe (III):

$$C = 8.55 \times 10^{-3} \times \text{Abs} \text{ mg} \cdot \text{L}^{-1}$$

Hence, the calculated Sandell's sensitivity index [16] for FeCl_3 in a column with a cross-section equal to 1 cm^2 and minimum subdivision of the device equal to 0.001 is:

$$(\text{Sensitivity}) = 1.531 \times 10^{-4} \times 0.001 \times 162.2 \times 1 \times 10^{-6} \times 10^{-3} = 0.0248 \text{ } \mu\text{g} \cdot \text{cm}^{-2}$$

or expressed as μg Fe (III):

$$(\text{Sandell's sensitivity index}) = 8.5 \times 10^{-3} \text{ } \mu\text{g} \cdot \text{cm}^{-2}.$$

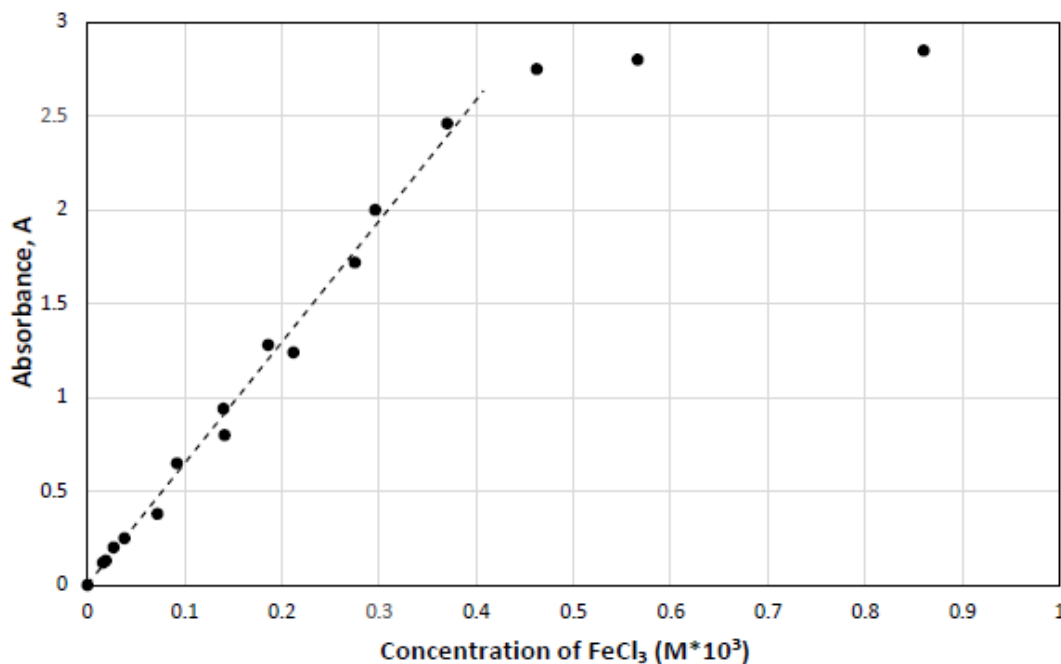


Figure 4. Linear absorbance-concentration relationship ($R^2 = 0.992$) up to 0.37×10^{-3} M FeCl_3 , or the equivalents 60 mg L^{-1} FeCl_3 , and 20.70 mg L^{-1} Fe (III).

3.4 Validation of the method

The results of this method were compared with gravimetric measurements of FeCl₃ dissolved in methyl ethyl ketone after its transformation to FeOCl. Thus, samples of known content in FeCl₃ were evaporated to dryness and then heated in an air oven at 180°C for 24 h to transform FeCl₃ to FeOCl. These measurements were 4 % lower than the initial quantities tested, that is recovery was found to be 95.98 ± 0.72 (RSD = 0.75) as shown in Table 1. This is attributed to the partial decomposition of FeOCl, which normally decomposes at 200°C [17].

The method was further validated against real measurements in a chlorination reactor of p-xylene at 90°C and the results are shown in Table 2. Samples of 1 mL volume were taken from the reactor during the chlorination of p-xylene. The reactant chlorine and the byproduct hydrogen chloride that interfere due to their complexes with the organic compounds present were successfully eliminated by the removal of these gases after passing a stream of nitrogen through the samples for 10 minutes. Subsequently, after the addition of 4 mL of methyl-ethyl-ketone, the weak complex of the aromatic hydrocarbons and the FeCl₃ that started to precipitate due to freezing of the samples re-dissolves and dissociates in favor of the more stable MEK-FeCl₃ complex.

Table 1. Gravimetric measurements of FeCl₃ dissolved in methyl ethyl ketone after its transformation to FeOCl.

Quantity of iron in mg		Recovery %
as FeCl ₃	as FeOCl	
6	5.8	96.67
9	8.6	95.56
12	11.4	95
15	14.4	96
18	17.4	96.67
Average =		95.98
SD =		0.72

Table 2. Measured and corrected concentrations of FeCl₃ in a chlorination reactor of p-xylene.

Conversion degree, x	Absorbance (after 5 times dilution of the samples)	Catalyst (FeCl ₃) concentration (mol/L)	Corrected catalyst concentration (mol/L)
0	1.170	8.96	8.96
0.099	1.201	9.19	8.97
0.224	1.241	9.50	8.97
0.295	1.265	9.69	8.98
0.409	1.306	10.0	8.99
Average =			8.97
SD =			0.01

The absorbances of these samples were measured at 360 nm with pure MEK as reference solution in a PerkinElmer Coleman 124 Double Beam spectrophotometer with 10 mm fused silica cells. The 1 mL samples from the reactor were diluted with 4 mL MEK for the formation of the complex with FeCl₃. Thus, the concentrations of FeCl₃ calculated by the linear relationship of concentration and absorbance derived in this work have to be multiplied by a factor of 5 to determine the real concentration.

The continuous increase of the corrected concentration in Table 2 is due to the related decrease of the specific volume of the reaction mixture as long as the extent of the reaction proceeds, taken into account that the chlorination product (mono-chloro-p-xylene) is denser than p-xylene. These measurements are corrected in the table with density-variation data of the p-xylene and mono-chloro-p-xylene mixture found in the literature [18]. It is clear from these measurements that the concentration of FeCl₃ in the reactor remains stable and there is no interference from the changing composition of the reactants.

The remaining slight increase of the concentration is probably due to the elevated reaction temperature (90°C) causing a slight loss of p-xylene and mono-chloro-p-xylene with the chlorine gas passing through the reactor.

This photometric method could be used in chemical kinetics studies of iron powder chlorination, which is further used in chlorinations of organic compounds. This catalytic effect is accomplished via the previous chlorination of iron to FeCl₃, which is the real catalyst. The study of these systems can be obtained, after a simple and reliable analytical method is developed, such as the present one.

4 CONCLUSIONS

The spectrophotometric method developed in this paper for the determination of iron (III) chloride in organic media is based on the σ -complex of iron with methyl ethyl ketone and is simple, sensitive, reliable, and fast.

For this method, Beer's law is valid up to absorbance 2.42, where iron (III) concentration is 20.7 mg·L⁻¹. Molar absorptivity is 6.532×10³ L·mol⁻¹·cm⁻¹ at 360 nm. The standing time for color development is of the order of a few seconds, whereas the stability of absorbance with time exceeds 12 months.

The method may be used for organic compounds chlorinations, where metallic iron is used as a catalyst, since measurements do not depend on the composition of the reaction mixture, concerning reactants, chloro-derivatives, or the content of methyl ethyl ketone.

Interferences of other metals were not investigated since these are not normally present in organic compound chlorinations.

For the above application, chlorine and hydrogen chloride interferences due to their complexes with the reacting organic compounds can be successfully eliminated by their removal by an inert gas stream through the samples.

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