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THE USE OF N,N'-DIMETHYL-N,N'-DIPHENYLMALONAMIDE FOR IRON(III) EXTRACTION

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N,N'-dimethyl-N,N,-diphenylmalomanide (DMDPHMA) has been proposed as selective reagent for extracting iron(III) from hydrochloric acid media. The influence of hydrochloric acid concentration on the extraction of Fe^{3+} ions was studied. Iron(III) ions were completely extracted from the concentrated hydrochloric acid solution (>8 M). When the concentration of chloride ions was maintained at 12 M by LiCl addition to the aqueous phase, the yield of iron(III) was nearly 100%. The stripping of iron(III) from the loaded organic phase (1,2-dichloroethane) was achieved by simple contact with water. The possible extraction mechanism and the composition of the extracted iron(III) species have been determined by using UV, IR and NMR spectroscopic techniques. The results showed that the metal ion was extracted as $FeCl_4^-$ complex.

Key words: extraction, iron(III),N,N'-dimethylN,N'-diphenylmalonamide, UV, IR, NMR spectroscopy

INTRODUCTION

The solvent extraction method is generally applied to the concentration of valuable metal ions from leaching solution. It can be used for eliminating these ions which trouble in recovery of the valuable metals presented in aqueous solution. For instance, the leaching solution after polymetalic copper ores treating contains Cu, Ni, Co and Fe. Dissolved metals can be separated using various procedures such as: cementation, precipitation, ions exchange or solvent extraction. The selective iron(III) separation is one of the targets for the precipitation of other metal ions from leaching solution (RABAH, 2000; RODRIGUEZ DE SAN MIGUEL, et al., 2000).

During bioleaching of gold-bearing minerals, metal ions such as Fe^{3+} are accumulated in the leaching liquor. The presence of an excess of Fe^{3+} ions in leaching

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solutions leads to jarosite precipitation (MARTINEZ et al., 1999; LANYN et al., 1999).

Malonamides belong to diamides that are amides with the functional group of (RCON).It has derived from malonic acid. The extractive properties of diamides, especially as extractants of multi-valent metal ions can be explained by the existence of hybrid forms of monoamides (TIAN, HUGHES, 1994, FERNANDES 1998). The chemical structure of the malonamide used in this investigation is shown in figure 1.

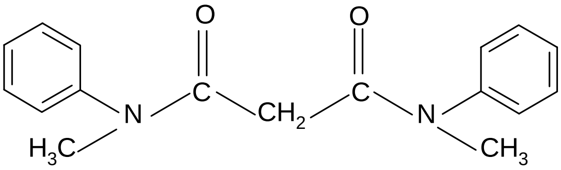

Fig. 1. General structure of DMDPHMA

The main objective of this study was to investigate the extractive features of the above structure for iron(III) extraction from hydrochloric acid solutions.

EXPERIMENTAL METHODS

REAGENTS

The extraction reagent was synthesised from the intermediate compounds: methylaniline and dimethylmalonate. These intermediate compounds were purchased from Aldrich (Germany). The malonamide was recrystallized from aqueous solution and its purity was established by both melting point and spectroscopic methods. 1,2 dichloroethane was used as organic diluent The stock solution of Fe(III) was prepared with $FeCl_3.6H_2O$. All other chemical reagents were of A.R. grade.

EXTRACTION PROCEDURE

The stock solution of the extraction reagent was prepared by dissolving appropriate weights of the compound in 12-dichloroethane. The organic phase was dichloroethane. The extraction experiments were carried out in Erlenmeyer’s flask. Equal volumes of the aqueous solution containing iron(III) and organic solution were agitated for 15 min at room temperature. Both phases were placed at separatory funnels. Then, the aqueous phase was separated. Iron(III) concentration in the aqueous phases before and after the extraction process was analysed by atomic absorption spectrometry (Shimatzu AA680).

NMR, IR SPECTROSCOPY

The Infrared spectra were recorded on a MATTSON 1000 FTIR spectrometer and the Nuclear Magnetic Resonance spectra were measured on a BRUKER (300 MHz) NMR spectrometer. In the case of NMR the chemical shifts were expressed with respect to an internal reference standard (TMS) and were δ values in *ppm.* The solvent in all cases was deuterated chloroform ($CDCl_3$), which frequency is attaining at about 77.0 – 79-0 ppm. In this study the observed for this solvent frequency was: 77.3 – 78.1 ppm.

In the present work IR spectra of the extractant molecule in different organic diluents, such as CCl_4, 1,2-dichloroethane, toluene and dichloromethane were analysed and compared. Similar spectra were obtained and that is why the results will be only presented for 1,2-dichloroethane (the diluent, which was chosen for DMDPHMA in this work).

RESULTS AND DISCUSSION

The influence of the ligand concentration on iron(III) extraction was studied using organic phases with different concentration of the extractant. The results obtained are shown in table1.

Table 1. Influence of ligand concentration on Fe^{3+} extraction

Ligand Concentration [mol/dm^3]	Initial Fe^{3+} concent. [mg/dm^3]	Final Fe^{3+} concnt. [mg/dm^3]	Fe^{3+} concent. organic faze [mg/dm^3]	Fe^{3+} extraction E [%]
0.10	582.7	1.4	581.3	99.8
0.010	582.7	7.0	575.6	98.8
0.0010	582.7	502.3	80.4	13.8

The experimental data show that Fe(III) is extracted quantitatively from the aqueous solution using 0.01 mol/dm^3 DMDPHMA dissolved in an organic phase. Experiments have also been conducted to establish the equilibrium isotherm curve (Fig. 2). The isotherm shows the dependence of the Fe^{3+} concentration in aqueous phase to the Fe^{3+} concentration in the organic phase.

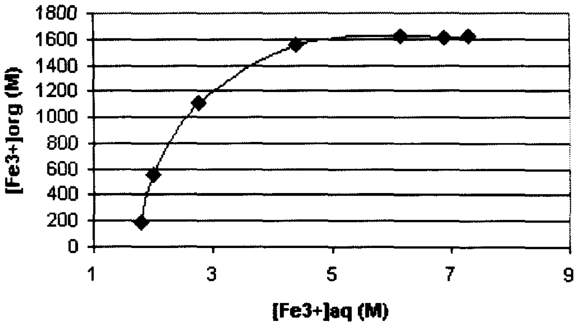

Fig. 2. The equilibrium isotherm curve

The shape of the obtained curve corresponds to the shape, which is characteristic for a ion-pair mechanism. The influence of hydrochloric acid concentration on the Fe^{3+}ions extraction was also studied using 1.0 M to 12 M range of concentration (Fig. 3).

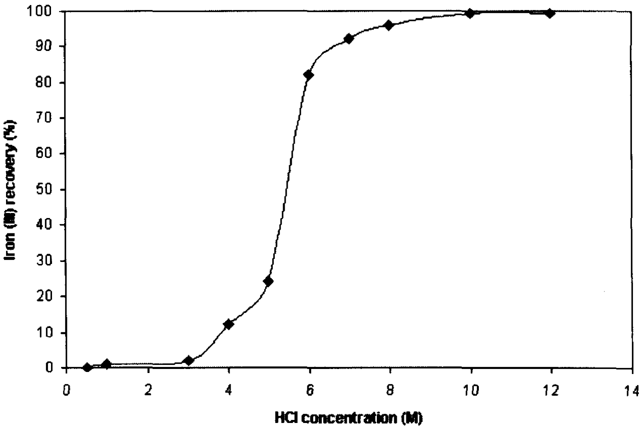

Fig. 3. Fe^{3+} ions extraction from HCl solutions

According to the obtained results it is possible to establish that the ability of DMDPHMA to extract Fe^{3+} from hydrochloric acid solutions is dependent on the acid concentration. This extraction behaviour is very close to the literature data (FERNANDES 1998; COSTA, et al. 1999, COSTA, PAIVA, 2002). The extraction of Fe^{3+} from 12 M of the total chloride concentration showed an absence of the acid concentration dependence (Table 2), when chloride concentration was achieved by LiCl addition.

Table 2. Fe^{3+} extraction from HCl solutions of 12 M of total Cl^- ions concentration

Total Cl^- conc.	12 M	12 M.	12 M	12 M	12 M
HCl conc. mol/dm^3	3	4	5	7	8
Initial Fe^{3+} conc. mg/dm^3	574.8	562.9	608.9	585.7	601.5
Final Fe^{3+} conc. mg/dm^3	5.6	5.4	5.8	8 .0	6.1
Fe^{3+} extraction E[%]	99.0	99.0	99.0	98.6	99.0

It is interesting to note that, when LiCl was replaced by sodium chloride the percentage of Fe^{3+} extraction was 20 %. According to the ion-pair formation mechanism, the lithium ion has a dimension like to a proton and is able to replace proton in the following process.

$$MAH^+Cl^-_{(org)} + Li^+_{(aq)} + FeCl_4^-{}_{(aq)} \rightarrow MaLi^+FeCl_4^-{}_{(org)} + H^+Cl^-_{(aq)}$$

When the hydrochloric acid solution was substituted by both nitric or sulphuric acid solutions, the results of Fe^{3+} extraction were unsuitable (HNO_3 8M, E[%] = 30.0; H_2SO_4 5M, E[%] = 20.0). In the case of malonamide as extractant, the possible protonation of its molecule should be taken into account, when metal extraction from concentrate acid solution is considered. Previous studies have shown that the protonation occurs on the carbonyl oxygen's rather that at the nitrogen atom (TIAN, HUGHES, 1994).

To find out, which iron(III) species are preferable extracted by DMDPHMA from hydrochloric acid media both aqueous and organic phases were analysed by UV spectroscopy. The UV spectra of the iron(III)-loaded organic phase show two peaks at 364.2 nm and 314.2 nm. (Fig. 4). According to the literature data these bands correspond to $FeCl_4^-$ species (LEVER, 1968). The peaks at about 364.0 nm and 314.0 nm were also identified in aqueous phases with chloride ion concentrations higher than 4 M. This can indicate that $FeCl_4^-$ is the predominant specie in HCl > 4 M.

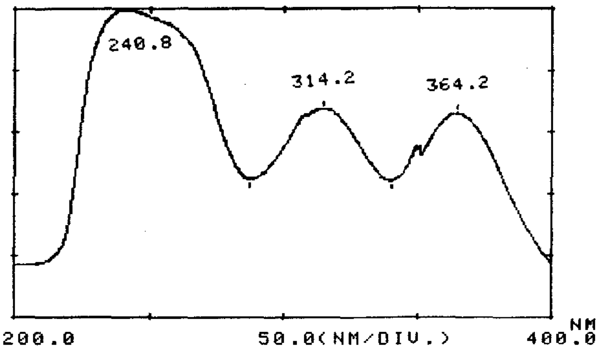

Fig 4. UV spectra of iron (III)-loaded organic phase in 1,2-dichloroethane after extraction from 8M HCl

Peaks corresponding to $FeCl_4^-$ were also observed in the spectrum of both organic and aqueous phases when the LiCl solution was used. NMR spectroscopy gives the possibility to investigate the structure of the extractant in different connections; before and after extraction. It is helpful to understand the mechanism of iron(III) extraction. NMR spectra of DMDPHMA in $CDCl_3$ are shown in Fig.5a,b.

Table 3. NMR assignments of DMDPHMA

^1H NMR δ(ppm)	^{13}C NMR δ(ppm)
3.01 (2H,s,a)	38.0 (2C,s,i)
3.23 (6H,s,b)	42.0 (1C,s,ii)
7.03-7.06 (4H,d,c)	128.1-130.3 (10C,m,iii)
7.28 7.38 (6H,m,d)	144.4 (2C,s,iv)
	167.7 (2C,s,v)

(s-singlet, d-doublet, t-triplet, m-multiplet)

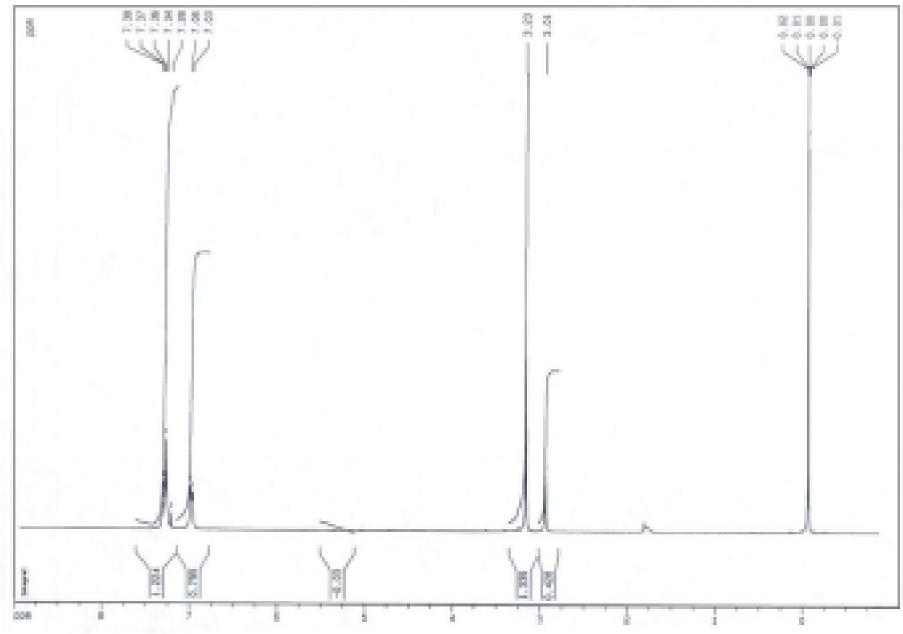

Fig. 5a. Proton NMR spectrum of DMDPHMA in $CDCl_3$ solution

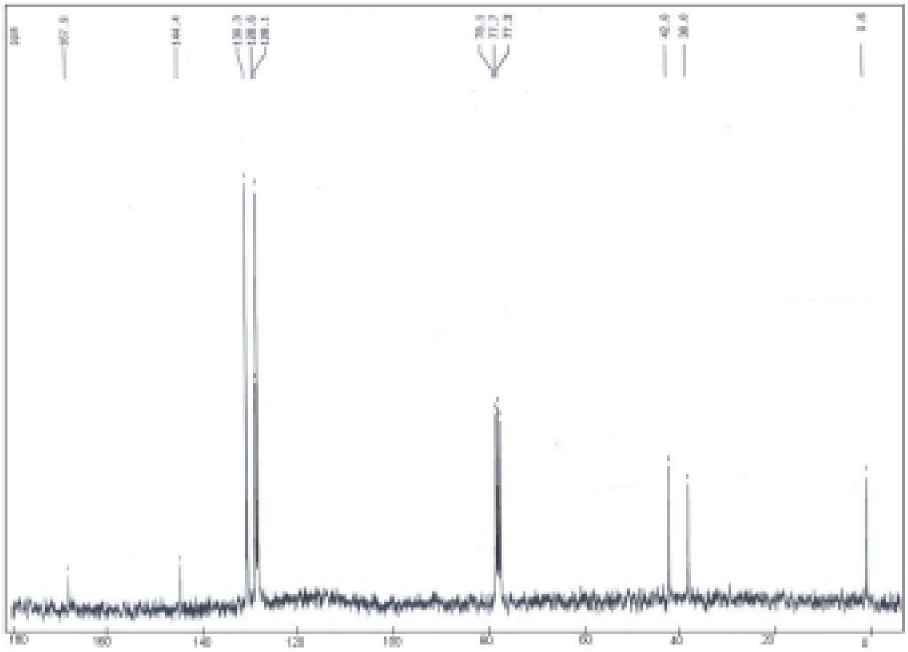

Fig.5b. Carbon NMR spectrum of DMDPHMA

Table 3 summarises the information of ^{1}H NMR and ^{13}C NMR spectra as well as NMR spectra of DMDPHMA after extraction and after contact with 8 M hydrochloric acid solution show the presence of four additional protons. This suggests that protonation occurs on both carbonyl oxygen atoms and on nitrogen atoms. According to previous IR-studies (FERNANDES, 1998), when coordination through the carbonyl oxygen occurs, a decrease in the C=O stretching band (1640 cm^{-1} in Fig. 6) intensity takes place. In the spectrum of DMDPHMA in 1,2-dichloroethane after extraction (Fig. 7), a decrease of intensity in the region of both groups (C=O and C-N) is observed. This suggests that protonation can occur on the carbonyl oxygen's and on the both nitrogen atoms.

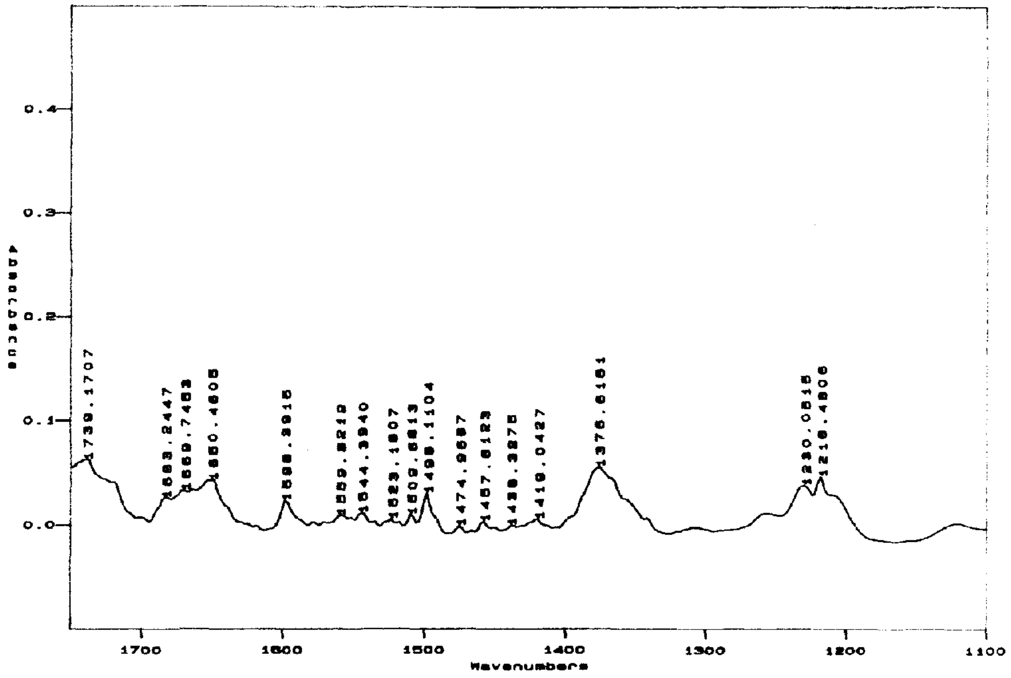

Fig. 6. IR spectra of DMDPHMA in 1, 2-dichloroethane

The titration of the aqueous phase with NaOH solution confirmed the fact that four moles of H^+ ions were attached to one mole of DMDPHMA. The kinetic study showed that the extraction of iron(III) from aqueous phase was realised in a very short period of time. Fig 8 shows that the iron recovery dramatically increased during the first 5 minutes of the extraction experiment.

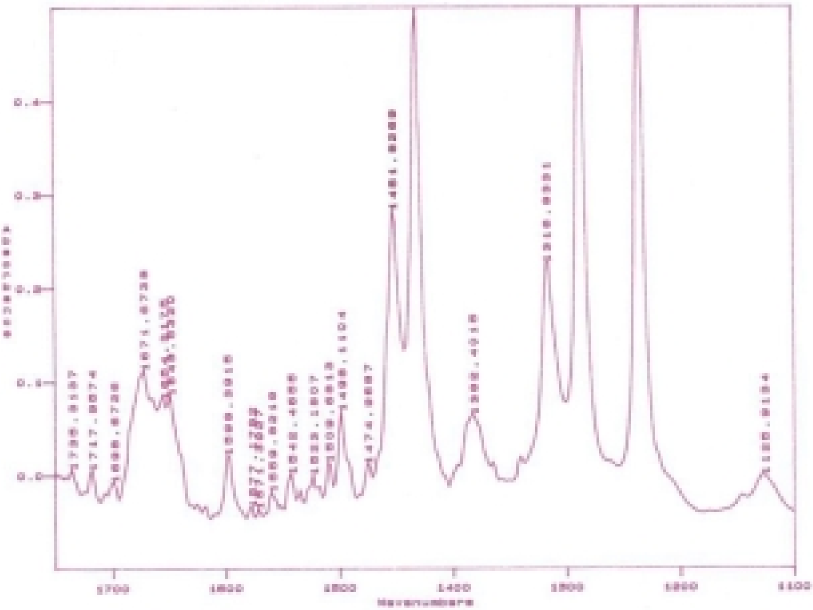

Fig. 7. IR spectra of DMDPHMA in 1, 2-dichloroethane after extraction of iron (III) from 8M HCl solution

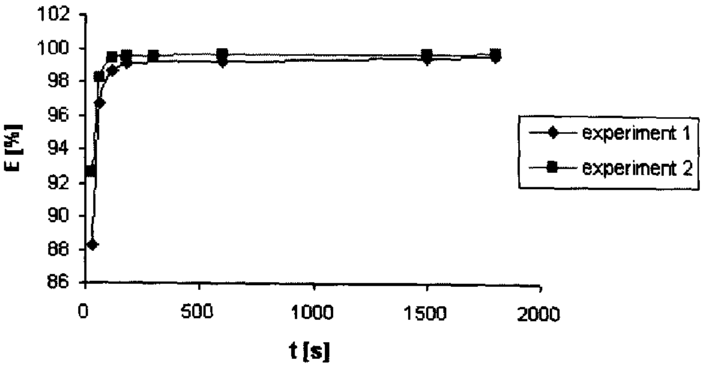

Fig. 8. Kinetic of iron (III) extraction using DMDPHMA

Further extraction experiments to test the selectivity of DMDPHMA through the presence of Cu(II), Zn(II) and Fe(II) ions in the aqueous solution were performed. No extraction of those ions was observed and in addition, their presence does not affect iron(III) extraction. In addition to the selectivity experiments stripping essays were conducted using water as the stripping agent. According to the results iron(III) can be totally stripped from the loaded organic phase with water.

The good selectivity of DMDPHMA for iron(III) is an important result considering that this metal is usually co-extracted together with zinc(II) and copper(II). It gives the better results then other extractants such as DZEHPA or TBP are used.

CONCLUSIONS

1. Iron(III) extraction depends on the extractant concentration in the organic phase, as well as on the concentration of hydrochloric acid in the aqueous phase.
2. The yield of iron(III) extraction was 100% when the chloride ions concentration was 12 M by adding LiCl to the aqueous phase.
3. UV spectroscopy studies confirmed that iron is extracted as $FeCl_4^-$.
4. NMR spectroscopy investigation proved that during extraction protonation of the extractant occurs and four protons are attached to one DMDPHMA molecule.
5. In IR spectra of DMDPHMA after contact with HCl solution (8M) and after iron (III) extraction small shifts were observed in the stretching frequency of the carbonyl group as a consequence of its protonation.
6. The rate of iron(III) extraction to the organic phase is high (3-4 minutes).
7. Good selectivity of DMDPHMA for iron(III) towards other base metal cations (Cu(II), Zn(II) and Fe(II)) is achieved.
8. Iron(III) can be easily and completely removed from the loaded organic phase by simple contact with water.
9. DMDPHMA can be an interesting alternative to commercial organophosphorous extractants.

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Costa M.C. , Uryga A., Sadowski Z., *Zastosowanie N,N'-dwumetylo-N,N'-dwufenyloamidy kwasu malonowego do ekstrakcji żelaza(III),* Fizykochemiczne Problemy Mineralurgii, 36, (2002) 317-326 (w jęz. ang.)

N,N'-dwumetylo-N,N'-dwufenyloamid kwasu malonowego został zaproponowany jako selektywny kstrahent dla ekstrakcji żelaza(III) z roztworów kwasu solnego. Badano wpływ stężenia kwasu solnego na proces ekstrakcji jonów Fe^{3+}, stwierdzając, że jony Fe^{3+} były całkowicie ekstrahowane z roztworów o wysokim stężeniu kwasu solnego (>8M). W przypadku, gdy wysokie stężenie jonów chlorkowych (12M) uzyskano przez dodanie chlorku litu (LiCl), odzysk jonów żelaza(III) był również bliski 100%. Zastosowanie innych roztworów chlorkowych (KCl,NaCl) nie przyniosło zadawalających wyników ekstrakcji. Reekstrakcje z fazy organicznej (dwuchloroetan) realizowano przy pomocy wody destlowanej. W celu wyjaśnienia mechanizmu selektywnej ekstrakcji żelaza(III) przeprowadzono badania spektrofotometryczne (UV,IR) oraz NMR. Wyniki tych badań wskazują, że odpowiedzialnym za ekstrakcję żelaza(III) jest kompleks $FeCl^{-}$.