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Synthesis under Microwave Irradiation, Characterization and Application of Alkyliminodimethylenediphosphonic Acids in Solvent Extraction of Iron (III)

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Abstract: The synthesis under microwave irradiation, characterization and application of new alkyliminodimethylenediphosphonic acids in solvent extraction of iron (III) has been investigated. The alkyliminodimethylenediphosphonic acids synthesized were: hexadecyliminodimethylenediphosphonic acid (HIDMP, H_4L^1) and decyliminodimethylenediphosphonic acid (DIDMP, H_4L^2). After purification, these products were characterized by elemental analysis and by FT-IR, 1H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy. In this study, we proposed a tentative assignment for the shifts of those two ligands and their specific complexes with iron (III). We also carried out the extraction of Fe (III) by HIDMP and DIDMP from [chloroform+2-octanol (v/v: 90%/10%)] solutions at an aqueous to organic phase ratio (1/1) and at room temperature. Experimental results showed that HIDMP and DIDMP are synthesised efficiently and rapidly in good yields (85-88%) under microwave irradiation. The extraction yields are more significant in the case of the HIDMP (99%) which is equipped with a hydrocarbon chain, longer than that of the DIDMP (95%). Logarithmic plots of the iron (III) distribution ratio vs. pH_{eq} and the extractant concentration showed that the ratios of extractant to extracted iron (III) are 3:1. The metal complexes formed in organic phase are $[Fe(H_3L^1)_3 \cdot 3H_2O]$ and $[Fe(H_3L^2)_3 \cdot 3H_2O]$ with HIDMP and DIDMP, respectively. A spectroscopic analysis of the metal complexes has showed that coordination of iron (III) takes place via oxygen atoms in the phosphonic groups, whereas the nitrogen atom remains rather uncoordinated. The equilibrium constants for the extraction of iron (III) were found to be 10.44×10^{-3} and 1.98×10^{-3} for HIDMP and DIDMP, respectively.

Key words: Alkyliminodimethylenediphosphonic acids, synthesis, microwave irradiation, extraction, iron

INTRODUCTION

Organophosphorus chemistry is exploring the properties and reactivity of organophosphorus in particular aminophosphonic acids compounds. Aminophosphonic acids, synthesized for the first time in 1945 by Schwarzenbach *et al.* (1949), Matczak-Jon *et al.* (1999) and Naydenova *et al.* (2010). These acids are very good ligands for the coordination of metal ions so they can be used for the extraction of metals such as uranium, iron, copper and nickel in hydrometallurgy (Villemin *et al.*, 2008; Naydenova *et al.*, 2010; Matczak-Jon *et al.*, 1999; Abderrahim *et al.*, 2006; Belkhouche *et al.*, 2006; Didi *et al.*, 2004; Sawaji *et al.*, 1992; Turner *et al.*, 2003; Nowack, 2002; Rao, 2010). Aminophosphonic acids form

also complexes on the surface of metal such as iron and are consequently are very good as anti-corrosion agents (Villemin *et al.*, 2008; Matczak-Jon *et al.*, 1999; Nowack, 2002). These acids are also used as insecticides, herbicides, bactericides, plant-growth regulators, enzyme inhibitors, anticancer agents, etc., (Naydenova *et al.*, 2010; Kukhar and Hudson, 2000; Matczak-Jon *et al.*, 1999; Juribasic *et al.*, 2009; Kurzak *et al.*, 2000; Kafarski and Lejczak, 2000, 2001; Sun *et al.*, 2003; Ying and Mao, 2005; Lebouc *et al.*, 2005; Yoshikawa, 1995; Redmore, 1972).

Aminophosphonic acids are generally obtained by hydrolysis of esters via Kabachnik-Fields reaction (Kabachnik and Medved, 1952; Fields, 1952; Moedritzer and Irani, 1966; Villemin *et al.*, 2008; Naydenova *et al.*, 2010). This reaction can be activated by

microwave irradiation; nevertheless there are often secondary reactions during the hydrolysis (Villemin *et al.*, 2008; Naydenova *et al.*, 2010; Juribasic *et al.*, 2009). The synthesis of Irani-Moedritzer is less general than the Kabachnik-Fields reaction, but it has the advantage of obtaining the aminophosphonic acids without a step of hydrolysis (Moedritzer and Irani, 1966). The Irani-Moedritzer reaction times are in general long, so the use of microwave for assisting the reaction is of interest (Villemin *et al.*, 2008; Naydenova *et al.*, 2010). This reaction is carried out in aqueous medium under microwave irradiation with an aqueous solution of formaldehyde in acidic aqueous medium without organic solvent. Water is an inexpensive, non flammable, non toxic solvent and has the advantage of warming up quickly under microwave irradiations. Carrying out reactions using microwave heating, as opposed to conventional heating, has the major advantage of shorter reaction times because of the rapid heating (Villemin *et al.*, 2008; Lidström and Tierney, 2005; Loupy, 2006). The Irani-Modzdrizer reaction can be compared to a Mannich reaction and takes place by the addition of the phosphorous acid on iminium salt formed by reaction of formaldehyde with the amine in acidic medium (Moedritzer and Irani, 1966).

In this study, we describe the synthesis two new alkyliminodimethylenediphosphonic acids under microwave irradiation. The synthesis of the iminodimethylenediphosphonic acids under microwaves irradiation is fast and efficient than a conventional heating (Didi *et al.*, 2007; Simeon, 1998; Villemin *et al.*, 2008; Naydenova *et al.*, 2010). These acids exhibited high complexation efficiency towards zinc (II), magnesium (II), calcium (II) and nickel (II) ions. This results from both dinegatively charged phosphonate groups as well as the imino-nitrogen present in their structure (Matczak-Jon *et al.*, 1999; Didi *et al.*, 2007; Naydenova *et al.*, 2010). In fact, we have synthesized hexadecyliminodimethylenediphosphonic acid, $C_{16}H_{33}N(CH_2PO_3H_2)_2$ (HIDMP, H_4L^1) and decyliminodimethylenediphosphonic acid, $C_{10}H_{21}N(CH_2PO_3H_2)_2$ (DIDMP, H_4L^1) for such a purpose. The characterizations of these products were carried out by elemental analyse and by FT-IR, 1H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy. We have also tested the chelating properties of these extractants towards iron (III) ion.

MATERIALS AND METHODS

This research project was conducted from January 2009 to March 2010 in the Nuclear Research Center of Draria, Algiers, Algeria.

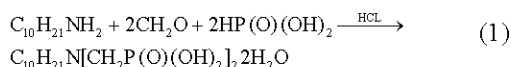
Reagents and solutions: The reagents used in this study were 1-hexadecylamine (90%, Alfa), 1-decylamine (95%, Merck), phosphorous acid (99%, Aldrich), formaldehyde (37.5%, Panreac), hydrochloric acid (36%, Merck) and iron (III) chloride hexahydrate (99%, Labosi). Chloroform (Merck) and 2-octanol (Prolabo) of analytical grade were used without further purification. The aqueous solutions of 0.015 M iron (III) were prepared from chloride hexahydrate and the organic solutions were prepared from of HIDMP and DIDMP (0.03 to 0.3 M) dissolved in the organic solvent [chloroform+2-octanol (v/v: 90%/10%)].

Instrumentation: The microwave experiments were conducted in Synthewave 402 microwave oven supplied from Prolabo. This microwave oven fitted monomode resonance cavity TE_{013} at 2450 MHz working with 800 W max and equipped with a universal generator MES 73-800 (Micro-ondes Energie Systèmes 2). $^{13}C\{-^1H\}$, $^{31}P\{-^1H\}$ and 1H -NMR spectra were measured on Bruker AC 250 working at 250 MHz in $CDCl_3$ solution. Infrared spectra were measured on a Perkin Elmer 16 PC-FTIR equipped with a thermostat to maintain the temperature of the sample cell at 25 \pm 0.1 $^\circ$ C. Elemental analysis were performed using a ThermoQuest NA2500 elemental analyser. pH measurement were taken on a potentiometer Consort C 831 with combined glass electrode was used to measure the pH of the aqueous solution before and after extraction. In a water-acetone mixture (5:15) a known mass of each sample titrated by a solution of NaOH (5×10^{-4} M). Metal ion was determined using the atomic absorption spectrophotometer, system GBC Avanta. Water was titrated in the organic phase by the use of a Mettler DL18 Karl Fisher Titrator.

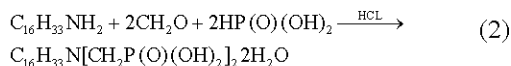
Synthesis of the extractants: HIDMP and DIDMP were prepared by a Mannich type reaction according to the procedures previously described (Moedritzer and Irani, 1966; Didi *et al.*, 2007; Simeon, 1998; Villemin *et al.*, 2008; Naydenova *et al.*, 2010; Turner *et al.*, 2003; Yoshikawa, 1995).

A mixture of phosphorous acid (1.64 g, 20 mmol), water (2 mL) and hydrochloric acid (2 mL) was added to a 2 mL 1-decylamine (10 mmol) placed in a tube made of quartz. The mixture is irradiated for 5 min at 240 W. Three milliliter formaldehyde (40 mmol) were then added quickly and the assembly is irradiated at 400 W for 8 min. The product precipitated directly into the tube, then it is filtered, then washed with acetone and rinsed with water.

The product was obtained as white solid. Its melting point is 248 $^\circ$ C. The yield is 88%. The reaction of the synthesis is of the following form:



The procedure above was analogously repeated using 2.144 g (10 mmol) of 1-hexadecylamine. The product was obtained as white solid. Its melting point is 214°C. The yield is 85%. The reaction of the synthesis is of the following form:



Extraction experiments: The extraction tests were performed using HIDMP and DIDMP as extracting agents. These substances were tested for iron (III) extraction from aqueous solutions. Equal volumes of organic and aqueous phases (10 mL) were shaken together at 25°C for 15 min. Preliminary experiments showed that equilibration was complete in 15 min (Didi *et al.*, 2002). The addition of 2-octanol in organic solution as modifier (10 vol.%) was necessary to improve phase separation. This alcohol also prevents micelle formation and solvated metal-extractant complexes (Didi *et al.*, 2002; Kahlweit *et al.*, 1991; Strey and Jonstromer, 1992; Mellah and Benachour, 2006). It is very important to note that no third phase or any precipitation was observed during the extraction process. After shaking, the organic phase was separated from the aqueous phase. The metal ion concentration was determined in aqueous phase by atomic absorption spectrophotometry. The metal ion concentration in the organic phase was calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction. The water was titrated in the organic phase by the use of a Karl Fisher Titrator.

RESULTS AND DISCUSSION

Analysis and characterisation of HIDMP and DIDMP: The results showed that The HIDMP and DIDMP are synthesised efficiently and rapidly in good yields (85-88%) under microwave irradiation (Didi *et al.*, 2007; Simeon, 1998; Villemin *et al.*, 2008; Naydenova *et al.*, 2010). The structure of the complexing agents synthesis were identified and characterized by elemental analyse and by FT-IR, ¹H NMR, ¹³C NMR, ³¹P NMR spectroscopy (Table 1).

HIDMP and DIDMP were titrated by potentiometry. The measurements indicated that, in the water-acetone medium these acids probably exist as zwitterions with three titratable protons, a strongly dissociated proton and two weak ones, with the fourth available proton being coordinated to the central nitrogen atom (Moedritzer and Irani, 1966).

The displacement of νP = O to lower frequency in the infrared spectra indicates the existence of intermolecular hydrogen bonds P = O...H-OP. The band appearing between 1650-1520 cm⁻¹ indicates the existence of bond N...H intermolecular of N... H-O-P.

Extraction of Fe (III) by HIDMP and DIDMP: The extraction experiments results are discussed in term of extraction yield (Y) and distribution ratio (D) defined as follows:

$$Y (\%) = \frac{m_i - m_f}{m_i} \times 100 \quad (3)$$

$$D = \left(\frac{m_i - m_f}{m_f} \right) \times \frac{V_{aq}}{V_{org}} \quad (4)$$

where, m_i is initial mass of Fe (III) in aqueous phase; m_f is mass of Fe (III) after extraction; V_{aq} is the volume of the aqueous phase; V_{org} is the volume of the organic phase.

The variable Q is the ratio of the number of moles of extractant in organic phase versus the number of moles of metal in aqueous phase before extraction.

$$Q = \frac{n_{extractant}}{n_{metal}} \quad (5)$$

The variation of the extraction yield test of 0.015M iron (III) as a function of Q is shown in Fig. 1.

Figure 1 shows the yield of extraction of iron (III) increases with Q. Working with extractants concentrations range 0.03 to 0.3 M (Q = 2 to 20), we reached a yield of 99% for HIDMP and 95% for DIDMP. The extractant with a longer alkyl group forms more hydrophobic complexes. HIDMP and DIDMP present a similar extraction power, but the hydrophobic character determines the amount of extraction. The hydrophobic character of ligand can be determined calculating log P which is defined as the partition coefficient between two phases of a substance, generally n-octanol and water.

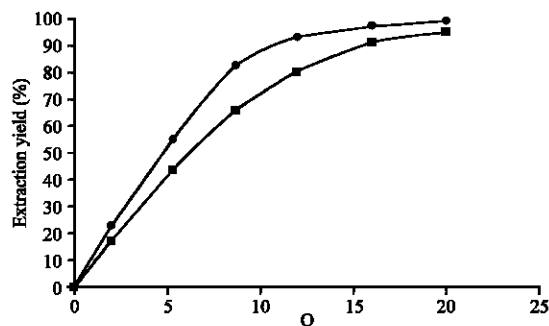


Fig. 1: Effect of the molar ratio on the extraction yield of Fe (III). [Fe³⁺] = 0.015 M, V_{aq}/V_{org} = 1, t = 25°C

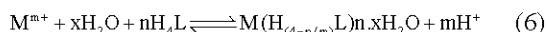
Table 1: HIDMP and DIDMP characteristics

Products	HIDMP	DIDMP
Formula	C ₁₆ H ₃₃ N(CH ₂ PO ₃ H ₂) ₂	C ₁₀ H ₂₁ N(CH ₂ PO ₃ H ₂) ₂
pKa	3.2, 6.5, 8.64 ± 0.05	3.7, 6.87, 8.8 ± 0.05
Elemental analysis	%C %H %N Exptl. 50.43 9.88 6.40 Calcd 50.34 9.62 6.17	%C %H %N Exptl. 41.25 8.61 6.40 Calcd 41.73 8.49 6.17
¹ H NMR δ (ppm)	0.85 (t, 3H, (CH ₃)), 1.38 (m, 26H, (CH ₂)), 0.83 (d, 2H, (=CH ₂ -)), 3.06 (t, 2H, (=CH ₂ -N)), 3.21 (t, 2H, (N-CH ₂ -P)), 4.89 (d, 4H, (P(O)(OH) ₂))	0.85 (t, 3H, (CH ₃)), 1.24 (m, 14H, (CH ₂)), 1.75 (d, 2H, (=CH ₂)), 3.40 (t, 2H, (=CH ₂ -N)), 3.39 (d, 2H, (N-CH ₂ -P)), 4.10 (d, 4H, (P(O)(OH) ₂))
¹³ C NMR (δ ppm)	14.80 (s, (CH ₃)), 22.90 and 32.10(14s, (CH ₂)), 53.80 (s, (CH ₂ -N)), 52 (d, J _{CP} = 142.1, (N-CH ₂ -P))	14.0 (s, (CH ₃)), 22.1 and 31.3(8s, (CH ₂)), 53.5 (s, (CH ₂ -N)), 51.2 (d, J _{CP} = 41.3, (N-CH ₂ -P))
³¹ P NMR δ (ppm)	+ 6.08 (s)	+ 5.57(s)
FT-IR (cm ⁻¹)	3590-3100 (vs. OH), 2928 (vs. CH), 2858 (vs. CH), 2750-2550 and 2380-2100(vs. POH), 1650-1520 (vs. N-H), 1180 (vs. P = O)	3700-3200 (vs. OH), 2924 (vs. CH), 2854 (vs. CH), 2770-2570 and 2364-2084 (vs. P-OH), 1648-1518 (vs. NH), 1168 (vs. P = O)

Exptl. and calcd: experimental and calculated percentages for the elemental analysis of the synthesized compounds, δ (ppm): chemical shift, s: singlet, d: doublet, t: triplet, m: multiplet, s: symmetric stretching, ias: antisymmetric stretching

Modern molecular modeling software allows the log p-values, calculated using ChemDraw Ultra (Cambridge Soft) are respectively 1.16 for DIDMP and 5.93 for HIDMP showing that HIDMP is strongly hydrophobic (Didi *et al.*, 2002, 2008).

Stoichiometry of extracted species: In the work on stoichiometric relation for the extraction of iron complex with HIDMP (H₄L¹) and DIDMP (H₄L²), we have supposed that the solubilities of the extractant and the iron-extractant complex in the aqueous phase are negligible; the overall reaction in the extraction of metal cations by cationic extractants, as the case of HIDMP and DIDMP, can be show as following:



where, H₄L is the molecule of extractant, M is the metal (Fe), m valency of metal (Fe³⁺), n molecules of extractant engaged in the reaction, n/m number of protons exchanged by each extractant and x number of molecules of water.

The equilibrium constant of the above reaction, K_{ex}, can be given as function of molar concentration:

$$K_{ex} = \frac{[M(H_{(4-n/m)}L)_n \cdot xH_2O][H^+]^m}{[M^{m+}][H_4L]^n} \quad (7)$$

Substitution of the distribution ratio, which is defined by the concentration of metal in organic phase divided by that in aqueous phase, into Eq. 8 results in:

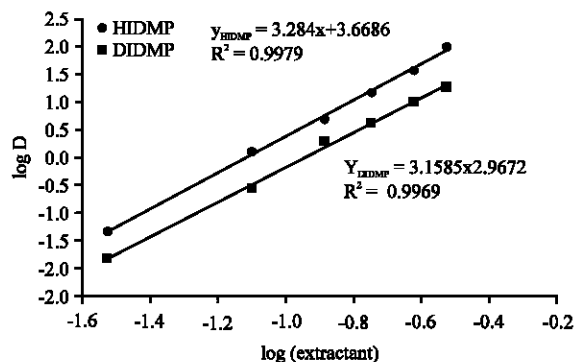


Fig. 2: Effect of extractant concentration on the distribution ratio for Fe (III). [Fe³⁺] = 0.015 M, V_{aq}/V_{org} = 1, t = 25°C

$$D = \frac{K_{ex} [H_4L]^n}{[H^+]^m} \quad (8)$$

Taking logarithms of Eq. 8, one obtains:

$$\log D = \log K_{ex} + n \log [H_4L] - m \log [H^+] \quad (9)$$

$$\log D = \log K_{ex} + n \log [H_4L] + m \text{pH} \quad (10)$$

The stoichiometry of the extracted species was determined by analysing the experimental data. The conventional slope analysis method was used. Figure 2 shows the plots of log D versus log [extractant] which gave two straight lines with good correlation coefficients 0.998 and 0.997 and slopes equal to 3.28, which is close

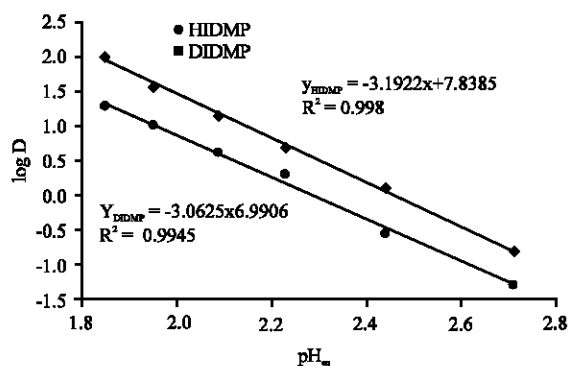
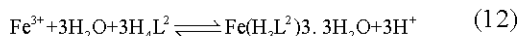
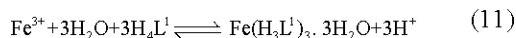


Fig. 3: Effect of equilibrium pH on the distribution ratio for Fe (III). $[Fe^{3+}] = 0.015\text{ M}$, $V_{aq}/V_{org} = 1$, $t = 25^\circ\text{C}$

to 3 and 3.15, which is close to 3 for HIDMP and DIDMP, respectively. This result suggests that three molecules of extractant react with one iron (III) ion. Figure 2 also shows that the distribution ratio of iron (III) increases with the increase in extractant concentration. The distribution ratios are more significant in the case of the HIDMP which is equipped with a hydrocarbon chain, longer than that of the DIDMP. Figure 3 shows the plots of log D versus pH_{eq} which also gave two straight lines with good correlation coefficients 0.998 and 0.994 and slopes equal to 3.19, which is close to 3 and 3.06, which is close to 3 for HIDMP and DIDMP, respectively. This indicates that three protons are released during the cation exchange reaction. The plots log D versus log [extractant] and the plots log D versus pH_{eq} suggest that the ratio of extractant to extracted iron (III) is 3:1 (Songling *et al.*, 1993; Kong *et al.*, 2004; Sun *et al.*, 2003; Kurzak *et al.*, 2000; Rao, 2010). The equations extraction equilibrium can thus be written as:



According to the above equations extraction equilibrium, The metal complexes formed in organic phase are $[Fe(H_3L^1)_3 \cdot 3H_2O]$ and $[Fe(H_3L^2)_3 \cdot 3H_2O]$ for HIDMP and DIDMP, respectively (Songling *et al.*, 1993; Sun *et al.*, 2003; Kurzak *et al.*, 2000). Protons, intervening in our extraction, correspond to the pK_a of HIDMP and DIDMP, 3.2 and 3.7, respectively. HIDMP and DIDMP extract the iron (III) ions in cationic exchange mode. The two last values of pK_a obtained by potentiometric measurement confirm that the extracting agent can exchange only one or two protons per molecule. We also

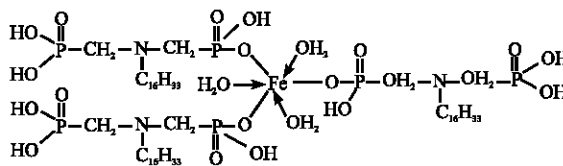


Fig. 4: Structure of the complex HIDMP-Fe (III). $3H_2O$

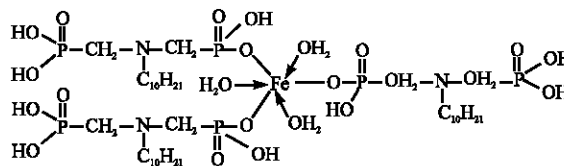


Fig. 5: Structure of the complex DIDMP-Fe (III). $3H_2O$

note that the extraction of iron (III) by HIDMP and DIDMP is accompanied by three water molecules extraction. The equilibrium constants for the extraction of iron (III) were found to be 10.44×10^{-3} and 1.98×10^{-3} for HIDMP and DIDMP, respectively.

The structures of the complex HIDMP-Fe (III). $3H_2O$ and HIDMP-Fe (III). $3H_2O$ are indicated in Fig. 4 and 5.

Figure 4 and 5 show that the iron complexes, $[Fe(H_3L^1)_3 \cdot 3H_2O]$ and $[Fe(H_3L^2)_3 \cdot 3H_2O]$, are formed by coordinating of each iron (III) ion to three phosphonate oxygen atoms from three molecules of extractant agent. Figure 4 and 5 show also that these complexes contain three water molecules. The HIDMP and DIDMP exhibited high complexation efficiency towards iron (III) ions. This results from both dinegatively charged phosphonate groups as well as the imino-nitrogen and the hydrophobic character present in their structure (Matczak-Jon *et al.*, 1999; Naydenova *et al.*, 2010; Kabachnik *et al.*, 1974, 1975; Van Hecke and Goethals, 2006; Sun *et al.*, 2003).

HIDMP-Fe (III) and DIDMP-Fe (III) spectra: The solid complex HIDMP-Fe was prepared by stirring the iminodimethylenediphosphonic acid in the organic solvent mixture (chloroform+2-octanol), with an aqueous solution of Fe (III). After separation of the phases and evaporation of the organic solvents, the solid complex was washed with water and dried. We have observed a shift of $P=O$ band from 1180 to 1081 cm^{-1} . In the complex, a new IR band appears at 631 cm^{-1} attributed to the distortion vibration $PO-Fe$. Similarly, comparison of the spectra of DIDMP and DIDMP-Fe show a shift the 1168 P=O band to 1069 cm^{-1} . A new band in DIDMP-Fe appears at 624 cm^{-1} attributed to the deformation

vibration of PO-Fe. The two deformation vibrations PO-Fe showed that the bond between P-O and Fe for HIDMP is stronger than with DIDMP. A spectroscopic analysis has showed that coordination of iron (III) takes place via oxygen atoms in the phosphonic groups, whereas the nitrogen atom remains rather uncoordinated (Kabachnik *et al.*, 1975; Kurzak *et al.*, 2000).

CONCLUSIONS

The obtained results from this study can be summarised as following:

- The HIDMP and DIDMP are synthesised efficiently and rapidly in good yields (85-88%) under microwave irradiation
- The yields of extraction of iron (III) increases with the ratio Q. HIDMP and DIDMP can complex and extract, respectively 99 and 95% of iron (III) by using a large excess extractant agent (Q = 20)
- HIDMP ligand has a stronger extracting power for iron(III) than DIDMP. This fact is related to more hydrophobic character of HIDMP vs. DIDMP
- The HIDMP and DIDMP exhibited high complexation efficiency towards iron (III) ions. This results from both dinegatively charged phosphonate groups as well as the imino-nitrogen and the hydrophobic character present in their structure
- Logarithmic plots of the iron (III) distribution ratio vs. pH_{eq} and the extractant concentration showed that the ratios of extractant to extracted iron (III) is 3:1. The metal complexes formed in organic phase are $[Fe(H_3L^1)_3, 3H_2O]$ and $[Fe(H_3L^2)_3, 3H_2O]$ for HIDMP and DIDMP, respectively. Protons, intervening in our extraction, correspond to the pK_a of HIDMP and DIDMP, 3.2 and 3.7, respectively. HIDMP and DIDMP extract the iron (III) ions in cationic exchange mode. The two last values of pK_a obtained by potentiometric measurement confirm that the extracting agent can exchange only one or two protons per molecule
- Extraction of iron (III) by HIDMP and DIDMP is accompanied by three water molecules extraction
- A spectroscopic analysis has showed that coordination of iron (III) takes place via oxygen atoms in the phosphonic groups, whereas the nitrogen atom remains rather uncoordinated
- The equilibrium constants for the extraction of iron (III) were found to be 10.44×10^{-3} and 1.98×10^{-3} for HHDPA and DHDPA, respectively

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