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ABSTRACT

In the present paper, a new, simple, and effective method for iron(III) extraction from acidic chloride solutions is described involving the use of a *N*,*N*,*N*′,*N*′-tetrasubstituted malonamide, *N*,*N*′-dimethyl-*N*,*N*′-dibutylmalonamide (DMDBMA). The behavior of this ligand towards iron(III) extraction was investigated for different experimental conditions with a particular emphasis on the influence of HCl, LiCl, and ligand concentrations. The extraction behavior of DMDBMA is compared

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with the ones shown by two similar malonamide derivatives, *N*,*N*′-dimethyl-*N*,*N*′-diphenylmalonamide (DMDPHMA) and *N*,*N*′-dimethyl-*N*,*N*′-diphenyltetradecylmalonamide (DMDPHTDMA), previously studied. The mechanism involved on iron(III) extraction, the structure of the metal–adducts formed, and also the relationship between the extraction mechanism and the ligand structures are clarified. Therefore, hydrochloric acid extraction, slope analysis, and spectroscopic data—UV and NMR—were used to collect information on the iron(III) extraction reactions. A solvation mechanism involving iron(III) extraction as chlorocomplexes such as $HFeCl_4$ and $FeCl_3$ is proposed. From aqueous feed solutions with HCl concentrations higher than 4 M, iron(III) is mainly extracted as the anionic chlorocomplex, while from solutions with lower HCl concentrations ($2\,M < C_{HCl} \leq 4\,M$) the metal is probably removed as $FeCl_3$. The results also suggest that different malonamides (e.g., DMDBMA, DMDPHMA, and DMDPHTDMA) extract iron(III) through diverse mechanisms, thus showing the important role played by the chemical structure on the metal ion transfer reactions to the organic phase. The efficient extraction of iron(III) from aqueous chloride solutions and the selectivity of the ligand for this metal ion when in the presence of interfering ions such as copper, zinc, nickel, cobalt, lead, and silver, in binary and in multicomponent mixtures, are also reported. The high selectivity towards iron(III), the complete stripping of this metal by simple contact of the loaded organic phase with water and the efficient reutilization of DMDBMA are very promising results that can justify an eventual industrial application.

Key Words: Iron(III); DMDBMA; Aqueous phase; Extraction.

INTRODUCTION

The expansion of industrial activities in the last century has been responsible for a great increase of iron in the environment. Metal plating and extractive metallurgical industries, especially those that use ferric ion as a leaching agent—and even others that generate iron pregnant leaching solutions—are important examples, since this metal is frequently found dissolved in high concentrations and its removal and disposal constitutes a major operation problem. Iron oxide manufacturers that use waste chloride pickle liquors from steel plants, blue dust, flue dust iron scrap, etc., also produce high iron levels to the environment.[1]

Separation of iron from complex matrices is an important objective for the production of iron oxides and for the treatment of iron contaminated waste waters. Several methods are available for separation, purification, and recovery of iron(III) from different sorts of aqueous solutions. Iron is often removed using precipitation techniques, as used in the zinc industry.[2] Although its effectiveness, this technique implies a significant consumption of neutralizing agents and a large accumulation of complex iron residues, that may cause environmental problems. Moreover, the need to find easy and reliable methods for the separation of metals has been stimulated by stricter environmental regulations—which have forced the industries to reduce their emissions to water systems—and by increasing costs, thus imposing more effective separation technologies. Due to its inherent simplicity, liquid–liquid extraction is a remarkable alternative, widely used for the separation of metal ions from aqueous solutions and avoiding the undesirable features associated with the precipitation processes. In fact, solvent extraction plays an important role in hydrometallurgical industries, and thus a great effort has been continuously devoted to the development of new extractant molecules.

The selective separation/or pre-concentration of iron(III) from mineral pregnant leaching solutions or from industrial waste water streams are topics of large relevance that justify the present research. In the last decades, several iron extractants have been used, the most relevant being *bis*(2-ethylhexyl)phosphoric acid (D2EHPA)[3–10] and tributylphosphate (TBP).[11–13] Synergistic mixtures as for example TBP + D2EHPA and D2EHPA + Kelex 100 have also been tested.[1,14–16]

Recently, Costa et al.[17] have demonstrated that *N*,*N*,*N*′,*N*′-tetrasubstituted malonamides are efficient and selective extractants for the separation of iron(III) from acidic chloride media. *N*,*N*′-dimethyl-*N*,*N*′-diphenylmalonamide (DMDPHMA) and *N*,*N*′-dimethyl-*N*,*N*′-diphenyltetradecylmalonamide (DMDPHTDMA) were the molecules investigated, both presenting high iron(III) extractive performances. In this paper, a new malonamide derivative, *N*,*N*′-dimethyl-*N*,*N*′-dibutylmalonamide (DMDBMA) is presented, and its behavior is compared with the ones shown by both reported ligands.

This work intends to be a contribution for the development of an effective and simple method for the removal of iron(III) from aqueous solutions, particularly for the treatment of effluents and for the separation and/or pre-concentration of this metal in hydrometallurgical systems. In fact, only one reference has been found concerning the extraction of iron(III) from nitric acid medium using *N*,*N*,*N*′,*N*′-tetraalkylmalonamides,[18] in which Fe(III) distribution ratios between *N*,*N*′-dimethyl-*N*,*N*′-dioctylmalonamide (DMDOMA) and aqueous HNO_3 solutions were determined.

The extractive properties of this family of compounds have already been extensively investigated over a number of years for the separation of actinides and lanthanides from nitric media,[18–31] considering the need of efficient extractants (alternative to TBP) for the nuclear processing industry.

With this purpose, several malonamide structures have been studied and, in general, very promising results have been achieved.[32,33] Using DMDBMA specifically, research works with a similar aim have also been carried out.[34–36]

Presently, the most investigated malonamide seems to be *N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide (DMDBTDMA),[37] which is an alkylated form of DMDBMA with a long chain of 14 carbon atoms in the central carbon, used as the reference molecule in the French DIAMEX process for the partitioning of minor actinides from high-level liquid radioactive wastes.[27,28] This reagent extracts tri-, tetra-, and hexavalent actinides from nitric acid solutions with a concentration higher than 4 M into conventional (normal or branched alkane) diluents.[37]

Among the advantages reported for this type of reagents are the relatively innocuous nature of extractant degradation products and their "ash-free" incineration character.[37] The disadvantages mentioned are their relative structural complexity and the somewhat narrow range of nitric acid concentrations from which trivalent actinides are extractable.[37]

EXPERIMENTAL

Synthesis of DMDBMA

Several methods are reported in the literature for the synthesis of *N*,*N*,*N*′,*N*′-tetrasubstituted malonamides.[17,19,34,36] One of those methods is the reaction of a secondary amine HNRR′ with an acyl chloride in the presence of $(C_2H_5)_3N$, according to Eq. (1),

$$2\mathrm{HNRR'} + \mathrm{CH_2(COCl)_2} \longrightarrow 2\mathrm{HCl} + \mathrm{CH_2(CONRR')_2} \tag{1}$$

in which R and R′ are alkyl groups.

Thus, DMDBMA was synthesized as follows: 100 mL of *N*-methyl-*N*-butylamine (0.9 mol) and 90 mL of dichloromethane were introduced in a 500 mL reaction vessel. After the addition of triethylamine, $(C_2H_5)_3N$, the vessel was cooled down to 5°C using an ice–salt bath. Then, 30 mL of malonyl dichloride (0.3 mol), dissolved into 90 mL of dichloromethane were slowly added. The temperature was raised to the CH_2Cl_2 boiling point and maintained at reflux for 4–8 hr. After cooling to room temperature, the triethylamine hydrochloride and the unreacted triethylamine were washed out by water. The aqueous phase was removed. The organic phase was evaporated to dryness under vacuum to yield a dark brown liquid which was distilled at

140–144°C under low pressure (3 mm Hg). Finally, the yellow distillate was crystallized at 5°C from *n*-hexane, giving a yield of about 26%.

A fraction of the solid obtained was further purified by column chromatography in order to characterize the product and to carry out the slope analysis and other specific experiments. The synthesized compound was characterized by melting point and elemental analysis (CE Instruments EA 1110 CHNS-O), Table 1, and by spectroscopic techniques such as mass spectroscopy (MS), ^{1}H NMR, ^{13}C NMR, and IR. For MS a Trio 1000 equipment was used. The ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained with a Bruker 400 Avance spectrometer, using $CDCl_3$ as solvent and TMS as internal reference. MS data are presented in Table 2 and ^{1}H and ^{13}C NMR data are presented in Table 3. The infrared spectrum (4000–650 cm^{-1}) was recorded on a Hitachi I-3001 spectrometer (with a resolution of 2 cm^{-1}). The sample was prepared by mixing DMDBMA with KBr. The carbonyl stretching frequency ($\nu_{C=O}$) was clearly identified by the presence of a strong peak at 1638 cm^{-1}. This value is in agreement with the ones reported in two studies.[30,36] The first one mentions a characteristic IR band for DMDBMA at 1641 cm^{-1} due to $\nu_{C=O}$. In the second one, the carbonyl stretching frequency of DMDBMA was observed for the organic compound dissolved in various diluents: values between 1626 cm^{-1} for chloroform and 1644 cm^{-1} for *n*-pentane, *n*-hexane, and *n*-dodecane were reported.

Solvent Extraction Experiments

Solutions of, 0.05 M, of DMDBMA in 1,2-dichloroethane (1,2-DCE) were equilibrated for 15 min with the iron(III) aqueous phases for preliminary evaluation. After the phase disengagement, aliquots of the aqueous phases were sampled for iron(III) analysis.

Table 1. Melting point and elemental analysis for DMDBMA.

		Melting point (°C)	
Literature		51[4]	
This work		37–39	
Elemental analysis	C (%)	H (%)	N (%)
Theoretical	64.5	10.7	11.6
Experimental	60.9	10.9	11.4

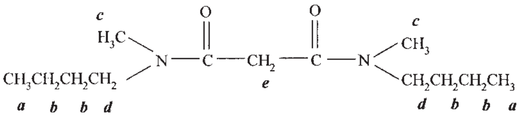
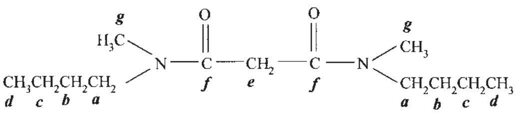
Table 2. MS data for DMDBMA.

Molecular and fragmentation peaks (m/z)
$C_{13}H_{26}N_2O_2]^+ = 242$ (<1%)
$C_{13}H_{22}N_2O_2]^+ = 238$ (5%)
$C_{12}H_{17}N_2O_2]^+ = 221$ (5%)
$C_{10}H_{16}N_2O_2]^+ = 196$ (5%)
$C_9H_{14}N_2O_2]^+ = 182$ (5%)
$C_8H_{12}NO_2]^+ = 154$ (40%)
$C_8H_{15}NO]^+ = 141$ (5%)
$C_6H_{10}NO]^+ = 112$ (47%)
$C_5H_{11}N]^+ = 85$ (100%)
$C_4H_9]^+ = 57$ (29%)

Dichloromethane has also been used as a diluent for specific purposes such as NMR sample preparation. For slope analysis, different concentrations of the extractant were employed.

Hydrochloric acid and lithium chloride solutions, with concentrations varying between 1 and 12 M, and metal feed solutions with ~0.01 M of iron(III) (prepared by dissolving $FeCl_3 \cdot 6H_2O$), were used as aqueous phases. In some aqueous solutions, the total chloride concentration was maintained at 12 M by adding LiCl.

Table 3. ^{1}H NMR and ^{13}C NMR assignments for DMDBMA.

Molecular structure	^{1}H NMR (ppm)
	0.90–0.98 (6 H, 2t, *a*) 1.29–1.60 (8 H, 2m, *b*) 2.94 (3 H, s, *c*) 3.03–3.07 (3 H, 2s, *c*) 3.34–3.41 (4 H, 2t, *d*) 3.49 (2 H, s, *e*)
	13.9 (2 C, *d*) 20.0 (2 C, *c*) 27.8–32.9 (2C, *g*) 36.1(2 C, *b*) 40.4–41.6 (2 C, *a*) 47.8–50.4 (1 C, *e*) 166.9 (2C, *f*)

Note: s, singlet; d, doublet; t, triplet; m, multiplet.

For the selectivity tests, binary mixtures containing ~0.01 M of iron(III) and one metal ion (~0.005 M of Cu(II), Zn(II), Co(II), and Ni(II) as chloride salts or Ag(I) and Pb(II) as nitrate salts) were prepared. A multicomponent mixture containing iron(III) and all those mentioned metal ions simultaneously was prepared as well.

Extraction and stripping experiments were carried out by shaking equal volumes of aqueous and organic phases ($A/O = 1$) for 15 min, at room temperature and at a constant stirring speed of 1000 rpm, which was enough to guarantee a good emulsion. A similar procedure was also adopted for the evaluation of the selectivity properties of the extractant. For the investigation of the extraction reactions and the influence of acidity on iron(III) extraction, a double-wall cell with circulation of water from a thermostat, in order to control the temperature (25°C), was used instead.

The experiments concerning the reutilization of the extractant were performed by several successive contacts of the same organic phase (0.05 M of DMDBMA in 1,2-DCE), after stripping of its iron(III) content by distilled water, with aqueous phases of 8 M HCl containing ~0.01 M Fe(III) as ferric chloride salt.

In the HCl extraction studies, the acid remaining in the aqueous phase was analyzed by acid–base titration using phenolphthalein as indicator and NaOH as titrant, previously standardized with potassium hydrogen phthalate ($KHC_8H_4O_4$).

The organic phases after contact with the acid were analyzed by NMR spectroscopy. For application of ^1H and ^{13}C NMR, the equilibrium organic phases were filtrated, dried with anhydrous magnesium sulfate, evaporated to dryness, and a suitable amount was dissolved in $CDCl_3$.

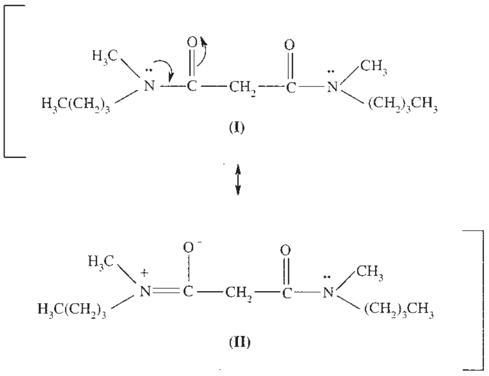
The metal content in the aqueous phases was analyzed before and after extraction by flame atomic absorption spectroscopy (AAS) using a Shimatzu AA 680 model. For each sample, three aliquots were analyzed and the values were critically treated and only accepted when a reasonable standard deviation was obtained. Metal ion concentrations in the organic phases were found by mass balance. The aqueous and the iron(III) loaded organic phases were analyzed by UV-Visible spectroscopy (Shimatzu UV 160).

Stripping experiments were performed by contact of the iron(III) loaded organic phases with an equal volume of distilled water ($O/A = 1$) for 15 min.

All the chemicals used were of analytical grade and were utilized without further purification.

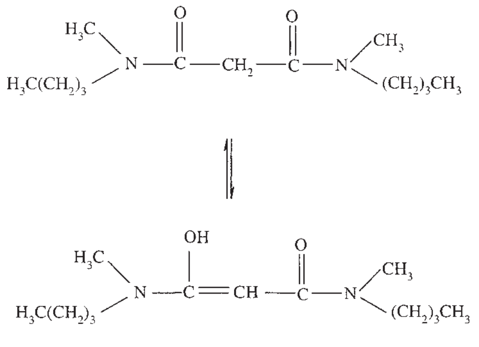
The obtained MS spectrum is in accordance with the expected fragmentation of the molecule.

^1H NMR data are in agreement with previous reported results.[36] However, in the ^1H spectrum reported on Table 3, some signals appear duplicated (two triplets, two multiplets, and two singlets) most probably due to the following resonance structures:



Tian and Hughes[36] have already reported resonance for diamides, due to the lowered carbonyl infrared stretching frequency observed for these molecules in comparison to other carbonyl compounds. According to the same authors, in substituted malonamides more than in the non-substituted ones, the occurrence of the resonance form II is higher. The contribution of form (II) should not only weaken the carbonyl bond, but should also increase the electron density at the oxygen atom. This behavior can be responsible for the high capacity of these ligands to extract iron(III), as well as other reported metals, such as actinides and lanthanides.

The occurrence of a spontaneous rearrangement of the carbonyl group to give a sort of an enol, phenomenon well known as tautomerism and here described by the following equilibrium,



can also be responsible for the duplication of peaks observed in the ^{1}H NMR spectrum.

^{13}C NMR spectrum is in accordance with the expected spectroscopic results for DMDBMA.

RESULTS AND DISCUSSION

Preliminary Considerations

Choice of the Diluent, Ligand Concentration and Equilibration Time

In the present work, 1,2-DCE was chosen as the diluent for DMDBMA taking into account the results reported by Nakamura et al.,[30] who measured the solubility of this compound into various organic diluents, and also previous solubility tests carried out with DMDPHMA.[17] The former authors found that aliphatic hydrocarbons are unsuitable as DMDBMA diluents and they also verified that the solubility of DMDBMA increases as the polarity of the diluents increases as well. In both cases, 1,2-DCE was considered to be one of the most suitable diluents amongst the ones tested, and in the preparation of a 0.05 M solution of DMDBMA a clear solution was obtained. A poor solubility was achieved for DMDBMA when using the usual commercial diluents (e.g., kerosene).

In this work, it was assumed that there is no significant influence of using different diluents for DMDBMA on its iron(III) extraction performance from HCl solutions, since just some slight differences were observed for DMDPHMA,[17] those attributed to the distinct degree of the extractant solubility and its adducts on the diluents tested (the iron(III) extraction was higher when 1,2-DCE was used as a diluent, and it was a bit lower for toluene and tetrachloromethane, following the DMDPHMA order of solubility in these diluents).

No third phase formation was observed after extraction; good and fast phase separations were also achieved for all the extraction experiments that were carried out.

The selection of the ligand concentration (0.05 M) was based on preliminary studies made with solutions containing different concentrations of DMDBMA in 1,2-DCE. When a concentration of 0.05 M was used, the Fe(III) extraction was about 100%.

The selection of the equilibration time was also based on previous experiments performed with DMDPHMA and DMDPHTDMA to evaluate the period of time necessary to reach iron(III) extraction equilibrium by malonamides.[17] For both ligands, the Fe(III) extraction process was completed even before 5 min of contact between the two phases. Thus, a contact period of 15 min between the aqueous and the organic phases was selected for the subsequent extraction experiments. The short equilibrium time necessary to achieve a very good Fe(III) extraction is an important result for the development of an appropriate extraction process with industrial application.

Extraction of Iron(III) from Chloride Media

The ability of DMDBMA to extract iron(III) from hydrochloric acid solutions depends on the hydrochloric acid content in the aqueous phases, Fig. 1.

Iron(III) extraction increases as the hydrochloric acid concentration increases and no extraction was detected for $C_{HCl} \leq 2\,M$. For $2\,M < C_{HCl} < 6\,M$, iron(III) removal increases continuously with the acid concentration and from $C_{HCl} \geq 4\,M$ the iron(III) extraction is always >50%. The metal ion is totally removed from $C_{HCl} \geq 8\,M$ (%E ≥ 99%).

The results of iron(III) extraction from HCl solutions until 12 M, with a 12 M total chloride concentration achieved by addition of LiCl, are shown in Fig. 2.

Iron(III) is totally removed regardless the acid concentration in the aqueous phase. Even in solutions containing only LiCl (12 M), the metal ion is also completely extracted.

The influence of different chloride sources on iron(III) extraction by DMDBMA was also investigated. Therefore, aqueous solutions containing only LiCl (0–12 M), or NaCl (saturated aqueous solution), in addition to iron(III), were tested. The results of iron(III) extraction obtained from LiCl solutions are illustrated in Fig. 3.

The metal ion is almost completely extracted from solutions with concentrations on LiCl higher than 4 M. For solutions with lower LiCl concentrations ($C_{LiCl} \leq 4\,M$), iron(III) is only partially removed: percentages of iron(III) extraction around 20% to 30% were achieved.

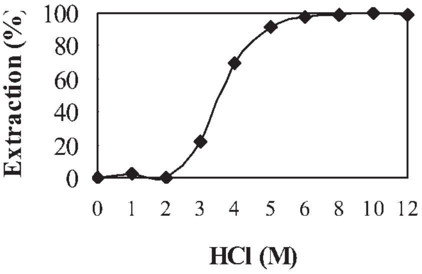


Figure 1. Iron(III) extraction by DMDBMA (0.05 M in 1,2-DCE) from HCl solutions.

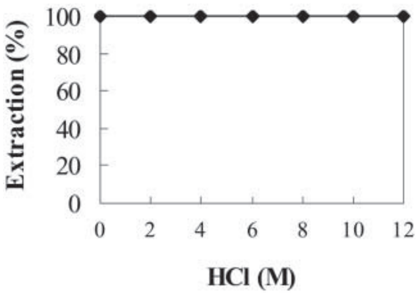


Figure 2. Iron(III) extraction by DMDBMA (0.05 M in 1,2-DCE) from HCl solutions with 12 M total chloride concentration (achieved by the sum of HCl and LiCl concentrations).

When lithium chloride was replaced by another chloride salt such as sodium chloride, the efficiency of iron(III) recovery by DMDBMA was comparatively much lower. Only 11% of iron(III) was extracted from a saturated sodium chloride solution (∼6 M).

Iron(III) Extraction from Other Aqueous Media than Chloride

The extraction of iron(III) from aqueous media containing other than chloride ions has also been tested. The results related with the extraction of ∼0.01 M Fe(III) in different acidic media, obtained by dissolution of distinct iron(III) salts, are presented in Table 4.

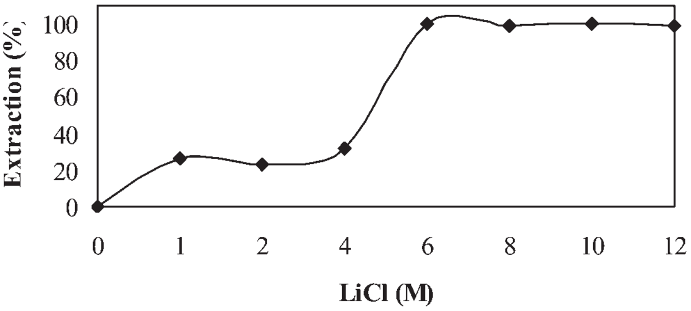


Figure 3. Iron(III) extraction by DMDBMA (0.05 M in 1,2-DCE) from LiCl aqueous solutions.

Table 4. Iron(III) extraction by DMDBMA from several aqueous media containing different metal salts.

	DMDBMA in 1,2-DCE			
Extraction (%)	HCl (8 M)	HNO_3 (8 M)	H_2SO_4 (8 M)	H_2O
$FeCl_3 \cdot 6H_2O$	99	17	20	0
$Fe(NO_3)_3 \cdot 9H_2O$	—	3	—	—
$Fe_2(SO_4)_3 \cdot 7H_2O$	—	—	6	—

When HNO_3 or H_2SO_4 are used instead of hydrochloric acid, iron(III) extraction decreases considerably, even when a chloride iron(III) salt was employed as the metal ion source. In these cases, only a partial iron(III) recovery was achieved (17% and 20% from nitric and sulfuric media, respectively).

From water, no iron(III) extraction was found, most probably due to the replacement of the chloride ions of the salt by water molecules in the metal ion coordination sphere. When iron(III) is added as a nitrate or a sulfate source, only a vestigial metal extraction is observed.

These data demonstrate the great importance of the iron(III) chlorocomplex existence in the aqueous solutions, for which malonamide derivatives show a particular affinity.

Slope Analysis

The plot of log D as a function of log[L] for DMDBMA is presented in Fig. 4.

In Fig. 4, it can be seen that the iron(III) distribution data from HCl 8 M lay on a straight line with a good correlation factor and presenting a slope of about 2.6. The slope tends to increase for high ligand concentrations, where values near 3 were obtained and, on the contrary, it decreases for lower concentrations, where values lower than 2 were observed. Therefore, for the ligand concentration range tested ($[L] = 0.0025$ to 0.05 M), the collected results suggest that an average of two molecules of the extractant must be involved in iron(III) extraction.

Acid Extraction

The investigation concerning the extraction of HCl by DMDBMA can be an important tool for a better understanding of the behavior of this compound towards iron(III) removal from hydrochloric acid solutions.

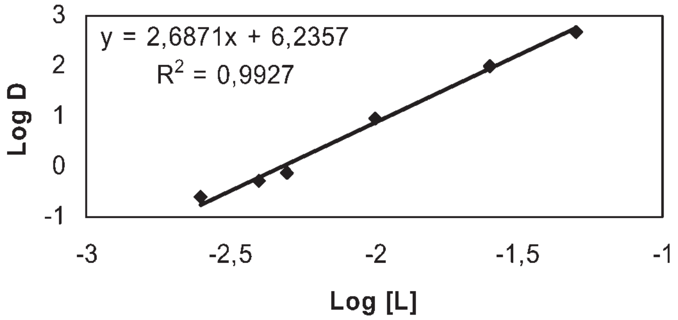


Figure 4. Dependence of log D on log[L] for DMDBMA (in 1,2-DCE): extraction of ~0.01 M iron(III) from HCl 8 M.

Nitric acid extraction by DMDBMA has already been reported by Nakamura and Miyake,[30] who studied its extraction at the initial concentration of 3.0 M HNO_3. The slope obtained by plotting the distribution ratios of nitric acid versus the concentration of DMDBMA exhibited a straight line with a slope of 1, which suggests that the ratio between the ligand and the acid is about one.

In the present work, the extraction of hydrochloric acid by DMDBMA was also investigated by acid–base titration analysis of the acid content in the aqueous phases before and after contact with a 0.05 M solution of the ligand.

The presence of hydrochloric acid in the DMDBMA organic phase after contact with a 8 M HCl aqueous solution was confirmed, and the ratio between HCl and malonamide appeared to be of about four. However, when ~0.01 M Fe(III) was added to the 8 M HCl aqueous solution, no HCl transfer to the organic phase was detected by the titration analysis. Nevertheless, the pH of distilled water before and after contact with the iron(III) loaded organic phase, during stripping, decreased from 5.5 to 1.8, thus indicating the occurrence of some acid transfer. A decrease of pH from 5.7 to 3.3 of the distilled water after contact with a HCl loaded organic phase of DMDBMA was also observed. In both extraction systems [with and without Fe(III)], HCl transfer to the organic phase seems to take place.

Spectroscopic Studies and Extraction Mechanisms

Spectroscopic studies were undertaken to clarify the mechanism of iron(III) extraction by DMDBMA. In fact, the data provided by spectroscopic techniques was analyzed in order to better understand the reactions involved on iron(III) extraction by DMDBMA.

UV-Visible Spectroscopy

UV-Visible spectroscopy is particularly useful to help in the identification of the iron(III) species in the organic phase after extraction.

The presence of $FeCl_4^-$ species in the loaded organic phases of DMDBMA after contact with aqueous phases of iron(III) in 8 M HCl was detected, thus supporting the transfer of this iron(III) chloro-complex to the organic solution. In fact, the UV-Visible spectrum of DMDBMA in 1,2-DCE after contact with iron(III) in 8 M HCl solutions, Fig. 5, shows two peaks at 364 and 314 nm, assigned to the anionic chloro-complex $FeCl_4^-$, since the literature refers to the existence of intense charge-transfer bands at those wavelengths for this complex.[38,39]

The two peaks at about 364 and 314 nm were also identified in the spectra of the iron(III) aqueous phases containing hydrochloric acid concentrations higher than 4 M,[40,41] Table 5. These spectra present a third peak at 242 nm, also assigned to $FeCl_4^-$. The increase in chloride ion concentrations facilitates the formation of $FeCl_4^-$ and therefore iron(III) extraction by DMDBMA. In fact, $FeCl_4^-$ is referred to in the literature as the predominant

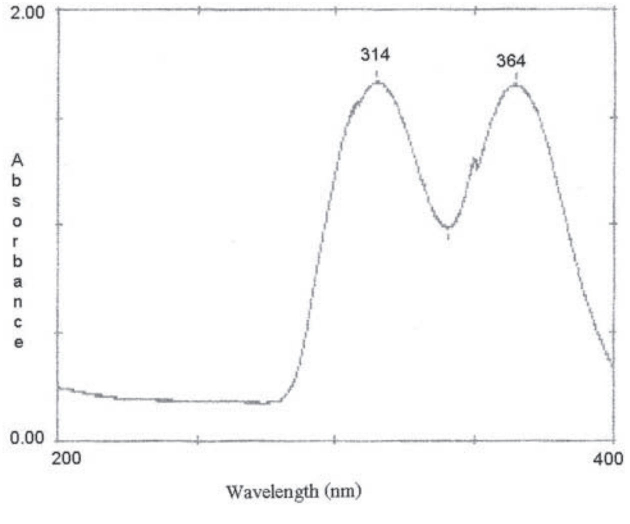


Figure 5. Region of the UV-Visible spectrum of the iron(III) loaded DMDBMA in 1,2-DCE (after extraction from 8 M HCl).

Table 5. Peaks of UV spectra of aqueous feed solutions of $FeCl_3 \cdot 6H_2O$ for different HCl concentrations.

Wavelength (nm)		
HCl (3 M)	HCl (4 M)	HCl (>4 M)
338	342	364
—	—	314
218	223	242

species at high Cl^- concentrations.[42–44] These UV data are in agreement with previously reported results.[17,40,41,45]

Different spectra—with two peaks varying between 215–223 and 338–342 nm—were obtained for iron(III) in the 3 and 4 M HCl aqueous phases before and after contact with the organic solutions of DMDBMA in 1,2-DCE (Table 5). Actually, the UV spectra of the iron(III) aqueous solutions with hydrochloric acid concentrations of 4 M or lower (e.g. 3 M) show two peaks, whose wavelengths are shifted to lower values as indicated in Table 5. These data can be explained by the predominance of other than $FeCl_4^-$ iron(III) chlorocomplexes, such as $FeCl_3$, $FeCl_2^+$, and $FeCl^{2+}$.

Taking into account that iron(III) is also extracted by DMDBMA from HCl solutions with concentrations of 4 M or even lower, more than 20% of Fe(III) was extracted from a 3 M HCl solution (where $FeCl_4^-$ is not the iron(III) predominant species), an UV spectrum of the iron(III) loaded organic phase (DMDBMA in 1,2-DCE) after contact with iron(III) in a 3 M HCl feed solution was obtained. The mentioned spectrum is shown in Fig. 6.

In this case, instead of the peaks assigned to $FeCl_4^-$ species, two different peaks at about 309 and about 355 nm were identified, which are most likely associated to other than $FeCl_4^-$ iron(III) species also extracted by DMDBMA. Considering the shift presented by these peaks, they are probably due to the $FeCl_3$ complex, which should be one of the iron(III) species presented in HCl solutions with concentrations between 2 and 4 M. The extraction of $FeCl_3$ species suggests a solvation mechanism occurring at least for the extraction of the metal ion from HCl solutions with concentrations between 2 and 4 M. Below 2 M HCl, no extraction was achieved, probably due to the predominance of different iron(III) complexes, such as $FeCl_2^+$ and/or $FeCl^{2+}$, which should not be extracted by the ligand.

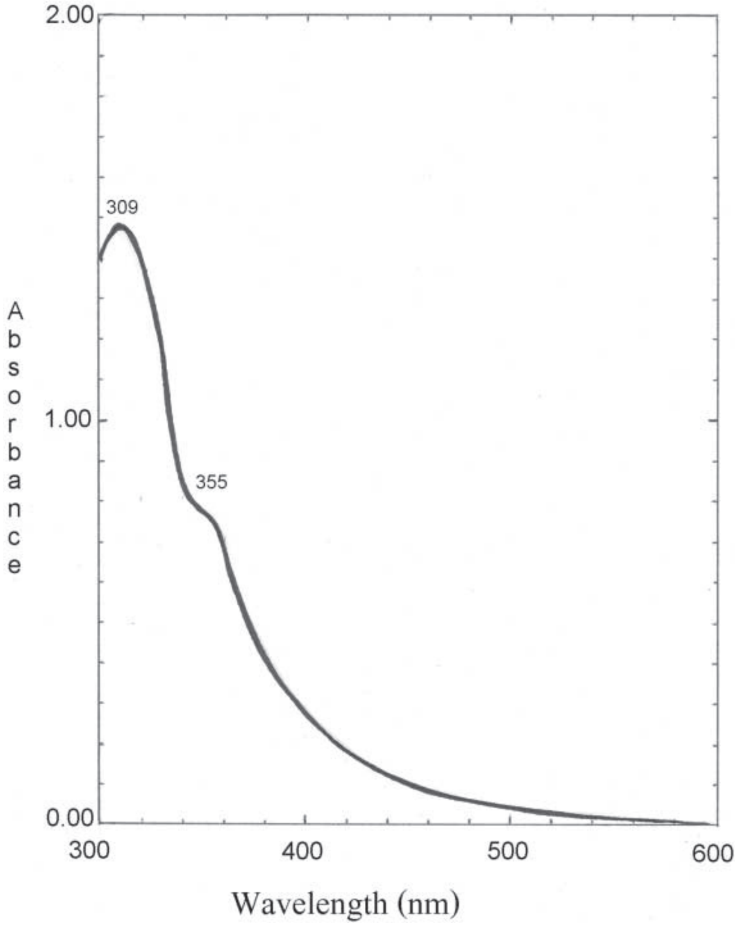


Figure 6. Region of the UV-Visible spectrum of the iron(III) loaded DMDBMA in 1,2-DCE (after extraction from 3 M HCl).

NMR Spectroscopy

In order to obtain concluding data on the iron(III) extraction reactions when DMDBMA is involved, NMR studies were carried out.

The ^{1}H NMR spectrum of DMDBMA, obtained after contact of the organic phase with an aqueous solution containing 8 M HCI, is displayed in Fig. 7.

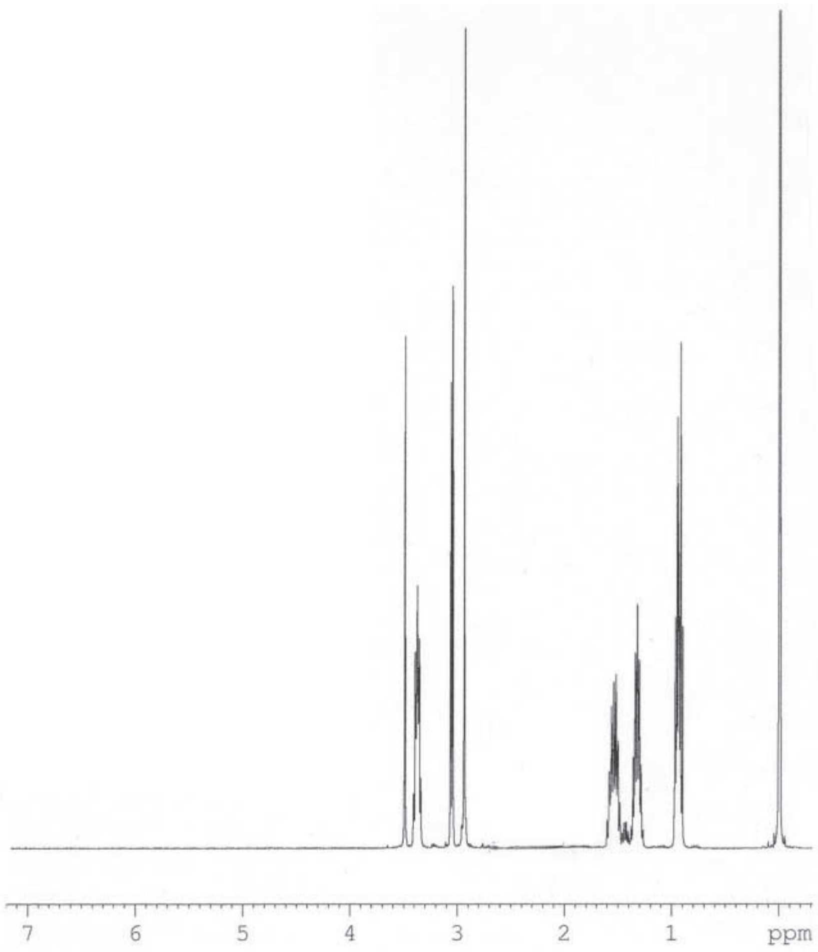


Figure 7. ^{1}H NMR spectrum of DMDBMA after contact with 8 M HCl.

In this spectrum, no additional peaks appear as it should happen when protonation of the ligand occurs.[17] This result emphasizes that iron(III) extraction should involve a solvation mechanism in which $FeCl_3$ and/or $HFeCl_4$ are the predominant extracted species, depending on the chloride ion concentrations of the aqueous phase. ^{13}C NMR spectra for DMDBMA before and after contact with HCl 8 M are similar: the chemical shift for the carbon of the carbonyl group did not suffer any deviation, as well as the other additional peaks.

Fe(III) Extraction Reactions

At this stage it is already possible to propose the most probable reaction pathways involving iron(III) recovery from chloride media, using DMDBMA.

When DMDBMA (L) is involved, the data collected points out to the predominance of an iron(III) solvation reaction from $\mathrm{HCl} > 4\,\mathrm{M}$ such as that depicted in Eq. (2).

$$n\mathrm{L}_{(\mathrm{org})} + \mathrm{HFeCl}_{4(\mathrm{aq})} \Leftrightarrow n\mathrm{L} \cdot \mathrm{HFeCl}_{4(\mathrm{org})} \tag{2}$$

According to the slope analysis results, when $\mathrm{HCl} = 8\,\mathrm{M}$, $n \simeq 2$.

For HCl concentrations varying from 2 to 4 M, the predominant iron(III) species extracted by DMDBMA should be $\mathrm{FeCl_3}$, therefore the correspondent chemical equation can be depicted such as in Eq. (3).

$$n\mathrm{L}_{(\mathrm{org})} + \mathrm{FeCl}_{3(\mathrm{aq})} \Leftrightarrow n\mathrm{L} \cdot \mathrm{FeCl}_{3(\mathrm{org})} \tag{3}$$

Selectivity Studies

The selectivity of DMDBMA towards Fe(III) extraction in the presence of several metal ions was also investigated.

With that aim, solvent extraction experiments with DMDBMA were accomplished using aqueous phases containing a 0.005 M concentration of one of the following metals—Cu(II), Zn(II), Pb(II), Ni(II), Co(II), Ag(I)—in combination with $\approx$0.01 M of iron(III), from 8 M HCl. The extraction of iron(III) and the above mentioned metals from a multicomponent mixture containing all those elements was also investigated. The results are illustrated in Table 6.

With exception of Ag(I) and Pb(II), no significant metal ion extraction is observed in the presence of iron(III) from either binary or multicomponent metal aqueous solutions. A slight increase in the extraction of Cu(II), Zn(II), and Ni(II) is observed when all the mentioned metals are together in the aqueous phase. Nevertheless, their extraction is lower than 10%. The values obtained for the extraction of Ag(I) and Pb(II) in binary and multicomponent mixtures can be due not to a real extraction but to a precipitation phenomena, considering the known low solubility of both metals in chloride media. Further data should be obtained to confirm this possibility.

Taking into account that most iron(III) commercial extractants (e.g., TBP, D2EHPA, Alamine 336, and Amberlite LA) co-extract Fe(III) together with

Table 6. Extraction of iron(III) and other metals in binary and multicomponent mixtures by DMDBMA (0.05 M in 1,2-DCE) from 8 M HCl solutions.

	Metal extraction (%)	
Mixture	M	Fe
Binary		
Cu(II) + Fe(III)	0	97
Zn(II) + Fe(III)	0	98
Ni(II) + Fe(III)	2	99
Co(II) + Fe(III)	0	99
Ag(I) + Fe(III)	20	99
Pb(II) + Fe(III)	8	99
Multicomponent		
Cu(II)	6	98
Zn(II)	7	
Ni(II)	8	
Co(II)	0	
Ag(I)	18	
Pb(II)	48	

Zn(II) or Cu(II),[46–48] the high selectivity of this ligand towards several metals, including Zn(II) and Cu(II), is a very promising result.

Stripping of the Iron(III) Loaded DMDBMA Organic Solutions and Reutilization of the Extractant

Distilled water was tested as a stripping agent for iron(III) from the malonamide derivative under study, after the extraction of the metal ion from HCl 8 M. The metal is quantitatively re-extracted and, as it was already mentioned, a large pH variation of the aqueous phase, after stripping, was verified. This difference is probably due to the transfer of H_3O^+ ions to the new aqueous phase, supporting the following stripping mechanism depicted in Eq. (4).

$$n\mathrm{L}\cdot \mathrm{HFeCl}_{4(\mathrm{org})} \Leftrightarrow n\mathrm{L}_{(\mathrm{org})} + \mathrm{FeCl}_{-4(\mathrm{aq})} + \mathrm{H_3O}^{+}_{(\mathrm{aq})} \qquad (4)$$

These results are very encouraging considering the difficulties usually verified for iron(III) stripping from usual commercial extractants, e.g., organophosphorus extractants such as D2EHPA and TBP.[15,16]

A solution of 0.05 M of DMDBMA in 1,2-DCE was reutilized three times, each one after stripping of its iron(III) content with distilled water, by successive contact with aqueous phases of 8 M HCl containing ~0.01 M Fe(III) as a ferric chloride salt. The percentages of iron(III) recovery in each stage are summarized in Table 7.

The data presented in Table 7 indicate that DMDBMA can be successively reutilized for iron(III) extraction from HCl solutions without significant loss of efficiency, taking into account that recoveries higher than 93% were obtained even after a fourth contact with the aqueous feed solution. These results denote that no extensive degradation of the extractant in the adopted experimental conditions seems to occur. However, better results can possibly be expected if a more diluted HCl solution is used as aqueous medium (e.g., HCl 6 M).

In addition to other results described in this and in previous papers,[17,40,41] the possibility of successive reutilizations of DMDBMA, which can probably be extended to other malonamide derivatives, reinforces the potentialities of this family of extractants in view of their industrial application.

Comparison of the Extraction Behavior of DMDBMA Towards Iron(III) with the Already Studied Malonamide Derivatives

In a previous work, two malonamide derivatives—DMDPHMA and DMDPHTDMA—have already been investigated regarding their extraction capacity towards iron(III) recovery from chloride media.[17] Thus, a comparison with the behavior of DMDBMA can be easily made. For the three malonamide derivatives, iron(III) extraction depends directly on HCl

Table 7. Iron(III) extraction by DMDBMA after three reutilization stages of the organic phase (0.05 M in 1,2-DCE).

Stage of contact	Extraction (%)
1	99.8
2	98.6
3	96.5
4	94.0

concentration, and their efficiency is enhanced as the acid concentration in the aqueous phase increases. When the aqueous phase reaches a 8 M HCl concentration, all the malonamide derivatives extract iron(III) with an efficiency higher than 99%.

However, DMDBMA presents an intermediate extraction ability for iron(III) contained in HCl solutions from 3 to 4 M, because at this concentration range it is a better extractant than DMDPHMA but poorer than DMDPHTDMA.

The same iron(III) extraction behavior was found for DMDPHMA and DMDBMA from HCl solutions with 12 M total chloride concentration containing both the acid and LiCl. In these cases, the metal ion extraction is always quantitative, independently on the acid and salt concentrations in the aqueous solutions.

For the three malonamides, an average of two molecules of extractant seems to be involved on iron(III) extraction from 8 M HCl media.[17]

The spectroscopic data collected for the three malonamides—UV and ^{1}H NMR—denote that iron(III) is most likely extracted in the $FeCl_4^-$ form, therefore pointing out the relevance of using a concentrated aqueous chloride media to achieve the predominance of this anionic chlorocomplex iron(III) species. These data is also reinforced by the fact that no iron(III) extraction was observed in the total absence of chloride ions, as it was confirmed from the results obtained for the iron(III) extraction from other media than chloride.[17] For each malonamide, iron(III) extraction efficiencies always depend on several parameters that govern the overall equilibria, leading to the formation of the chloro-complex extractable species.

Concerning the chemical reactions responsible for iron(III) extraction, it was found earlier that DMDPHMA extracts the metal ion by an anion-exchange reaction, $FeCl_4^-$ being the extracted species, whereas a solvation mechanism was proposed for DMDPHTDMA for the extraction of $HFeCl_4$.[17] For DMDBMA, the evidences collected from the ^{1}H NMR point out to the extraction of $HFeCl_4$ through a solvation chemical reaction, from 8 M HCl, but $FeCl_3$ should be the predominant species extracted by DMDBMA from 3 M HCl, as it was suggested from the correspondent UV-Visible spectrum obtained from the analysis of the respective loaded organic phase.

Iron(III) stripping from the studied *N*,*N*,*N*′,*N*′-tetrasubstituted malonamides is easily achieved by a simple contact with water, which is a very good result from a practical point of view. In addition, the results for their selectivity towards iron(III) when this metal ion is in presence of several other metals are also remarkable, considering that no significant contamination of the organic phases occurs. Moreover, the data concerning the reutilization of DMDBMA is also promising.

Table 8. More relevant chemical data obtained for DMDBMA.

Collected data	DMDBMA
Iron(III) extraction from chloride media	>99% Fe(III) extraction at 8 M HCl and 6 M LiCl; Fe(III) extraction is always quantitative from 12 M Cl^-, independently on the HCl and LiCl concentrations
Iron(III) extraction from other media (sulfuric and nitric acids)	Partial extraction when the source of iron(III) is a chloride salt only
Spectroscopic studies	
UV spectroscopy	$FeCl_4^-$ was detected in the loaded organic phases after extraction from 8 M HCl, while it was not detected in the loaded organic phase after extraction from 3 M HCl, in spite of iron(III) being extracted
^{1}H NMR spectroscopy	No additional peak was observed in the ^{1}H NMR spectra of the ligand after contact with HCl solutions with a concentration of 8 M
Iron(III) stripping	Quantitative when water is used as stripping agent
Selectivity towards iron(III)	Fe(III) is always efficiently extracted when involved in binary and multicomponent aqueous mixtures—Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Ag(I). For the tested experimental conditions, these metals are not significantly co-extracted
Solvent re-utilization	DMDBMA still shows a high extractive Fe(III) performance even after four stages of utilization

CONCLUSIONS

The most important chemical data obtained for DMDBMA, previously discussed, are summarized in Table 8.

The chemical structure of the malonamide derivatives seems to affect the type of the metal ion transfer reactions from the aqueous to the organic phase.[17] For DMDBMA, a solvation mechanism involving the extraction of $HFeCl_4$ from 8 M HCl seems to be the predominant one. However, according to the obtained UV data, the extraction of iron(III) as $FeCl_3$ is likely to occur when a 3 M HCl solution is involved.

The stripping of iron(III) from the DMDBMA loaded organic phase, the selectivity patterns and the reutilization data collected are considered to be very interesting results in view of a practical application.

Further studies regarding the use of different chemical malonamide structures, towards Fe(III) extraction, are currently underway.

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