



STUDY AND RESEARCH REGARDING BINARING SISTEM WITH TIOBIS - β – NAFTOL

Olga MITOSERIU, Stela CONSTANTINESCU,
Lucica ORAC

“Dunarea de Jos” University of Galati
email: stelaconstantinescu@email.ro

ABSTRACT

This paper presents the results for contribution of determining the manganese from waters and steel. Manganese, due to its properties, cannot be found but in acid waters and usually associated with iron. In small amounts, the manganese is a necessary nutrient above all as activator of certain enzymes. In large amounts, though, coming from contaminated waters, the manganese is noxious and may cause brain damage. It is considered that drinking water should not contain more than 0,1 ppm manganese. From the studies carried out, the tiobis- β -naftolul dissolved in etilic alcohol or isobutyl alcohol may be used to determine the Mn (II) ion, under certain conditions as described in the paper. To determine manganese (II) in water, a photometric extraction method has been developed. The method is new, useful and accurate and enables determining Mn in surface, underground and fishery waters.

KEYWORDS: manganese, tiobis- β -naftolul, waters, photometric extraction method

1. Introduction

Finding efficient extraction agents is one the major research directions in the field of extraction process chemistry. From an analytical point of view, the metal ion extraction systems using organic reactants are highly important. The chelate polyketides agents containing acid and coordination groups in their molecule are the most widely used for this purpose. Metal separation by means of etheric sulphide organic compounds is, however, less studied than other classes of compounds. [1] Researches have revealed that certain substances from tiobisphenol class can be used as remarkable reactants for the separation of metals by extraction. Thus, di- β -naftolmonosulphide has groups of -OH in its molecule, with mobile hydrogen and etheric sulphide which, under favorable conditions, produces donor-acceptor bounds therefore it can form complex combinations.

The literature only points out to combinations reached by ions Ca(II) and Ba(II) [2], Pb(II) [3], Cu(II) [4] and alkaline metals. [5,6,7,8]

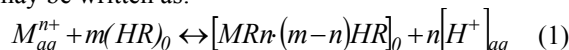
Di- β -naftolmonosulphide, dissolved in a suitable organic solvent, non-miscible with water,

extracts the metal ions from the water environment, thus proving to be a very good extracting agent.

2. The extraction mechanism

Di- β -naftolmonosulphide is a poor-acid organic ligand. Dissolved into organic solvents such as higher alcohols, it is able to form with ion Mn(II) extractable soluble green species. To study the extraction mechanism a calculation model was used and applied to the chelate extraction system. [9,10,11]

In a first approximation, the extraction balance may be written as:



Symbols 0 and aq represent the compounds in organic-phase and water-phase respectively.

As to the balance this can be written as:

$$K_{ex} = \frac{[MRn \cdot (m-n)HR]_0 \cdot [H^+]_{aq}^n}{[M^{n+}]_{aq} [HR]_0^m} \quad (2)$$

For the case under study the authors suggest:



- Under the conditions provided the metal ion does not form significant amounts of acid-compounds;

- Concentration of species $M(OH)$, formed by auxiliary balances, becomes negligible due to the more stable chelate MR_n , and its extraction in organic phase;

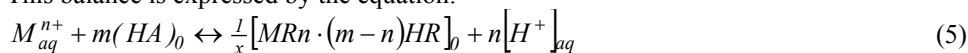
- Concentration of species MR_n in water phase and those of the intermediate water species are also small and therefore negligible.

By denoting D the repartition coefficient, and by applying logarithms and differential calculation to equation (2) with respect to pH , we have:

$$\left[\frac{\partial \lg D}{\partial pH} \right]_{(HR)_0} = n \quad (3)$$

Relation (3) enables determination of n , i.e. the cation charge and implicitly the form of the

This balance is expressed by the equation:



Where x is the number of monomer units in the polymer phase.

For the repartition coefficient, we have:

$$D = \frac{[M]_0}{[M^{n+}]_{aq}} ; D = \frac{\left\{ \frac{[M]_0}{x} \right\}^{\frac{1}{x}} [M]_0^{\frac{x-1}{x}}}{[M^{n+}]_{aq} \left(\frac{1}{x} \right)^{\frac{1}{x}}} \quad (6)$$

By applying a logarithm and re-arranging the terms in the extraction constant relation, we have:

$$\lg D = \lg K_{ex} + n pH + m \lg HA + \frac{1}{x} \lg x + \frac{x-1}{x} \lg M_0 \quad (7)$$

At the pH where extraction is 50% $M_0 = M_{total}/1$ therefore:

$$\left[\frac{\partial pH_{50\%}}{\partial \lg [M]_{total}} \right]_{HR_0, x} = - \frac{x-1}{nx} \quad (8)$$

The graphic representation under coordinates $\lg D$ vs $pH_{50\%}$ at different metal concentrations shall have, in some areas, straight lines. From the slope of this line it can be calculated the x value. [12]

2. Experimental

The experiments were carried out using an organic phase -water phase ratio =1:2. The pH was varied by different buffer solutions ($NH_4OH + NH_4Cl$). Funnels were stirred for 20 minutes; after the balance had become stable, the water solution was analyzed to determine the pH (with a pH -meter MV-S4) and the concentration $M(II)$ (complexometric titration in the presence of ascorbic acid, using violet

species where the metal ion in water phase is to be found.

The graphic illustration is performed in the coordinates $\lg D$ - pH , while keeping constant the concentration of the reactant HR .

At the pH where an extraction of 50% $\lg D=0$ is obtained we shall have:

$$pH_{50\%} = \frac{1}{n} \lg K_{ex} - \frac{m}{n} \lg [HR]_0 \quad (4)$$

From the graphic $pH_{50\%} - \lg [HR]_0$ the value of m can be determined.

When the variation of the metal ion concentration influences the repartition coefficient, some polymer species are assumed to be in organic phase.

pirocatehine as indicator). The ion strength was still present with solution of KNO_3 1m.

3. Results and discussions

The experimental results concerning the variation of the repartition coefficient depending on the pH value are presented in fig.1. Applying the mathematical quantitative approach to the described extraction procedure the slope of the straight lines of $n=1,92 \approx 2$ is obtained. The n value, even at this pH , is consistent with the second oxidation state of the manganese; this takes part in the complexation reaction with di- β - naftolmonosulphide as a Mn^{2+} species and complexes two ligand molecules. The occurrence of a family of straight parallel lines in the $\lg D$ - pH graphic, for different ligand concentrations, indicates the possibility of solvating the complex compound consisting of two reactive molecules. From the graphic illustration under coordinates $pH_{50\%} - \lg C_{HR}$ (fig.2), we get a straight line from which slope we can calculate $m \approx 3$.

The species extracted will add a ligand molecule which can be written as:
 $[MnR_2 \cdot HR]$

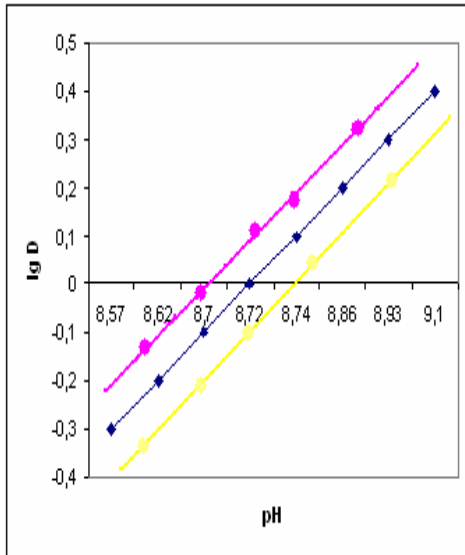


Fig.1. Extraction Mn(II) with di - β- naftol
 lgC_{HR} upon Mn(II) extraction

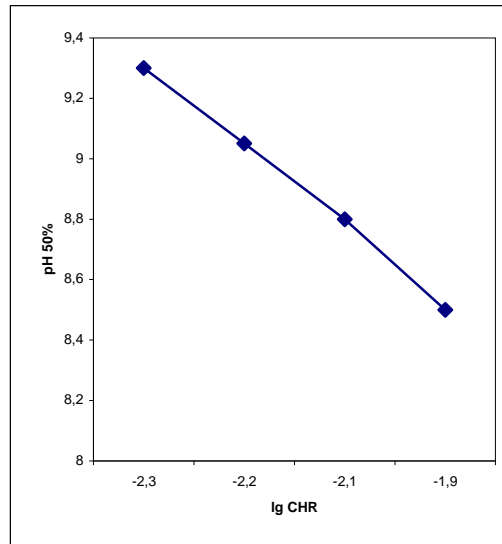


Fig.2. Variation of $pH_{50\%}$ with monosulphide
 $C_{Mn} = const.$, $C_{HR} = variable$

Experimental researches performed, while keeping the reactive concentration constant, at different metal ion concentrations, were focused on the variation of the repartition coefficient depending on the pH of the water phase. Within the concentration range concerned, $4 \cdot 10^{-4}$ - $6 \cdot 10^{-4}$ mol Mn^{2+} / l, the repartition coefficients do not depend

on the initial concentration of the Mn^{2+} ion which indicates the absence of the polymerization of the species extracted in organic phase (fig.3.) Therefore, the di-β-naftolmonosulphide, dissolved in isobutyl alcohol forms with Mn^{2+} ion a green combination, extractable in non water medium.

The extraction balance is described by the following chemical equation:

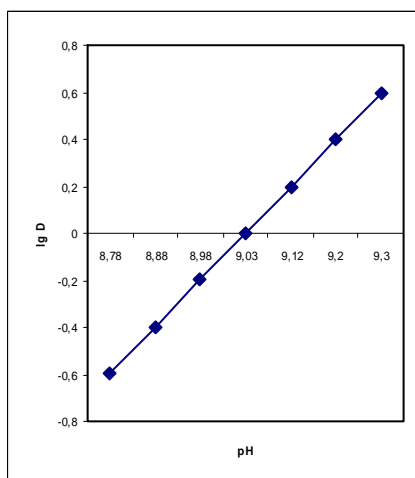
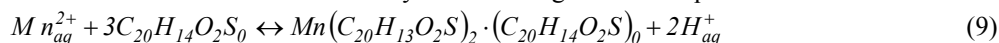


Fig.3. Extraction Mn(II) with di- β- naftolmonosulphide:
 $C_{Mn} = variable$; $C_{HR} = const.$

Based on the studies carried out the optimum extraction conditions have been established (wave length , pH, reactive concentration, extraction time , influence of foreign ions) and an efficient method of determining the manganese from waters was finally reached.

The following way of working is recommended: in a separating funnel of 50 ml, 10ml reactive solution is poured into $1 \cdot 10^{-2}$ mol/l isobutyl alcohol, 10 ml buffer solution of pH 10 (clorura de amoniu- amoniac) and V ml solution to be analyzed are poured. After 5 min stirring , phases are separated and the water layer is removed.

The extract in isobutyl alcohol is brought to level in a measuring flask of 25 ml. With higher Mn^{2+} concentrations, it is recommended to repeat extraction.



To remove water traces, the extract is filtered through cotton or a layer of anhydrous Na₂SO₄.

The absorbance of solutions flasks supplemented with isobutyl alcohol was measured after 30 minutes.

The variation of absorbance versus the Mn²⁺ ion concentration results in a linear dependence, in a very large range of [Mn²⁺](Table1).

Table 1. Processing the experimental results to verify Lambert- Beer law

$C_{Mn} \cdot 10^{-2}$ mol/litru x_i	A_{560} y_i	$x_i^2 \cdot 10^8$	$x_i y_i \cdot 10^4$	A calculate y_i	$(y_i - Y_j) \cdot 10^3$	$(y_i - Y_j)^2 \cdot 10^6$
1	0,072	1	0,072	0,073	-1	1
2	0,145	4	0,290	0,145	0	0
3	0,220	9	0,660	0,218	2	4
4	0,290	16	1,160	0,290	0	0
5	0,362	25	1,810	0,363	-1	1
6	0,435	36	2,610	0,436	-1	1
7	0,508	49	3,556	0,508	0	0
8	0,582	64	4,656	0,581	1	1

5. Conclusion

$$y = 0,5 \cdot 10^{-4} + 0,0726 \cdot 10^4 x$$

$$y_{sup} = 2,88 \cdot 10^{-3} + 0,0726 \cdot 10^4 x$$

$$y_{inf} = -2,88 \cdot 10^{-3} + 0,0726 \cdot 10^4 x$$

where:

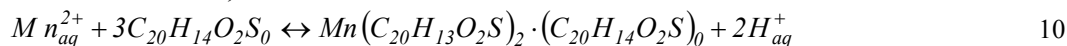
y- absorbance

x – concentration C_{Mn}

- Di-β-naftolmonosulphide, organic polydentat ligand, can be used as an efficient extract agent in the extract process chemistry;

- The Mn²⁺ ion reacts with di-β-naftolmonosulphide resulting in a green compound, extractible in organic water non-miscible solvents, such as high alcohol;

- When isobutyl alcohol is used as solvent in the concentration range concernd, at pH 8-10, the extraction balance of Mn²⁺, is written as:



- The extraction procedure depends on the pH of the water phase, the ligand concentration in organic phase and the stirring time. Under certain conditions, the extraction can be carried out quantitatively.

References

- [1]. Mitoşeriu O., *Doctor's degree thesis*, Jassy Polytechnic Institute, 1980
- [2]. Mitoşeriu O., Constantinescu S., sa., *Metode moderne de investigare a proprietatilor materialelor metalice*, Editura Universitatii „Dunarea de Jos” Galati, 1998, p. 56-83.
- [3]. Constantinescu S., Mitoşeriu O., Orac L., *Influence of manufacturing technology on chemical and structural homogeneity of X60 steel*, TEHNOMUS XIV a XIV-a Conferinta Stiintifica Internationala, 4-5 Mai 2007, Suceava, p. 267-272.
- [4]. Mitoşeriu L., Nastase G., Orac L., *„Identificarea ionilor Fe(II) si Cu(II) din materiale metalice”*, Lucrarile Conferinței Stiintifice cu participare Inetrnațională ARTCAST 2006, 4-5 mai, Galati, Faculty of Metallurgy and Science Materials, Editura ACADEMICA, 2006, p.237-241, ISBN973-8937-00-0
- [5]. Popa G., Moldovanu S., *Reactivi organici în chimia analitică*, Editura Academiei, București, 1976.
- [6]. Liteanu C., *Volumetric quantitative analytical chemistry*, Didactic and Pedagogic Publishing House, Bucharest, 1964
- [7]. Odochian L., Mihai E., Fişel S., Mitoşeriu O., *Rev. Roumain Chim. R.S.R.*, 26, 3, 1981 p. 383.
- [8]. Mitoşeriu O., Hartoapeanu A., Cioroi M., *Analytical chemistry. Separation and identification of cations*, Ed. “Ars Docendi” University from Bucharest, 2001, ISBN 973-8118-51-4.
- [9]. Holzbecher Y., Divis L., Kral M., Lucha L., Vlacil F., *Organiceschie reagenti v neorganicescom analize*, Izd., Mir, Moscova, 1979, p 427.
- [10]. Mitoşeriu O., Musat V., Popescu M., Benea L., Bodi V., *Analize tehnice*, Universitatea Dunarea de Jos Galati, 1995.
- [11]. Liteanu C., *Studii și cercetări*, Chimie, Cluj, 1, 1963, p.181
- [12]. Ceașescu D., *Use of mathematical statistics in analytical chemistry*, Technical Publishing House, Bucharest, 1982.
- [13]. Mitoşeriu O., Levcovici D., Filip G., *Reactiv organic selectiv pentru determinarea mai multor metale grele din diferite materiale*, The Anals of “Dunărea de Jos “University of Galați Fascicula IX, Faculty of Metallurgy and Materials Science, year XXIV (XXIX), May 2006, no.1, ISSN 1453-083X, p.95-101
- [14]. Mitoşeriu O., Levcovici D., Filip G., *Determinarea mercurului din apele poluate accidental prin metoda colectării gravimetriceIn stadiul organic*, The Anals of “Dunărea de Jos “University of Galați. Fascicula IX, Faculty of Metallurgy and Materials Science, year XXIV (XXIX), May 2006, no.1, ISSN 1453-083X, p.31-35