Complexation of Cobalt with a Heteropolyanion of Dawson Type and Recovery by Emulsified Liquid Membrane

Nacéra Zabat¹, Mostefa Abbessi²
Department of Process Engineering, Badji Mokhtar-Annaba University
P.O. Box 12, 23000, Annaba, Algeria
¹zabatnassira@yahoo.fr; ²mostefa_abbessi@yahoo.fr

Abstract
In this study, a lacunar heteropolyanion (HPA) of Dawson type \((\text{P}_2\text{W}_{15}\text{Mo}_2\text{O}_{66})^{10-}\) was prepared and tested in the complexation of aqueous (Co²⁺). The complex formed was recovered after that using an emulsified liquid membrane (ELM). The results showed that the complex \((\text{P}_2\text{W}_{15}\text{Mo}_2\text{O}_{66}\text{Co})^{8-}\) was very stable with constant stability of \(\beta = 4,073.10^3\). The recovery of this complex formed by (ELM) attained the yield of 70%.

Keywords
Polluted Water; Heavy Metals; Cobalt; Complexation; Heteropolyanions; Emulsified Liquid Membrane

Introduction
The qualitative and quantitative analysis of toxic metals likely to be present in water of industrial wastes generally requires a preliminary complexation.

Experimental
Preparation of Metallic Complex
The heteropolyanion \((\text{P}_2\text{W}_{15}\text{Mo}_2\text{O}_{66}\text{Co})^{8-}\) was prepared by addition of cobalt nitrate on the lacunar compound...
(P₂W₁₅Mo₂O₆₈)₁₀⁻ based on methods described in the literature [Contant, 1997; Abbessi1989; Abbessi, 1991]. The monovacant compound (P₂W₁₅Mo₂O₆₈)₁₀⁻ was obtained by reaction of addition of two molybdate MoO₄²⁻ on the trivacant compound (P₂W₁₅), this later was obtained by reaction of elimination of a tritungstic grouping which occupied the site “a” in the saturated species αP₂W₁₈O₆₂₆⁻. The various structures of these heteropolyanions are presented in figure 1.

![Figure 1. Different structures of heteropolyanions](image)

**Study of the Formation of Metallic Complex**

Before extracting the complex (P₂W₁₅Mo₂O₆₈Co)₈⁻ by emulsified liquid membrane, it is useful to study its stability according to the pH, the time and to determine its constant of stability. The analysis was carried out with a spectrophotometer 6405 UV/VIS (JENWAY).

**Stability of the Complex According to pH**

A UV-Visible sweeping with different pH was carried out in order to choose the optimum pH for the complex (P₂W₁₅Mo₂O₆₈Co)₈⁻. In this case of the equimolaires solutions made up of ligand, metal and buffer were used. The results obtained for the complex (P₂W₁₅Mo₂O₆₈Co)₈⁻, with different pH, are gathered in table 1.

It is noticed that the degree of formation of the formed complex is deducted from the value of the recorded maximum absorptance. The formation of the complex is very weak in acid medium; on the other hand, the basic medium is more favorable to its formation. The optimal pH for the formed complex (P₂W₁₅Mo₂O₆₈Co)₈⁻ is pH= 9 with a maximum wavelength \( \lambda_{\text{max}} = 304 \text{ nm} \).

**Stability of the Complex According to Time**

To determine the time for which the complex is stabilized, the variation of the absorptance according to the time was followed (Figure 2).

The result reveals that the formed complex is stable in a rather broad time interval (one hour).

![Figure 2. Variation of the absorptance of the complex (P₂W₁₅Mo₂Co)₈⁻ according to the time](image)

**Determination of the Constant of Stability of the Complex**

The determination of the constant of stability was carried out by using statistical methods of calculation (method of isomolaires series, method of saturation and method of balance displacement) [Hamlaoui, 1990]

1) Method of Isomolaires Series

In this method, the volume of the buffer solution (pH=9) is maintained constant whereas the volumes of the solutions of ligand and cobalt, of the same concentration (5.10⁻⁴M) are mixed in variable proportions in order to keep constant total volume.

According to the principle of the method of isomolaires series, the stoechiometry is deduced from report \( C_L/C_M \) leading to the maximum value of the absorptance. The result shows that the stoechiometry of the formed complex is equal to 1 (figure 3).

![Figure 3. Variation of the absorptance of the complex (P₂W₁₅Mo₂Co)₈⁻ according to the report \( C_L/C_M \) by method of isomolaires series](image)

2) Method of Saturation

This method consists in varying volumes of the ligands and the buffer solution, and maintains the volume of constant metal. Total volume is kept constant. The values of this method become source data in calculation of the constant of stability by the means of balance displacement.

The results represented in figure 4 showed that the
intersection of the tangents of the two parts of the curves (left ascending and the stage) makes it possible to deduce stoechiometry from the reaction which indicates the ratio CL/CM close to 1.

The stoechiometry and constant of stability of the formed complex are determined by the method of displacement of balance based on the study of the linear dependence of the Equation (1):

$$\log \left( \frac{A_i}{A_{\text{max}} - A_i} \right) = n \log C_{Li} + \log \beta$$  \hspace{1cm} (1)

$A_i$: absorptance of the complex corresponding to the increasing part of the curve of saturation.

$A_{\text{max}}$: maximum absorptance corresponding to the stage of the curve of saturation.

$n$: stoechiometric report (CL/CM).

$C_{Li}$: concentration of the ligand correspondent to each value of $A$.

$\beta$: constant of stability.

By tracing $\log \left( \frac{A_i}{A_{\text{max}} - A_i} \right)$ according to $\log C_{Li}$ for three points of the ascending part of the curve of saturation, figure 5 was plotted.

The stoechiometry of the complex $(P_2W_{15}Mo_2O_{61}Co)$ determined based on the graph(Figure 5) is equal to 1. The value of $\log \beta$ is deduced also from this graph ($\log \beta = 3,610$) from where $\beta = 4,073.10^3$ thus revealing a sufficiently stable compound.

Recovery of the Complex Formed $(P_2W_{15}Mo_2O_{61}Pb)^+$ by Emulsified Liquid Membrane

1) Preparation of the Emulsified Liquid Membrane

The membrane intended to extract the complex $(P_2W_{15}Mo_2O_{61}Co)^+$ was prepared with a mixture of extractant triethylamine $(C_3H_7)_3N$ (Aldrich) of thinner n-heptane (Riedel-in Hean) and surfactant monooleate of sorbitane SPAN80 (Federated) [Samar,1992]. The choice of the nature of extractant, the thinner and surfactant was made leave a bibliography search [Bourenane, 2003; Frites,2005].

For favorite emulsion water in oil (W/O), this emulsion was prepared by mixing a volume of the internal NaOH phase (0.2M) with a volume of the liquid membrane. The mixture was agitated at a number of revolutions of 5000 tr/min during 5 min with the aid of a homogenizer models ULTRA-TURRAX T 18-10. A stable emulsion was obtained.

2) Procedure of the Extraction by Emulsified Liquid Membrane:

To extract the complex considered, it was as follows: A volume of the membrane was taken and dispersed in a beaker containing 200 ml solution to be treated (external phase), whose initial concentration of the complex to be extracted is equal to 100 ppm. The mixture was agitated using a mechanical agitator (type RW20 Kjank & Kunkel). The pH evolution of the external phase was followed by means of a pH meter (type HANA Hi 8519N). In order to follow the variation of the kinetics of extraction of the complex formed, $(P_2W_{15}Mo_2O_{61}Co)^+$according to time, was carried out to take away of the external phase for following times of contact: (2, 4, 6 and 8min). After filtration, these samples were proportioned by a spectrophotometer 6405 UV/VIS (JENWAY).

The experimental study carried out described the evolution of the yield of extraction in function of a variety of parameters. This yield is calculated by the following formula:

$$Y_{\text{ext}} = \frac{C_{\text{ext}} - C_{\text{fext}}}{C_{\text{ext}}}$$  \hspace{1cm} (2)
Results and Discussion

Optimization of Extraction Parameters

All the parameters are maintained constant except the parameter to optimize.

Operartories conditions

- Emulsification rate: 5000 revs/min;
- Emulsification time: 5 min;
- Temperature: 25°C;
- Concentration of internal phase (NaOH): 0,2 M;
- Concentration of external aqueous phase (solution to treat): 100 ppm;
- pH of the external phase: 9;
- Stirring velocity: 250 revs/min;
- Ratio of the organic phase on the internal phase (O/A)= 1;
- Ratio of the external phase volume on the emulsion volume (Vext/Vemul) =1.

1) Composition of the Membrane

Mass of Extractant. The Variation of the mass percentage of extractant varied automatically the composition of the membrane. The compositions of triethylamine, SPAN80 and n-heptane studied are: (15%, 12,5% and 72,5%); (25%, 12,5% and 62,5%); (30%, 12,5% and 57,5%); (35%,12,5% and 52,5%).

The experimental results are illustrated in figures 6 and 7.

Results showed that the optimal percentage of extractant in the membrane is 30% which corresponds to the best performance (Yext= 44%). Beyond, this percentage yield of extraction decreases. This can be explained by the fact why the increase in the mass of extractant destabilizes the emulsion and supports the emulsion oils in water. For percentages of extractant lower than 30%, yield also decreases, probably for that the mass of extractant is less important to extract the aqueous solution.

Mass of Surfactant. The parameters optimized previously are kept constant and the membranes were prepared with various percentages from surfactant which are the following: 12,5%,15%,25% and 35%.

Results indicate that the percentage of surfactant (Fig. 9) giving the best yield (Yext= 44%) is 12,5%. For values higher than 12,5%, the yield decreases. It seems that the membrane becomes very thick, which slows down the kinetics of extraction (Fig. 8).

pH of External Phase

The kinetics of extraction of the metallic complex was studied according to the different pH (fig.10). It is noticed that the best yield of extraction is (Yext=44%) obtained for pH=9 (fig.11). For the pH lower than 9, the yield of extraction decreases. This can be explained by the fact that in acid medium
the extractant which is an amine becomes degraded after a reaction with medium.

3) Stirring Velocity

The stirring velocities used are: 100, 200, 250, 300, and 350 revs/min.

Results of the stirring velocity influence on the kinetics are represented in figure 12.

It was noted that the best yield (Fig.13) of extraction (Yext=44%) is obtained for a stirring velocity equal to 250 revs/min after 2 min of contact. Beyond this speed, the yield of extraction decreases because of the bad transfer of the aqueous solution following slow kinetics of extraction.

4) Ratio of the Organic Phase on the Internal Phase (O/A)

Different values from 0.5 to 3 of O/A ratio have been studied. Results of the influence of the O/A ratio on the kinetics of extraction are represented by curves in Fig. 14 and the yield in Fig. 15.

Results showed that the extraction is bad for the ratio of O/A lower than unit and it is worse for the ratio O/A higher than unit. This phenomenon can be explained by the fact that more volume of emulsion increases more the membrane becomes thick thus involving an increase in the viscosity of the emulsion, consequently, the aqueous solution to be extracted diffuses with difficulty through the membrane. The optimal ratio (O/A=1) is obtained for yield of extraction (Yext= 44%) at a time of contact equal to 2 min.
5) **Ratio of the External Phase Volume on the Emulsion Volume (Vext/Vemul)**

In order to study the influence of the ratio (Vext/Vemul) on the kinetic (Fig. 16) and yield of extraction (Fig. 17), the ratios varying from 5 to 15 were used. It is observed that for a report Vext/Vemul higher than 10, the extraction of metallic complex is less effective. This can be due to the volume of the external phase which increases and with the decreasing volume of emulsion, consequently, the mass of extractant becomes less important to extract the aqueous solution. If the ratio Vext/Vemul is lower than 10, the extraction is even less effective, probably because of the emulsion volume which is more important than that of the external phase that involves more thickness of the membrane film, therefore, a kinetic of extraction becomes low. The optimal ratio is Vext/Vemul=10 gives the best yield (Yext=44%).

6) **Initial Concentration of the External Phase**

This study was carried out by fixing the optimal parameters found previously and by varying the initial concentration of the external phase to extract: 50 ppm, 100 ppm and 150 ppm.

Results of the kinetics of extraction are illustrated in Figure. 18 and the yield in Figure. 19.

These figures indicate that when the initial concentration of the complex in the external aqueous phase is lower than 100 ppm, the extraction gives an important yield. For a concentration generally higher than 100 ppm, the extraction is unsatisfactory. The best yield of extraction (Yext= 70%) is obtained for an optimal initial concentration equal to 50 ppm for a time of contact equal to 4 min; which confirms the theory stipulating that one of the advantages of the emulsified liquid membranes is their use for much diluted concentrations.

7) **Description of the Mechanism of Transport Through the Emulsified Liquid Membrane**

To recover the complexe (aqueous solution) by emulsified liquid membrane (ELM), a mechanism of aqueous solution-extractant transport is described, for better understanding its chemical reaction with the interface of the membrane. The mechanism proposed is the following:

\[
\text{R}_3\text{N} + \text{OH}^- \xrightarrow{\text{R}_3\text{N}, \text{OH}^{-}} (\text{R}_3\text{N})_8(\text{HPACo}) + 8\text{OH}^- \\
8(\text{R}_3\text{N}, \text{OH}^-) + (\text{HPACo})^8 \xrightarrow{\text{R}_3\text{N}, \text{OH}^{-}} (\text{R}_3\text{N})_8(\text{HPACo}) + 8\text{OH}^- 
\]

HPA: \( \text{P}_2\text{W}_{15}\text{Mo}_{2}\text{O}_{63} \)

OH: basic medium where the extraction is favored, moreover the complex \((\text{P}_2\text{W}_{15}\text{Mo}_{2}\text{O}_{63}\text{Co})^8\) is stable in this pH=9 medium.

The mechanism of transport of the heteropolyanion...
through the emulsified liquid membrane is schematized according to figure 20.

External phase I       Liquid membrane      Internal Phase II

[ R3N, (HPACo)8- ]

[(HPACo)8-,OH-]           ( (HPACo)8-

Extraction                                                   Desextraction

FIGURE 20. MECHANISM OF TRANSPORT OF HETEROPOLYANION THROUGH THE EMULSIFIED LIQUID MEMBRANE

Conclusion

The lacunar heteropolyanion prepared (P2W15Mo2O610-) seems to have remarkable properties of complexation. Of this fact, it can be used in the field of water treatment to fix toxic metals, as used in catalytic reaction as well as proposed in chemical analysis. This is confirmed by the analysis of spectra IR of the prepared complex, showing that the metal element (Co²⁺) is in the vicinity of the gap of the ligand (P2W15Mo2O610-). Moreover, the constant of given stability indicates the use potential of this compound, particularly in aqueous mediums, without risk of decomposition. Indeed, the constant of stability is rather high; which is equal to β = 4,073.10³.

The extraction by emulsified liquid membrane of the complex (P2W15Mo2O61Co)8- which could serve with effective manner in the electrocatalytic reduction of nitrates in a slightly acid solution, was the object of this work. The study of membrane made up of SPAN80 as surfactant and TEA as extractant according to the various parameters, showed that the increase in the concentration of extractant and surfactant stabilizes the emulsion. The increase in the pH of medium (basic pH), favorites the extraction of complex. The increase of the stirring velocity would cause a shearing and the phenomenon of osmosis (swelling). The increase in O/A ratio involves an increase in the viscosity of the emulsion. The increase in Vext/Vemul ratio would cause the instability of the membrane. It has been found that the parameter of the initial concentration of the external phase plays an important role in improving the extraction yield. Hence, the decrease of the initial concentration of the external phase significantly increased the extraction yield, rising from 44% (Co=100ppm) to 70% (Co=50ppm). It was deduced then that the extraction by ELM is favored for very dilute concentrations of the external phase.

The yield of extraction for the complex formed (P2W15Mo2O61Co)8- is of 70%; under the following optimal operating conditions:
- pH of the external phase to extract is equal to 9;
- Stirring velocity = 250 revs/min;
- Ratio O/A is equal to 1;
- Mass percentage of surfactant in the membrane is 30%;
- Mass percentage of surfactant in the membrane is 12,5%;
- Ratio Vext/Vemul is equal to 10;
- Initial concentration of the external aqueous phase for the complex (P2W15Mo2O61Co)8- is equal to 50 ppm.

REFERENCES


Dawson, B. “The structure of the 9(18)-heteropolyanion in potassium 9(18)-tungstophosphate,K$_6$(P$_2$W$_{18}$O$_{62}$).14H$_2$O”.

Devulapalli, R., Jones, F. “Separation of aniline from aqueous solutions using emulsion liquid membranes”.


HU, S. B., Li, J., Wieneck, J. “Feasibility of surfactant-free supported emulsion liquid membrane extraction”.

Kargari, A., Kaghazchi, T., Soleimani, M. “Role of emulsifier in the extraction of gold (III) ions from aqueous solutions using the emulsion liquid membrane technique”.

Keita, Bineta., Girard, Francois., Nadjo, Louis., Contant, Roland., Canny, Jacqueline., Richet, Martine. “Metal ion complexes derived from the α$_1$ isomer of (P$_2$W$_{17}$O$_{61}$)$^{10-}$: comparison with the corresponding α$_2$ species”. Journal of Electroanalytical Chemistry 478 (1999): 76-82.


