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**STUDIES REGARDING Au(III) EXTRACTION IN AQUEOUS  
TWO PHASE SYSTEMS BASED ON POLYETHYLEN GLYCOL  
WITH DIFFERENT MOLECULAR WEIGHTS**

BY

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**Abstract.** This study presents the efficiency of Au(III) ions extraction in aqueous two phase systems (ATPS) based on polyethylene glycol (PEG) 40% (w/w) and  $(\text{NH}_4)_2\text{SO}_4$  40% (w/w), in the presence of chloride ions with a concentration of 0.5 mol/L as extracting agents and a pH of 4.5 of the inorganic salt. The influence of two experimental parameters was studied: PEG molecular weight and volume ratio between the two phases. Experimental results showed that with the increasing of the PEG molecular weight the quantity of Au(III) ions extracted in PEG rich phase increases (67.78% for PEG(2000), 75% for PEG(4000) and 86.19% for PEG(6000), values obtained for a volume ratio  $(\text{NH}_4)_2\text{SO}_4$  : PEG of 5:4). Also, the extraction efficiency showed an important decrease for a  $(\text{NH}_4)_2\text{SO}_4$  : PEG volume ratio  $>2$  because of the hydrophobicity of the environment that decreases.

**Keywords:** Au(III) ions extraction; aqueous two phase systems; PEG; green chemistry.

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## 1. Introduction

Over the time, metal ions from ore and industrial wastes were extracted using various methods, such as chemical precipitation, ionic exchange, adsorption on different types of materials, solvent extraction etc. However, these methods have a series of disadvantages, like: high costs, only partial removal of metals from waste water, low selectivity, high consumption of energy, especially when are used for recovery of precious metals ions (Bulgariu and Bulgariu, 2013). In this case, the most efficient method is liquid-liquid extraction, in which the precious metal ions are removed with organic solvents.

The liquid-liquid extraction with organic solvents method can be successfully used for selective separation and concentration of metal ions traces from an aqueous system. This method is efficient also due to the fact that a variety of solvents, extracting agents and aqueous phases can be used. Some of the other advantages of the organic solvents extraction are: the extraction is done in a relatively short time, the method can be adapted to a variety of solutes and experimental conditions (concentration of solute, pH, temperature, ionic strength), the possibility of recycling the solvent. However, the high quantities of solvent required, the high costs, toxicity, inflammability and volatility of organic solvents made it necessary to find other extraction methods, which are not as aggressive for the environment and humans as the methods with organic solvents (Bulgariu and Bulgariu, 2013). One of these methods is extraction in aqueous two phase systems, this method being of interest in the recent years.

The aqueous two phase systems are prepared with two immiscible aqueous phases: a certain water soluble polymer and another hydrophilic polymer (dextran, ficoll) or a suitable inorganic salt (for example:  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{HPO}_4$ ), in specific concentrations (Bulgariu and Bulgariu, 2007). The top phase – rich in PEG – has the same role as the organic solvent from traditional extraction methods, whilst the bottom phase is rich in inorganic salt (Bulgariu *et al.*, 2006; Bulgariu and Bulgariu, 2008; Graber *et al.*, 2000). These systems can be use both for biomolecules and metal ions separation (Rogers *et al.*, 1996).

PEG is the most common polymer used for extraction in aqueous two phase systems because it is not toxic, flammable or volatile, is stable, biodegradable and inexpensive. These advantages eliminate most of the problems linked to environment pollution, which are frequent in traditional extraction methods with organic compounds (Bulgariu, 2006).

A low hydration degree of the metal ions makes it easier to partition between the two phases of the aqueous two phase system. The use of extracting agents that form metal complexes has an important role in decreasing the hydration degree (Bulgariu and Bulgariu, 2007). The extracting agents can be either organic complexing agents, which form with the metal

ions stable chelates, or inorganic complexing anions, which can form with metal ions inorganic complexes, that are easily extracted in PEG rich phase (Bulgariu, 2006).

The use of halide ions in these systems is due to high solubility of halide alkaline salts in water, but also due to low and negative value of Gibbs free energy of hydration, which makes possible the extraction of these ions in PEG rich phase in absence of the metal ions. Moreover, the halide ions are not expensive and are commercially available (Bulgariu and Bulgariu, 2007).

The efficiency of metal ions extraction in aqueous two phase systems has already been proved for heavy metal ions (Pb(II), Cd(II), Zn(II), Co(II), Hg(II)) (Bulgariu and Bulgariu, 2013; Akama *et al.*, 2000; Bulgariu and Bulgariu, 2007; Bulgariu *et al.*, 2006), but also for gold ions (Au(III)) (Bulgariu and Bulgariu, 2011).

In PEG based aqueous two phase systems, the metal ions partition is done between the two phases. The extraction is influenced by physicochemical properties of the phases, which are represented as different hydration media. Therefore, in order to partition from salt rich phase (where the hydration media is well ordered because of the H bonds) to PEG rich phase (where the hydration media is less ordered), a metal ion does not have to strongly interact with water (Bulgariu and Bulgariu, 2006).

This study presents the influence of volume ratio of the two phases from system and the influence of PEG molecular weight over the efficiency of Au(III) ions extraction in PEG – (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> based aqueous two phase systems, with chloride ions as extracting agents. Studies like this are necessary to establish the optimum conditions for extraction, in order to attain extraction % as high as possible, but with small amounts of inorganic salt and PEG.

## 2. Experimental

### 2.1. Materials

The experiments were carried out with 40% (w/w) PEG aqueous solutions prepared by dissolving a suitable quantity of solid PEG with average molecular weights of 2000, 4000 and 6000 g/mol in distilled water. The inorganic salt aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 40% (w/w) was prepared by dissolving the solid salt weighted at technical balance in distilled water.

Sodium chloride solution with a concentration of 1 mol/L was used as extracting agent. The solution was prepared by dissolving the solid sodium chloride, weighted at analytical balance, in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 40% (w/w) stock solution. This way was avoided the decrease of salt rich phase concentration.

A stock solution of 1000 µg/mL solution of AuCl<sub>3</sub> was used for experimental extraction studies.

Starting with the calibration graph, a spectrophotometric method was used to determine the concentration of Au(III) ions from PEG rich phase. The color reagent was Rhodamine R (0.05% w/w) and was prepared by dissolving the solid Rhodamine R in ethanol.

## 2.2. Methods

The extraction systems based on PEG and  $(\text{NH}_4)_2\text{SO}_4$  were prepared in 9 graded tubes. In each tube were added 1 to 8 mL of  $(\text{NH}_4)_2\text{SO}_4$  40% (w/w), 0.5 mL of extracting agent (NaCl 1mol/L) and 0.5 mL of 1000  $\mu\text{g/mL}$   $\text{AuCl}_3$  solution. In the end, volumes of 1 to 9 mL of PEG 40% (w/w) were added in order to adjust the system to 10 mL. The PEG used for experiments had average molecular weight of 2000, 4000 and 6000 g/mol.

The experiments were performed at a temperature of 20°C. The pH of salt stock solution was maintained constant at 4.5. Also, the Au(III) ions concentration was maintained constant throughout the experiments.

The prepared systems were centrifuged for 10 min at 2000 rpm in order to attain a clear separation of the two phases. The volumes of the two phases were read at the tubes graduation after a 24 h rest, then the separation of the phases was realized. The PEG rich phase was carefully extracted and placed into different tubes with Pasteur pipettes.

Different volumes from the PEG rich phase were used for Au(III) ions spectrophotometric analysis with Rhodamine R (500 nm wave length, 1 cm glass cell, against blank solution).

The calibration curve (Fig. 1) was used for determination of Au(III) ions concentration from PEG rich phase. In 25 mL volumetric flasks were added 1 mL of 2N HCl solution, 1 mL of Rhodamine R solution, different volumes of 50  $\mu\text{g/mL}$   $\text{AuCl}_3$ , then the volume was adjusted to 25 mL with distilled water. The absorbance values from spectrophotometric determination were used for the calibration curve.

In order to determine the efficiency of Au(III) ions extraction in PEG based aqueous two phase system, the experimental results were used to calculate the distribution coefficient ( $D_{\text{Au}}$ ) and the extraction percentage ( $E_{\text{Au}}\%$ ), according to Eqs. (1) and (2):

$$D_{\text{Au}} = \frac{c_{\text{Au}}^{\text{PEG}}}{c_{\text{Au}}^{\text{sare}}} \quad (1)$$

$$E_{\text{Au}}\% = \frac{D_{\text{Au}}}{D_{\text{Au}} + \vartheta'} \quad (2)$$

where:  $c_{\text{Au}}^{\text{PEG}}$  and  $c_{\text{Au}}^{\text{sare}}$  represents the Au(III) ions concentration from PEG rich phase and from salt rich phase,  $\mu\text{g/mL}$ ,  $\vartheta'$  represents the volume ratio between the salt rich phase and PEG rich phase.

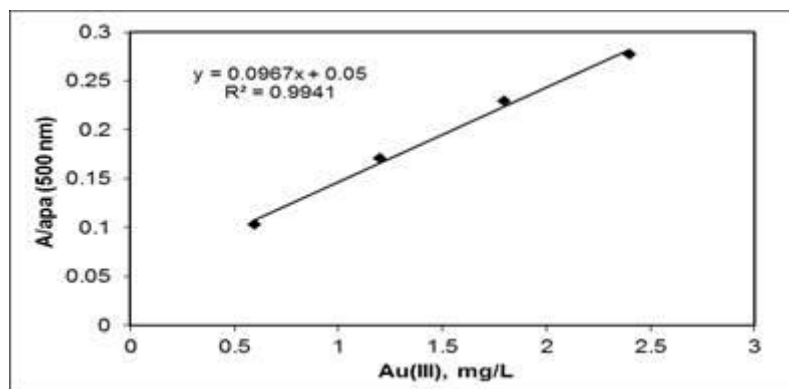


Fig. 1 – The calibration curve obtained for the spectrophotometric determination of Au(III) ions with Rhodamine R ( $\lambda = 500$  nm, 1 cm glass cell).

### 3. Results and Discussions

The chloride ions were chosen as extracting agents in PEG –  $(\text{NH}_4)_2\text{SO}_4$  aqueous two phase system because, as a previous study already showed (Bulgariu and Bulgariu, 2011), they form anionic complexes with gold ( $\text{AuCl}_4^-$ ) with a lower hydration degree, which makes it easier to partition in PEG rich phase.

Fig. 2 shows the variation of distribution coefficient of Au(III) ions ( $D_{\text{Au}}$ ) as a function of the volume ratio of the two phases,  $v_{\text{salt}}/v_{\text{PEG}}$ , for the three average molecular weights studied for PEG (2000, 4000 and 6000 g/mol).

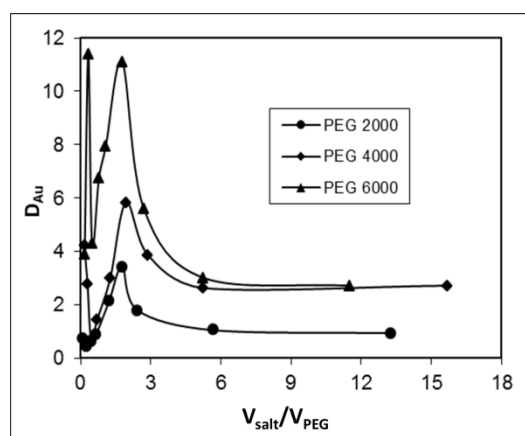


Fig. 2 –  $D_{\text{Au}}$  variation as a function of the volume ratio between the two phases of the system for PEG with average molecular weights of 2000, 4000 and 6000 g/mol.

The highest value for the distribution coefficient for an aqueous two phase system with PEG(2000) was attained for a  $(\text{NH}_4)_2\text{SO}_4$ : PEG volume ratio of 5:4. Also, for a system based on PEG(4000) and the same volume ratio of the phases the distribution coefficient had the highest value.

For PEG(6000) based aqueous two phase systems, the distribution coefficient had the highest value for a  $(\text{NH}_4)_2\text{SO}_4$ : PEG volume ratio of 1:8, but the distribution of Au(III) ions was significant also for a volume ratio of 5:4.

Low values of Au(III) ions distribution in PEG rich phase were obtained for a  $(\text{NH}_4)_2\text{SO}_4$ : PEG volume ratio higher than 2 in all three cases presented.

The efficiency of Au(III) ions extraction in PEG rich phase as a function of the volume ratio of the two phases is illustrated in Fig. 3. As the quantity of inorganic salt from the system increases, the efficiency of the extraction decreases, the decrease being more visible for a volume ratio higher than 2-2.5.

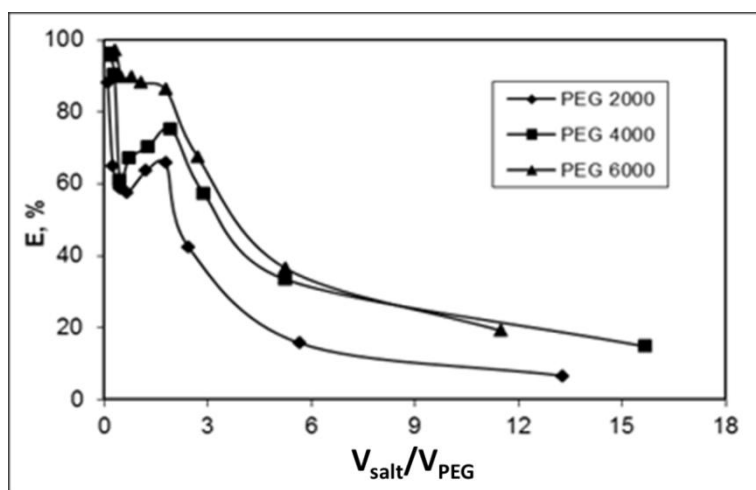


Fig. 3 –  $E_{\text{Au}}\%$  variation as a function of the volume ratio of the two phases of the system for PEG with average molecular weights of 2000, 4000 and 6000 g/mol.

The highest values for the  $E_{\text{Au}}\%$  were obtained for systems in which the  $(\text{NH}_4)_2\text{SO}_4$  was present only as a solvent for NaCl, these systems being prepared only with PEG (2000, 4000, 6000), 1 mol/L NaCl solution and 1000  $\mu\text{g}/\text{mL}$   $\text{AuCl}_3$  solution.

The  $E_{\text{Au}}\%$  of Au(III) ions was significant for PEG(6000) based aqueous two phase systems, when volumes between 1 to 5 mL of the inorganic salt were added to the system (between 86.19% and 97.15%). The  $E_{\text{Au}}\%$  decreases with the decrease of PEG(6000) quantity from the system, the decrease being more significant for a  $(\text{NH}_4)_2\text{SO}_4$ : PEG(6000) volume ratio higher than 6:3.

For systems prepared with PEG(4000) and volumes of inorganic salt between 2 and 5 mL, the  $E_{Au}$ % shows an increase (from 60.94% to 75%). Once the quantity of inorganic salt from system increases, the  $E_{Au}$ % decreases significantly.

In case of systems with PEG(2000) and for a  $(NH_4)_2SO_4$ :PEG volume ratio of 2:7 and 5:4, the  $E_{Au}$ % has close values (64.82% and 65.78%), registering an important decrease, as for PEG(4000) and PEG(6000), from a  $(NH_4)_2SO_4$ :PEG(2000) volume ratio higher than 6:3.

The influence of PEG molecular weight on  $E_{Au}$ % is showed in Fig. 4 for a  $(NH_4)_2SO_4$ : PEG volume ratio of 5:4. As the molecular weight of PEG increases, the Au(III) ions are extracted more efficiently in PEG rich phase. This is the result of the decrease of the OH terminal groups from the structure of PEG with the increase of molecular weight, which increases the hydrophobicity of the environment, making the partition of  $AuCl_4^-$  complexes in PEG rich phase easier.

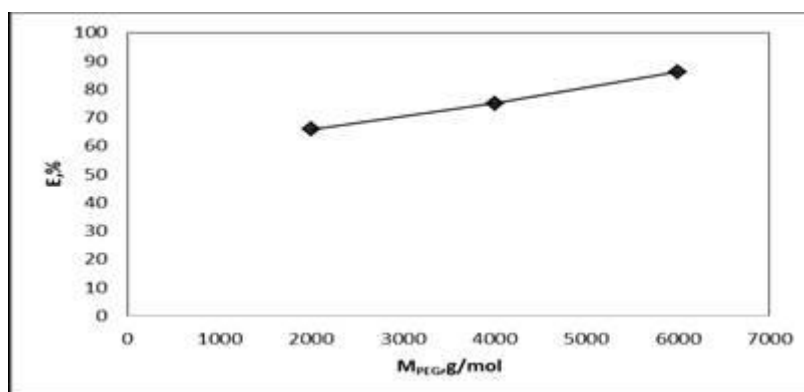


Fig. 4 – The influence of PEG average molecular weight on efficiency of Au(III) ions extraction for a  $(NH_4)_2SO_4$ :PEG volume ratio of 5:4.

#### 4. Conclusions

The influence of PEG molecular weight and volume ratio between the 40% (w/w)  $(NH_4)_2SO_4$  solution and 40% (w/w) PEG solution on efficiency of Au(III) ions extraction was investigated in this study.

Considering that the previous studies showed that the extraction is improved if extracting agents are added to the system, which lead to a low hydration degree of metal complexes that partition easier into PEG rich phase, the experiments were performed with extracting agents.

The results showed that with the increasing of the average molecular weight of PEG, the quantity of Au(III) ions extracted into PEG rich phase increases, this being the result of the hydrophobicity of PEG rich phase. The

studies showed also that the volume ratio of the two phases has an influence on extraction, the optimum value for all three average molecular weights of PEG studied being 5:4. For higher quantities of inorganic salt, the extraction of Au(III) ions in PEG rich phase becomes insignificant.

## REFERENCES

- Akama Y., Ito M., Tanaka S., *Selective Separation of Cadmium from Cobalt, Copper, Iron (III) and Zinc by Water-Based Two-Phase System of Tetrabutylammonium Bromide*, *Talanta*, **53**, 645-650 (2000).
- Bulgariu L., *Studii privind extracția cu solvenți a unor ioni metalici toxici*, Ph.D. Thesis, Iași, 2006.
- Bulgariu L., Bulgariu D., *Hg(II) Extraction in a PEG-Based Aqueous Two-Phase System in Presence of Halide Ions. I. Liquid Phase Analysis*, *Central European Journal of Chemistry*, **4**, 2, 246-257, DOI: 10.2478/s11532-006-0009-1 (2006).
- Bulgariu L., Bulgariu D., Sârghie I., Măluțan T., *Cd(II) Extraction in PEG-Based Two-Phase Aqueous Systems in the Presence of Iodide Ions. Analysis of PEG-Rich Solid Phases*, *Central European Journal of Chemistry*, **5**, 1, 291-302, DOI: 10.2478/s11532-006-0048-7 (2006).
- Bulgariu L., Bulgariu D., *The Partition Behavior of Zn(II) Using Halide Ions Extractants in Aqueous PEG-Based Two-Phase Systems*, *Separation Science and Technology*, **42**, 1093-1106 (2007).
- Bulgariu L., Bulgariu D., *Extraction of Metal Ions in Aqueous Polyethylene Glycol-Inorganic Salt Two-Phase Systems in the Presence of Inorganic Extractants: Correlation Between Extraction Behavior and Stability Constants of Extracted Species*, *Journal of Chromatography*, **1196-1197**, 117-124 (2008).
- Bulgariu L., Bulgariu D., *Extraction of Gold (III) from Chloride Media in Aqueous Polyethylene Glycol-Based Two-Phase System*, *Separation and Purification Technology*, **80**, 620-625 (2011).
- Bulgariu L., Bulgariu D., *Selective Extraction of Hg(II), Cd(II) and Zn(II) Ions from Aqueous Media by a Green Chemistry Procedure Using Aqueous Two-Phase Systems*, *Separation and Purification Technology*, **118**, 209-216 (2013).
- Graber T.A., Andrews B.A., Asenjo J.A., *Model for the Partition of Metal Ions in Aqueous Two-Phase Systems*, *Journal of Chromatography B*, **743**, 57-64 (2000).
- Rogers R.D., Bond A.H., Bauer C.B., Zhang J., Griffin S.T., *Metal Ion Separations in Polyethylene Glycol-Based Aqueous Biphasic Systems: Correlation of Partitioning Behavior with Available Thermodynamic Hydration Data*, *Journal of Chromatography B*, **680**, 221-229 (1996).



STUDIU PRIVIND EXTRACȚIA Au(III) ÎN SISTEME  
CU DOUĂ FAZE APOASE FORMATE DIN POLIETILENGLICOL CU  
DIFERITE MASE MOLECULARE

(Rezumat)

În acest studiu este prezentată eficiența extracției ionilor de Au(III) în sisteme cu două faze apoase formate din polietilenglicol (PEG) 40% și  $(\text{NH}_4)_2\text{SO}_4$  40%, în prezența ionilor clorură ca agenți de extracție, având o concentrație de 1M, și la un pH al sării anorganice de 4.5. Pentru aceasta s-a urmărit influența a doi parametri experimentali: masa moleculară a PEG și raportul volumic dintre cele două faze ale sistemului de extracție. Rezultatele obținute în urma determinărilor spectrofotometrice au arătat că o dată cu creșterea masei moleculare a PEG crește și cantitatea de Au(III) care trece în faza bogată în PEG (67.78% pentru PEG(2000), 75% pentru PEG(4000) și 86.19% pentru PEG(6000), valori obținute pentru un raport volumic  $(\text{NH}_4)_2\text{SO}_4$  – PEG de 5:4). De asemenea, pentru un raport volumic  $(\text{NH}_4)_2\text{SO}_4$  – PEG mai mare de 2, eficiența extracției prezintă o scădere semnificativă datorită scăderii hidrofobicității mediului.