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EFFICIENT RECOVERY OF METALS FROM AQUEOUS MEDIA BY TWO PHASE MICROEMULSION SYSTEM

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Two nonionic microemulsions for heavy metal recovery from a synthetic solution have been investigated. The constructed pseudo ternary phase diagrams presented a large Winsor II domain which is preferred for metals ions recovery. The results showed that 4 mol·L^{-1} sodium thiocyanate is the optimum concentration for cobalt salt recovering in 0.05 mol·L^{-1} concentration. The maximum amount of cobalt salt that can be recovered using the optimum sodium thiocyanate concentration was 0.1 mol·L^{-1} for both systems. This investigation is important from economical and environmental points of view for the recovery of heavy metals from aqueous or solid wastes.

Keywords: ternary phase diagrams, microemulsion, recovery efficiency

1. Introduction

High rate of industrial growth imposed by the increasing requirements of the world market is a major cause for the release of heavy metals into the environment [1]. Industries such as tannery, metallurgy, dyes, explosives, ceramics, paints, textile, etc. disposed in the environment significant amounts of heavy metals both as aqueous waste stream and solid waste [2].

By recycling metals from these wastes, not only the risks to environmental and public health could be avoided, but also the shortage of some metals used as the raw materials during production of electronic devices could be accomplished [3].

Through a substantial number of critical metals contained in the solid wastes, cobalt is of particular significance. It is used to generate deep blue glass,

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ceramics, pottery and tiles, paint pigments, batteries, catalysts and in combination with other metals it is used to make alloys which are employed to create strong magnets, jet engines and gas turbine engines [1, 4]. Consequently, the recovery of cobalt from these wastes represents an important issue as it has a potential economic value as non-renewable (and increasingly rare) natural resource [5, 6].

Moreover, in the case of aqueous waste streams, the presence of heavy metals has become a serious problem due to their persistent nature in the environment [1, 7].

Beside its economically importance, cobalt plays a crucial role in biological systems, as it is part of vitamin B12, which is essential for human health [2, 8-10]. However, the ingestion or inhalation of large doses of this analyte, may lead to accumulation in muscle, liver and gills causing toxic effects [8, 11]. Also, it may change the abundance of other compounds and their reactivity, determining neurotoxicological and genotoxic disorders in human beings. In chronic cases, the excess of cobalt may cause cancer [8]. Therefore, it is necessary to treat industrial effluents before discharge into the aqueous streams [1].

Many papers have been published regarding the removal of metal ions from industrial effluents. The most conventional methods for treating such effluents are ion exchange, chemical precipitation, adsorption, biosorption, reverse osmosis and membrane filtration [1, 2, 6].

The utilization of microemulsified systems has been introduced as an innovative and very efficient method [12-14], compared with other conventional methods that present low reactivity, low bio degradability, high thermal, chemical and photolytic stability [15-19]. In order to recover metallic cations from aqueous phase the microemulsion must be oil continuous. Hence, Winsor II system (WII), which represent water in oil microemulsion with excess of water (W/O, W) is usually used for this purpose as it is very effective for the improvement of extractability as well as for the acceleration of extraction due to an enormous rise of the microinterfacial surface area in the W/O microemulsion phase [20-22]. Various type of metallic cations, such as chromium [23-25], copper [26], gold [27], lanthanide [28-30] and other metals [2, 31, 32] can be extracted by this type of microemulsion and trapped in the inner aqueous phase microemulsion. The extraction of cobalt has been investigated using bis (2-ethylhexyl) sulfosuccinate sodium salt (AOT)/n-pentanol/n-heptane/NaCl or Cetyltrimethyl-ammonium bromide (CTMAB)/n-pentanol/heptane/HCl Winsor II microemulsions, where CTMAB or AOT are used as cationic or anionic surfactants, *n*-pentanol as cosurfactant and heptane as organic phase [4, 10].

The aim of the present study is to reduce the effective cost of the process and the toxicity of the systems by introducing two non-ionic environmental-friendly systems that can be used to investigate the recovery of cobalt ions from synthetic aqueous solutions by Winsor II microemulsions. The proposed systems contain polyoxyethylene (4) lauryl ether (Brij30) as nonionic surfactant and ethyl acetate or butyl acetate as organic phases. The optimum sodium thiocyanate concentration and the maximum metal ions concentration that can be removed using certain thiocyanate concentration were investigated. Prior to these studies, the pseudo-ternary phase diagrams were constructed at room temperature.

2. Experimental section

2.1. Materials

Ethyl acetate (EtOAc) 99.8% and butyl acetate (BuOAc) 99% purchased from Sigma-Aldrich were used as organic phases. Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$ and sodium thiocyanate, NaSCN, were supplied by Merck. Nonionic surfactant, polyoxyethylene (4) lauryl ether (Brij 30) with molecular formula $C_{12}H_{25}(OCH_2CH_2)_4OH$ was provided from Across Organics. Distilled water was used for the preparation of the microemulsion samples. All chemicals were used as received without further purification or distillation.

2.2. Methods

Phase diagram construction. In order to find out the region where microemulsion (μE) can be formed, pseudo ternary phase diagrams were constructed using the surfactant titration method at room temperature (298 K), following the procedure described in reference [33]. This involves successive addition of small quantities of surfactant in established water/oil ratio. The samples were taken in sealed test tube and vigorously shaken to ensure a proper mixing of the components.

Recovery procedure. The microemulsions used in this study were composed by water, sodium thiocyanate solution, Brij30 and organic phase (EtOAc or BuOAc). In order to recover cobalt ions, the synthetic aqueous phase was obtained by dissolving appropriate quantities of cobalt nitrate in distilled water. Sodium thiocyanate salt was used as a complexing agent for cobalt ions and was dissolved in a mixture of water:acetone 1:1 (w/w) . The Winsor II (WII) compositions used in this study for cobalt ions extraction are presented in Table 1.

The detailed experimental recovery was fully illustrated by the authors elsewhere [34-36]. The experiments were carried out in a hermetically sealed glass container in order to preserve the composition of the system, as the organic phase contains volatile compounds. The microemulsion was shaken vigorously for about 1 min, and was allowed to equilibrate at room temperature for a minimum of 12 h. Finally, two clear phases were obtained: the upper phase represented by

W/O microemulsion and the down phase represented by clean aqueous phase. The microemulsion is strongly colored due to its rich content in cobalt thiocyanate complex, while the aqueous phase is colorless. At the end of the procedure, after the thermodynamic equilibrium was achieved, the two phases were collected separately using syringes.

UV-VIS measurements. After the two phases separation, NaSCN 0.1 mol·L^{-1} was added to the aqueous phase in order to react with the remained metal ions. Spectrophotometric measurements of cobalt concentration in aqueous solution were performed with a Jasco UV–VIS spectrophotometer V-670 type, using glass cuvettes with 1.00 cm optical path length and the cobalt concentration in organic solution was calculated by mass balance.

Recovery efficiency. The recovery efficiency (E%) was calculated using the following formula:

$$E\% = \frac{C_{in} - C_{fin}}{C_{in}} \times 100 \qquad (1)$$

where: $C_{in} = \frac{Abs_{in}}{\varepsilon \times l} \times DF$ and $C_{fin} = \frac{Abs_{fin}}{\varepsilon \times l} \times DF$

ε = molar extinction coefficient (1709.82 M^{-1}·cm^{-1}) obtained from the calibration curve of cobalt thiocyanate complex, l = flow-cell path length (1 cm), C_{in} = initial cobalt concentration in aqueous solution, C_{fin} = final cobalt concentration in aqueous phase after cobalt recovery, Abs_{in} = initial cobalt thiocyanate complex absorbance, Abs_{fin} = absorbance of cobalt complex in aqueous phase after cobalt recovery, DF = dilution factor of cobalt thiocyanate solution.

All the measurements were performed in triplicate and the precision of the methods was found to be 1-5% for diagram phase construction and 1-2% for UV-VIS measurements.

3. Results and discussion

3.1. Phase diagrams in water/nonionic surfactant/acetate esters/acetone pseudo ternary systems

The pseudo ternary phase diagram was visually determined by mixing the surfactant with oil/water mixtures until a clear, homogenous and transparent solution appeared. The nonionic surfactant has been used as self-assembling agent. The phase diagrams drawn in pseudo ternary systems water/Brij30/acetate esters/acetone, realized at room temperature, are shown in Fig. 1. The acetate esters used in this study are ethyl acetate and butyl acetate and the aqueous phase is represented by a cobalt thiocyanate complex obtained by mixing cobalt nitrate

0.05 mol·L^{-1} (dissolved in water) with sodium thiocyanate 5 mol·L^{-1} (dissolved in a mixture of water:acetone 1:1 (w:w)). From Fig. 1 one can observe that in both cases the solubilisation of water and organic solvent increases proportionally with the surfactant concentration for a given water/oil volumetric ratio, R = V_W/V_O. In the case of Brij30/EtOAc/$Co(SCN)_4^{2-}$ two microemulsion systems are formed, namely Winsor IV (WIV) and WII, compared with Brij30/BuOAc/$Co(SCN)_4^{2-}$ system, when a small region of Winsor III (WIII) microemulsion can be observed. When using the system with BuOAc, for R > 1, the WII microemulsion area was increased.

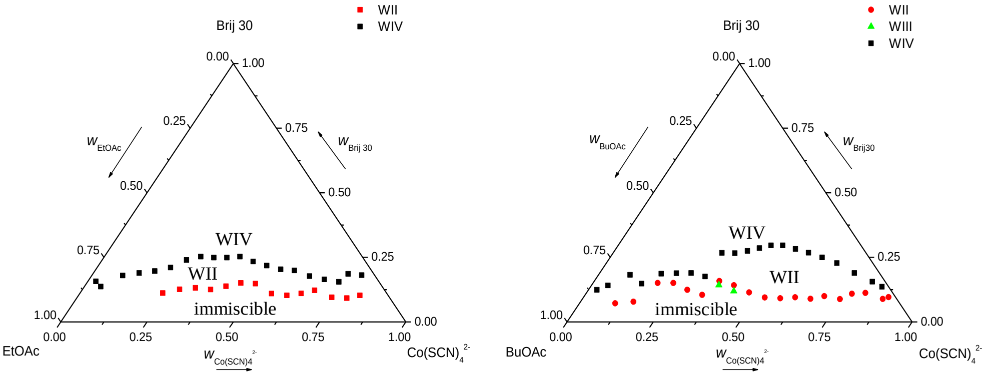

Fig. 1. Phase diagrams of pseudo ternary systems: a) Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone; b) Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone; where *w* = mass fraction

From the phase diagrams (Fig. 1), two WII compositions were chosen for the further studies (Table 1).

Table 1

Winsor II compositions for Brij 30/BuOAc/$Co(SCN)_4^{2-}$/acetone and Brij 30/EtOAc/$Co(SCN)_4^{2-}$/acetone systems

System	$^*w_{Brij30}$	$w_{Organic\ phase}$	$w_{Aqueous\ phase}$ (66.66% Co^{2+} + 33.33% SCN^-)
Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone	0.10	0.135	0.765
Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone	0.10	0.09	0.81

$^*w$ = mass fraction

3.2. The optimization of cobalt extraction from aqueous media by microemulsion

3.2.1 Choosing the optimum sodium thiocyanate concentration for cobalt recovery efficiency

The sodium thiocyanate concentration influences the transfer of cobalt ions from the aqueous phase into the microemulsion phase. In order to study this aspect, different NaSCN concentrations in the range of 0.5 - 10 mol·L^{-1} were investigated for both systems. The cobalt nitrate concentration was 0.05 mol·L^{-1} and was kept constant.

The electronic spectra of aqueous phase treated with NaSCN 0.1 mol/L after cobalt ions removal are presented in Fig. 2. For Brij30/BuOAc/Co(SCN)$_4^{2-}$/acetone system one can observe a decrease of the maximum absorbance values with the increasing of sodium thiocyanate concentration. More exactly, using 4 mol·L^{-1} NaSCN concentration in the initial composition, all cobalt ions were extracted from the aqueous phase. Thus, the increasing of sodium thiocyanate concentration from 0.5 to 10 mol·L^{-1} leads to an increasing trend of the recovery yields in the range of 80 to 99.7% for the system with butyl acetate as organic phase (Fig. 3).

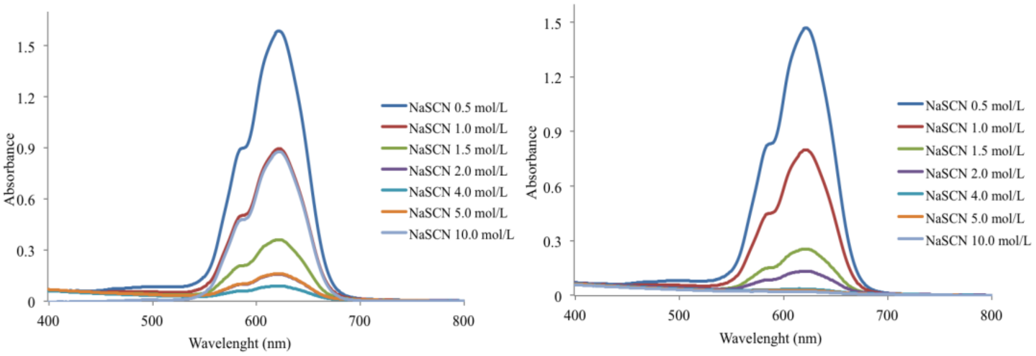

Fig. 2. Electronic spectra of aqueous phase treated with NaSCN 0.1 mol·L^{-1} after extraction of cobalt nitrate 0.05 mol·L^{-1} using different sodium thiocyanate concentration in the case of: a) Brij30/EtOAc/Co(SCN)$_4^{2-}$/acetone and b) Brij30/BuOAc/Co(SCN)$_4^{2-}$/acetone

In the case of Brij30/EtOAc/Co(SCN)$_4^{2-}$/acetone system, the lowest maximum absorbance value, corresponding to the best cobalt ions recovery, was also obtained using NaSCN 4 mol·L^{-1}. Therefore, the recovery efficiency increases from 77.2 % (at 0.5 mol·L^{-1} NaSCN) to 98.7 % (at 4 mol·L^{-1} NaSCN). Above this concentration, an increase of maximum absorbance value can be observed corresponding to a decrease of cobalt recovery yield up to 87.4 %.

By increasing the NaSCN concentration over 4 mol·L^{-1} in Brij30/EtOAc/Co(SCN)$_4^{2-}$/acetone system, the distribution of the sodium thiocyanate between the aqueous and the microemulsion phases leads to a similar metallic cations behavior.

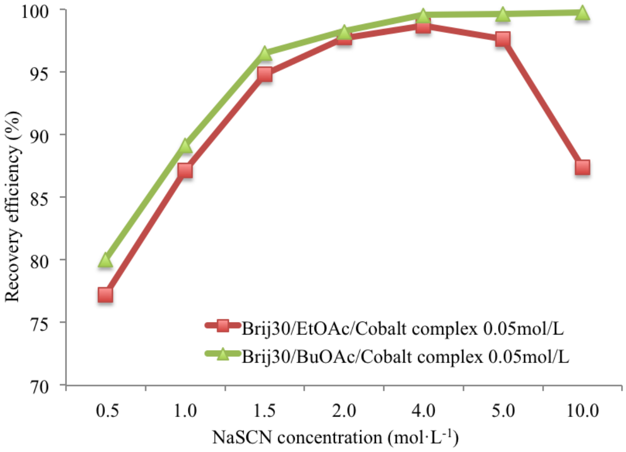

Fig. 3. Effect of NaSCN concentration on cobalt recovery efficiency for Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone systems

The lowest maximum absorbance values for both systems were obtained using 4 mol·L^{-1} NaSCN concentration, which correspond to a good cobalt ions recovery from aqueous media. The electronic spectra of the aqueous phases are presented in Fig. 4

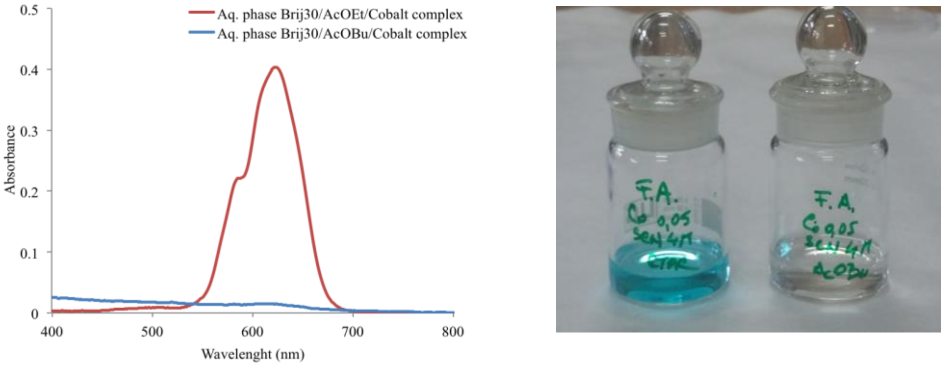

Fig. 4. Electronic spectra of aqueous phases after cobalt ions recovery with NaSCN 4 mol·L^{-1} for Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone systems

In order to find out if the complexation of the remained cobalt ions in the aqueous phase is influenced by the sodium thiocyanate concentration, which is added after the two phases separation, several NaSCN concentration between 0 – 2.5 mol·L^{-1} (dissolved in a mixture of water:acetone 1:1 ratio) were investigated.

From Fig. 5 one can notice that the maximum absorbance values vary from 0.078 (NaSCN 0 mol·L^{-1}) to 0.105 (NaSCN 2.5 mol·L^{-1}) in the case of Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and from 0.028 (NaSCN 0 mol·L^{-1}) to 0.042 (NaSCN 2.5 mol·L^{-1}) in the case of Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone pointing out an insignificant influence of NaSCN concentration.

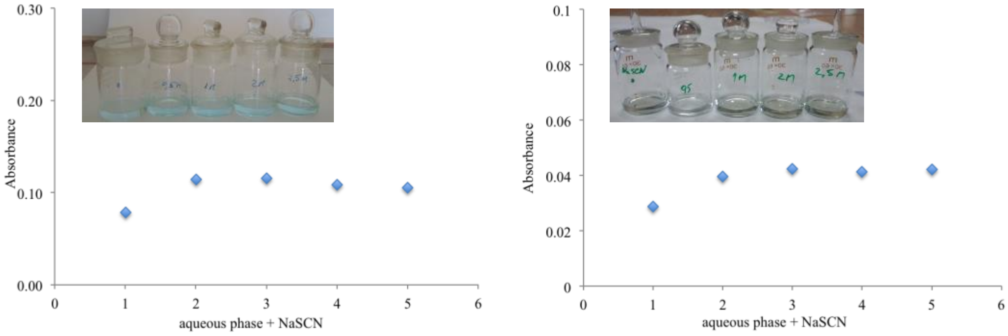

Fig. 5. Effect of NaSCN concentration (dissolved in water:acetone 1:1 ratio) on absorbance values for Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone systems where 1) aq. ph. + NaSCN 0 mol·L^{-1}, 2) aq. ph. + NaSCN 0.5 mol·L^{-1}, 3) aq. ph. + NaSCN 1 mol·L^{-1}, 4) aq. ph. + NaSCN 2 mol·L^{-1}, 5) aq. ph. + NaSCN 2.5 mol·L^{-1}

3.2.2. Loading capacity of the microemulsion systems

To find out what is the maximum cobalt concentration that can be recovered using 4 mol·L^{-1} NaSCN concentration, five different concentrations of cobalt nitrate in the range of 0.05 mol·L^{-1} - 0.15 mol·L^{-1} have been used. In Fig. 6 are presented the electronic spectra of aqueous phases treated with sodium thiocyanate 0.1 mol·L^{-1} after cobalt ions recovery. As it was expected, the absorbance value increased with the concentration of cobalt salt.

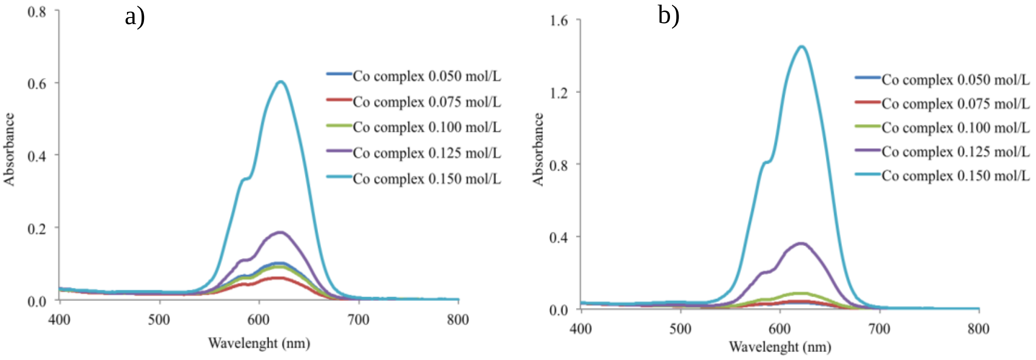

Fig. 6. Electronic spectra of aqueous phase treated with NaSCN 0.1 mol·L^{-1} after recovery of different cobalt nitrate concentration using sodium thiocyanate 4 mol·L^{-1} in the case of: a) Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and b) Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone

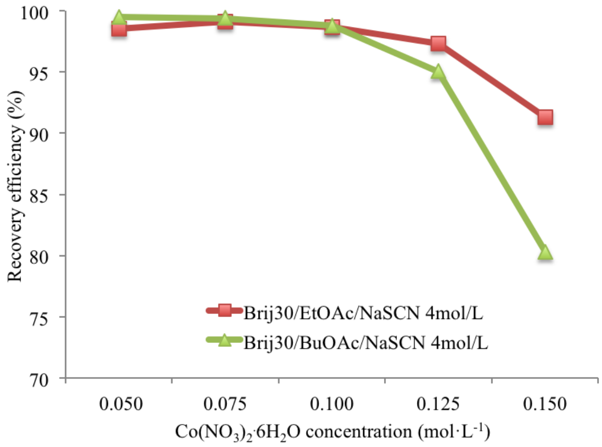

Fig. 7. Effect of $Co(NO_3)_2 \cdot 6H_2O$ concentration on cobalt recovery efficiency for Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone and Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone systems

The recovery efficiency of cobalt ions from aqueous media was calculated based on the electronic spectra previously presented. By increasing the cobalt nitrate concentration from 0.050 to 0.100 $mol \cdot L^{-1}$ no significant decrease of recovery efficiency can be observed (Fig. 7). At cobalt concentrations higher than 0.100 $mol \cdot L^{-1}$ the Brij30/EtOAc/$Co(SCN)_4^{2-}$/acetone system presented better efficiency than the Brij30/BuOAc/$Co(SCN)_4^{2-}$/acetone system.

4. Conclusions

The phase diagrams in pseudo ternary systems composed by aqueous solution of cobalt thiocyanate complex, Brij 30 and ethyl acetate or butyl acetate have been drawn in order to determine the microemulsion domains. Based on these diagrams, two compositions containing 10% surfactant were chosen to study the recovery of cobalt ions from a synthetic aqueous solution.

The experimental results obtained from the variation of NaSCN concentration in the range of 0.5 - 10 $mol \cdot L^{-1}$ showed that in both polyoxyethylene (4) lauryl ether/Ethyl acetate/water and polyoxyethylene (4) lauryl ether/Butyl acetate/water systems, the best cobalt ions recovery efficiency were obtained using 4 $mol \cdot L^{-1}$ NaSCN concentration (when the cobalt salt concentration was 0.05 $mol \cdot L^{-1}$).

While keeping the NaSCN concentration constant (4 $mol \cdot L^{-1}$), the cobalt salt concentration has been increased in the range of 0.05 - 0.15 $mol \cdot L^{-1}$. Up to 0.10 $mol \cdot L^{-1}$ cobalt salt concentration no significant decrease of the recovery efficiency can be observed. Above this concentration, the system containing ethyl acetate as organic phase presented higher efficiency than the system with butyl acetate.

In conclusion, the results of this paper showed that both polyoxyethylene (4) lauryl ether/Ethyl acetate/water and polyoxyethylene (4) lauryl ether/Butyl acetate/water systems can be successfully used to transfer heavy metals ions from aqueous phase into the microemulsion phase. Thus, by removing the metal ions from different wastes, not only the environmental risk could be avoided, but also the shortage of these metals used as the raw materials during the production of some electronic devices could be fulfilled.

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