Conference Paper

"Green" Extractants in the Recovery Processes of Non-ferrous Metal Ions from Technological Solutions

Andrey A. Voshkin[1,2], Yulia A. Zakhodyaeva[1], and Inna V. Zinov'eva[1]

[1]Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky Prospect, Moscow, 119991 Russia
[2]MIREA – Russian Technological University, 86 Vernadsky Avenue, Moscow, 119571 Russia

Abstract

The extraction of non-ferrous metal ions (Co, Ni, Cu, Al) from chloride solutions with poly(propylene glycol) 425 was studied. The values of the distribution coefficients and the degree of metal ions extraction are determined in the system under study. The mechanism of metal extraction in the poly(propylene glycol) 425 – sodium chloride – water extraction system in the presence of KSCN is described. The possibility of selective extraction of Co (II), Ni (II), Cu (II) and Al (III) from chloride solutions with poly(propylene glycol) 425 in the presence of KSCN is shown.

Keywords: aqueous two-phase system, metal extraction, liquid–liquid equilibria, e-waste, poly(propylene glycol), sodium chloride

Corresponding Author:
Andrey A. Voshkin
voshkin@igic.ras.ru

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1. Introduction

A huge number of new electronic devices are appearing in the modern world, and it causes an increasing number of electronic wastes that contain toxic heavy metals (Hg, Pb) and various aggressive chemicals, on the one hand, and a number of valuable metals on the other hand [1–5]. Surface and underground waters around the landfills, where the waste in question are disposed of as municipal waste, are especially highly polluted with toxic metals, so failure to address the problem of their disposal can lead to serious negative environmental impact. Electronic waste, such as printed circuit boards, contains precious metals such as gold, silver, platinum, as well as a number of non-ferrous metals (Cu, Al, Co, Ni), etc. Today, an environmentally friendly and cost-effective technology that would allow processing waste electronic devices to produce products of adequate quality does not exist. Therefore, it is important and relevant to create new environmentally friendly technological processes for the separation of valuable components from aqueous solutions with the subsequent production of pure substances [6–15].

This paper presents the results of experimental studies of Co (II), Ni (II), Cu (II) and Al (III) extraction from chloride solutions with an aqueous two-phase system based on poly(propylene glycol) 425.

2. Experimental

The following chemicals were used in this study: cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, $\geq$ 99.0%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, $\geq$ 99.0%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, $\geq$ 99.0%), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, $\geq$ 99.0%), sodium chloride produced by Sigma-Aldrich (ACS chemical, $\geq$ 99.0%), 4-(2-pyridylazo)resorcinol (PAR) (CAS no. 1141-59-9), xylenol orange (CAS no. 3618-43-7), hydrochloric acid (chemically pure), and poly(propylene glycol) with a molecular weight of 425 produced by Acros Organics.

Double distilled water was used to prepare the solutions. All chemicals were used as is, without additional purification. The initial solutions of extracted metals chloride were obtained by dissolving precisely weighed quantities in double distilled water slightly acidized with hydrochloric acid (pH = 2.5) in order to prevent the generation of hydroxide metal formations.

All extraction experiments were carried out at a temperature of 25°C and an atmospheric pressure of $\approx$100 kPa in a temperature-controlled shaker (Enviro-Genie SI-1202, Scientific Industries, Inc., USA).

To create the extraction system, poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water of poly(propylene glycol) 425, aliquot and sodium chloride were dissolved in double distilled water and mixed until two-phase equilibrium was generated. All the experiments were conducted in graduated centrifugal test tubes (15 mL). The chemicals were weighed on an analytical balance with an accuracy of $\pm$0.0001 g (HR-100AZ, AND Company, Korea). Then, an aliquot of extracted metal salt acidized with hydrochloric acid and a 0.1 mol·L^{-1} (pH = 2.5) concentrated were added to the created aqueous two-phase system.

The test tubes were placed into the temperature-controlled shaker and intensely mixed at constant temperature over the course at a rotation speed of 30 rpm to reach the thermodynamic equilibrium (20 min). Then, the samples were centrifuged at 2,500 rpm for 10 minutes in order to facilitate the phase separation in the centrifuge (CM-6MT, SIA ELMI, Latvia). The volumes of the top and bottom phases were measured as well. Then, the phases were separated and concentration of metal ions were determined in both phases.

The quantitative estimation of metals in the initial solution in the equilibrium polymer and salt phases after the extraction was performed using the spectrophotometric method based on obtaining complexes of metals with 4-(2-pyridylazo)resorcinol absorbing in the visible spectrum had the following wavelengths, nm: 492 (Ni), 508 (Co), and 494 (Cu) in the Cary-60 spectrophotometer (Agilent Tech., USA) (wavelength accuracy ±0.06 nm). The concentration of aluminum was also determined spectrophotometrically using xylenol orange at pH = 3.5 and a wavelength of 550 nm. The concentration determination error was < 5%.

Quantitative determination of thiocyanate ions in solution was carried out by spectrophotometric method with iron (III) chloride at 460 nm.

Absorption spectra in the wavelength range from 190 to 1000 nm were recorded on the device *Cary*-60 (*Agilent Tech.*) in a quartz cell with a thickness of 1 and 10 mm relative to a blank solution.

For the purpose of the quantitative description and efficiency estimation of metal ions' extraction recovery, the distribution coefficient (D_M) was used, which was determined by equation:

$$D_M = \frac{[M]_{TP}}{[M]_{BP}} \tag{1}$$

where $[M]_{TP}$ is the metal concentration in the top phase, mol/L, $[M]_{BP}$ is the metal concentration in the bottom phase, mol/L.

All the obtained results were reproduced three times and processed via mathematical statistics methods.

3. Results and Discussion

The ions distribution of Co^{2+}, Ni^{2+}, Cu^{2+} and Al^{3+} ($[M]_{in}$ = 0.01 mol/L) in the extraction system poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water was studied. It is established that the extraction of the studied metals occurs with very low distribution coefficients (D_{Co} = 0.12, D_{Ni} = 0.18, D_{Cu} = 0.24, D_{Al} = 0).

To increase the extraction of metal ions into aqueous two-phase systems, complexing agents of an organic and inorganic nature (dithizone, PAN, arsenazo III, eriochrome black T, thoron, alkali metal iodides, etc.) are additionally introduced. These reagents provide effective extraction of metal ions into aqueous two-phase systems, however, due to the high toxicity of these complexing agents, these extraction systems lose their attractiveness.

Thiocyanate complexes are widely used in analytical chemistry for photometric and extraction-photometric determination of a number of metal ions. We used potassium

thiocyanate as a complexing agent for extracting Co^{2+}, Ni^{2+}, Cu^{2+}, Al^{3+} metal ions from dilute chloride solutions.

Extraction of metals from thiocyanate solutions is in many ways similar to the extraction of metal halide compounds, however, thiocyanate metal complexes are much larger than the corresponding compounds with halide ions; therefore, they are less hydrated and more strongly disrupt the water structure, which results in an increase in the extractability of metal cation ions into the polymer phase.

Experimental studies of Co^{2+}, Ni^{2+}, Cu^{2+}, Al^{3+} metal ions extraction were carried out in the poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water system in the presence of KSCN in an amount of from 0.001 to 0.011 mol/L. The dependence of the distribution coefficient of metal ions on the KSCN content was obtained (Fig. 1).
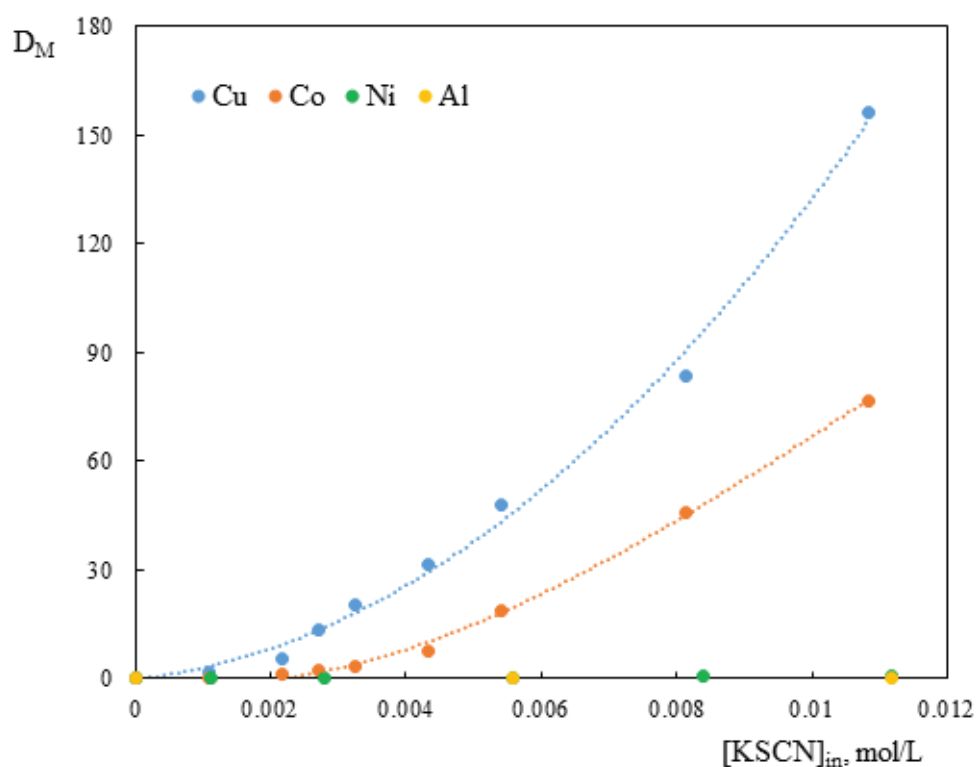

Figure 1: Dependence of the distribution coefficient of Co (II), Ni (II), Cu (II), and Al (III) on the KSCN content in the system with poly(propylene glycol) 425 (30 wt%) and sodium chloride (8 wt%). The initial concentration of metal in the extraction system is 0.01 mol/L.

As can be seen, the introduction of potassium thiocyanate into the extraction system leads to an increase in the distribution coefficients of Co^{2+} and Cu^{2+} ions and practically does not affect the extraction of Ni^{2+} and Al^{3+} ions. Varying the KSCN content in the system allows selective extraction of metal ions from solutions. The difference in the extractability of metal ions is determined by their ability to complex with the thiocyanate ion.

In the absence of the extracting species (SCN⁻), all metallic ions concentrated in the bottom phase. This behavior is caused by specific interactions of the metallic cations with the chloride anion, thereby forming a complex species [16]:

$$M^{n+}_{aq} + xCl^-_{aq} \leftrightarrow MCl_x^{(x-n)-}{}_{aq} \tag{2}$$
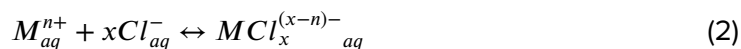
$$K = \frac{\gamma_{MCl_x^{(x-n)-}} \cdot [MCl_x^{(x-n)-}]}{\gamma_{M^{n+}} \cdot [M^{n+}] \cdot \gamma_{Cl^-}^x \cdot [Cl^-]^x} \tag{3}$$

where K – the standard thermodynamic constant of formation of the metal–chloride complex, γ – the activity coefficient of the ionic species, and $[X]$ – the concentration of ionic species.

The stability constant depends on the electronic structure of the central metal ion. The metal extraction efficiency is inversely proportional to the constant of formation of the complex if only the metal–chloride interactions are considered.

However, an incremental addition in the amount of potassium thiocyanate affect the extraction behavior of the metallic ions, and the metal extraction percentages were observed to increase. This is due to the formation of different anionic complexes between the metallic ion and the thiocyanate species and also because of the ultimate preferential transfer of such complexes from the bottom phase to the phase that is more concentrated in top phase. The formation process of the new complexes and the stability constant are represented by Eqs. (4) and (5) [16]:

$$M^{n+}_{aq} + xSCN^-_{aq} \leftrightarrow M(SCN)_x^{(x-n)-}{}_{aq} \tag{4}$$
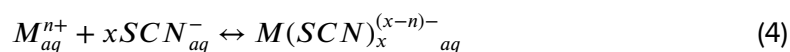
$$K = \frac{\gamma_{M(SCN)_x^{(x-n)-}} \cdot [M(SCN)_x^{(x-n)-}]}{\gamma_{M^{n+}} \cdot [M^{n+}] \cdot \gamma_{SCN^-}^x \cdot [SCN^-]^x} \tag{5}$$

The extraction of a metallic complex into the top phase is governed by two main factors: the competition between the anionic binding agents (SCN⁻ versus Cl⁻) for the metal and the interaction of the resultant complex with the macromolecule PPG present in the top phase.

Metal complexes with thiocyanate ion are more stable than systems with chloride ion. After the formation of the complexes with thiocyanate ion, they are spontaneously transferred to the top phase as a result of polymer and anion interactions. As the concentration of the anion increases in the top phase, its concentration in the bottom phase is reduced, which causes the equilibrium shown by Eq. 4 to be displaced toward the formation of the metal–SCN⁻ complex.

Figure 2 shows the bilogarithmic dependence of the Co (II), Ni (II), Cu (II), and Al (III) distribution coefficient in the poly(propylene glycol) 425 (30 wt%) - sodium chloride (8

wt%) - water extraction system on the concentration of SCN⁻ polymer phase. As can be seen, the dependences are straightforward with an inclination angle for Co (II) and Cu (II) equal to 3, Ni (II) - 1 and Al (III) - 0. According to the data obtained, we can conclude that the components pass into the polymer phase in the following proportions: Co^{2+}: SCN^- = 1: 3; Cu^{2+}: SCN^- = 1: 3 and Ni^{2+}: SCN^- = 1: 1. The low values of coefficient distribution for the Ni(II) ions in these systems may be attributed to the formation of complexes, which interact weakly with the polymer. Aluminum does not form stable thiocyanate complexes, so it does not pass into the polymer phase.
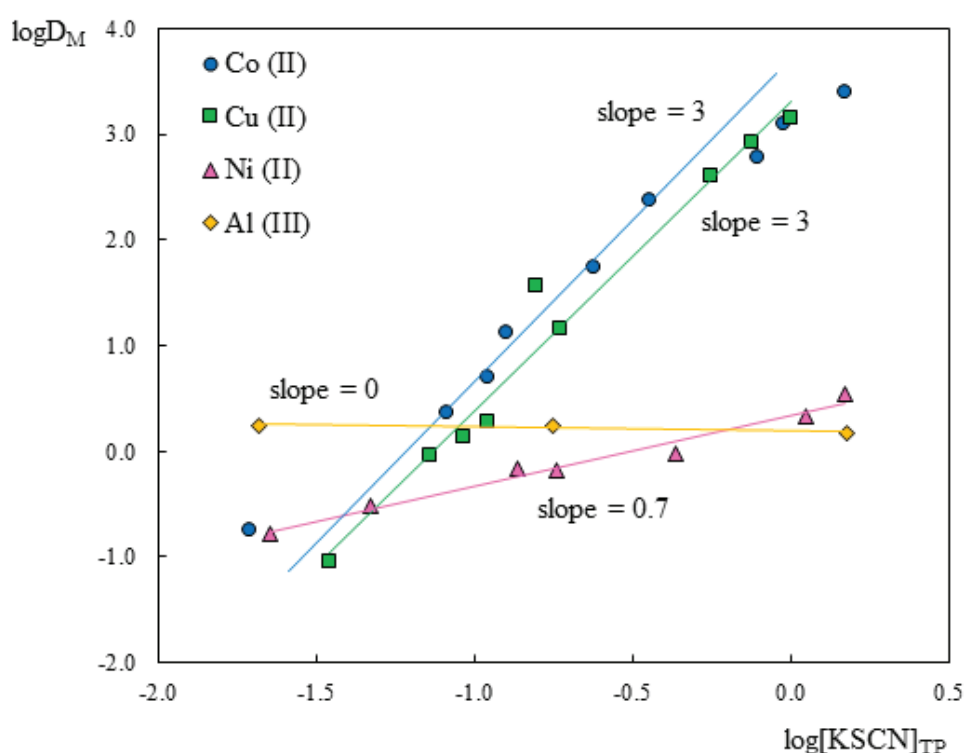

Figure 2: Plots of $logD_M$ against $log[KSCN]_{TP}$ for Co (II), Ni (II), Cu (II) and Al (III). The initial concentration of metal in the solution is 0.01 mol/L.

To evaluate the composition of extractable compounds, studies of the metals complexing with thiocyanate ions were carried out by spectrophotometry. Electronic absorption spectra were obtained of the initial solutions of metal chlorides and equilibrium phases after extraction. Figures 3–5 show electronic absorption spectra of the initial solutions and solutions after extraction of the studied metal ions in the poly(propylene glycol) 425 (30 wt%) - sodium chloride (8 wt%) - water extraction system in the presence of potassium thiocyanate.

The research results show that the Co^{2+} ion in the initial solution (Fig. 3a) and the equilibrium salt phase after extraction (Fig. 3a) exists mainly in the form of the $[Co(H_2O)_6]^{2+}$ aqua complex, as indicated by the presence of an absorption band at 510 nm and
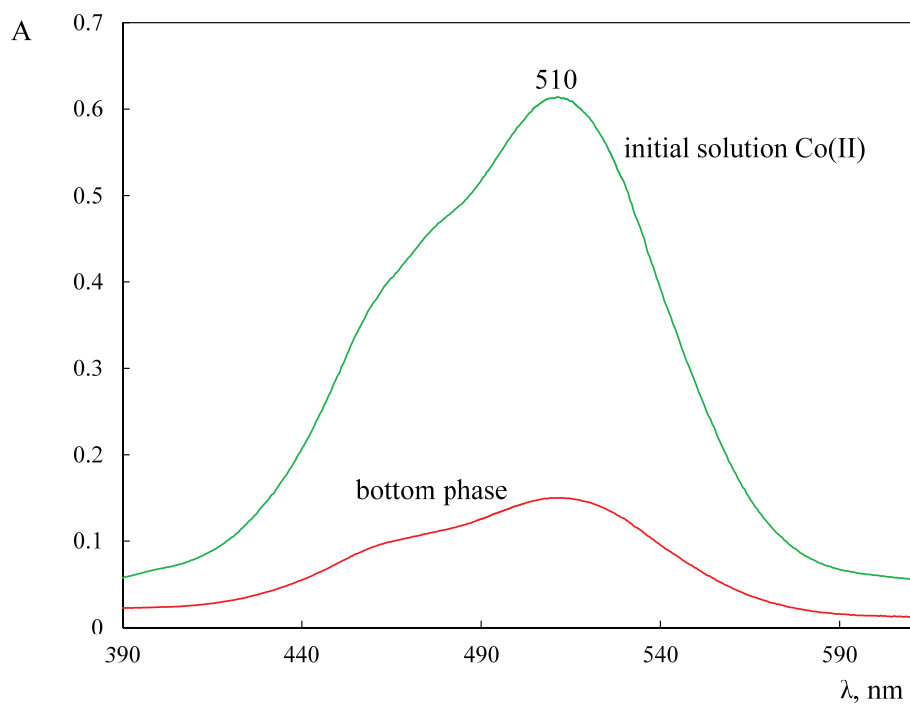
(a)
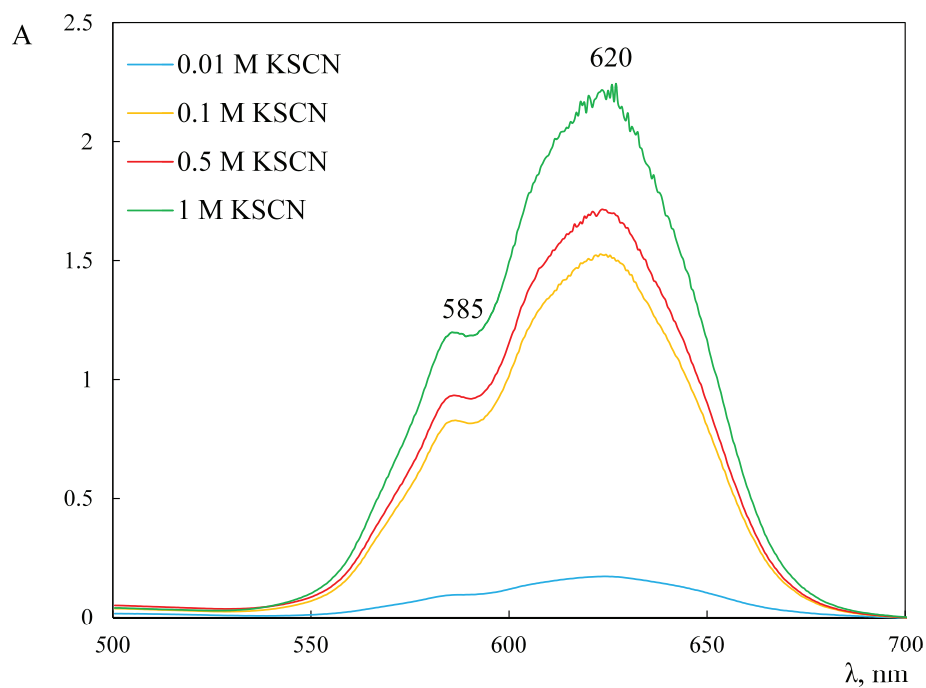
(b)

Figure 3: Electronic absorption spectra of a 0.01 M solution of cobalt chloride (a), equilibrium salt (a) and polymer phases (b) after extraction of Co (II) ($[M]_{in}$ = 0.005 mol/L) in the poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water system in the presence of KSCN.

shoulder at 480 nm [17, 18]. The electronic spectrum of the polymer phase contains an absorption band with a broad maximum at 620 nm, which corresponds to the formation of complexes of the composition $[Co(SCN)_3]^-$ and $[Co(SCN)_4]^{2-}$ [18]. Also, a plateau is observed in the spectrum at 580 nm, which belongs to the $[Co(SCN)_2]^0$ complex (Fig. 3b). Thus, it is seen that a mixture of Co (II) complexes with a general Co ratio is extracted into the polymer phase: SCN = 1: 3, moreover, depending on the content of SCN $^-$ this or that form prevails.

Figure 4 shows similar electronic spectra of solutions for Cu (II). The absorption spectra of the initial solution of copper (II) chloride and the salt phase after Cu (II) extraction are similar and have an absorption band at 800 nm that is characteristic of the $[Cu(H_2O)_6]^{2+}$ aqua complex [17, 18]. In the polymer phase, there is no peak at 810 nm and a wide absorption band appears in the area of 450 nm. With a change in the KSCN concentration, the absorption spectra differ from each other, the absorption maximum shifts to the long-wavelength area, which indicates the formation of mixed copper thiocyanate complexes with the general Cu (II) ratio: SCN = 1: 3 (Fig. 2).

The spectra of the initial solution of $NiCl_2$ and the salt phase after extraction of Ni (II) are similar (Fig. 5) and have absorption maxima at 395 and 730 nm and a shoulder at 655 nm related to the $[Ni(H_2O)_6]^{2+}$ octahedral ion [17, 18]. After extraction, the absorption band at 395 nm is also observed in the spectra of the polymer phase, the band at 730 nm and the shoulder at 655 nm disappear and bands appear at 500 and 665 nm, which indicates the formation of mixed nickel (II) thiocyanate complexes [18].

The studies showed that in the salt phase metal ions are in the form of cationic octahedral aquatic complexes, only neutral or anionic metal complexes that can form intermolecular bonds with the polymer pass into the polymer phase.

4. Conclusion

Thus, the extraction of Co (II), Ni (II), Cu (II), and Al (III) from chloride solutions with poly(propylene glycol) 425 was studied. The distribution coefficients and the degree of metal ions extraction are determined in the system under study. The mechanism of metal extraction in the poly(propylene glycol) 425 – sodium chloride – water extraction system in the presence of KSCN is described. The prospects of the proposed extraction system for the selective extraction of metal ions from chloride solutions are shown.
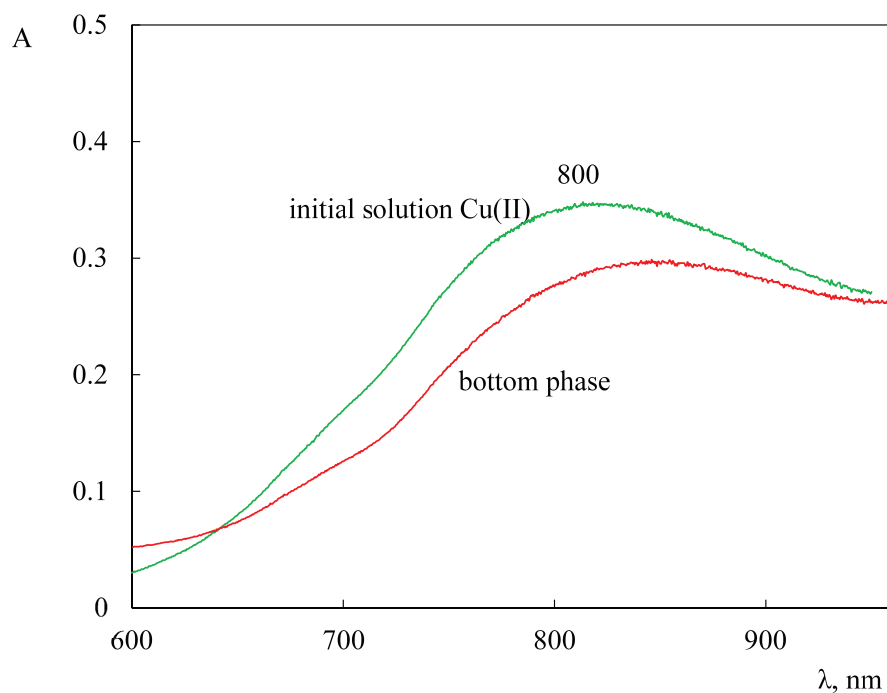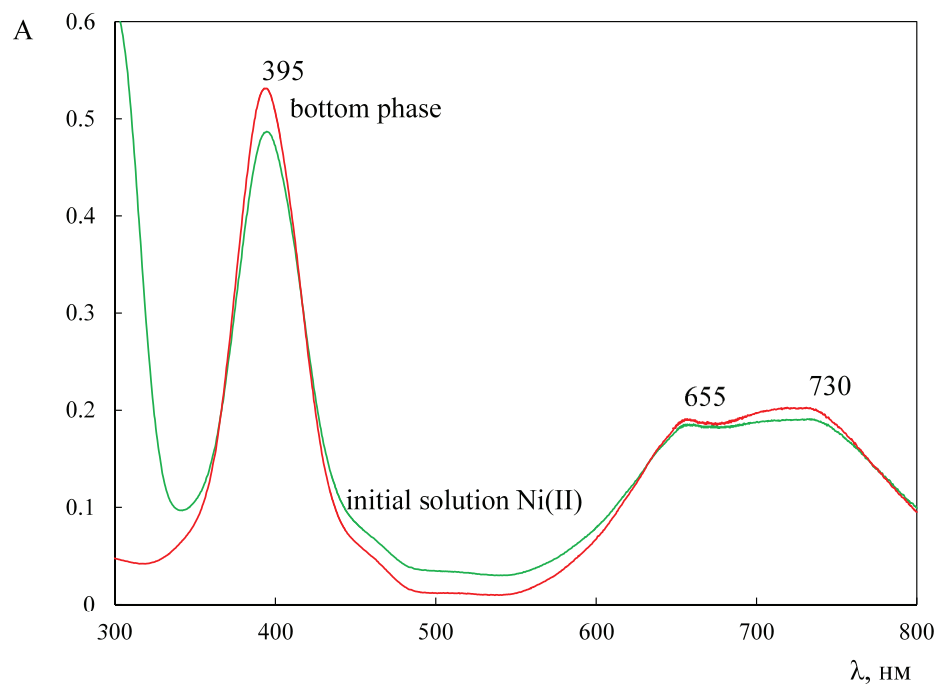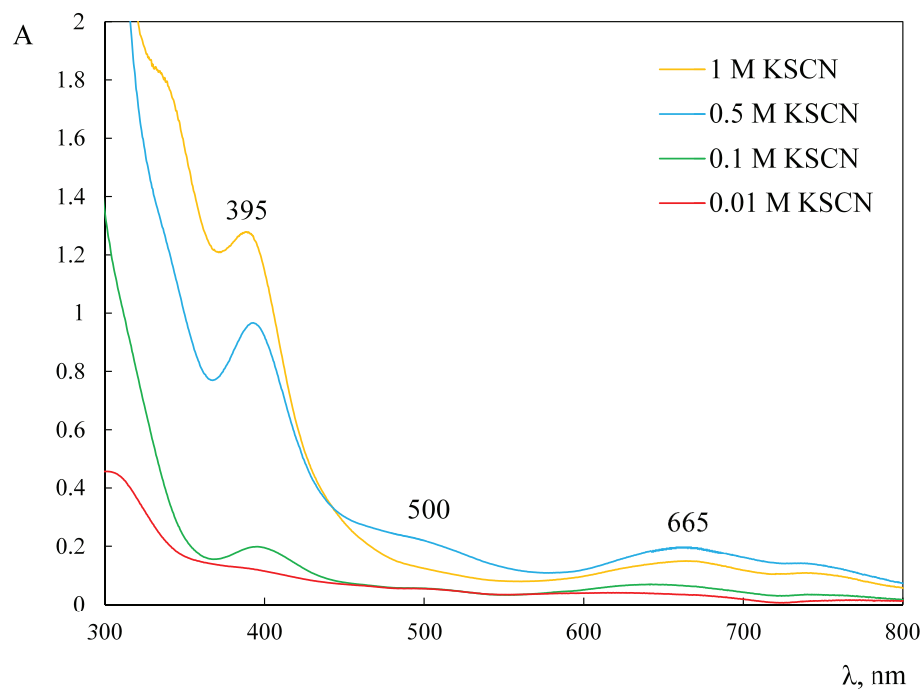
(a)
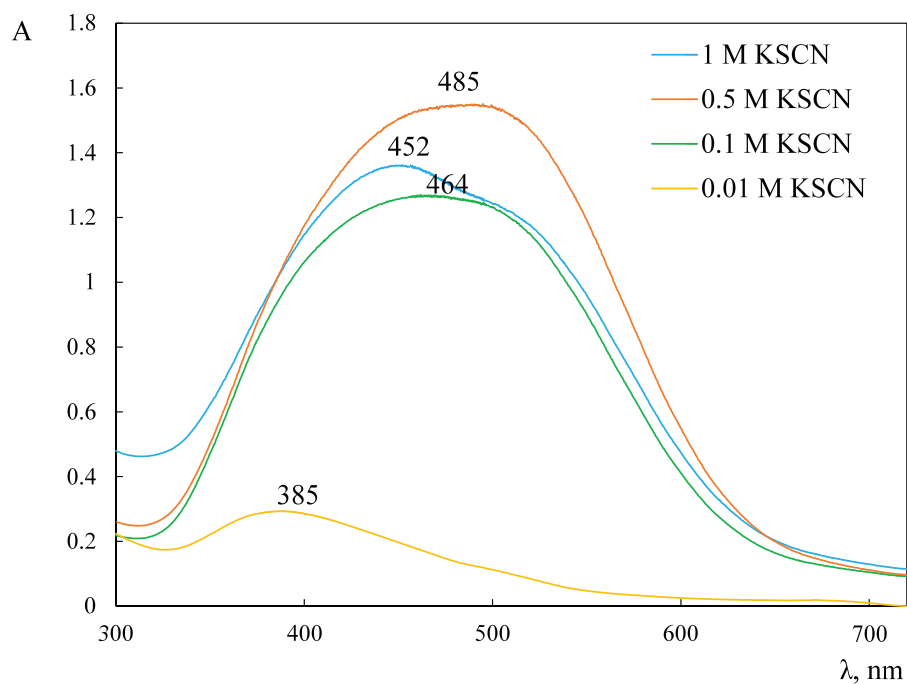
(b)

Figure 4: Electronic absorption spectra of a 0.01 M solution of copper (II) chloride (a), equilibrium salt (a) and polymer phases (b) after extraction of Cu (II) ($[M]_{in}$ = 0.005 mol/L) in the poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water system in the presence of KSCN.

(a)

(b)

Figure 5: Electronic absorption spectra of a 0.01 M solution of nickel chloride (a), equilibrium salt (a) and polymer phases (b) after extraction of Ni (II) ($[M]_{in}$ = 0.01 mol/L) in the poly(propylene glycol) 425 (30 wt%) – sodium chloride (8 wt%) – water system in the presence of KSCN.

Acknowledgements

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