



Application of aqueous two-phase systems for the development of a new method of cobalt(II), iron(III) and nickel(II) extraction: A green chemistry approach

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ABSTRACT

We have investigated the extraction behavior of the metallic ions Co(II), Fe(III) and Ni(II) as a function of the amount of potassium thiocyanate used as an extracting agent, using the following aqueous two-phase systems (ATPS): PEO + (NH₄)₂SO₄ + H₂O, PEO + Li₂SO₄ + H₂O, L35 + (NH₄)₂SO₄ + H₂O and L35 + (Li)₂SO₄ + H₂O. Metal extraction from the salt-rich phase to the polymer-rich phase is affected by the following parameters: amount of added extractant, pH, and the nature of the electrolyte and polymer that forms the ATPS. Maximal extraction percentages were obtained for Co(II) (99.8%), Fe(III) (12.7%) and Ni(II) (3.17%) when the ATPS was composed of PEO1500 + (NH₄)₂SO₄ + H₂O containing 1.4 mmol of KSCN at pH 4.0, providing separation factors as high as $S_{Co,Fe} = 3440$ and $S_{Co,Ni} = 15,300$. However, when the same ATPS was used at pH 2.0, the maximal extraction percentages for iron and nickel were 99.5% and 4.34%, respectively, with $S_{Fe,Ni}$ equal to 4380. The proposed technique was shown to be efficient in the extraction of Co(II) and Fe(III), with large viability for the selective separation of Co(II) and Fe(III) ions in the presence of Ni(II).

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1. Introduction

Nickel and cobalt are important metals because they are extensively employed in commerce and industry [1]. They are used in the fabrication of the electrodes of rechargeable batteries. These batteries are used mainly as components of electro-electronic items such as cell phones and portable computers [2–4].

The worldwide demand for electro-electronic equipment is growing drastically due to the importance of information technology. As a result, there has been a sharp increase in the production of rechargeable batteries [5,6], whose internal components contribute to environmental pollution when disposed [5]. Therefore, for the benefit of the environment, efficient recycling processes for the metallic content of these materials must be developed to avoid the discharge of dangerous residues [7–9]. Economic advantages can also be obtained from the high added value of such metals [10,11].

The recovery of nickel and cobalt from electronic waste and natural resources is usually achieved by applying pyrometallurgical or hydrometallurgical processes [12,13]. However, the

pyrometallurgical route consumes a large amount of energy, and polluting gases are emitted during the process, which may cause considerable damage to human health and the environment [2,8,14].

The hydrometallurgical route consists of the dissolution of the desired metals by means of alkaline or acid leaching. After the leaching step, the generated metal solutions can be further submitted to the processes of separation, namely chemical precipitation, solvent extraction and electrodeposition [15,16].

A serious problem in the separation of nickel and cobalt from aqueous solutions is the similarity in the properties and characteristics of these metals [4,17,18]. Solvent extraction is the most efficient and widely used technique for the separation of these metallic ions from aqueous solutions [19–22]. However, this technique involves the use of organic solvents that are mostly toxic and/or flammable [23].

In recent years, alternative technologies for the separation and recovery of metals have been implemented. In these new approaches, aqueous two-phase systems (ATPS) are proposed for the development of environmentally safe techniques for the extraction and/or recovery of metals [24–26]. These are efficient liquid–liquid extraction operations that have high extraction yields, low cost and do not require organic solvents because the main component of the chemical systems used is water [27–33].

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ATPS are spontaneously formed by mixing aqueous solutions of two chemically different hydrophilic polymers or by combining aqueous solutions of a polymer and an electrolyte under specific thermodynamic conditions, thereby promoting the separation of two immiscible aqueous phases in equilibrium. In general, one of the phases is rich in one polymer, whilst the other contains more electrolytes or the other polymer [34–38].

In this work, the extraction behaviors of the metallic ions Co(II), Fe(III) and Ni(II) were separately investigated with the following ATPS: L35 + Li₂SO₄ + H₂O, L35 + (NH₄)₂SO₄ + H₂O, PEO1500 + Li₂SO₄ + H₂O and PEO1500 + (NH₄)₂SO₄ + H₂O, in the presence of KSCN as an extracting agent. The influence of some parameters on the extraction percentage (%E) of the metallic ions was also analyzed, namely the chemical structure of the polymer, the nature of the ATPS-forming electrolyte, the pH and the amount of extractant added.

2. Experimental

2.1. Equipment

A WTW pH-meter (Wissenschaftlich-Technische Werkstätten, pH 330i/SET) was used to measure the pH of all solutions. The ATPS were prepared by weighing proper amounts of all components on a Shimadzu AY 220 analytical balance, with precision of ±0.0001 g. A Thermo Scientific (Heraeus Megafuge 11R) centrifuge and a Microquímica (MQBTC 99-20) thermostatic bath were also used in the preparation of the ATPS. The concentrations of cobalt, iron and nickel in the standard solutions and the top phase of the ATPS were determined by flame atomic absorption spectroscopy (AAS) with a VARIAN AA-240 spectrometer. Cobalt, iron and nickel were determined with an air-acetylene burner at wavelengths of 240.7, 248.3 and 232.0 nm and lamp currents of 7, 5 and 4 mA, respectively. The aperture width was 0.2 nm.

2.2. Materials and chemicals

All chemicals were of analytical grade and used as received without further purification. The ATPS were prepared with the triblock copolymer L35, HO-(EO)₁₁(PO)₁₆(EO)₁₁-H, with an average molar mass (MM) of 1900 g mol⁻¹, or with poly(ethylene oxide) (PEO1500), with MM = 1500 g mol⁻¹, both acquired from ALDRICH (Milwaukee, WI, USA). The chemicals (NH₄)₂SO₄, Li₂SO₄·H₂O, H₂SO₄, KSCN, FeCl₃·6H₂O, CoCl₂·6H₂O and Ni(CH₃COO)₂·4H₂O were purchased from VETEC (Rio de Janeiro, Brazil). Deionized water (Milli-Q, Millipore) was used in the preparation of all solutions used in the experiments.

2.3. Composition of ATPS

Four different ATPS were tested in the extraction assays, as follows: L35 + Li₂SO₄ + H₂O, L35 + (NH₄)₂SO₄ + H₂O, PEO1500 + Li₂SO₄ + H₂O, and PEO1500 + (NH₄)₂SO₄ + H₂O. Each ATPS was prepared at the desired concentration, as shown in Tables 1 and 2, and was formed with the addition of 2.0 g of the copolymer (or polymer) solution containing different amounts of the KSCN extractant with 2.0 g of the electrolyte solution containing the metallic ion at a concentration of 0.500 mmol kg⁻¹. For each amount of added extractant, all respective ATPS were prepared in triplicate.

2.4. Liquid–liquid extraction

After mixing specific amounts of the polymer and salt solutions, the ATPS were manually stirred for approximately 5 min and then centrifuged at 20,257 × g s⁻¹ for a further 5 min to induce phase

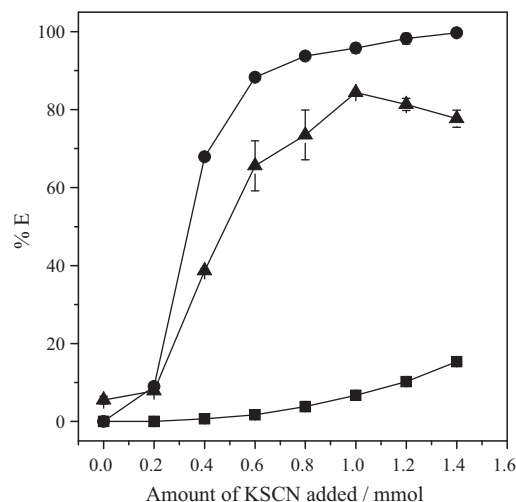


Fig. 1. The effect of the amount of KSCN added to the ATPS top phase on the %E of Co(II), Fe(III) and Ni(II) using the L35 + (NH₄)₂SO₄ + H₂O system at pH 1.0: (●) cobalt; (▲) iron; (■) nickel; [metal] = 0.250 mmol kg⁻¹; T = 25.0 °C.

separation. Then, they were placed in the thermostatic bath at 25.0 °C for 20 min to attain thermal equilibrium. Aliquots from the top phase were collected and diluted, and the concentrations of the metallic ions were determined in the flame AAS. The extraction percentages (%E) of all ions were then calculated with Eq. (1):

$$\%E = \frac{n_M^{TP}}{n_M^T} \times 100 \quad (1)$$

where n_M^{TP} is the number of moles of the desired metallic ion in the top phase and n_M^T is the total number of moles of metallic ions in the system.

2.5. Effect of the amount of added extractant

The %E of Co(II), Fe(III) and Ni(II) was assessed by adding different amounts of the KSCN extractant to the top phase of each system, ranging between 0 and 1.4 mmol, with increments of 0.2 mmol.

2.6. Effect of pH

The initial pH of the deionized water was 5.30. The pH was adjusted by adding H₂SO₄ solution (18 mol L⁻¹). The polymer and salt solutions were then prepared at the desired concentrations using these acidic solutions as solvents, with pH 1.0, 1.5, 2.0 or 4.0.

3. Results and discussion

3.1. Extraction behavior

The liquid–liquid equilibrium data of the ATPS used in this work are described elsewhere [40], and the largest tie-line lengths (TLL) of each ATPS were selected, corresponding to phases with very distinct intensive thermodynamic properties, which allow for higher extraction percentages [28].

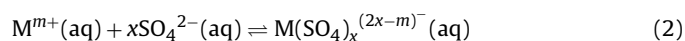
Fig. 1 summarizes the %E of the metallic ions Co(II), Fe(III) and Ni(II) added to the L35 + (NH₄)₂SO₄ + H₂O system at pH 1.0 as a function of the amount of KSCN in the ATPS top phase. The results indicate that the metallic ions cannot be extracted to the top phase from the bottom phase with low amounts of KSCN (≤0.2 mmol). The extraction of Co(II) and Fe(III) only occurs when the amount of added KSCN is 0.4 mmol, with yields as high as 68.0% for Co(II) and 39.0% for Fe(III), with insignificant extraction of Ni(II). Any small variations in the amount of KSCN higher than 0.4 mmol abruptly

Table 1
Concentrations of polymer and salt in the top phase, bottom phase and overall composition of the ATPS examined at 25.0 °C for the tie-line length tested.

ATPS	Composition/% (w/w)					
	Overall Salt	Polymer	Top phase Salt	Polymer	Bottom phase Salt	Polymer
L35 + (NH ₄) ₂ SO ₄ + H ₂ O	10.66	29.92	1.21	57.16	20.11	2.68
L35 + Li ₂ SO ₄ + H ₂ O	10.03	27.60	0.50	54.25	19.55	0.95
PEO + (NH ₄) ₂ SO ₄ + H ₂ O	17.11	30.44	1.76	56.04	32.45	4.84
PEO + Li ₂ SO ₄ + H ₂ O	12.14	29.43	2.15	53.26	22.12	5.60

enhances the %E of Co(II) and Fe(III), and maximal yields were obtained with 1.0 mmol of KSCN for Fe(III) and 1.4 mmol of KSCN for Co(II) and Ni(II). These maximal values were (99.7 ± 0.4)% for Co(II), (84.4 ± 0.3)% for Fe(III) and (15.3 ± 0.3)% for Ni(II).

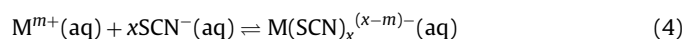
In the absence of the extracting species (SCN⁻), all metallic ions concentrated in the salt-rich phase. This behavior is caused by specific interactions of the metallic cations with the sulfate anion, thereby forming a complex species (Eqs. (2) and (3)).



$$K_{M(SO_4)_x^{(2x-m)-}}^\theta = \frac{\gamma_{M(SO_4)_x^{(2x-m)-}} \cdot [M(SO_4)_x^{(2x-m)-}]}{\gamma_{M^{m+}} \cdot [M^{m+}] \cdot \gamma_{SO_4^{2-}} \cdot [SO_4^{2-}]^x} \quad (3)$$

In Eq. (3), $K_{M(SO_4)_x^{(2x-m)-}}^\theta$ is the standard thermodynamic constant of formation of the metal–sulfate complex, γ_X is the activity coefficient of the ionic species X, and [X] is the concentration of such species ($X = M^{m+}$ or SO_4^{2-} or $M(SO_4)_x^{(2x-m)-}$). The stability constant depends on the electronic structure of the central metal ion. The metal–sulfate complexes can be preferentially formed in the following order: Fe (log K = 5.38) [41] > Co (log K = 2.50) > Ni (log K = 2.40) [42]. The metal extraction efficiency is inversely proportional to the constant of formation of the complex if only the metal–sulfate 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 electrolyte-rich phase to the phase that is more concentrated in L35. The formation process of the new complexes and the stability constant are represented by Eqs. (4) and (5), respectively:



$$K_{M(SCN)_x^{(x-m)-}}^\theta = \frac{\gamma_{M(SCN)_x^{(x-m)-}} \cdot [M(SCN)_x^{(x-m)-}]}{\gamma_{M^{m+}} \cdot [M^{m+}] \cdot \gamma_{SCN^-} \cdot [SCN^-]^x} \quad (5)$$

where $K_{M(SCN)_x^{(x-m)-}}^\theta$ is the standard thermodynamic constant of formation of the metal–thiocyanate complex, γ_X is the activity coefficient of the ionic species X and [X] is the concentration of such species ($X = M^{m+}$ or SCN^- or $M(SCN)_x^{(x-m)-}$).

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 SO₄²⁻) for the metal and the interaction of the resultant complex with the macromolecule present in the top phase.

The stability constant of the Fe–sulfate complex (log K₁ = 4.04; log K₂ = 1.34) [41] is higher than that of the Fe–thiocyanate complex (log K₁ = 1.96; log K₂ = 2.02; log K₃ = -0.41; log K₄ = -0.14; log K₅ = -1.57; log K₆ = -1.51) [43], which does not enable the extraction of Fe(III) to the top phase. However, after the formation of the M(SCN)_x^{(x-m)-} complexes, they are spontaneously transferred to the top phase as a result of polymer and anion interactions. As the concentration of the M(SCN)_x^{(x-m)-} 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. The EO–M(SCN)_x^{(x-m)-} interaction depends on the nature of the central atom. da Silva et al. [44] have demonstrated that the partition of the [M(CN)₅NO]^{x-} anion is strongly affected by the central atom. The low values of %E for the Ni(II) ions in these systems may be attributed to the formation of complexes such as [Ni(SCN)₄]²⁻, which interact weakly with the polymer segments [27].

An important aspect that must be noted is that Fe(III) and/or Co(II) may be separated or pre-concentrated in the presence of Ni(II) if the ratio of [SCN⁻]/[M^{m+}] ≥ 600.

The results of this work are similar to the ones reported by Shibukawa et al. [25], thereby corroborating the efficiency of the ATPS in the preferential extraction of some metallic ions [27]. Shibukawa et al. [25] prepared ATPS with PEO and Na₂SO₄ and investigated the extraction behavior of metallic ions in the presence of thiocyanate (SCN⁻) and iodide (I⁻) as extracting agents. They observed %E values as high as 75% for Cd(II) ions and over 90% for Co(II), Cu(II), Fe(III) and Zn(II) ions when thiocyanate was used.

3.2. Effect of pH

Fig. 2 shows the influence of pH on the extraction percentages of Co(II), Fe(III) and Ni(II), as a function of the amount of KSCN, for the PEO1500 + (NH₄)₂SO₄ + H₂O system. The results demonstrate that, regardless of the pH, only a small amount of the metallic ions was extracted with low amounts of KSCN added.

Similar to the ATPS prepared with L35, the increase in the amount of KSCN favored the extraction of Co(II) and Fe(III) into the top phase; however, the same effect was not observed for Ni(II)

Table 2
Concentrations of polymer and salt in the stock solutions used for the preparation of the ATPS.

ATPS	TLL ^a /(m/m)	Concentration/(m/m)		Reference
		Polymer	Electrolyte	
L35 + (NH ₄) ₂ SO ₄ + H ₂ O	57.67	59.84	21.32	[34]
L35 + Li ₂ SO ₄ + H ₂ O	56.60	55.20	20.05	[35]
PEO + (NH ₄) ₂ SO ₄ + H ₂ O	59.69	60.88	34.21	[39]
PEO + Li ₂ SO ₄ + H ₂ O	51.67	58.86	24.27	[40]

^a Tie-line length.

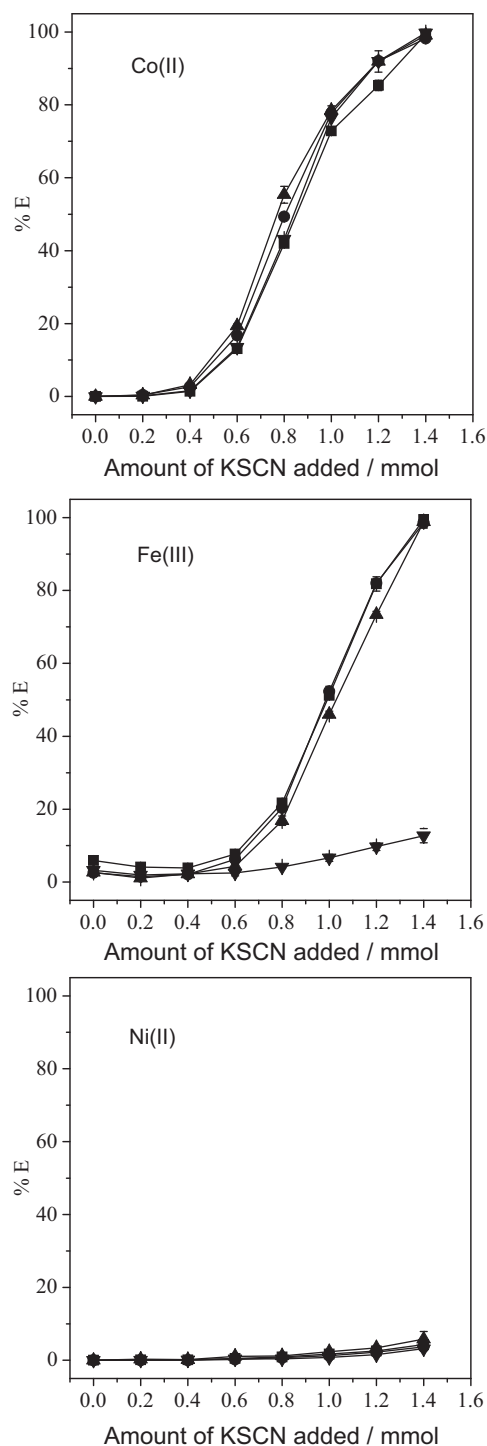


Fig. 2. The influence of pH on the %E of Co(II), Fe(III) and Ni(II) with different amounts of KSCN added to the ATPS top phase: PEO1500 + (NH₄)₂SO₄ + H₂O system at (●) pH 1.0; (▲) pH 1.5; (■) pH 2.0; (▼) pH 4.0; [metal] = 0.250 mmol kg⁻¹; T = 25.0 °C.

ions. Between pH 1.0 and pH 4.0, no significant influence of pH on the extraction of ions was detected, except for Fe(III), which was extracted with a yield of only (12.7 ± 1.9)% at pH 4.0.

For systems formed with L35 + (NH₄)₂SO₄ + H₂O, there was almost no influence of pH on the extraction of Co(II), with a maximal %E of (93.8 ± 1.0)% at pH 1.5 and (99.7 ± 0.4)% at pH 1.0. However, the %E for Fe(III) ranged between (24.5 ± 0.8)% at pH 4.0 and (98.3 ± 2.0)% at pH 1.5. For Ni(II), no significant influence of pH on the %E was observed. For systems formed with L35 + Li₂SO₄ + H₂O,

variations in pH did not significantly affect the extraction of the three metallic ions examined.

Similarly, there were no significant differences in the metal extraction percentages for the ATPS PEO1500 + Li₂SO₄ + H₂O at pH 1.0 and pH 2.0. However, at pH 4.0, the %E of all metals with this ATPS was reduced, with values as high as (76.9 ± 7.5)% for Co(II) and (14.5 ± 0.3)% for Ni(II). The Fe(III) ions could not be extracted because precipitation occurred at pH 4.0.

3.3. Effect of the electrolyte

Fig. 3 is a comparison of the %E values for Co(II) and Ni(II) in systems formed with L35 (59.84%, w/w) and (NH₄)₂SO₄ (21.32%, w/w), and L35 (55.20%, w/w) and Li₂SO₄ (20.05%, w/w), both in the presence of KSCN as an extracting agent.

The maximal extraction percentages for Co(II) ions were (98.6 ± 1.2)% when (NH₄)₂SO₄ was used as electrolyte and (99.6 ± 0.3)% in the presence of Li₂SO₄. For Ni(II) ions, the maximal %E values were (14.6 ± 0.2)% with (NH₄)₂SO₄ and (45.9 ± 0.2)% with Li₂SO₄.

In Fig. 4, the same comparison is shown for Co(II) and Ni(II) in systems formed with PEO1500 (60.88%, w/w) and (NH₄)₂SO₄ (34.21%, w/w), and PEO1500 (58.86%, w/w) and Li₂SO₄ (24.27%, w/w), both in the presence of KSCN. The Co(II) ions could be extracted with a maximal yield of (99.4 ± 0.8)% in the presence of (NH₄)₂SO₄ and a maximal yield of (96.1 ± 1.0)% when Li₂SO₄ was used. For Ni(II) ions, the maximal %E values were (4.34 ± 0.18)% with (NH₄)₂SO₄ and (19.7 ± 0.5)% with Li₂SO₄.

The ATPS containing Li₂SO₄ as electrolyte were more efficient than those that contained (NH₄)₂SO₄ in the extraction of the metals examined in this work. This effect is evident in Figs. 3 and 4.

The significant increase in the values of %E for lithium-containing ATPS results from the strong interactions between Li⁺ cations and the ethylene oxide units (EO) of the macromolecule. The cation–EO interactions induce the formation of a pseudopolymer. Consequently, a positive charge density forms along the macromolecules of both the PEO1500 and L35 polymers, and the anionic complexes interact electrostatically with such pseudopolymerizations, thereby being preferentially transferred to the top phase of the ATPS [45].

3.4. Effect of the hydrophobicity of the phases

Only few reports found in the literature focus on the study of ion transfer in ATPS, but almost all refer to systems formed with PEO and different electrolytes. To the best of our current knowledge, only two investigations discuss the effect of hydrophobicity in the partition of ions. Rodrigues et al. [27] examined the extraction behavior of Ni(II), Fe(III), Cd(II), Co(II), Zn(II) and Cu(II) as a function of the amount of extractant added into the ATPS formed with a triblock copolymer (L35) and Na₂SO₄ in the presence of iodide or thiocyanate. The molecular interaction between the L35 copolymer and the electrolytes is less intense than that observed in the ATPS formed with PEO and inorganic salts. This fact suggests that the extraction is more efficient in PEO/salt ATPS when both biphasic systems are prepared in the same overall composition. Thus, the extraction efficiency of the metallic ions is highly dependent on both the species to be partitioned and the chemical structure of the polymer that forms the ATPS.

da Silva et al. [46] studied the partition behavior of [Fe(CN)₅(NO)]²⁻ and [Fe(CN)₆]³⁻ in ATPS formed with a triblock copolymer or PEO and potassium phosphate. Two triblock copolymers with different hydrophobicities were tested: L35 (EO 50% and 1900 g mol⁻¹) and F68 (EO 80% and 8400 g mol⁻¹). The relative magnitude of the partition coefficient for the anions tested followed

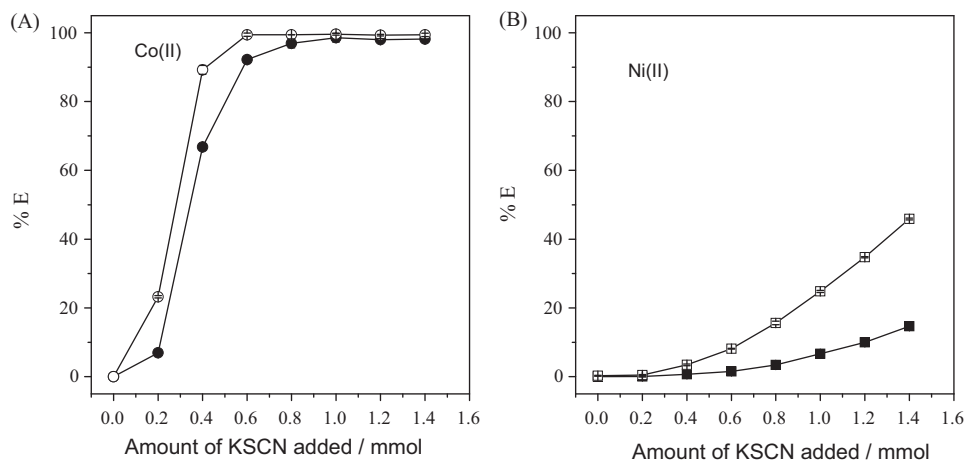


Fig. 3. The effect of the ATPS-forming electrolyte on the %E of the metals with different amounts of KSCN added to the ATPS top phase; systems formed with L35 at pH 2.0: (A) Co(II) + (●) $(\text{NH}_4)_2\text{SO}_4$ or (○) Li_2SO_4 ; (B) Ni(II) + (■) $(\text{NH}_4)_2\text{SO}_4$ or (□) Li_2SO_4 ; [metal] = 0.250 mmol kg⁻¹; T = 25.0 °C.

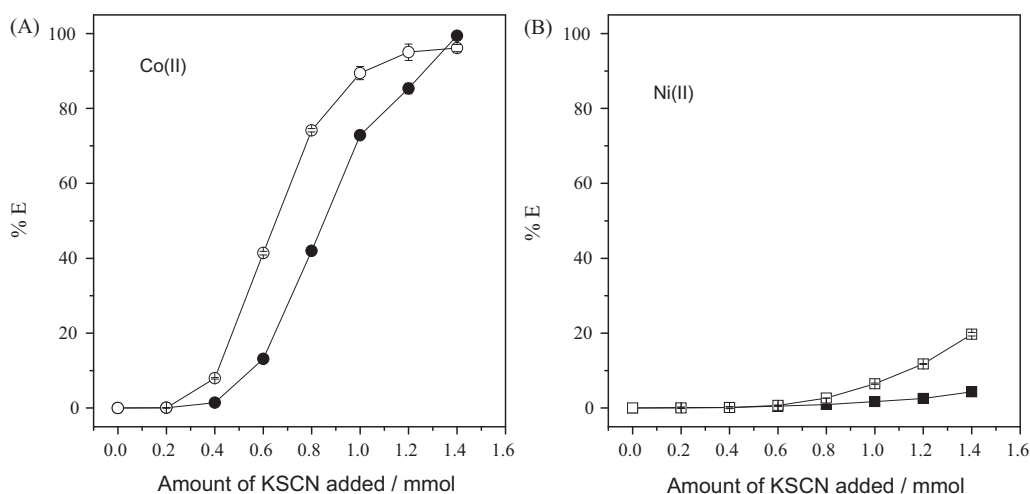


Fig. 4. The effect of the ATPS-forming electrolyte on the %E of the metals with different amounts of KSCN added to the ATPS top phase; systems formed with PEO1500 at pH 2.0: (A) Co(II) + (●) $(\text{NH}_4)_2\text{SO}_4$ or (○) Li_2SO_4 ; (B) Ni(II) + (■) $(\text{NH}_4)_2\text{SO}_4$ or (□) Li_2SO_4 ; [metal] = 0.250 mmol kg⁻¹; T = 25.0 °C.

the order of L35 < F68 < PEO. Thus, it is clear that the partition coefficient depends on the hydrophilic-hydrophobic balance (HLB) of the polymer used. The typical effect observed is the decrease in the partition coefficient when hydrophobicity increases.

From these studies, it could be verified that the effect of hydrophobicity of the phase rich in macromolecules on the partition of ions is very high. The partition of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ is impaired with increasing hydrophobicity, whilst the

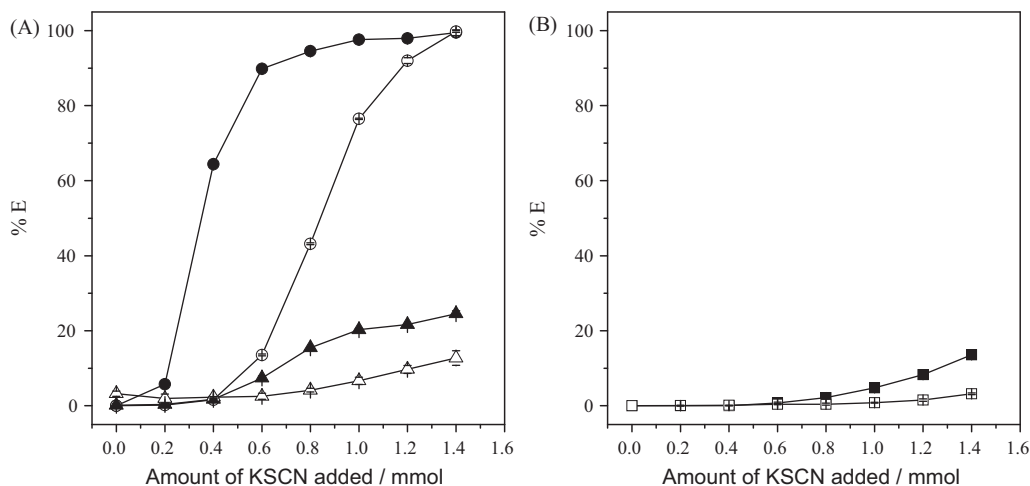


Fig. 5. The influence of the hydrophobicity of the ATPS phases on the %E of the metals with different amounts of KSCN added to the ATPS top phase; systems formed with $(\text{NH}_4)_2\text{SO}_4$ at pH 4.0: (A) Co(II) + (●) L35 or (○) PEO; Fe(III) + (▲) L35 or (△) PEO; (B) Ni(II) + (■) L35 or (□) PEO; [metal] = 0.250 mmol kg⁻¹; T = 25.0 °C.

opposite is observed for complexes with the general structure of $M(\text{SCN})_x^{(x-m)^-}$, which tend to be more partitioned when the hydrophobicity increases.

Fig. 5 shows the results of the study on the effect of the hydrophobicity of the ATPS top phases on the extraction efficiency of Co(II), Fe(III) and Ni(II), with various amounts of KSCN added.

The results indicate the preferential transfer of Co(II) ions to the phases enriched with PEO1500 or L35. However, the extraction behavior is significantly different for the examined ions, depending on the structure of the macromolecules that form the ATPS.

The addition of an extracting agent to the system favored the extraction of Co(II), with maximal yields of $(99.5 \pm 0.8)\%$ for the $\text{L35} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$ system and $(99.8 \pm 0.2)\%$ for the $\text{PEO1500} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$ system. The same effect could not be observed for Ni(II) and Fe(III), which could be extracted with maximal yields of only $(13.6 \pm 0.3)\%$ and $(24.5 \pm 0.8)\%$, respectively, when using the L35 ATPS, and $(3.17 \pm 0.22)\%$ and $(12.7 \pm 1.9)\%$, respectively, when using the PEO1500 ATPS. All maximal extraction percentages are affected when 1.4 mmol of the KSCN extractant was added to the top phase of the ATPS.

Furthermore, these results highlight that Co(II) ions can be separated or pre-concentrated in the presence of Ni(II) and Fe(III) when using both ATPS. However, the amount of KSCN required for such separation is very different in each system. In the L35 ATPS, the amount of KSCN must be higher than 0.4 mmol, whilst the system formed with PEO1500 requires more than 0.9 mmol of KSCN to produce reasonable extraction levels.

This difference in behavior is justified by the enhanced hydrophobicity of the copolymer macromolecule, which features propylene oxide (PO) units on its chain. Although the macromolecules are solvated in the aqueous medium, there is less interaction between the PO units and the water molecules, thereby favoring intermolecular interactions of the PO units themselves. This is a result of the so-called hydrophobic effect. Above the critical micelle concentration (CMC) of the L35 copolymer, self-assembled micelle aggregates appear, each one comprising a hydrophilic corona formed by EO units and a hydrophobic core composed of PO units.

Therefore, it is believed that thiocyanate ions are coordinated with Co(II) ions by the nitrogen atom with the purpose of generating tetrahedral complexes such as $[\text{Co}(\text{NCS})_4]^{2-}$. It is known that such complexes do not readily form in aqueous solution and, therefore, must be transferred to the ATPS top phase, where hydrophobic regions exist as a result of the copolymer aggregation nuclei [27].

Rodrigues et al. [27] have confirmed that the hydrophobicity of the top phase caused by the presence of L35 micelles significantly enhances both the extraction percentage and the selectivity of the metallic ions, corroborating the results presented herein.

3.5. Separation Factor ($S_{M,N}$)

The separation factor ($S_{M,N}$) expresses the efficiency of separation of two species, M and N , in liquid–liquid extraction operations [21]. It can be given by Eq. (6):

$$S_{M,N} = \frac{D_M}{D_N} \quad (6)$$

where D_M is the distribution coefficient of species M and D_N is the distribution coefficient of the concurrent species N . The distribution coefficient of any given species is expressed by Eq. (7):

$$D_M = \frac{\%E}{100 - \%E} \quad (7)$$

For the effective separation of the metallic ions, it is essential that the values of $S_{M,N}$ range between 10^3 and 10^4 .

Table 3
Separation factors $S_{\text{Co,Ni}}$, $S_{\text{Co,Fe}}$ and $S_{\text{Fe,Ni}}$ obtained for different ATPS as a function of pH.

SAB	$S_{\text{Co,Ni}}$			$S_{\text{Co,Fe}}$			$S_{\text{Fe,Ni}}$		
	pH 1.0	pH 2.0	pH 4.0	pH 1.0	pH 2.0	pH 4.0	pH 1.0	pH 2.0	pH 4.0
L35 + $(\text{NH}_4)_2\text{SO}_4$	$(1.83 \pm 0.05)10^3$	$(9.93 \pm 0.38)10^2$	$(1.27 \pm 0.04)10^3$	$(9.54 \pm 0.39)10^1$	(1.66 ± 0.07)	$(6.12 \pm 0.29)10^2$	$(1.92 \pm 0.09)10^1$	$(5.99 \pm 0.31)10^2$	(2.07 ± 0.12)
PEO + $(\text{NH}_4)_2\text{SO}_4$	$(1.43 \pm 0.05)10^3$	$(3.66 \pm 0.22)10^3$	$(1.53 \pm 0.15)10^4$	(0.776 ± 0.014)	(0.834 ± 0.013)	$(3.44 \pm 0.73)10^3$	$(1.84 \pm 0.06)10^3$	$(4.38 \pm 0.26)10^3$	(4.43 ± 1.03)

The ATPS that produced the largest differences in the %E values were those formed by ammonium sulfate ((NH₄)₂SO₄). The corresponding values of $S_{\text{Co,Ni}}$, $S_{\text{Co,Fe}}$ and $S_{\text{Fe,Ni}}$ were then calculated at different pHs, and the results are shown in Table 3. The $S_{\text{Co,Ni}}$, $S_{\text{Co,Fe}}$ and $S_{\text{Fe,Ni}}$ values obtained for the L35 + (NH₄)₂SO₄ + H₂O ATPS at pH 2.0 were calculated with the addition of 1.0 mmol of KSCN to the top phase. The separation factors obtained for all other ATPS were calculated with the addition of 1.4 mmol of KSCN.

Co(II) ions can be separated from Ni(II) ions by using the PEO1500+(NH₄)₂SO₄+H₂O system at pH 4.0, because in this case, $S_{\text{Co,Ni}} = (1.53 \pm 0.15) \times 10^4$. If this ATPS is again used at pH 4.0, one can separate Co(II) from Fe(III), with $S_{\text{Co,Fe}} = (3.44 \pm 0.73) \times 10^3$. The separation of Fe(III) and Ni(II) can be effected by using the PEO1500 + (NH₄)₂SO₄ + H₂O system at pH 2.0, with $S_{\text{Fe,Ni}} = (4.38 \pm 0.26) \times 10^3$.

Based on the results listed in Table 3, it is evident that the PEO1500 + (NH₄)₂SO₄ + H₂O system is responsible for the selective extraction of Co(II) and Fe(III) in the presence of Ni(II) and also for the selective extraction of Co(II) in the presence of Fe(III).

4. Conclusion

An alternative technique that can replace traditional liquid–liquid extraction operations has been proposed in this work for the extraction and/or separation of Co(II), Fe(III) and Ni(II) ions. The technique employs aqueous two-phase systems (ATPS) that are based on the principles of green chemistry, with good efficiency and economical viability. The ATPS were prepared with either the L35 triblock copolymer or poly(ethylene oxide), with an average molar mass of 1900 g mol⁻¹ and 1500 g mol⁻¹, respectively, and with either ammonium sulfate ((NH₄)₂SO₄) or lithium sulfate (Li₂SO₄) as the electrolyte. KSCN was also used as an extracting agent. It has been demonstrated that the extraction efficiency of these metals is affected by the following parameters: amount of added extracting agent, pH, type of electrolyte and the nature of the ATPS-forming polymer. The use of Li₂SO₄ as an ATPS-forming electrolyte instead of (NH₄)₂SO₄ produces higher extraction percentages (%E) of the metallic ions examined, particularly in comparison with nickel. For this metal, the values of %E varied from (14.6 ± 0.2)% to (45.9 ± 0.2)% when the L35 system was used, and from (4.34 ± 0.18)% to (19.7 ± 0.5)%, with systems formed by PEO1500 at pH 2.0, when (NH₄)₂SO₄ was replaced with Li₂SO₄. It could also be observed that with lower amounts of KSCN, the L35 copolymer could produce %E values close to 100% for Co(II) and Fe(III). However, higher separation factors could be obtained with the PEO1500 + (NH₄)₂SO₄ + H₂O system at pH 4.0 containing 1.4 mmol of KSCN, namely $S_{\text{Co,Fe}} = (3.44 \pm 0.73) \times 10^3$ and $S_{\text{Co,Ni}} = (1.53 \pm 0.15) \times 10^4$, with maximal %E for Co(II), Fe(III) and Ni(II) equal to (99.8 ± 0.2)%, (12.7 ± 1.9)% and (3.17 ± 0.22)%, respectively. However, if the same ATPS is prepared at pH 2.0 with the same amount of KSCN, the maximal extraction percentages were (99.5 ± 0.8)% for Fe(III) and (4.34 ± 0.18)% for Ni(II), with $S_{\text{Fe,Co}} = (4.38 \pm 0.26) \times 10^3$. The technique proposed in this work has proven to be efficient for the extraction of Co(II) and Fe(III), with great viability for the selective separation of Co(II) in the presence of Ni(II) and Fe(III) at pH 4.0. Also, the selective separation of Fe(III) can be effected in the presence of Ni(II) at pH 2.0, due to strong interactions between the anionic complex and the macromolecules in the ATPS.

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