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Counter-current separation of cobalt(II)–nickel(II) from aqueous sulphate media with a mixture of Primene JMT-Versatic 10 diluted in kerosene

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ABSTRACT

This work claims the use of the mixture of Primene®JMT-Versatic 10 [HJMT⁺-Versatic⁻] IL diluted in Kerosene as an extractant for cobalt/nickel separation from sulphate media by solvent extraction technique, its application on a continuous counter-current device is possible because the presence of Primene®JMT in the organic phase allows us to maintain the pH of the equilibrated aqueous phase at an almost stable value. The solvent extraction of cobalt and nickel ions is studied as a function of the extractant concentration in the organic phase and the concentration of both metals. By constructing the McCabe-Thiele diagram, we found that four steps are necessary to separate the cobalt(II) from the nickel(II) in sulphate media. A simulated continuous counter-current experiment corroborated the McCabe-Thiele predictions, obtaining a raffinate containing 83% of the inlet nickel with a purity of 99.9%, working with an A:O ratio 1:2.

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Mixture extractants; ionic liquid; continuous counter-current; cobalt; nickel; sulphate media

Introduction

Cobalt and nickel are two important metals because they are extensively applied in different branches of industry such as superalloys in aerospace, gas turbine engines, automotive, military, electronics and catalyst in the petroleum industry, moreover as pigments in ceramics, glass, plastic materials, magnets, electroplat-

ing and other chemical applications, but their main

market is the battery components.^[1] Nowadays, cobalt is included in the list of critical raw materials (CRMs) created by the European Commission, which combines, to each material, the economic importance for the EU with its supply risk (Report on Critical Raw Materials for The EU^[2]). In this sense, it is forecasted that the refined cobalt world supply growth will increase at a lower rate than the cobalt world consumption, which is mainly due to the strong growth in the rechargeable

batteries and aerospace industries.^[1] In fact, about 4.5–

8% per year is the demand growth expected until 2020

(Report on Critical Raw Materials for The EU^[2]). In the

near future, the natural resources of these metals could be insufficient and expensive to supply this strong demand.

According to the European Directive 2006/66/CE and considering the extensive use of batteries as green energies in the electronic devices and also in the hybrid or electric vehicles, it is needed to develop specific routes to recovery the valuable metals prior to a safe disposal. In this way, these processes will be worthwhile economically and environmentally favoured. These processes include the

the supercritical fluids for metal leaching and extraction and the solvent extraction.^[5-13]

Spent catalysts and waste alloys are recognized as secondary sources of these metals. The use and exploitation of these other secondary sources to metal recovery gives rise to the interest for more intensive cobalt and nickel separation processes.^[14-18]

So far, many achievements for cobalt or nickel enrichment are made in the field of solid-phase extraction^[19]
[20]

cloud point extraction,

salting-out liquid-liquid

extraction,^[21]

adsorption,^[22]
[24]

liquid membranes,^[23]

micro-
[25]

emulsion extraction

and hollow fibre membranes.

Liquid-liquid (i.e., solvent) extraction continues representing a separation technology of significance in both metal ion separations and commercial scale separation

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processes.^[26] Solvent extraction offers some advantages over competing techniques, like the flexibility of the chemistry employed in the extraction process (e.g., nature and concentration of extractant, aqueous phase composition) and the concomitant "tailorability" of the separations, account for the ongoing popularity of the technique.

The published literature data gave big attention to the separation of cobalt and nickel and most of these studies used cationic extractants such as Cyanex 272, Versatic10 acid, D2EHPA, PC88A, etc.^[6,27-35] When cationic extractants are used in a counter-current extraction process, the aqueous phase pH decreases, the pH of the aqueous phase decreases, making the

are shown in Table 1. Kerosene, which is supplied by Sigma Aldrich, is used as the diluent. CoSO₄, NiSO₄ and Na₂SO₄ are obtained from Panreac Applichem and all the used chemicals are analytical reagent grade. The Na₂SO₄ is used to adjust the sulphate concentration at 0.5 M in all experiments. To make the stripping, a solution 1 M of the H₂SO₄ is used.

The extractant used in this work is prepared by mixing equimolar quantities of Primene®JMT (RNH₂, basic characteristic) and Versatic10 (HA, acidic properties) at room temperature (22 ± 2°C) (Fig. 1). The acid-base reaction that takes place between these compounds is as follows:

metal transfer to the organic phase impossible without



pH readjusting. One way to avoid this problem is the use of bifunctional ionic liquids as selective extractant agents because they are compatibles with the continuous counter-current conditions. The possibility to combine different cation/anion pairs to develop new ionic liquids for specific tasks promoted their extensive use

in the field of the metal ion separations.^[36-48]

This work presents the extraction and separation of cobalt(II) and nickel(II) from sulphate media using the acid-base couple [HJMT⁺Versatic10⁻] as a tailored extractant. The purpose is to produce an ionic liquid able to make the selective separation of cobalt(II)/nickel(II) from an aqueous sulphate solution using a continuous counter-current extraction process without conditioning the inter-step pHs. The study of the JMT/Versatic ratio in the mixture and the concentration of the extractant allow us to find the best conditions to carry out the separation. The procedure to simulate the counter-current process using separatory funnels is an improvement comparing to the methodology applied in other studies and allows a reduction in the needed phase volumes.

Experimental

Reagents

The neodecanoic acid, commercially known as Versatic 10 Acid (Versatic) and Primene®JMT (JMT), a tertiary alky(C₁₆-C₂₂) primary amine are kindly donated from Momentive Specialty Chemicals and Dow Chemical, respectively. The physical properties of both compounds

$$3 \cdot A_{\text{org}} \beta$$

This reaction allows the formation of the stable ion-pair arrangement which is able to extract Co(II) and Ni(II) from the aqueous media conditions proposed in this work. The obtained extractant is diluted in Kerosene until the decided concentrations.

Solvent extraction

Bearing in mind that the objective of this paper is the Co(II)/Ni(II) separation, the working conditions were established on the basis industrial applications. So, the feed solution contained 500 mg Co(II)/L and 5000 mg Ni(II)/L in 0.5 M SO₄²⁻. These metal ion concentrations are chosen because the Co(II):Ni(II) concentration ratio is usually 1:10 (mg/L) in the real leachings.^[52]

Equal volumes of aqueous and organic phases are mixed in a separatory funnel and are maintained under agitation at room temperature (22 ± 2°C). After 20 min of agitation in a horizontal mechanical shaker (SBS Mechanical Shaker), a sample is taken from the aqueous phase to determine the metal concentrations by inductively coupled plasma Atomic Emission Spectroscopy using a 4100 MP-AES spectrophotometer (Agilent Technologies). The concentrations of metal ions in the organic phase are calculated from the difference between the metal concentration in the aqueous phase before and after extraction. Then, the loaded organic phases are stripped, using the same extraction procedure, with 1 M H₂SO₄, and the metal concentration in this solution allows us to close the mass balance.

4

Table 1. Physical properties of the IL precursors.

Commercial name	Content, %	Avg. mol. weight, g/mol	Acid value, mgKOH/g	Neutral equivalent, g/mol	Density, kg/m ³	Viscosity, mPa.s
Primene®JMT	80-90 ^b	269 ^a		325 ^a , 316 ^c	834 (25°C) ^a	11.59 (22.8°C) ^a
Versatic 10 ^d	90 min.	172.26	318-300		910 (20°C)	40.95 (20°C)

4

^aTechnical data sheet Primene J-MT, Global CTM.^[49]

^bTechnical data sheet Primene J-MT, Dow Chemical Company.^[50]

^cExperimental data by potentiometric titration in water/ethanol.

^dTechnical data sheet Versatic acid 10, Hexion.^[51]

O

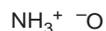


Figure 1. Structure of [HJMT⁺Versatic⁻]IL.

The extraction yield (%E), the distribution coefficient (D) and the separation factor (β) are defined as follows:

$$\frac{1}{2}M^{b2}]_{mi} \quad \frac{1}{2}M^{b2}]_{aq}$$

order to make a multistep counter-current extraction process, the equilibrium metal distribution (isotherm) and the mass balances are required. The simulation of the continuous counter-current process is done using a set of separatory funnels. Figure 2 shows a conceptual scheme of the counter-current contacts during the transitory period until to achieve the steady-state conditions. The methodology depicted in allows minimizing the volume of solutions required to carry out the counter-current simulation. Also, compared to other procedures in the literature^[53,54], this reduces the number of used funnels to accomplish the steady-state for the same number of the separation steps.

$E\%$

$\frac{1}{2}M^{p2}]_{ini}$

$\frac{1}{2}M^{p2}]_{org}$

$\times 100$ (1)

To begin the process, 14 mL of organic phase (0.47 mol/L JMT-Versatic II) and 7 mL of aqueous phase (500 mg/L of Co(II) -5000 mg/L of Ni(II) in 0.5 M of sulphate medium) at pH 6.2 are contacted in four separatory funnels, shaken for 20 min and let

$$D \quad \frac{1}{2}M^{p2}]_{aq} \quad D_{Co} \quad Ni$$

(2)

(3)

stand until both phases are completely separated. Once the phases are separated, it must perform the following procedure:

- Take a new separatory funnel (the separatory funnel

$\frac{1}{4}$

D

where $[M^{+2}]_{ini}$, $[M^{+2}]_{aq}$ and $[M^{+2}]_{org}$ represent the initial, the equilibrium and the organic metal concentrations, respectively.

Counter-current extraction

To use the bifunctional JMT/Versatic ionic liquid proposed in this work for the Co(II)/Ni(II) separation at these conditions will be necessary more than a simple contact. In

$\frac{1}{4}$

D

5 in Fig. 2) and introduce a fresh organic phase

- Take out the aqueous phase of the funnel 4 as a raffinate
- Transfer the aqueous phase from the separatory funnel 3 to the funnel 5, 2 to 4 and 1 to 3 and introduce a fresh aqueous phase in the funnel 2
- Put aside the separatory funnel 1 and keep the organic phase to make the stripping.
- Place the other funnels to shake for 20 min

$\frac{1}{4}$

Figure 2. Scheme of the methodology applied to simulate the four stages of counter-current extraction process.

This procedure is repeated until the process stabilization, in fact is running 11 times to reach it. At this point, all the aqueous phases are collected and all the loaded organic phases are twice stripped with H_2SO_4 1 M. The samples are analysed to determine the metal concentrations of the raffinate and the extract of each one of the four stages needed for the metal ion separation process.

Results and discussion

Effect of the JMT concentration on the separation of cobalt and nickel

To determine the JMT/Versatic ratio in the extractant that promotes the best selectivity to the Co(II)/Ni(II) separation, different organic phases containing a fixed concentration of Versatic (10% (v/v)), and JMT concentration in the range 0 to 25% (v/v) are prepared. Figure 3 shows the effect of this parameter on the Ni/Co extraction when the aqueous phase contains 500 mg/L of cobalt(II) and 5000 mg/L of nickel(II) in 0.5 M of sulphate media. It can be observed that the extraction percentage of cobalt increases when the JMT concentration in the extractant is increased whereas in the case of the nickel, the percentage of extraction barely rises and it achieves only 15–18%. Also, it can be seen that low extraction yields for both metal ions are obtained by using Versatic 10 acid 10% (v/v) alone. In fact, it is necessary to increase the JMT concentration beyond 5% to have significant extraction of the metal ions. This behaviour is due to the low equilibrium pH of the aqueous phase, which is equal to 4.4, compared to the pH of the initial solution, equal to 6.2. Therefore, the addition of JMT neutralizes this effect and makes possible the metal extraction possible. In Fig. 3, it is possible to appreciate the increase in the Co(II) extraction from the mixture by the addition of JMT linked

to the rise in equilibrium pH of the aqueous phase from 6.4 to pH 7.4.

On the other hand, the separation factor represented in Fig. 4 increases to the maximum value of 10.2. It corresponds to a JMT concentration equal to 18% (v/v) and for higher concentrations of JMT, β remains constant. This result suggests that 18% JMT-10% Versatic is the ideal IL composition able to separate Co (II) from Ni (II) in the mixture and it corresponds to a 0.47 M of each constituent in the binary mixture (equimolar ratio).

Effect of the ionic liquid concentration on the cobalt/nickel separation

After determining that the optimal JMT/Versatic molar ratio producing the extractant is equal to 1, the effect of $[HJMT^+Versatic^-]$ IL concentration on the extraction of

Figure 4. Effect of the JMT concentration on the separation factor using constant 10% (v/v) of Versatic 10 acid in kerosene. Aqueous phase: 500 mg/L of Co(II) and 5000 mg/L of Ni(II) in 0.5 M sulphate solution and pH 6.2.

Figure 3. Effect of the JMT concentration on the extraction of Co(II) and Ni(II) and pH of the equilibrated aqueous phase maintaining 10% (v/v) of Versatic 10 acid in kerosene. Aqueous phase: 500 mg/L of Co(II) and 5000 mg/L of Ni(II) in 0.5 M sulphate solution and pH 6.2.

cobalt and nickel ions from the mixture is studied in the range 0.1–0.8 M. As can be seen in Fig. 5, the extraction of cobalt(II) increases as the extractant concentration increases, while nickel extraction does not appear to be

Versatic 10 (HA), it is well known that the extraction process promotes a reduction of the pH in the aqueous phase because of the cationic exchange reaction:

influenced by the variation of the $[HJMT^+Versatic^-]$. Also, Fig. 5 shows an almost stable pH of the equilibrated aqueous



(4)



eous phase for all the organic solutions used because the ratio between both components of the mixture JMT/Versatic is maintained. Figure 6 demonstrates that the maximum separation factor are obtained using 0.47 M of ionic liquid. This concentration is the best to separate cobalt from nickel and therefore it is chosen for the subsequent experiments.

Chemical extraction mechanism

Extraction and separation of the Co(II)/Ni(II) in the



this behaviour prevents its use as extractant in a continuous process without inter-steps conditioning. On the other hand, the extraction of Co(II) or Ni(II) with the primary amine JMT generates a precipitate in the organic phase and this makes the separation impossible.

The mixture of the amine with the Versatic 10 promotes the IL formation, $RNH_3^+A^-$, and this compound modifies the extraction mechanism as can be seen in these two options:



experimental conditions depicted in this study pre-



$2RNH^p$



$2p \quad 2$



sent some problems. For a cationic extractant like



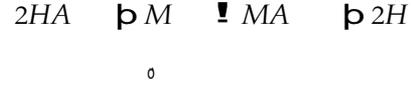
or:



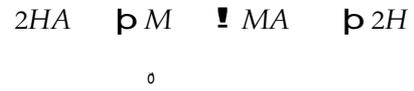
$2RNH^p A$



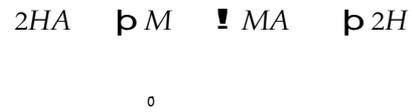
M^{2p}



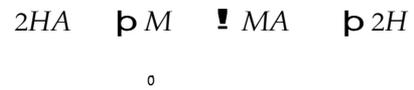
pSO²



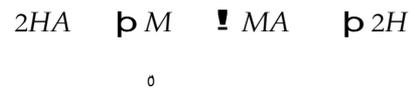
MA_{2 org}



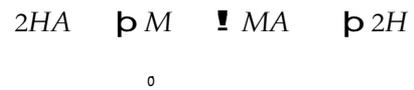
δ_{org}



δ_{aq}

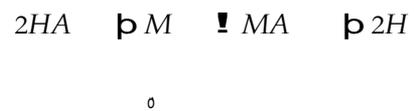


δ_{aq} δ

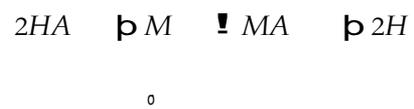


The pH in the aqueous phase for both proposed mechanisms is maintained and the continuous extraction can take place.

The experimental data fit very well with the mechanism of the reaction (6). Equation (7) depicts the extraction constant corresponding at this reaction:



K_{ext} 1/4 RNH₃ p₂



(7)

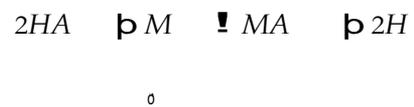
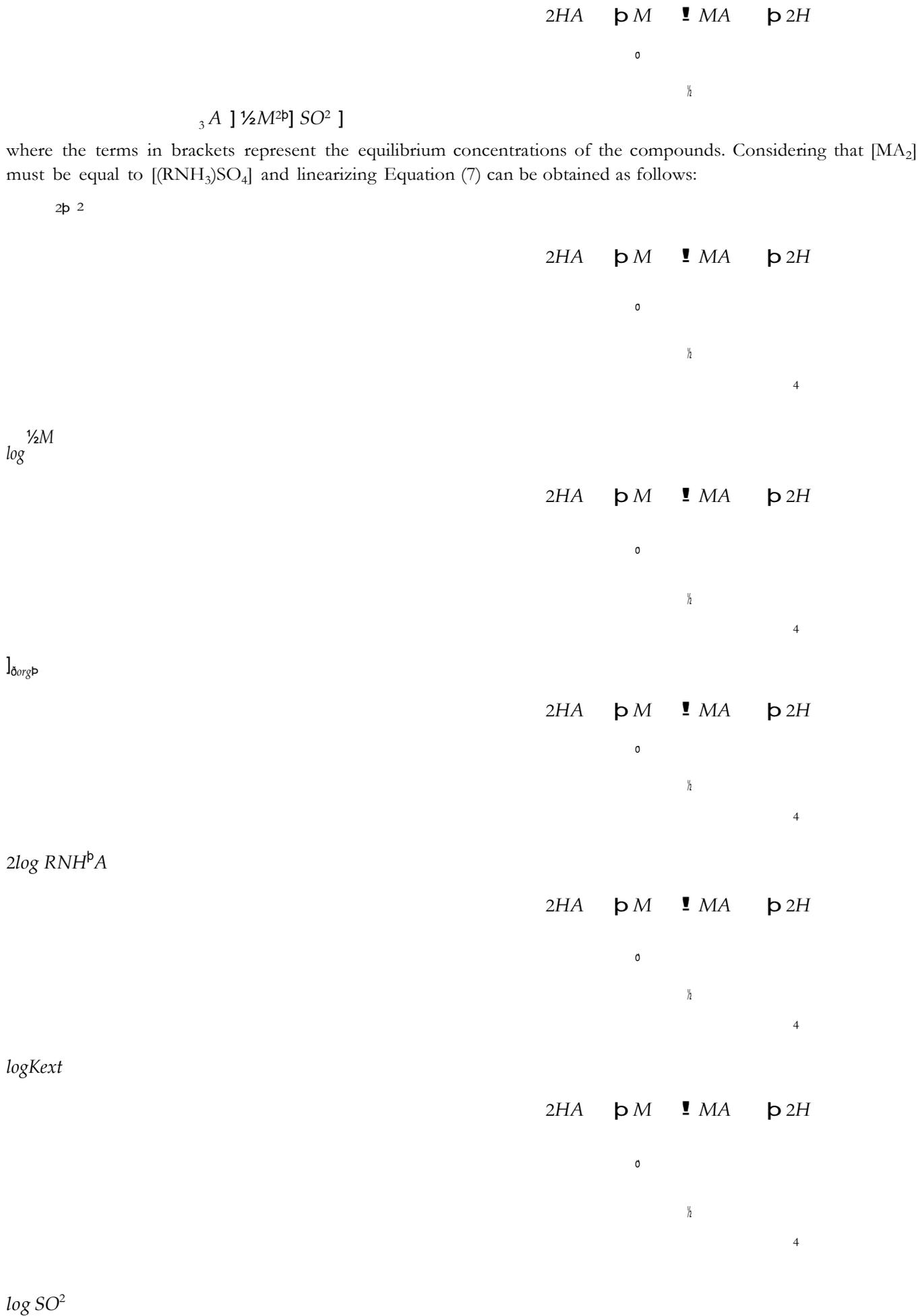
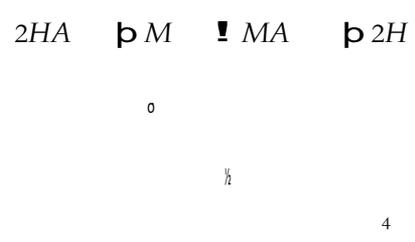
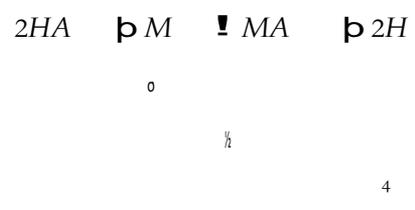
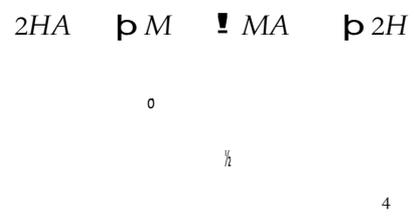


Figure 5. Effect of the [HJMT+Versatic⁻] IL concentration on the Co(II) and Ni(II) extraction and the pH of the equilibrium. Aqueous phase: 500 mg/L of Co(II) and 5000 mg/L of Ni(II) in 0.5 M sulphate solution and pH 6.2. JMT/Versatic molar ratio equal to 1.



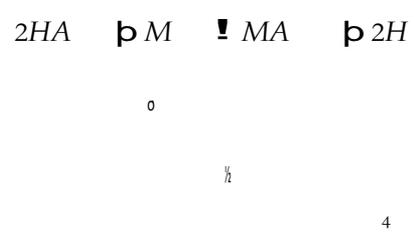
$$\frac{1}{2}M^{2p}]_{aq}^{1/4}$$

3 p p 4



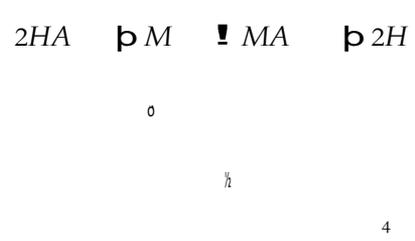
0 P

and as can be seen in Fig. 7, for the Co(II) extraction, the straight line obtained by plotting $\log([Co^{2+}_{(org)}]^2 /$



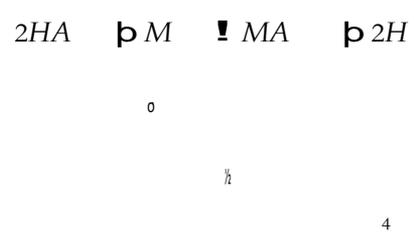
0 P

$$[Co^{2+}$$

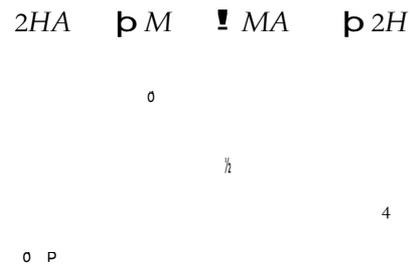


0 P

) versus $\log[RNH^+A^-]$ has a slope value



0 P



equal to 2. This suggests that the extraction mechanism of Co(II) corresponds to the model proposed in Equation (6).

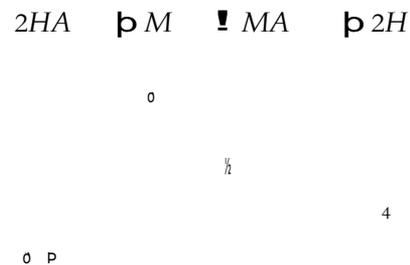
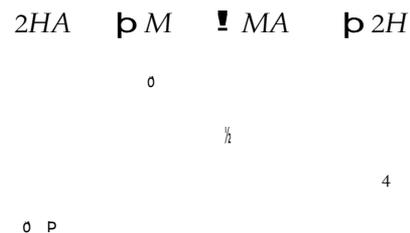


Figure 6. Effect of the [HJMT+Versatic] IL concentration on the separation factor. Aqueous phase: 500 mg/L of Co(II) and 5000 mg/L of Ni(II) in 0.5 M sulphate solution and pH 6.2. JMT/Versatic molar ratio equal to 1.



Effect of the CO/NI ratio on the separation of cobalt and nickel

On the other hand, this study also carried out the individual metal ions, 500 mg/L Co(II) and 5000 mg/L

Despite these last results, where low Ni(II) concentration in the mixture allows us to get better cobalt extraction, to make the separation, a solution containing relatively a high concentration of nickel (Co/Ni 1:10) is chosen because this ratio is often found in industrial applications.

Figure 7. Plot of $\log([Co^{2+}]_{(org)})/[Co^{2+}]_{(aq)}$ vs. \log

$\log([Co^{2+}]_{(org)})/[Co^{2+}]_{(aq)}$

vs. \log

Isotherm extraction

The equilibrium isotherm for the extraction of the individual metals ions as well as the extraction isotherm of the cobalt(II) in mixtures containing a constant concentration of nickel(II) (5000 mg/L) as shown in Fig. 9. The concentration of the ionic liquid is 0.47 M and the aqueous solutions contain metals ions in the

[HJMT⁺Versatic⁻] at constant 0.5 M of SO₄²⁻ and 0.47 M of the IL in the organic phase.

L Ni(II), and for a cobalt(II)/nickel(II) mixture containing 500 mg/L of each metal. The results in Fig. 8 indicate that the percentage of extraction in the case of cobalt alone and nickel alone increases by increasing [HJMT⁺Versatic⁻] IL even though cobalt is more influenced by this variable than the nickel. The observed extraction behaviour for the cobalt ion from the mixtures (with a ratio 1:1 and 1:10 w/w) is the same that it shows individually, but as can be seen in this figure, the extraction percentage increment is higher in the case of Co(II) from the mixture Co/Ni ratio of 1:1 compared to the Co(II) from the mixture Co/Ni ratio of 1:10. Independently on the extractant concentration, the extraction percentage of nickel(II) from the mixtures is maintained near to 10%, a value smaller than it gets for Ni(II) alone. The cobalt ion is preferentially extracted from the mixture, but the presence of a high amount of nickel makes it more difficult.

2 2+

range 50–5000 mg/L in 0.5 M of SO₄²⁻.

In all the cases, the equilibrium pH is in the range 7.2–7.3. For the individual metal ions, this figure shows again that the cobalt extraction gives better yields than the nickel extraction.

Comparing the cobalt isotherms, we can see that the presence of 5000 mg/L of nickel(II) (constant concentration) in the feed solution decreases the extraction of Co(II). In the same experiments, the concentration of Ni(II) in the organic phase decreases when the concentration of cobalt ion in the aqueous phase increases. This behaviour can be observed in Fig. 10 and it suggests that the preferential extraction of Co(II) hinders the extraction of Ni(II) and this fact will be exploited in the counter-current process.

Counter-current extraction

The McCabe–Thiele graphical method was used to calculate the number of theoretical equilibrium steps for the separation of Co(II) from the mixture using 0.47 M of IL. According to this method, the distribution equilibrium curve of the cobalt (isotherm) in the working range

2 2+

Figure 8. Effect of the [HJMT⁺Versatic⁻] IL concentration on the Co(II) and Ni(II) extraction for the individual metal ion and for the mixtures of the 1:1 and 1:10 Co/Ni ratios.

2 2+

Figure 9. Extraction isotherms for individual metal ion and for Co(II) in the mixture with 5000 mg/L of Ni(II). Aqueous phase: 0.5 M sulphate solution. Organic phase: 0.47 M of the IL.

Figure 10. Effect of the cobalt ion concentration on the nickel(II) extracted. Aqueous phases: 5000 mg/L Ni(II) and variable concentration of Co(II) in 0.5 M SO₄²⁻.

Figure 12. Evolution of the Co(II) and Ni(II) concentrations during the transitory period up to the steady state.

tration of Co(II) in 0.5 M SO₄²⁻

. Organic phase: 0.47 M of the IL.

state conditions are given in the scheme in Fig. 13. The metal ion concentrations obtained experimentally

(0–500 mg/L) and the mass balance line at a phase ratio A: O of 1:2 are represented in Fig. 11. Taking in consideration that the aim of this work is to separate the Co(II) from a mixture containing 5000 mg/L of nickel(II), constructing the McCabe–Thiele diagram confirms that four counter-current steps will be necessary.

The counter-current experiment is carried out by the procedure and at the conditions depicted previously in the experimental section. To be sure that the steady-state has been achieved, 14 runs were done. The evolution of Co(II) and Ni(II) concentrations in the fourth stage raffinate during the transitory period as shown in Fig. 12. We can see, after 11 runs, that the concentrations of these metal ions are constants (2 mg/L and near 4100 mg/L, respectively) meaning that 11 runs would be enough to achieve the steady-state.

The nickel(II) and cobalt(II) concentrations and the pHs obtained in each one of the four stages of the counter-current process after achieving the steady-

are in concordance with the values predicted by the McCabe–Thiele method and it can be seen in Fig. 11 where the experimental points are included as bold ticks. It is noticeable that the Co(II) concentration in the raffinate is reduced from 500 to 2 mg/L, obtaining a flow rich in nickel (99,95%) and practically cobalt free. These results indicate a good separation between nickel and cobalt using this ionic liquid in a four steps counter-current extraction process. As can be observed in

Fig. 13, the extraction by [HJMT⁺Versatic⁻] IL allows

us to maintain the pH nearly constant during the separation process avoiding the addition of an alkali to condition the aqueous phases. This is a great advantage via other extraction systems used to separate this challenging mixture.

Conclusions

In this article, an improvement on the separation of cobalt from nickel in sulphate medium is carried out using the cheap HJMT⁺Versatic⁻ ionic liquid.

The more important points that can be drawn from this work are as follow:

- Stoichiometric JMT/Versatic mixtures allow us to maintain the pH nearly constant during the counter-current process without conditioning the aqueous phases.
- The optimal concentration of the [HJMT⁺Versatic⁻] IL to carrying out the Co (II)/ Ni (II) separation is 0.47 mol/L.
- The applied counter-current procedure enables the reduction of the amount of the required reagents to simulate the separation process.

520 M. HADJ YOUCEF ET AL.

Figure 13. Concentration of the Co(II) and Ni(II) in each stage of the counter-current extraction process. A:O ratio = 1:2. Feed solution 500 mg/L of Co(II) and 5000 mg/L of Ni(II), pH = 6.2 and 0.5 M SO₄²⁻.

- The McCabe–Thiele diagram shows that at an A/ O phase ratio of 1/2, four theoretical stages are needed to separate cobalt from a solution containing 500 mg/L Co(II) and 5000 mg/L Ni(II) in 0.5 M SO₄²⁻ medium.
- The counter-current simulation confirms the McCabe–Thiele prediction and shows that four stages are enough to reduce the cobalt concentration from 500 mg/L to 2 mg/L.
- The raffinate contains 83% of the inlet nickel with a purity of 99.9%.

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