

# Nickel-cobalt separation by solvent extraction method

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Separation of cobalt(II), and nickel(II) ions from nitrate solutions using liquid-liquid extraction process was reported. The measurements were run at 25°C and at fixed ionic strength equal to 0.5 (KNO<sub>3</sub>, HNO<sub>3</sub>). Initial concentrations of Co(II) and Ni(II) nitric acid in the aqueous phase were constant (0.01 M and 0.15 M, respectively). Both 1-hexylimidazole (1), and 1-hexyl-2-methylimidazole (2), both in dichloromethane were used as extractants. Their concentrations in organic phase were varied from 0.01 to 0.25 M. Cobalt(II) in an aqueous solution forms both tetrahedral and octahedral complexes. Nickel(II) forms only a six-coordinate complexes. These general differences help to provide the basis for the various separation processes currently used for cobalt-nickel separation. The steric effect for extractant 2 facilitates the extraction of tetrahedral Co(II) complexes. Extraction percent (%E) of cobalt(II) and nickel(II) in the systems studied were calculated. The percentage extraction increases for increasing values of pH of aqueous phase and is the highest for pH = 7.2. In the aqueous phase, of which the pH = 7.2, there remain 75% Ni(II) and 40% Co(II) for extractant 1 and the respective values for extractant 2 are 85% Ni(II) and 20% Co(II).

The steric effect increases selectivity coefficients Co(II)/Ni(II). The highest selectivity coefficients for both extractants were obtained at a pH of aqueous phase = 6.2; their values were 5 and 8.9 for extractants 1 and 2, respectively.

**Keywords:** separation ions, solvent extraction, cobalt(II), nickel(II), alkylimidazole

## Introduction

The separation of cobalt from nickel in aqueous solution has always been a problem for hydrometallurgy. Their adjacent positions in transition metal series in the periodic table results in aqueous chemical behavior that is too similar for easy their separation. Although both cobalt and nickel preferentially exist as divalent hexahydrated ions in dilute aqueous solution, the rate exchange of water molecule in the coordination sphere for the cobalt ion is very much higher than for nickel. Cobalt(II) in an aqueous solution forms both tetrahedral and octahedral complexes. By contrast, Ni(II) having a rigid coordination sphere forms only a six-coordinate complexes, and in the particular conditions of flat square complexes. These general differences help to provide the basis for the various separation processes currently used for cobalt-nickel separation. These differences are used in the extraction methods of separation of these two ions [1].

The separation of Co(II) and Ni(II) by solvent extraction has been studied over the last 25 years or so [2]. At present many commercial plants use the phosphoric (D2EHPA) [3], [4], phosphinic (Cyanex 272, Cyanex 301, Cyanex 302, DDPA) [4]–[7] or phosphonic acids (PC88A, DDPA) [3], [6]–[8] and their mixture [3] as extractant. The separation factor increases in the series phosphoric < phosphonic < phosphinic acids [10]. Also used phosphoric acid and derivatives of oximes mixtures [11], [12], derivatives of carboxylic acids or sulfonic with aliphatic hydroxoximes [12]–[14], hydroxamic acids (LIX1104, LIX63,

VERSATIC) [15], [16], and pyridine derivatives [17]. The separation process was carried out with acidic sulphate [5], [18] or chloride [16] solutions or from concentrated HCl using a water insoluble amine (Alamine 336) [19].

Alkyl derivatives of imidazole are a convenient group of bases of which the complex-forming properties in respect of transition metals may be predicted and programmed in order to differentiate their extraction properties so as to improve the selectivity of recovery of selected metals [20]–[23].

In this work, the authors present results of their investigation of the liquid-liquid extraction of the cobalt(II) and nickel(II) ions from nitrate solutions. 1-Hexylimidazole (1), and 1-hexyl-2-methylimidazole (2) both in dichloromethane were used as extractants. The values extraction percent (%E), and selectivity coefficient ( $S_{M(1)/M(2)}$ ), were calculated for the analysis of the extraction process.

## Experimental

### Reagents

Inorganic chemicals: cobalt(II), nickel(II), and potassium nitrates from POCh (Gliwice, Poland) were of analytical grade and were purchased. Aqueous solutions were prepared with double distilled water (conductivity 5  $\mu$ S/m). Concentration of the Co(II) and Ni(II) salts were determined by titration with EDTA and that of potassium nitrate gravimetrically as sulfate. Nitric acid (analytical reagent, POCh) was standardized against anhydrous sodium carbonate and sodium tetraborate decahydrate.

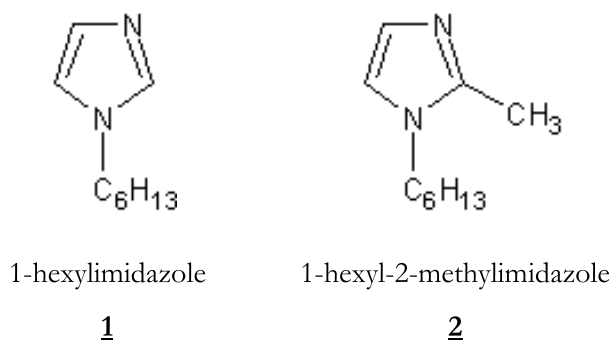


Fig. 1. Structural diagrams of extractants

Dichloromethane (from Fluka) was of analytical grade and was used without further purification. Alkylimidazoles **1** and **2** (Fig.1) were synthesized as described [24].

The pH-meter was calibrated using commercial buffer solutions (Radiometer) of  $\text{pH } 4.01 \pm 0.01$  and  $7.00 \pm 0.01$ . The pH was also checked against hydrochloric acid according to IUPAC recommendations [25].

### Extraction Procedure

The measurements were run at  $25^\circ\text{C}$  and at fixed ionic strength (0.5) maintained in the aqueous phase with  $\text{KNO}_3 + \text{HNO}_3$ . Before extraction, concentrations of the metal ions and nitric acid in the aqueous phase were constant (0.01 M and 0.15 M, respectively) and the extractants (**1** – **2**) concentrations in organic phase were varied from 0.01 to 0.25 M. Six  $\text{cm}^3$  of the aqueous phase were placed in a graduated test tube and an equal volume of extractants (**1** – **2**) solution in dichloromethane was added. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes, however, no longer than 30 min. After that the phases were separated, and the pH of the aqueous phase was measured.

The Co(II) and Ni(II) concentrations in the aqueous phase were determined on emission spectrophotometer.

### Results and discussion

Extraction percent (%E) of cobalt(II) and nickel(II) in the systems studied were calculated on the basis of the metal concentrations in the aqueous phase before and after attaining partition equilibrium from the following equation:

$$\%E = \frac{C_M}{C_M^0} * 100\% \quad (1)$$

where:  $C_M^0$  and  $C_M$  denote analytical metal ions concentrations in the aqueous phase before and after attaining partition equilibrium, respectively.

A graph of the relationship %E vs. pH of aqueous phase after extraction was plotted for every system (Fig. 2).

An analysis of the data shown in Fig. 2 indicates that the percentage extraction increases for increasing values of

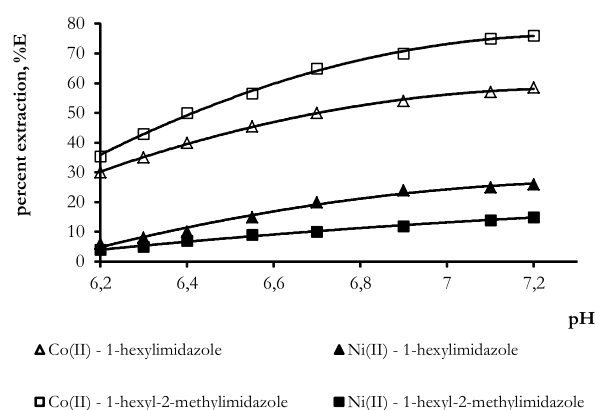
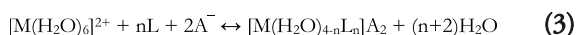
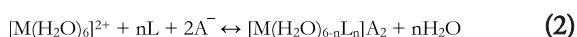


Fig. 2. Percent extraction vs. pH

pH of aqueous phase and is the highest for  $\text{pH} = 7.2$ , although the percentage extraction for Ni(II) is not higher than 25% while for Co(II), it is ab. 60% for extractant **1** and ab. 80% for **2**. The steric effect of the methyl substitute in position 2 in the molecule of extractant **2** makes difficult the extraction of Ni(II) complexes (lower values of %E, compared with extractant **1**) and is accountable for the higher percentage extraction of Co(II) ions.

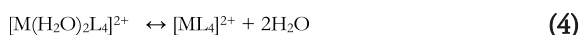
In the aqueous phase, of which the  $\text{pH} = 7.2$ , there remain 75%Ni(II) and 40% Co(II) for extractant **1** and the respective values for extractant **2** are 85% Ni(II) and 20% Co(II).

The steric effect much less hinders the formation of tetrahedral complexes of 1-alkyl-2-methylimidazoles with cations which have an ability to change the shape of a coordination polyhedron from an octahedron to a tetrahedron (Eqs 2, 3) [22], [26]–[28].



where L denotes the extractant molecule.

The reactions, described by Equation (3) and involving a change in the coordination number, are typical for Co(II), especially for the fourth stage of complexation ( $n=4$ ). In such cases, configuration equilibria are established (Eq.4) between  $\text{ML}_n$  complexes, which have different coordination sphere structures, for instance:



The occurrence of configuration equilibria in the  $n$ -th stage of complexation will lead to higher values of its corresponding stability constant,  $\beta_n$  (Table 1), because it is a sum of the stability constant of the tetrahedral complex,  $\beta_t$  and the octahedral complex  $\beta_o$  ( $\beta_n = \beta_t + \beta_o$ ) [26]–[28]. There was a decrease in the stability of all the metal

Table 1. Comparison of the stability constants  $\beta_n$  of Co(II), and Ni(II) complexes with 1-hexylimidazole (1), and 1-hexyl-2-methylimidazole (2), at 25°C, ionic strength 0.5 mol/dm<sup>3</sup> (KNO<sub>3</sub>)

Ligand/pKa <sup>[29]</sup>	metal ions	log $\beta_1$	log $\beta_2$	log $\beta_3$	log $\beta_4$
1-hexylimidazole 7.32	Co(II) [28]	3.47	5.64	7.14	8.38
	Ni(II) [30]	3.29	5.34	7.07	7.95
1-hexyl-2-methylimidazole 8.35	Co(II) [22]	1.96	2.18	3.02	5.61
	Ni(II) [27]	2.08	4.62		

complexes due to steric hindrance, which in turn, depends on the kind of the central ion.

Separation coefficients ( $S_{M(I)/M(II)}$ ) for cobalt were calculated in the case of each extraction system, from the following formula:

$$S_{M(I)/M(II)} = \frac{\%E_{M(I)}}{\%E_{M(II)}} \quad (5)$$

The results of the calculations are presented in Figure 3.

The calculated selectivity coefficients for extractant **2** are nearly twice as high as those for **1**. The highest selectivity coefficients for both extractants were obtained at a pH of aqueous phase = 6.2; their values were 5 and 8.9 for extractants **1** and **2**, respectively.

From a practical point of view, for the selective separation of Co (II) should be chosen concentrations of reactants (metal ions, 1-hexyl-2-methylimidazole, nitric acid) to obtain a pH close to 6.4. This pH is also preferred to the environment. The steric effect of the substituent in a position 2 allows selective separation of the Co (II) and Ni (II), and consequently obtaining metals with a high degree of purity.

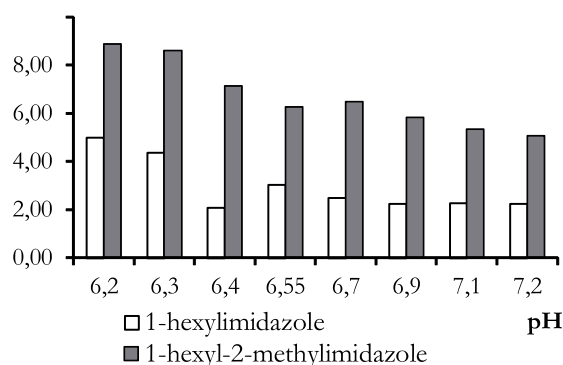


Fig. 3. Separation coefficients cobalt/nickel vs. pH of the aqueous phase.

## Conclusion

The alkylimidazoles that were used in the present work enable extraction from solutions having nearly neutral pH values.

The steric effect, caused by the presence of the  $-CH_3$  group in the molecule of 1-hexyl-2-methylimidazole accounts for higher concentrations of cobalt tetrahedral complexes, thereby increasing extraction of the metal.

The steric effect increases selectivity coefficients Co(II)/Ni(II). The highest selectivity coefficients for both extractants were obtained at a pH of aqueous phase = 6.2; their values were 5 and 8.9 for extractants **1** and **2**, respectively.

Possibly, selectivity for this type of extractant could be increased by placing, in position 2, an imidazole ring of a larger or more branched substitute (for instance, ethyl or isopropyl substitute), thus intensifying the steric effect. *The new developments presented above were carried out within the 2007-2013 Innovative Economy Operational Programme, Sub-action 1.3.2., Support of the protection of industrial property generated by scientific entities as result of R&D works within project no. UDA-POIG.01.03.02-04-077/12-00, financed by the European Regional Development Fund (ERDF) (85% of co-financing) and from a designated subsidy (15% of co-financing).*

## References

- [1] Flett D.S., Cobalt-nickel separation in hydrometallurgy: a review. *Chem.Sust.Dev.*, 12, pp. 81-91, 2004.
- [2] Ritcey G.M., in: Nickel'96, *The Australasian Institute of Mining and Metallurgy*, 1996, p. 251.
- [3] Sarangi K., Reddy B.R., et al., Das, Extraction studies of cobalt (II) and nickel (II) from chloride solutions using Na-Cyanex 272.: Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. *Hydrometallurgy*, 52, pp. 253-265, 1999.
- [4] Darvishi D., Haghshenas D.F., et al., Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. *Hydrometallurgy*, 77, pp. 227-238, 2005.
- [5] Tsakiridis P.E., Agatzini S.L., Simultaneous solvent extraction of cobalt and nickel in the presence of manganese and magnesium from sulfate solutions by Cyanex 301. *Hydrometallurgy*, 72, pp. 269-278, 2004.
- [6] Xing P., Wang Ch., et al., Cobalt separation from nickel in sulfate aqueous solution by a new extractant: Di-decylphosphonic acid (DDPA). *Hydrometallurgy*, 113-114, pp. 86-90, 2012.
- [7] Tait B. K., Cobalt-nickel separation: the extraction of cobalt(II) and nickel(II) by Cyanex 301, Cyanex 302 and Cyanex 272. *Hydrometallurgy*, 32, pp. 365-372, 1993.
- [8] Dreisinger D.B., Cooper W.Ch., The solvent extraction separation of cobalt and nickel using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester. *Hydrometallurgy*, 12, pp. 1-20, 1984.
- [9] Luo L., Wei J., et al., Extraction studies of cobalt (II) and nickel (II) from chloride solution using PC88A. *Trans. Nonferrous Met. Soc. China*, 16, pp. 687-692, 2006.
- [10] Preston J.S., Solvent extraction of cobalt and nickel by organophosphorus acids I. Comparison of phosphoric, phosphonic

- and phosphonic acid systems. *Hydrometallurgy*, 9, pp. 115-133, 1982.
- [11] Zhang P., Yokoyama T., et al., The synergistic extraction of nickel and cobalt with a mixture of di(2-ethylhexyl) phosphoric acid and 5-dodecylsalicylaldoxime. *Hydrometallurgy*, 61, pp. 223-227, 2001.
- [12] Preston J.S., Solvent extraction of nickel and cobalt by mixtures of carboxylic acids and non-chelating oximes. *Hydrometallurgy*, 11, pp. 105-124, 1983.
- [13] Cheng Ch. Y., Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxoxime. *Hydrometallurgy*, 84, pp. 109-117, 2006.
- [14] Osseo-Asare K., Renninger D.R., Synergic extraction of nickel and cobalt by LIX63-dinonylnaphthalene sulfonic acid mixtures. *Hydrometallurgy*, 13, pp. 45-62, 1984.
- [15] Zhang W., Pranolo Y., et al., Extraction and separation of nickel and cobalt with hydroxamic acids LIX®1104, LIX®1104SM and the mixture of LIX®1104 and Versatic 10. *Hydrometallurgy*, 119-120, pp. 67-72, 2012.
- [16] Coll M.T., Fortuny A., et al., Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. *Hydrometallurgy*, 125-126, pp. 24-28, 2012.
- [17] Zhou T., Pesic B., A pyridine-based chelating solvent extraction system for selective extraction of nickel and cobalt. *Hydrometallurgy*, 46, pp. 37-53, 1997.
- [18] Longao Z., Impurity removal and cobalt-nickel separation from sulphate solution by solvent extraction with B312. *Hydrometallurgy*, 24, pp. 167-177, 1990.
- [19] Sayar N.A., Filiz M., et al., Extraction of Co(II) and Ni(II) from concentrated HCl solutions using Alamine 336. *Hydrometallurgy*, 96, pp. 148-153, 2009.
- [20] Cupery M.E., N-Imidazole Compounds and Their Complex Metal Derivatives. *US Patent*, 3843667, October 22, 1974.
- [21] Schakers, J.M., du Preez, et al., Solvent Extraction Mixture Comprising Substituted Imidazole or Benzimidazole for the Purification of Groups of Base Metals. *US Patent*, US 20040208808 A1, October 21, 2004.
- [22] Radzimska-Lenarcik E., Witt K., The influence of alkyl chain length and steric effect on stability constants and extractability of Co(II) complexes with 1-alkyl-2-methylimidazoles. *Sep. Sci. Technol.*, 2014, DOI: 10.1080/01496395.2014.959600 to be published.
- [23] du Preez, J.G.H., et al., Nitrogen reagents in metal ion separation. XI. The Synthesis and Extraction Behavior of a New NS Imidazole Derivative. *Solv. Extr. Ion Exch.*, 19, pp. 143-154, 2001.
- [24] Pernak J., Krysinski J., et al., Bakterizide wirkung von iminimverbindungen, *A. Tenside Surfact. Det.*, 24, pp. 276-286, 1987.
- [25] Braibanti, A.; Ostacoli G., et al., Potentiometric Apparatus and Technique for the pH-metric Measurement of Metal-complex Equilibrium Constants, *Pure Appl. Chem.*, 59, pp. 1721-1728, 1987.
- [26] Radzimińska-Lenarcik E., Search for the possibility of utilizing the differences in complex-forming capacities of alkylimidazoles for selective extraction of some metal ions from aqueous solutions. *Polish J. Chem. Technol.*, 10, pp. 73-78, 2008.
- [27] Lenarcik B., Adach A., et al., The influence of steric effect and alkyl chain length on the extraction of the complexes of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with 1-alkyl-2-methylimidazole. *Polish Journal of Chemistry*, 73, pp. 1273-1281, 1999.
- [28] Lenarcik B., Ojczenasz P., Investigation of the stability constants of Co(II) complexes with a homologous series of 1-alkylimidazoles in aqueous solution by using a partition method with several solvents, *Sep. Sci. Technol.*, 39, pp. 199-226, 2004.
- [29] Lenarcik B., Ojczenasz P., The Influence of the Size and Position of the Alkyl Groups in Alkylimidazole Molecules on Their Acid-Base Properties, *J. Heterocyc. Chem.*, 39, pp. 287-290, 2002.
- [30] Lenarcik B. Rauckyte T., The influence of alkyl length on extraction equilibria of Ni(II) complexes with 1-alkylimidazoles in aqueous solution/organic solvent systems. *Sep. Sci. Technol.*, 39, pp. 3353-3372, 2004.

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