Solvent Extraction of Ni(II) from Sulfate Solutions with LIX 84I: Flow-Sheet for the Separation of Cu(II), Ni(II) and Zn(II)

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This paper reports on solvent-extraction studies of Ni(II) from sulfate solutions with LIX 84I (2-hydroxy-5-nonylacetophenoneoxime) as the extractant. The extraction of metal depends on the equilibrium pH of the aqueous phase and the extractant concentration. The transfer of metal follows a cation exchange-type mechanism: $\text{Ni}^{2+} + 2\text{HA} \rightarrow \text{NiA}_2 + 2\text{H}^+$. Extraction varies with the nature of the diluents. Temperature has no effect on the extraction of metal. The extraction behavior of associated metals clearly demonstrates the application of LIX 84I as the extractant for the separation of Cu(II), Ni(II) and Zn(II). Based on the results, a flow sheet of the process was developed.

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Introduction

Nickel is primarily used as an alloying metal. The other uses of nickel are in electroplating and batteries, and as catalysts. Sulfidic, oxidic nickel ores and various nickel bearing secondary materials, such as super alloy scrap, spent batteries and catalysts, dust *etc.*, are potential sources for nickel production.

Nickel-bearing ores/concentrates/other raw materials are treated either by hydrometallurgical or pyrometallurgical routes. In general, untreated or pretreated materials are leached in an ammoniacal or acidic medium. Sulfuric acid, hydrochloric acid or their mixtures are used for the dissolution/leaching of secondaries, such as super-alloy scrap. Thus-obtained leach solutions chiefly contain nickel and cobalt, along with other impurities, such as iron, copper, chromium, aluminum and silica. From such solutions, iron, chromium, aluminum, silica are removed by lime precipitation. Liquid-liquid extraction has been applied to many solutions to obtain either metals or salts in highly pure form. The most widely used extractants are phosphoric acid based alkyl phosphorous reagents D2EHPA, PC 88A, Cyanex 272, or their equivalents. These alkyl phosphorous acid extractants, although they extract both cobalt and nickel, have selectively for cobalt over nickel.¹⁻⁶ In our earlier studies, LIX 84I was used for the recovery of Ni(II) from ammoniacal sulfate liquor containing Ni: 20.5 g L⁻¹, Co: 0.2 g L⁻¹ and (NH₄)SO₄: 23.6 g L⁻¹.⁷ Literature reveals that this extractant was extensively used for copper extraction.⁸⁻¹² Price and Reid¹³ described the separation of nickel from cobalt, both present as amines, using modified LIX 84 I.

In this paper, we report on the solvent extraction of nickel(II) from sulfate solutions using LIX 84I as the extractant. The parameters studied are: the effect of the pH, the extractant concentration, diluents, loading capacity of the extractant, regeneration and recycling, stripping, extraction behavior of associated metals and finally the development of a flow-sheet

for the separation and recovery of copper(II), nickel(II) and zinc(II) from a typical synthetic sulfate solution using LIX 84I.

Experimental

Apparatus and reagents

A Perkin Elmer Model A300 atomic absorption spectrometer and a digital Digisun (DI 707 Model) pH meter with a combined glass electrode were used. The IR spectrum of the metal complex was recorded using a FTIR-Nicolet (USA)-740-spectrophotometer.

A stock solution of a 0.1 mol dm⁻³ nickel(II) solution was prepared by dissolving the requisite quantity of Analar NiSO₄ in distilled water. The nickel solution was standardized against a 0.05 mol dm⁻³ EDTA solution¹⁴ using a murexide indicator. Working standard solutions were prepared by suitable dilution of this stock solution. LIX 84I is a proprietary product of M/s. Cognis is a 2-hydroxy-5-*t*-nonylacetophenoneoxime having a molecular weight of ~263¹³ was used as such. Distilled kerosene (bp. 433–473 K) was used as the diluent. All other chemicals and reagents used were of Analar grade.

General extraction procedure

A suitable aliquot (10 ml) of a solution containing metal ion was equilibrated with an equal volume of LIX 84 I for 20 min in a separating funnel. Initial experiments on the effect of time on metal extraction indicated that 15 min is sufficient to reach an equilibrium reaction. Adding dilute H₂SO₄ or NaOH adjusted the equilibrium pH of the aqueous solution to the desired value. After phase disengagement, the aqueous phase was separated and the metal concentrations were analyzed by AAS. The distribution ratio, (*D*) was calculated as the concentration of the metal present in the organic phase to that part in the aqueous phase at equilibrium. As and when required, the metal concentration in the organic phase was determined after filtration through a 1PS paper and stripping a suitable aliquot with 1 mol dm⁻³ HCl, followed by analysis. All of the experiments were carried out at room temperature (303 ± 1 K).

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Fig. 1 Plot of the equilibrium pH vs log D . Extraction conditions: Ni(II), 0.0025 mol dm⁻³; LIX 84I, 0.01 mol dm⁻³.

Fig. 3 Plot of log[Ni(II)]_{aq} vs. log[Ni(II)]_{org}. Extraction conditions: LIX 84I, 0.01 mol dm⁻³; equilibrium pH, 7.50.

Fig. 2 Plot of log[extractant], mol dm⁻³ vs. log D . Extraction conditions: Ni(II), 0.005 mol dm⁻³; equilibrium pH, 7.50.

Results and Discussion

Extraction mechanism and species

The extraction equilibrium of nickel(II) from sulfate solutions with LIX 84I as an extractant may be represented as:

where K_{ex} denotes the equilibrium constant.

$$K_{\text{ex}} = \frac{[\text{NiA}_2][\text{H}^+]^2}{[\text{Ni}^{2+}][\text{HA}]^2}, \quad (2)$$

$$K_{\text{ex}} = \frac{D[\text{H}^+]^2}{[\text{HA}]^2}, \quad (3)$$

$$\text{where } D = \frac{[\text{NiA}_2]}{[\text{Ni}^{2+}]}. \quad (4)$$

Taking the logarithm of Eq. (3) and rearranging,

$$\log D = \log K_{\text{ex}} + 2\log[\text{HA}] + 2\text{pH}. \quad (5)$$

Analyzing the experimental data of distribution ratio (D) as a function of the equilibrium pH and the extractant concentration at constant value of other parameters allows an estimation of the

number of extractant molecules associated with the extracted metal complex.

The extraction of nickel (0.0025 mol dm⁻³) with LIX 84I (0.01 mol dm⁻³ and 0.005 mol dm⁻³) as a function of the pH showed an increase in the percentage extraction with an increase in the equilibrium pH. Further, a plot of log D vs. equilibrium pH (Fig. 1) gave a straight line with a slope of 2.0, indicating the exchange of two moles of H⁺ for every mole of metal ion during the extraction process.

The effect of the LIX 84I concentration (0.005 to 0.05 mol dm⁻³) on the extraction of Ni(II) (0.005 mol dm⁻³) was investigated. It was observed that the extraction of nickel increased with an increase in the extractant concentration. A plot of log D vs. log[HA] (Fig. 2) gave a straight line with a slope of 2, indicating that two moles of the extractant (HA = LIX 84I) were involved with the extracted complex.

The effect of nickel concentration (0.001 – 0.003 mol dm⁻³) on the extraction was investigated using LIX 84I (0.01 mol dm⁻³) at an equilibrium pH of 7.50. The extraction of nickel(II) was found to be independent of the metal ion concentration in the aqueous phase. A log-log plot (Fig. 3) of the equilibrium organic phase metal concentration against the aqueous phase metal concentration is linear with a slope of 1.0, indicating the extraction of mononuclear species into the organic phase. The species extracted into the organic phase appears to be NiA₂.

Effect of salts

The effect of salts, such as NaCl, Na₂SO₄, NaNO₃ and NaSCN, was studied in the concentration range 0.2 – 2.0 mol dm⁻³ on the extraction behavior of 0.001 mol dm⁻³ Ni(II) with 0.01 mol dm⁻³ LIX 84I. It was observed that there was a decrease in the percentage extraction of Ni(II) from 100 – 88.6% along with an increase in the salt concentration, when NaNO₃ was used as the salt. With other salts, the decrease in the percentage of extraction was marginal (100 – 95%). At a given concentration of metal and extractant, the percentage extraction followed in decreasing order as NaNO₃ > Na₂SO₄ > NaCl > NaSCN.

Effect of diluents and temperature

The extraction of Ni(II) (0.001 mol dm⁻³) using LIX 84I (0.01 mol dm⁻³) at an equilibrium pH of 7.5 in various diluents was investigated. The results demonstrate that the extraction of Ni(II) varies with the nature of the diluent, and decreases in the following order: xylene ($D = 1.15$) < chloroform ($D = 3.61$) < toluene ($D = 7.33$) < carbon tetrachloride ($D = 10.32$) < benzene

Fig. 4 Plot of the stage number vs. loading of organic phase by Ni(II). Loading conditions: Ni(II), 0.005 mol dm⁻³; LIX 84I, 0.01 mol dm⁻³; equilibrium pH, 7.50.

($D = 17.3$) < cyclohexane ($D = 32$) < *n*-hexane ($D = 47.8$) < kerosene ($D = 233.3$). In the present study, kerosene was used, considering the point that it is the cheapest commercially available diluent. The variation of the temperature in the range of 303 – 333 K ($\pm 1^\circ$) on the extraction of metal from an aqueous solution containing 0.0025 mol dm⁻³ Ni(II) and 0.01 mol dm⁻³ LIX 84I at an equilibrium pH of 7.5 was studied. The results demonstrated that the temperature had no effect on either the percentage extraction or stripping of Ni(II), and remained constant with an increase in temperature ($D = 1.015 \pm 0.002$).

Loading capacity of the extractant

An aliquot of 10 ml of 0.01 mol dm⁻³ LIX 84I was repeatedly contacted at 303 ± 1 K for 15 min with the same volume of aqueous solutions containing 0.005 mol dm⁻³ of Ni(II). After equilibration, the phases were analyzed for nickel content. The amount of nickel transferred into the organic phase in each contact was calculated based on the difference, and the cumulative concentration of nickel in the organic phase after each stage of contact was determined. A plot of the cumulative [Ni(II)]_{org} of LIX 84I versus the contact number is shown in Fig. 4. It is clear that nickel existing in the aqueous phase was extracted into the organic phase up to 10th contact, and thereafter remained constant. An analysis of L.O. containing 0.283 g L⁻¹ Ni(II), which corresponds to a loading efficiency of 97% of the extractant, indicated that the extractant used was in the pure form.

Stripping studies

The behavior of acids on the stripping of loaded organic containing 0.283 g L⁻¹ Ni(II) was studied using different stripping agents, such as HCl, H₂SO₄ and HNO₃, in the concentration range of 0.5 – 8.0 mol dm⁻³. The results show a marginal variation of the stripping efficiency (from 95 – 99.3%) with increasing acid concentration.

Regeneration and recycling capacity of LIX 84

The recycling capacity of 0.01 mol dm⁻³ LIX 84I for the extraction of Ni(II) (using 0.0025 mol dm⁻³ metal and equilibrium pH 5.32) was carried out by first loading the extractant with Ni(II), and then stripping with 1 mol dm⁻³ H₂SO₄ at the unit phase ratio. Single-stage extraction gave L.O. containing 0.055 g L⁻¹ Ni(II), corresponding to an extraction efficiency of 50% (Fig. 1). The stripped organic phase was washed with distilled water once and then used for extraction.

Fig. 5 Extraction behavior of associated metals as a function of the equilibrium pH. Extraction conditions: Ni, Cd, Co, Cu, Mn, and Zn, 0.0025 mol dm⁻³; LIX 84I, 0.1 mol dm⁻³.

The results revealed a practically insignificant change in the extraction (50%) and stripping efficiency (100%) of these extractants up to ten cycles of extraction.

IR studies

Characterization studies for confirming the Ni-LIX 84I complex in the organic phase were studied by FT-IR. L.O. containing 0.283 g L⁻¹ Ni(II) was used for this study. In the IR spectrum of the complex, the characteristic N-OH group of the LIX 84I that is present around 3500 cm⁻¹ (LIX 84I reference sample) is absent in the complex, since the metal appeared to be bonded to nitrogen. Also, the stretching frequency of the band increased from 950 cm⁻¹ to 974.94 cm⁻¹ (which is the characteristic of aryl group), showing a shift in that region, thus confirming bond formation.

Extraction behavior of associated elements

The extraction behavior of Ni(II) with other commonly associated metal ions, namely Cd, Co, Cu, Mn and Zn, of 0.0025 mol dm⁻³ concentration was studied with 0.1 mol dm⁻³ LIX 84I. Figure 5 gives the extraction curves of these metals with LIX 84I. It was observed that the percent extraction of metals depended mainly on the equilibrium pH of the aqueous phase. The extraction of Cu(II) started at pH values of < 0.2, and reached quantitative extraction at equilibrium pH ~4.0. Under these conditions, the extraction of Co and Cd was less than 5 and Mn ~20%. The extraction of Ni and Zn was nil. These results indicate that the extraction of nickel started after equilibrium at pH 4, and reached more than 90% upon equilibrium at pH 5.7, which is much below Zn extraction starting pH. Finally, the results clearly demonstrate the possible separation of Cu(II), Ni(II) and Zn(II) from their mixtures.

Flow sheet for the separation and recovery of Cu, Ni and Zn

Based on the data for the extraction behavior of Ni(II) with the associated elements, a flow sheet for the separation of Ni from Cu and Zn has been proposed while taking into account differences in their percentage extraction as a function of the equilibrium pH of the aqueous phase. For this purpose, a synthetic solution containing Ni, Cu and Zn (Cu: 0.150 g L⁻¹, Ni: 0.140 g L⁻¹, Zn: 0.161 g L⁻¹) was prepared.

The flow-sheet of the process for the recovery of Cu, Ni and Zn using 0.5 mol dm⁻³ LIX 84I is shown in Fig. 6. The solution was first subjected to copper extraction in a single stage at an equilibrium pH of 4.0 and an A:O ratio of 1:1, which gave

Fig. 6 Flow sheet for the separation of nickel, copper and zinc. Conditions: Cu, 0.150 g L⁻¹; Ni, 0.140 g L⁻¹; Zn, 0.161 g L⁻¹; LIX 84I, 0.5 mol dm⁻³.

99.7% Cu extraction efficiency. Further, a two-stage counter-current simulation test for the separation of Cu at an A:O ratio of 1:1 gave a copper extraction efficiency of 99.9%. The Cu raffinate contained Cu (0.0002 g L⁻¹), Ni (0.140 g L⁻¹) and Zn (0.161 g L⁻¹). Then a two-stage counter current simulation for the stripping of Cu from loaded organic (Cu: 0.1498 g L⁻¹) with 50 g L⁻¹ H₂SO₄ in two stages at A:O ratio of 1:1.75 gave a stripping efficiency of 99.8% copper. Ni extraction for Cu raffinate was carried at an equilibrium pH of 7.50, which gave a Ni extraction efficiency of 92% at an A:O ratio of 1:1.2. A two-stage counter current simulation for the extraction of Ni at A:O of 1:1.2 was conducted. This resulted in Ni raffinate containing 0.001 g L⁻¹ of Ni and 0.161 mg L⁻¹ of Zn, corresponding to Ni extraction efficiency of 99.3%. The Ni from L.O. (Ni: 0.1159 g L⁻¹) was stripped with 50 g L⁻¹ H₂SO₄ in two stages at an A:O ratio of 1:1.5, which gave a stripping efficiency of 98.9%. The resultant Ni raffinate was further processed for Zn extraction at an equilibrium pH of 9.0. Single-stage extraction data with the same extractant indicated extraction efficiency of 99.5% at A:O ratio of unity. Zinc from L.O. (Zn: 0.1602 g L⁻¹) was then subjected to stripping with 150 g L⁻¹ H₂SO₄ in two stages at an A:O ratio of 1:1, which gave a stripping efficiency of 99%.

Conclusions

LIX 84I, a commercial extractant supplied by Cognis, Ireland, was exploited for solvent-extraction studies of Ni(II) from a sulfate medium and the recovery of Cu(II), Ni(II) and Zn(II) from a synthetic solution. The extraction of Ni(II) depends on

the equilibrium pH of the aqueous phase and the extractant concentration, and follows a cation-exchange mechanism. Based on the differences in the extraction behavior of various metals, this extractant clearly indicated the possible separation of Cu(II), Ni(II) and Zn(II). Complete flow sheet of the process was developed, and the obtained metals were in pure form.

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References

1. D. S. Flett and D. W. West, "Complex Metallurgy 78", Paper International Symposium, ed. M. J. Jones, **1978**, Inst. Min. Metall., London, England, 49 - 57.
2. J. S. Preston, *Hydrometallurgy*, **1982**, 9, 115.
3. W. A. Rickelton, D. S. Flett, and D. W. West, *Solvent. Extr. Ion Exch.*, **1984**, 2, 815.
4. A. W. Ashbrook and G. M. Ritcey, paper presented at the Conference of Metallurgists, **1971**, Montreal, Canada, August 30, 45.
5. B. R. Reddy and P. V. R. Bhaskara Sarma, *Miner. Metall. Process.*, **2001**, 18, 172.
6. P. V. R. Bhaskara Sarma and B. R. Reddy, *Miner. Eng.*, **2002**, 15, 461.
7. C. Parija, B. R. Reddy, and P. V. R. Bhaskara Sarma, *Hydrometallurgy*, **1998**, 49, 255.
8. G. A. Kordosky, S. M. Olafson, R. G. Lewis, V. L. Deffner, and J. E. House, *Sep. Sci. Technol.*, **1987**, 22, 215.
9. A. I. Ali, J. A. Daoud, and H. F. Aly, *J. Chem. Technol. Biotechnol.*, **1996**, 67, 137.
10. J. Yang, "Proceedings of International Solvent Extraction Conference, ISEC'1993", ed. D. H. Logsdail and M. J. Slater, **1993**, Vol. 1, York, UK, 183 - 188.
11. J. H. Russell and R. L. Rickel, *Solvent. Extr. Ion Exch.*, **1990**, 8, 855.
12. F. Hu, "Proceedings of International Solvent Extraction Conference, ISEC'1996", ed. D. C. Shallcross, R. Paimin, and L. M. Prvcic, **1996**, Vol. 1, Melbourne, Australia, 727 - 732.
13. M. J. Price and J. G. Reid, "Proceedings of International Solvent Extraction Conference, ISEC'93", ed. D. H. Logsdail and M. J. Slater, **1993**, Vol. 1, York, UK, 159 - 166.
14. A. I. Vogel, "A Text Book of Quantitative Analysis Including Elementary Instrumental Analysis", 3rd ed., **1961**, ELBS and Longmans, Green and Co Ltd., 435.