

Solvent Extraction and Separation of Al(III) and Ni(II) from Aqueous Medium by Cyanex-272 [Bis-(2,4,4-Trimethylpentyl) Phosphinic Acid] in Kerosene

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Abstract. The solvent extraction and separation of Al(III) and Ni(II) from aqueous medium using Cyanex-272 [bis-(2,4,4-trimethylpentyl) phosphinic acid] in kerosene has been investigated as functions of contact time, aqueous phase acidity (pH), concentration of extractant in the organic phase, temperature, and loading capacity of the extractant. The equilibrium was reached within 9 min for Al(III) and 2 min for Ni(II). It was observed that the amount of Al(III) extraction was about 65% with 0.1 mol/l Cyanex-272 in kerosene at $(26 \pm 1)^\circ\text{C}$ and pH 4.2, whereas at the same time the amount of Ni(II) extraction was about 8.5% with the same condition. In both cases, the metal ion [Al(III) and Ni(II)] concentration in the organic phase gradually increased with the time of extraction until the curves levelled off. The extraction of Al(III) increased with increasing concentration of the extractant, aqueous phase acidity (pH), and the temperature. However, the amount of Ni(II) extraction at all temperatures was negligible and decreased with increasing extractant concentration. The temperature dependence data gave $\Delta H = 15.23$ kJ/mol up to 60°C , suggesting endothermic extraction. The loading capacity of Al(III) and Ni(II) was about 25.75 g and 0.5 g, respectively per mole of Cyanex-272, with 0.2 M Cyanex-272 at pH 4.1. Loading data indicates Al : Cyanex-272 ratio varied from 0.95 : 1 to 1.6 : 1 for Al(III) extraction indicating almost 1 : 1 complex formation in the organic phase.

Keywords: solvent extraction, Al-Ni separation, Cyanex-272, kerosene medium, bis-(2, 4, 4-trimethylpentyl) phosphinic acid

Introduction

One of the most important groups of extraction reagents used in the field of hydrometallurgy is the group of organophosphorus acid derivatives. Among these, the dialkylphosphinic acids were commercialized in 1982 by Cyanamid under the name Cyanex-272, in which the active component was bis-(2,4,4-trimethylpentyl) phosphinic acid. This reagent has been studied extensively for the extraction of cobalt and nickel yielding better separation than dialkylphosphoric and dialkyl phosphinic acids (Rickelton, 1996; Chou and Beckstead, 1990; Sastre *et al.*, 1990; Xun *et al.*, 1990; Rickelton and Boyle, 1988; Xun and Golding, 1987; Preston, 1983). Similar findings have also been reported for zinc-cadmium separation (Sastre *et al.*, 1990). Cyanex-272 has been widely studied for the extraction of several metal ions, mostly from sulfate and chloride medium (Wang and Li, 1994), and is commercially available for more than a decade. Al(III) and Ni(II) separation has been tried by tolyl phosphate by using NH_3 medium in the presence of fluoride ions (Islam and Mostafa, 1995). Most of the commercially available extractants possess poor separating ability for Al(III) and Ni(II) from a mixture of the two cations. The solvent extraction and separation of Al(III) and Ni(II) in aqueous medium have been attempted in the

present study by adding Cyanex-272 in kerosene. The study is of commercial importance as the acid leaching of the spent nickel catalyst from fertilizer factories produces aluminum and nickel containing solutions (Islam and Mostafa, 1993), the treatment of which is necessary to separate the two metals.

Materials and Methods

A stock solution of Al(III) was prepared by dissolving exactly 24.66 g of analytical grade aluminum sulfate in 1 litre of distilled water containing 1% of conc HNO_3 by volume. Another 1 litre of Ni(II) was prepared by dissolving exactly 8.96 g of analytical grade nickel sulfate in 1 litre of distilled water containing 0.1 N HCl. After mixing, the phases were quickly separated to guard against mass transfer of metal ions through diffusion from aqueous to the organic phase for the contact time dependence study. Cyanex-272 (85% purity) was used as such without further purification. The diluent, kerosene, was purchased from the local market and distilled to collect the fraction obtained in the range of $200\text{--}260^\circ\text{C}$. All other chemicals were of reagent grade and used without further purification.

20 ml aliquots containing definite amounts of Al(III) and Ni(II) in the aqueous phase and organic Cyanex-272 in kerosene in the organic phase were collected in 125 ml reagent bottles.

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The aqueous phase acidity in the aqueous solution for extraction was adjusted by adding either anhydrous Na_2CO_3 or conc H_2SO_4 , if necessary. The reagent bottles were shaken at a definite rate with an electric shaker for predetermined time (15 min) at a constant temperature ($26 \pm 1^\circ\text{C}$); except for the studies on the effect of temperature. The aqueous raffinate phase was taken in a beaker and the equilibrium pH was recorded by using a pH meter (pH S-25 model; China). The organic phase was then taken in a test tube and shaken with an equal volume of 2 N HCl as a stripping agent for 5 min to transfer metal contact to the aqueous HCl phase. Two layers formed and phases were settled for 5 min. The aqueous HCl phase was separated and measured spectrophotometrically to obtain metal extracted in the organic extractant phase. The contents of the extracted aqueous phase (raffinate) metal ions [Al(III) and Ni(II)] were determined by subtracting the values of organic phase metal ion contents from the initial aqueous phase values. Metal contents [Al(III) and Ni(II)] in the aqueous phase were determined by the Aluminon method (Scott, 1939) for Al(III) and dimethyl-glyoxime colourimetric method for Ni(II) (Vogel, 1989) using spectrophotometer ANA-75 (Tokyo Photoelectric Company, Japan). In the loading capacity determination, the raffinate phase metal contents were determined directly after each extraction.

Results and Discussion

Effect of phase-contact time. The extraction coefficient E_{Al}° for extracting Al(III) from 1.3 mg/l and Ni(II) from 0.9 g/l aqueous solutions by 0.1 M Cyanex-272 in kerosene was investigated at different phase-contact times with the initial aqueous pH of 4.2 (Fig. 1, 2 and 3). In both the cases, it was observed that E_{Al}° and E_{Ni}° increased with increasing phase-contact time upto 9 and 1 min respectively, and after that the curves levelled off. The extraction plots became horizontal after 9 min for Al(III) and 1 min for Ni(II). Therefore, about 15 min of mixing time was sufficient for the extraction study. About 65% Al(III) was extracted in 9 min and 8.5% Ni(II) was extracted in 1 min. Equilibrium attainment time for Ni(II) was almost similar for Cyanex-272 and (hydrogen di-tolyl phosphate) HDTP (Islam and Mostafa, 1993). However, the equilibrium attainment was obtained much faster with Cyanex-272 than HDTP for Al(III) extraction. This may be advantageous as less time would be required for the solvent extraction operation.

The results obtained from the contact time study of Al(III) and Ni(II) by using Cyanex-272 in kerosene is plotted (Fig. 3) as the separation factor (β) versus contact time (min). It may be observed that there were extensive possibilities for Al(III) to be well separated from Ni(II) after the 10 min

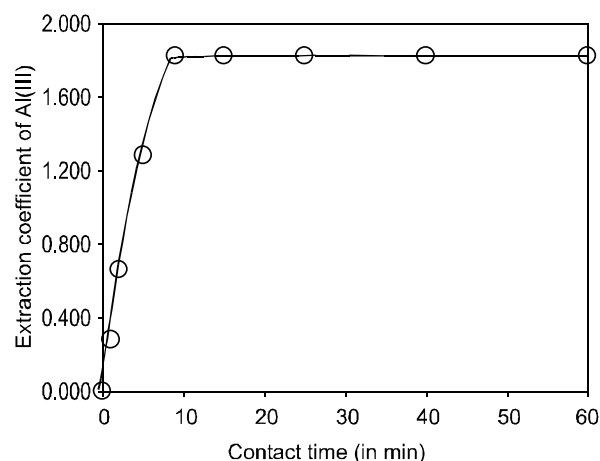


Fig. 1. Variation of extraction of Al(III) by Cyanex-272 as related with contact time; experimental condition: initial concentration of Al(III) = 1.30 g/l, initial concentration of Ni(II) = 0.90 g/l, phase ratio = 1 : 1, temperature = $26 \pm 1^\circ\text{C}$, extractant concentration = 0.10 M Cyanex-272 in kerosene, initial aqueous phase pH = 4.2.

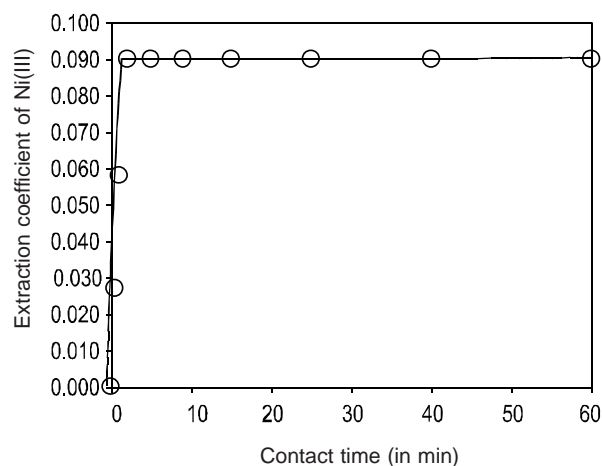


Fig. 2. Variation of extraction of Ni(II) as related with contact time; experimental conditions: initial concentration of Al(III) = 1.30 g/l, initial concentration of Ni(II) = 0.90 g/l, phase ratio = 1 : 1, temperature = $26 \pm 1^\circ\text{C}$, extractant concentration = 0.10 M Cyanex-272 in kerosene, initial aqueous phase pH = 4.2.

contact time for the specified conditions of extraction, namely, extraction concentration and acidity (pH). Thus for efficient separation or removal of Al(III) from Ni(II) from the acidic aqueous phase, longer contact time was not necessary for the separation of Al(III), as the maximum separation factor (β) 20 was obtained within 10 min.

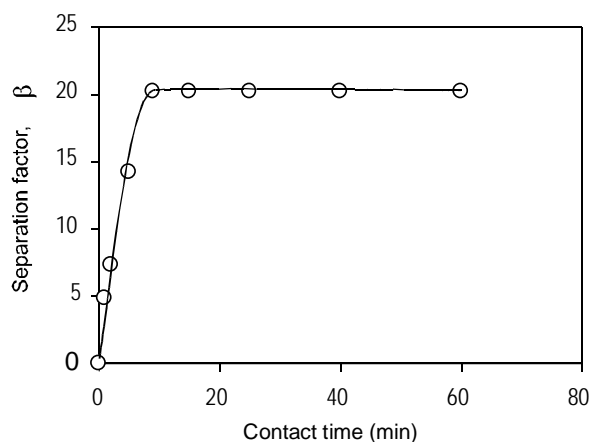


Fig. 3. Dependence of separation factor for Al(III)-Ni(II) as related with contact time; experimental conditions: initial concentration of Al(III) = 1.30 g/l, initial concentration of Ni(II) = 0.90 g/l, phase ratio = 1 : 1, temperature = 26 ± 1 °C, extractant concentration = 0.10 M Cyanex-272 in kerosene, initial aqueous phase pH = 4.2.

Effect of temperature. For 0.10 M Cyanex-272 in kerosene, the $\log E_{Al}^{\circ}$ versus $1/T^{\circ}$ plots at the equilibrium pH 2.8 are shown in Fig. 4. The plot shows that $\log E_{Al}^{\circ}$ value for Al(III) increased rapidly with increasing temperature, almost linearly up to 60 °C. With a slope of - 3.33 giving enthalpy change (ΔH) as 15.23 kJ/mol, the positive ΔH value indicated that the extraction process was endothermic.

Though the percentage of Al(III) extraction increased with increasing temperature, the temperature had little effect on the percent extraction at the lower equilibrium pH.

On the contrary, the amount of Ni(II) extraction at all temperatures was negligibly small at the lower equilibrium pH. Therefore, higher temperature may be used for the separation of Al(III) from Ni(II) from mixtures.

Dependence of extraction on acidity and the extractant concentration. Keeping all the other parameters fixed, the effect of extractant concentration and acidity on extraction was studied within the concentration range 0.05-0.20 mol/l Cyanex-272 in kerosene at the different equilibrium pH values of 1, 1.5, 2, 2.5. The results obtained are given in Fig. 5, as $\log E_{Al}^{\circ}$ Al(III) versus pH. It may be observed that when pH was increased, the amount of extraction increased almost linearly at the fixed extractant concentration. However, at low pH level (near 1.0) the extraction ratio was less even though the higher extraction concentration was used. It may be observed, nevertheless, that the extraction increased sharply with an increase in the extractant concentration after pH 2.0. It is probable that at high aqueous acidities near pH 1.0 the disso-

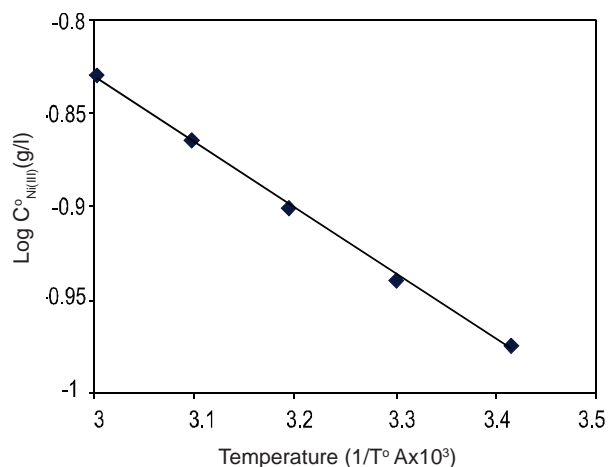


Fig. 4. Variation of extraction of Al(III) by Cyanex-272 as related with temperature; experimental conditions: initial concentration of Al(III) = 1.30 g/l, initial concentration of Ni(II) = 0.90 g/l, phase ratio = 1 : 1, extractant concentration = 0.10 M Cyanex-272 in kerosene, initial aqueous phase pH = 4.

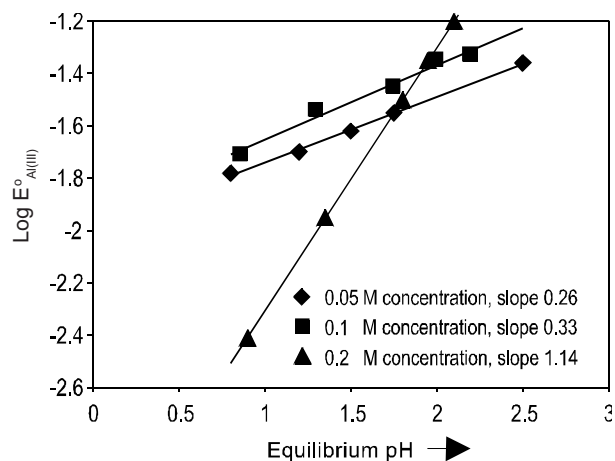


Fig. 5. Dependence of extraction of Al(III) as related with aqueous acidity; experimental conditions: initial concentration of Al(III) = 1.30 g/l, initial concentration of Ni(II) = 0.90 g/l, phase ratio = 1 : 1, temperature = 18 ± 1 °C, extractant concentration = 0.05-0.20 M Cyanex-272 in kerosene, initial aqueous phase pH = 1, 1.5, 2, 2.5.

ciation of acidic Cyanex-272 species was suppressed with the consequent decrease of extraction of the metal ion species. The effect may be more pronounced at the higher extractant concentration. However, the dissociation was facilitated at the lower aqueous acidities. Furthermore, with the same pH and extractant concentrations, extremely negligible amount of Ni(II) was extracted. As such, the extraction of Ni(II) may be

taken as zero. This may be explained by the assumption that with increasing extraction of Al(III), the extraction of Ni(II) was hindered. Thus, it may be concluded that Al(III) has higher affinity for Cyanex-272 than Ni(II). At the higher pH of the aqueous solution, Ni(II) and Al(III) precipitated as hydroxides. Therefore, investigations were made in the pH range of 1-3.

Loading capacity of Cyanex-272 for Al(III) and Ni(II).

The loading capacity is defined as the amount of metal ion in grams extracted per 100 g of pure extractant. This is a very important factor for commercial applicability. High values of loading capacity are desirable for any particular extractant metal system.

Aliquots of 20 ml 0.1M Cyanex-272 were repeatedly extracted for 15 min with the same volume of aqueous solution containing 2.52 g/l Al(III) and 3.00 g/l Ni(II). After equilibration, the phases were disengaged and the aqueous phases were analyzed for Ni(II) and Al(III) contents. The amount of metal ions [Ni(II) and Al(III)] transferred into the organic phase for each contact was then calculated by difference and the cumulative concentration of Ni(II) and Al(III) in the organic phase after each stage of contact was determined. The Al(III) cumulative $C_{Al(III)}^{\circ}$ versus the number of stages of contact have been plotted as Fig. 6, while the Ni(II) cumulative $C_{Ni(II)}^{\circ}$ versus the number of stages of contact have been plotted in Fig. 7. It may be noted that in both the cases, the organic phase was loaded to its saturation capacity with metal ions Ni(II) and Al(III) within 1-6 contacts for the experimental conditions

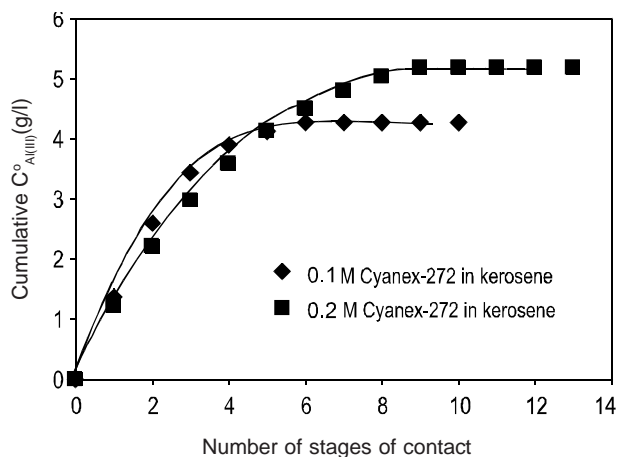


Fig. 6. The loading effect of organic phase in the extraction of Al(III) with Cyanex-272 in kerosene; experimental conditions; initial concentration of Al(III) = 2.52 g/l, initial concentration of Ni(II) = 3.00 g/l, phase ratio = 1 : 1, temperature = 21 ± 1 °C, initial aqueous phase pH = 4.1, contact time = 10 min.

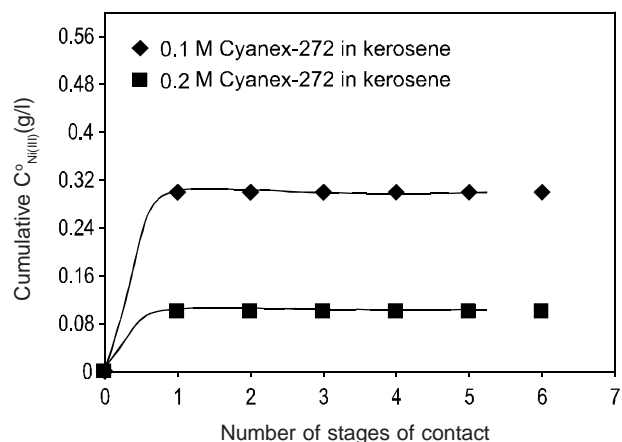


Fig. 7. The loading effect of organic phase in the extraction of Ni(II) with Cyanex-272 in kerosene; experimental conditions; initial concentration of Al(III) = 2.52 g/l, initial concentration of Ni(II) = 3.00 g/l, phase ratio = 1 : 1, temperature = 21 ± 1 °C, initial aqueous phase pH = 4.1, contact time = 10 min.

stated, for 0.1 M Cyanex-272 in kerosene. Though Ni(II) needed a single stage contact for saturation, multiple stages were required for Al(III). Eventually, the organic phase was saturated with the metal ions after the 5th contact stage. About 4.30 g/l Al(III) and 0.30 g/l Ni(II) were extracted at pH 4.1 and 0.1 M Cyanex-272, indicating the loading capacity of 43 g for Al(III) and 3 g for Ni(II) per mol of Cyanex-272 at pH 4.1.

At pH 4.1 and 0.2 M Cyanex-272 in kerosene, Al(III) and Ni(II), were loaded to full capacity of the organic within 10 contact stages. About 5.15 g/l Al(III) and 0.1 g/l Ni(II) were extracted with 0.2 M/l Cyanex-272 in kerosene, giving the loading capacity of 25.75 g for Al(III) and 0.5 g for Ni(II) per mol of Cyanex-272. The loading decreased with increase in the extractant concentration with respect to both Al(III) and Ni(II), which is difficult to explain. Similar observation was noted previously for Al(III) extraction (Fig. 5).

Cyanex-272 is a liquid cation exchanger and consequently the extraction is highly dependent on acidity. The presence of hydrogen ion in the aqueous phase hinders the ionization of the extractant. Therefore, extraction increased with decrease in the aqueous acidity. At pH 4.1, 0.1-0.2 M/l Cyanex-272 in kerosene showed the highest capacity or maximum extraction of the metal ions.

Conclusion

Cyanex-272 is an effective extractant for the extractive separation of Ni(II) from an aqueous solution containing Al(III)

and Ni(II). The equilibrium attainment was moderately fast for Al(III) and much faster for Ni(II). The loading capacity of Al(III) and Ni(II) were 43 and 3 g/l, respectively for 0.1 M Cyanex-272. Separation factor (β) of Al(III) with respect to Ni(II) was 20 at the experimental conditions (temperature = 26 ± 1 °C, extract concentration [HA] = 0.1 M Cyanex-272 in kerosene, phase ratio 1 : 1, pH = 4.2 initial) suggesting good separation from nickel. Temperature dependence suggests that a higher operating temperature may be used. Thus, the extractant Cyanex-272 has good possibility for use in the treatment of acidic leach liquors from the waste nickel catalyst from urea fertilizer plants.

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