Extractive Separation of Al(III) and Ni(II) by Di-2-Ethylhexyl Phosphoric Acid -Kerosene System from Aqueous Fluoride Medium

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Abstract. In the study of the extractive separation of Al(III) and Ni(II) by di-2-ethylhexyl phosphoric acid D2EHPAkerosene from aqueous fluoride medium, about 94% Al(III) and 2% Ni(II) were extracted with 0.3 M D2EHPA (pH 2.1 and temperature 30 ± 1 °C). Extraction of Ni(II) decreased with increasing extractant concentration. D2EHPA-kerosenefluoride system showed better extraction of Al(III) with higher extractant concentration and aqueous pH and *vice versa* for the extraction of Ni(II). The maximum separation factor (β ~1380) was obtained for Al(III) at 20 °C and decreased to (β ~732) at 60 °C. The separation of Al(III) from Ni(II) was favoured at normal temperature. Extraction followed the order Al(III) >>>Ni(II). About 99% stripping of Al(III) was attained from the loaded 0.20 M D2EHPA. Much faster extraction of Al(III) compared to Ni(II) and preferential loading were shown by D2EHPA-kerosene in the presence of fluoride ion in the aqueous phase. Separation of Al(III) was the most outstanding from Ni-Al-F-complex solution.

Keywords: Al-Ni separation, D2EHPA-kerosene system, fluoride medium

Introduction

Liquid-liquid extraction is one of the most promising and effective extraction and separation technique in hydrometallurgy. Particularly phosphorus-based extractant, D2EHPA, (a commercial extractant) has proved to be of particular significance for its wide range of use in the extraction (from divalent to heptavalent) as well as separation of metal ions from different acid solutions (Nasr-Eddine Belkhouche et al., 2005; Islam and Mostafa, 1995; Islam et al., 1988; 1979). Leaching of the spent nickel catalyst from fertilizer factories produces aluminium and nickel containing solutions (Islam and Mostafa, 1993) and a treatment is necessary to separate the two metal ions. Previously, for this purpose, in our laboratory some separation studies had been attempted using various extractants and also with tolyl phosphate using NH, medium in the presence of fluoride ions (Islam and Mostafa, 1993) and using Cyanex 272 (Islam and Rahman, 2006). Cobalt-nickel separation using Cyanex 272, Cyanex 301 and Cyanex 302 has also been reported by some workers (Reddy and Sarma, 2001; Tait and Brian, 1993; Chou and Beckstead, 1990; Danesi et al., 1984; Rickelton et al., 1984). However, no report was found on the extractive separation of Al(III) and Ni(II) by D2EHPA from fluoride medium, though several reports are available on Ni(II) and Al(III) from acidic medium.

Tributyl phosphate(TBP), di-*o*-tolyl phosphate (HDTP) and versatic acid-10 were attempted for extractive separation.

TBP and versatic acid-10 were unable to extract Ni(II) from Ni-Al-F solution in NH_3 medium. Di-2-ethylhexyl phosphate extracted Ni(II) from Ni-Al-F complex solution, but phase separation was very difficult owing to emulsion formation in ammoniacal media. It was observed that the waste nickel catalyst from urea fertilizer factories is leached by HF acid more effectively than other leachants like H_2SO_4 , HCl etc. However, it was difficult to separate Al-Ni from such leach solution by conventional precipitation methods.

The efficacy of D2EHPA for Al-Ni separation in acidic fluoride medium was tried in this laboratory and is reported here.

Materials and Methods

Standard solution of Al(III) was prepared by dissolving exactly 17.582 g of analytically pure KAl(SO₄)₂. 12H₂O in a one litre volumetric flask and made up to the mark with 1% HNO₃ solution and standardized using spectrophotometric technique as indicated below. Another 1 litre standard solution of Ni (II) was prepared by dissolving exactly 8.956 g of analytically pure NiSO₄. 6 H₂O in a 1 litre volumetric flask and made up to the mark with 0.1 N HCl solution and standardized. pH of the aqueous solutions was adjusted by using anhydrous Na₂CO₃/dilute H₂SO₄ if needed.

The extractant D2EHPA, having 98% purity, was used without further purification. All other chemicals were of reagent grade and used without further purification. The diluent kerosene was purchased from the local market and distilled to collect the colourless fraction obtained in the range of 200-260 °C.

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A stock solution of D2EHPA (1 M) was prepared by weighing out exactly 658.02 g of D2EHPA in a 1 litre volumetric flask and diluting by distilled kerosene. Extractant solutions of different concentrations were prepared by proper dilution of the stock with distilled kerosene.

A definite aliquot (20 ml) of an aqueous phase was taken in a 125 ml reagent bottle and to it same aliquot (20 ml) of organic phase was added. The bottle was stoppered and shaken for a definite time period in a thermostatic water bath at 30 $^{\circ}$ C (except for temperature dependence). After attainment of equilibrium, phases were allowed to settle and disengaged. The aqueous phase equilibrium, pH and the metal ion concentrations were determined.

For the stripping study, 20 ml organic phase of 0.20 M D2EHPA-kerosene loaded with Al(III) and Ni(II) were taken in a 125 ml reagent bottle and to it, 20 ml of 6 N HCl was added as a stripping agent and shaken for 5 min to transfer metal content to the aqueous HCl phase. Two layers are formed and settled for 5 min. The aqueous HCl phase was separated and measured spectrophotometrically to obtain metal extracted in the organic phase. The metal content, Al(III) and Ni(II), of the aqueous phases were determined by subtracting the values of organic phase metal ion contents from the initial aqueous phase values. In the case of loading test, the organic phase was repeatedly contacted with fresh equal volumes of aqueous solutions until saturation of the organic phase with the metal was attained.

Al(III) ion concentration in the aqueous phase was estimated by Aluminon method (Scott, 1939) and Ni(II) ion concentration was determined by dimethyl-glyoxime colorimetric method (Vogel, 1989) using spectrophotometer ANA-75 (Tokyo Photoelectric Company). In all the cases, phase separation occurred readily, pH values of the aqueous solutions were measured by the digital pH meter (HD-700, Japan). Distribution ratio (D) of metal ion was calculated as the ratio of metal ion concentration in the organic phase to that in the aqueous phase at equilibrium.

Results and Discussion

Effect of phase- contact time. Figure 1 represents variation of distribution ratio on contact time. In both the cases of Al(III) and Ni(II), it was found that the extraction ratio increased continuously with the increase of phase contact time up to a period of 9 min and after that it remained unchanged with further increase of contact time. Extraction plots became horizontal after 10 min for both Al(III) and Ni(II) and on further contact for a longer time, extraction ratio did not increase. Extraction of Al(III) is about 80% and 85% at 5 and 10 min,



Fig. 1. Effect of distribution ratio of Al(III) and Ni(II) extraction by D2EHPA- F⁻-kerosene system on contact time. Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{=})_{(ini)}$ =0.263 M; pH_(ini) = 2.10; D2EHPA = 0.10 M; phase ratio (O/A) = 1; F⁻ = 1.00 g/litre as NaF; temperature = $30\pm1^{\circ}$ C; diluent = kerosene.

respectively, for 0.10 M D2EHPA. On the contrary, extraction of Ni(II) was about 8% and 9% for the same duration. Therefore, it is concluded that equilibrium was attained within 10 min for both the metal ions. Equilibrium time was 9 and 2 min for Al(III) and Ni(II), respectively, by Cyanex 272 in kerosene systems (Islam and Rahman, 2006) and 30 and 10 min by HDTP in kerosene (Islam and Mostafa, 1995). It is concluded that extraction of Al(III) and Ni(II) from fluoride medium by analytical grade D2EHPA in kerosene system is much faster. Thus, in subsequent experiments, 10 min mixing was allowed to ensure equilibrium. Maximum separation factor β in this respect was found to be ~ 51 within 2 min.

Effect of equilibrium pH on the distribution of Al(III) and Ni(II) for extraction by D2EHPA- F⁻-kerosene system. The result obtained, from the experiments at different equilibrium pH, is plotted as log D (distribution ratio) *vs* equilibrium pH. Fig. 2 shows that extraction of Al(III) ions increases with increase of aqueous phase equilibrium pH. However, extraction of Ni(II) remain unchanged with the increase of aqueous phase pH. In the case of Al(III), slopes of lines were calculated and the values are 0.50, 0.54, 0.54 and 0.50 for 0.05, 0.10, 0.20 and 0.30 M D2EHPA systems, respectively. But in the case of Ni(II) extraction, slope of the plots became zero for all the extractant concentrations investigated. Thus, extraction of Al(III) by D2EHPA did not give a pH dependence value of 3 as expected from the equilibrium reaction:

 $Al^{3+} + 3/2 H_2 A_2 \leftrightarrow AlA_3 + 3 H^+ \dots (I)$ or

 $Al^{3+}+3 (HA) \leftrightarrow AlA_{3}+3 H^{+} \dots (II)$

where: dimeric(H_2A_2) and monomeric(HA) extractant species were assumed. A very low aqueous pH dependence slope cannot be accounted for by simple ion exchange mechanism though a linear dependence on aqueous acidity is observed. The existence of hydrolyzed species of the form Al(OH)²⁺ or Al(OH)⁺₂ in the aqueous phase formed by the hydrolysis reaction may promote Al(III) extraction by the following reactions.

$Al^{3+} + H_2O \leftrightarrow AlOH^{2*} + H^+$	(III)
$AlOH^+ + H_2O \leftrightarrow Al(OH)_2^+ + H^+$	(IV)

at the acidity of the aqueous phase, where complete hydrolysis to $Al(OH)_3$ is not supposed.

 $\begin{aligned} Al(OH)^{2+}+2HA &\longleftrightarrow Al(OH). A_2+2H^+....(V) \\ Al(OH)_2^++2HA &\longleftrightarrow Al(OH). A_2+H^+...(VI) \end{aligned}$

Where, HA is the monomer molecule of D2EHPA



● :[D2FHPA]=0.30 M; ■ :[D2EHPA]=0.20 M; ▲ :[D2EHPA]=0.10 M; ◆ :[D2EHPA]=0.05 M

Fig. 2. Effect of distribution ratio of Al(III) on equilibrium pH for D2EHPA- F⁻ kerosene system. Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{-})_{(ini)} = 0.263 \text{ M}$; pH_(ini) = 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30; phase ratio (O/A) = 1; F⁻ = 1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.

Thus, less than unity slope may indicate the hydrolyzed Al species extraction. Almost zero slope for Ni(II) extraction in the presence of F⁻ is difficult to explain. So, Ni(II) extraction is pH independent in the range of the studied pH. F⁻ ion may catalyze the formation of hydrolytic species in the case of Al and retard Ni extraction(Fig. 3).

Effect of D2EHPA concentration on extraction of Al(III) and Ni(II). Figures. 4 and 5 represent variations in distribution ratio (D) of cations on the extractant concentration. Experiments were carried out at extractant concentrations of 0.05, 0.10, 0.20 and 0.30 M and at aqueous phase pH of 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30. It was observed that the extraction of Al(III) increased with increasing extractant concentrations



■ : [D2EHPA]=0.05 M; □ : [D2EHPA]=0.10 M; ▲ : [D2EHPA]=0.20 M; △ : [D2EHPA]=0.30 M

Fig. 3. Effect of distribution ratio of Ni(II) on equilibrium pH.

Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{=})_{(ini)}$ = 0.263 M; pH_(ini)= 1.40,1.90, 2.40, 3.00, 3.70 and 4.30; phase ratio (O/A) = 1; F⁼ = 1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.



◆: pH=1.40; ■: pH=1.90; ▲: pH=2.40; •: pH=3.00; □: pH=3.70; ■: PH=4.30

Fig. 4. Effect of distribution ratio of Al(III) on extractant concentration for D2EHPA - F-kerosene system. Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{-1})_{(ini)} = 0.263$ M; (D2EHPA) = 0.05,0.10,0.20 and 0.30 M; phase ratio (O/A) = 1; F⁻ = 1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.

in the organic phase, and the straight-line relationship was obtained for distribution ratio and extractant concentration. Slopes of the lines are 0.60, 0.60, 0.50, 0.60, 0.50 and 0.50 for pH values of 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30 respectively. Here, linear relationship of the extraction ratio with the D2EHPA concentration indicated that with increasing extractant concentration, extraction of Al(III) improved. On the contrary, extraction of Ni(II) was extremely negligible and decreased with increasing extractant concentration and was independent of the pH of aqueous solutions. Since the extraction of Al(III) is significant and the extraction of Ni(II) is the same for



Fig. 5. Effect of distribution ratio of Ni(II) on extractant concentration for D2EHPA-F⁻- kerosene system. Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{=})_{(ini)}$ = 0.263 M; D2EHPA = 0.05,0.10,0.20 and 0.30 M; pH_(ini) = 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30; phase ratio (O/A) = 1; F⁻ = 1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.

different pH values, a single curve was obtained due to very low extraction of Ni(II). It is assumed that with increasing extraction of Al(III), extraction of Ni(II) is hindered. Thus, Al(III) cation has higher affinity than Ni(II) towards D2EHPA in fluoride medium. Converting the distribution coefficient to percentage extraction shows that about 94 % Al(III) and 2% Ni(II) were extracted at the equilibrium pH of 2.1.

The slope of extractant dependence indicates that normal ion exchange mechanism for unhydrolyzed Al(III) is not followed. Rather hydrolyzed and polymerized species extraction is indicated by the extraction data. Here the dependence of Al(III) on extractant concentration indicates that 2:1 complexes are formed in the extraction process, as suggested before which may explain low pH and extractant dependence.

Effect of temperature on Al(III) and Ni(II) extraction by D2EHPA- F⁻-kerosene system. Figure 6 shows variation of distribution ratio on temperature. In both the cases of metal ions, extraction ratio increased with increasing temperature. Slopes of the lines are 0.44 and 0.45 for Al(III) and Ni(II), respectively, at 0.20 M D2EHPA. Extraction reaction enthalpy changes (ΔH) has been calculated using Vant-Hoff equation. The calculated values are 8.50 and 8.70 kJ/mol for Al(III) and Ni(II), respectively. Positive enthalpy change suggests that the extraction process for both the ions is endothermic in nature. The distribution ratio/temperature relationship indicates that extraction reaction of the two is strongly influenced by temperature. Thus, the extraction using the system under study can be moderately increased by using a higher temperature.

Loading of D2EHPA by Al(III) and Ni(II). The loading capacity is defined as the amount of metal content in grams extracted per 100 g of an extractant. It is an important parameter for the



Fig. 6. Effect of distribution ratio of Al(III) and Ni(II) for D2EHPA- F⁻-kerosene system on temperature. $(SO_4^{=})_{(ini)} = 0.263 \text{ M}; \text{ pH}_{(ini)} = 4.00; \text{ D2EHPA} = 0.20 \text{ M};$ phase ratio (O/A) = 1; F⁻ = 2.45 g/litre as NaF; diluent = kerosene.

study of extraction mechanism and also for the industrial evaluation of the extractant, as a high value of loading capacity is desirable for any particular extractant metal system for industrial applications.

The same organic phase (20 ml) was repeatedly contacted for 10 min at 30 °C with the fresh equal volumes of aqueous solutions containing fixed concentration of Al(III) and Ni(II) ions. For loading, 0.10 and 0.20 M [D2EHPA] were used. Aqueous pH 4.10 was used because of the instability of the metal ions in the aqueous phase at higher pH values. After equilibration, the phases were rapidly disengaged to avoid any mass transfer and the aqueous phases were analyzed for metal content. The amount of metal ions transferred into the organic phase for each contact was then determined by difference and the cumulative concentration of ions in the organic phase was estimated. The obtained results plotted as cumulative metal content vs contact number is given in Fig.7 and 8. In these figures, it is seen that the organic phase is saturated with Al(III) and Ni(II) within 4 to 5 contacts. Under the stated, experimental conditions, 2.50 g Al(III) and 0.035 g Ni(II) are extracted at pH 4.10 with 0.20 M D2EHPA giving loading capacity of 12.50 g Al(III) and 0.00175 g Ni(II) for 1 mole D2EHPA. For 0.10 M D2EHPA at the same pH, loading capacity was 12.8 g Al(III) and 0.0035 g Ni(II). Loading test data suggests the extracted species as Al(HA),.

Separations studies: Effect of aqueous phase acidity and extractant concentration on Al-Ni separation factor (β). The separation factor (β) for Al(III) and Ni(II) is calculated for each extractant concentration 0.05, 0.10, 0.20 and 0.30 M D2EHPA, at initial aqueous pH values 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30, respectively, and plotted as separation factor



▲: D2EHPA = 0.10 M; ■: D2EHPA = 0.20 M



Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; (SO₄⁼)_(ini)=0.263 M; pH_(ini)=4.10; phase ratio (O/A) = 1; F⁻=1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.







(β) *vs* equilibrium pH in Fig. 9. It is seen from the plots that the separation factor increases with the decrease in aqueous phase acidities at all concentration of D2EHPA. Thus increase of pH favours the separation of Al(III) from Ni(II). The separation factor increases sharply with the increase of extractant concentration (Fig. 10). The increased extractant concentration decreases the Ni(II) concentration to a negligible value. Consequently, Al(III) can be almost completely removed from Ni(II) solution. Separation factor, β , values of more than ~650 were obtained at equilibrium pH 1.94 and 0.30 M extractant concentration, which may be due to the higher affinity of Al(III) for the extractant. It may be concluded that at high pH and higher extractant concentration, Al(III) and Ni(II) can be separated efficiently.



D2EHPA : ◆ = 0.05 M; ▲ = 0.10 M; ■ : 0.20 M; ●: 0.30 M

Fig. 9. Effect of aqueous phase acidity on separation factor (β).

Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; (SO₄⁼)_(ini)=0.263 M; pH_(ini)= 1.40, 1.90, 2.40, 3.00, 3.70 and 4.30 for each respectively; phase ratio (O/A) = 1; F⁻ =1.00 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.



Fig. 10. Effect of extractant concentration on separation factor (β).

Al(III) = 1.00 g/litre; Ni(II) = 0.50 g/litre; $(SO_4^{-})_{(ini)}$ = 0.263 M; D2EHPA = 0.05, 0.10, 0.20 and 0.30 M; phase ratio (O/A) = 1; F⁻ =1.00 g/litre as NaF, temperature = 30 ± 1 °C; diluent = kerosene.

Effect of temperature of extraction on separation factor (β). The separation factor (β) is graphically represented as function of absolute temperature(Fig. 11). It is evident from that the separation factor decreases with the increase in temperature. However, extraction is still much higher for Al(III) than Ni(II). Maximum separation factor β (1380) was obtained for Al(III) at 20 °C and decreased to 732 at 60 °C temperature. Thus, it is concluded that the ordinary temperature favoured better separation of Al(III) from Ni(II) ions from D2EHPA-kerosene-fluoride medium.



Fig. 11. Effect of temperature on separation factor (β). Al(III) = 1.84 g/litre; Ni(II) = 3.06 g/litre; (SO₄⁼)_(ini)= 0.263 M; pH_(ini)=4.00; D2EHPA = 0.20 M; phase ratio (O/A) = 1; F⁻ = 2.45 g/litre as NaF; diluent = kerosene.

Stripping of Al(III) and Ni(II) from loaded organic phase. In industrial applications, the back extraction of loaded organic phase is as important as the forward extraction. The metal loaded organic phase was stripped with aqueous HCl. The data obtained from the experiment is plotted (Fig. 12) as stripping duration (min) *vs* percentage of stripped metal ions. It was observed that about 87.18% and 70% of Al(III) and Ni(II) ions, respectively, were stripped from the organic phase within 5 min, about 96.8% and 90%, within 10 min by 6 N HCl and about 99% and 95%, within 15 min. However, with prolonged time for stripping, extraction percentage did not increase, which indicates that the back extraction equilibrium is attained within 15 min stripping of the loaded organic phase. However, the selective stripping of these metals is not pos-



Fig. 12. Effect of time on stripping of loaded organic phase. Al(III)_{org} = 0.78 g/litre; Ni(II)_{org} = 0.02g/litre; stripping agent = 6 N HCl; D2EHPA = 0.20 M; phase ratio (O/A) = 1; F⁻ = 1.0 g/litre as NaF; temperature = 30 ± 1 °C; diluent = kerosene.

sible. Separation is obtained only in the forward extraction of the aqueous phase.

Conclusion

D2EHPA is an exceptionally effective extractant for the extraction and separation of Al(III) and Ni(II)) from an aqueous fluoride medium containing Al(III) and Ni(II). The equilibrium is reached within 10 min for Al(III) and Ni(II)). The maximum separation factor (β ~1380) is obtained for Al(III) with respect to Ni(II) at 20 °C and decreased to (β ~732) at 60 °C temperature. D2EHPA loading capacity is 12.50 g Al(III) and 0.00175 g Ni(II)/ mole D2EHPA. The data indicates that simple ion exchange mechanism is not followed for the extraction of Al(III) from fluoride medium. Extraction involves the hydrolyzed species of Al(III) as the acid dependence values are only ~0.50. Extraction of Ni(II) is negligible in the fluoride medium. From the temperature dependence data, the extraction reaction enthalpy change (ΔH) value suggests that the extraction process is endothermic in nature and ΔH values are found to be 8.50 and 8.70 kJ/mol, respectively, for Al(III) and Ni(II) by D2EHPA.

Therefore, the extractant D2EHPA has good prospect for use in the treatment of leach liquors, from the waste nickel catalyst which may be obtained from HF leaching of the waste nickel catalyst from the reforming process of natural gas in the fertilizer plants.

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