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Hydrometallurgy 77 (2005) 227–238

hydrometallurgy

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Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA

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Received 29 September 2004; received in revised form 24 January 2005; accepted 1 February 2005

Abstract

Synergistic effects of Cyanex 272 mixed with D2EHPA and Cyanex 302 mixed with D2EHPA were investigated for the separation of cobalt and nickel from a dilute sulfate media with the aim of reducing the reagent cost. Selective extraction of cobalt over nickel improved with respect to D2EHPA, but worsened with respect to Cyanex 272. By the application of the slope analysis method, the stoichiometric coefficient of the extractant was found to be four for cobalt and five for nickel, in a mixture of D2EHPA with Cyanex 302. However, it was four for both cobalt and nickel in a mixture of D2EHPA with Cyanex 272. Fourier Transform Infrared Spectroscopy (FT-IR) was utilized to examine the organo-metallic complexes containing cobalt and nickel. Increasing the ratio of Cyanex 272 or Cyanex 302 to D2EHPA did not reveal a significant effect on the extraction curve of cobalt, but caused an increase in pH of the nickel extraction curve. Increasing the ratio of Cyanex 272 or Cyanex 302 to D2EHPA increased the pH_{50} difference ($\Delta pH_{50(Ni-Co)}$). Optimum separation was found with a Cyanex 302 to D2EHPA ratio of 0.3:0.3 when the pH_{50} difference ($\Delta pH_{50(Ni-Co)}$) was 0.9. Results showed that extraction of cobalt is more endothermic than that of nickel. Improved separation was hence achieved with a warm mixture.

Keywords: Synergistic effect; Extraction isotherm; Cobalt; Nickel; D2EHPA; Cyanex 272; Cyanex 302

1. Introduction

A review of the current research reveals that cobalt/nickel separation is a major hydrometallurgical problem when choosing a single component D2EHPA solution. Many researchers (Sahu et al., 2004; Tsakiridis and Agatzini, 2004a,b; Bhaskara Sarma and Reddy, 2002; Manski et al., 2002; Cheng, 2000; Devi et al., 1998) have explained that poor separation is because of similar physico-chemical properties of cobalt and nickel. Our observations show, however, that their separation

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doi:10.1016/j.hydromet.2005.02.002

would be feasible, provided that appropriate extractants are selected.

Alternative extractants have been proposed by previous authors to cope with this problem (Maljkovic and Lenhard, 2002; Lindell et al., 2000). reported a cobalt–nickel separation factor (defined as the ratio between the cobalt and nickel distribution coefficients) of 14 for D2EHPA, 280 for PC-88A and 7000 with Cyanex 272. Hubicki and Hubicka (1996) later investigated the purification of nickel using Cyanex 272. They showed that Cyanex 272 was most effective for the purification of nickel from cobalt. Nogueira and Delmas (1999) also investigated the separation of cobalt from nickel and found Cyanex 272 as the best reagent with a ($\Delta pH_{50(Ni-Co)}$)=1.48. However, the ($\Delta pH_{50(Ni-Co)}$) value for D2EHPA was 0.31. They also determined a separation factor of 204 at pH=4 and 1260 at pH=5.5 for Cyanex 272 (0.5 M) and a separation factor of 38 to 98 for Ionquest 801 (0.5 M). Tait (1993) showed that Cyanex 302 was a more effective reagent for cobalt/nickel separation than Cyanex 272 and found ($\Delta pH_{50(Ni-Co)}$)=2.6 for Cyanex 302 as compared to 1.7 for Cyanex 272.

Investigations on cobalt/nickel separation by mixtures of different extractants have also been carried out. For example, Preston (1983) found a synergistic effect with a mixture of D2EHPA and 2-ethylhexanal oxime (EHO) in the extraction of cobalt and nickel, and showed a reversal in the selectivity of the extractant for cobalt over nickel. Rejection of iron, manganese and aluminium was a problem in this system. Zhou and Pesic (1997) developed a new extractant mixture. They suggested that 2,6-bis-[5-N-nonylpyrazol-3-yl] (BNPP) mixed with di-nonyl naphthalene sulfonic acid (DNNSA) was the most efficient extractant. This system could extract cobalt and nickel prior to zinc, iron, manganese, calcium and aluminium. But the $pH_{0.5}$ values for cobalt and nickel were found to be less than zero, so it needed a strong acid for stripping which made the method undesirable.

Zhang et al. (1999) have reported that D2EHPA is not a suitable reagent for the separation of cobalt and nickel. In their work, TOA was used for the selective extraction of cobalt in the presence of nickel. In other work, Zhang et al. (2001) investigated the synergistic extraction of nickel and cobalt with a mixture of D2EHPA and 5-dodecyl-salicyl-aldoxime (LIX 860). They found $\Delta pH_{50}=pH_{50}^{D2EHPA}-pH_{50}^{D2EHPA+LIX860}$ was 0.89 for cobalt and 1.49 for nickel. They also found an unsatisfactory $\Delta pH_{50(Ni-Co)}$ separation factor of 0.24 for a mixture of D2EHPA and LIX 860; although it was claimed that cobalt and nickel could be separated from each other due to differences in their extraction rates.

Fourier Transform Infrared Spectroscopy (FT-IR) is one of the few analytical techniques currently available for studying a reactive extraction system. Utilization of this technique leads to a better understanding of the interaction between organic solvent and the organo-metallic complex present in the system (Morais and Mansur, 2004; Manski et al., 2002; Sainz-Diaz et al., 1996).

Although the Cyanex extractants offer good separation of cobalt and nickel, they are relatively expensive to be used commercially. While D2EHPA is much less expensive, its separation efficiency is unacceptable for this purpose. This paper therefore reports on the most recent results obtained from an extensive investigation of cobalt/nickel separation from sulfate media by mixed D2EHPA/(Cyanex 272 or Cyanex 302). The purpose is to investigate the synergistic effects of cobalt–nickel with D2EHPA/(Cyanex272 or Cyanex 302) mixtures in kerosene, and to explore the merits of these alternative organic solvents in providing desirable separation factors at reasonable prices. A further goal is to understand the thermodynamics and mechanism of the cobalt/nickel extraction with D2EHPA, Cyanex 272 and Cyanex 302 and their mixtures. Different stripping behaviors were observed with the different values of pH_{50} for the extraction of cobalt and nickel from the dilute synthetic solutions.

2. Experimental procedure

2.1. Materials

Commercial bis-2-ethylhexyl phosphoric acid (D2EHPA) was purchased from Sandong Chemical, Chengdu China, while di-2,4,4,-trimethylpentyl phosphinic (Cyanex 272) and di-2,4,4,-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) were obtained from Cytec Netherlands. Kerosene was purchased from Tehran Refinery Co. and was used

as a diluent. Sulfuric acid and ammonium hydroxide (ammonia solution) from Baran Chemical Company of IRAN were employed for adjusting the pH of the system.

2.2. Experiments

Batch experiments were carried out in a flask containing equal volumes (20 mL) of aqueous and organic solutions. Initial concentrations of both cobalt and nickel in the aqueous phase were 5 g/L. The mixture was agitated at a constant temperature of 25, 40 or 60 °C with a mechanical shaker. Although equilibrium could be achieved in less than 10 min (Lindell et al., 2000; Wassink et al., 2000; Owusu, 1998; Amer et al., 1995; Bart et al., 1992), agitation was carried out for 60 min to assure equilibrium conditions. Agitated samples were then retained in a flask for half an hour to allow complete separation of the two phases. The organic phase was subsequently separated and analyzed for metallic ions. Complete stripping with 200 g/L sulfuric acid was used to determine cobalt and nickel concentrations. EDTA and Muroxide titration indicators were used to analyze cobalt and nickel in the aqueous phase. Ammonium acetate was used to prevent the cobalt(II) ammine complex formation during titration procedure.

3. Results and discussion

A survey shows that Cyanex 272 and Cyanex 302 are not capable of extracting nickel at pH<6 while they are perfectly capable of extracting cobalt at pH<5. Extraction curves of cobalt and nickel using 0.6 M Cyanex 272 and Cyanex 302 are shown in Fig. 1 which illustrates their selectivity for cobalt.

3.1. Effect of Cyanex 272 or 302/D2EHPA concentration on cobalt and nickel separation

The following experiments were carried out to determine the extraction mechanism of cobalt and nickel and how D2EHPA and Cyanex 272 or Cyanex 302 associate together during the extraction. Fig. 2 illustrates the extraction curves of cobalt using different D2EHPA and Cyanex 272 or 302 mixtures with a fixed total extractant concentration of 0.6 M.

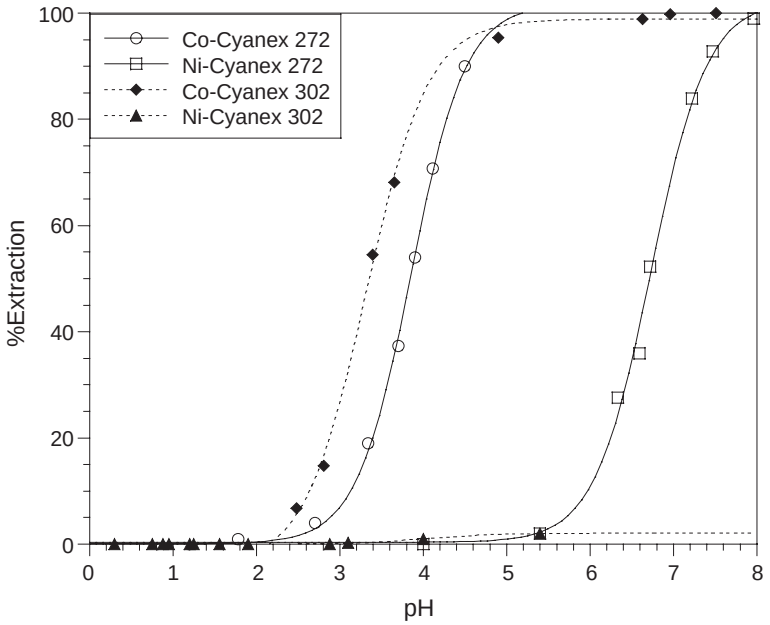

Fig. 1. Extraction of cobalt and nickel by 0.6 M Cyanex 272 and 0.6 M Cyanex 302 diluted in kerosene at 25 °C.

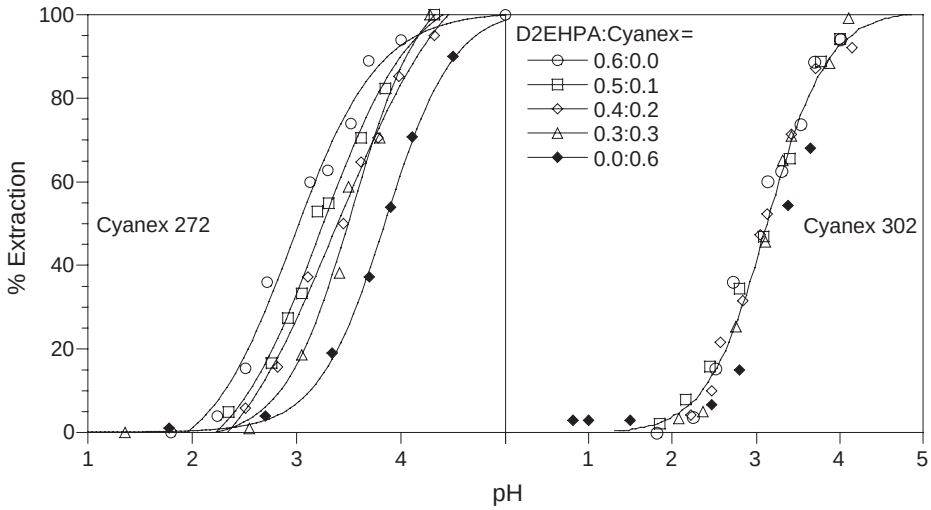

Fig. 2. Percent of cobalt extracted by D2EHPA/Cyanex 272 and 302 mixtures at 25°C (fixed extractant concentration=0.6 M).

As can be seen from the figure, variation of the D2EHPA to Cyanex 302 ratio does not significantly change the extraction curve and all experimental points coincide on one curve. Thus, the performance of Cyanex 302/D2EHPA mixtures is similar to that of D2EHPA and the extraction value of cobalt at different molar ratios of [D2EHPA]:[Cyanex 302] is constant. In contrast to Cyanex 302, there are some differences between D2EHPA and Cyanex 272 behavior during cobalt extraction and the extraction values of cobalt at different [D2EHPA]:[Cyanex 272] ratios do not remain exactly the same.

However, the extraction curves of nickel plotted for different D2EHPA/Cyanex 272 or 302 mixtures shift to the right by increasing the Cyanex to D2EHPA ratio (Fig. 3). In spite of the small shift using Cyanex 302 with D2EHPA, it can be expected that increasing Cyanex 302 in the mixture can improve the cobalt–nickel separation potential. A similar generalization can be made for increasing the

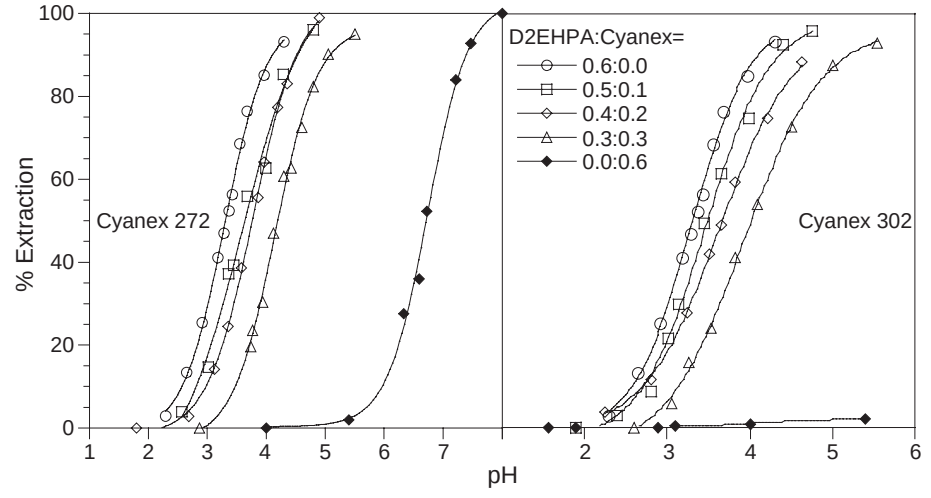

Fig. 3. Percent of nickel extracted by D2EHPA/Cyanex 272 and 302 mixtures at 25 °C (fixed extractant concentration=0.6 M).

Table 1
Values of pH_{50}^{Ni}, pH_{50}^{Co} and $pH_{50(Ni-Co)}^{Co}$ for different mole ratios of D2EHPA:Cyanex 272 or 302 at 25 °C

[D2EHPA]: [Cyanex]		pH_{50}				
		Ni	Co	$Ni–Ni_{[D2EHPA]=0.6\ molar}$	$Co–Co_{[D2EHPA]:=0.6\ molar}$	Ni–Co
272	0.6:0.0	3.30	3.04	0.00	0.00	0.26
	0.5:0.1	3.59	3.25	0.29	0.21	0.34
	0.4:0.2	3.76	3.39	0.46	0.35	0.37
	0.3:0.3	4.12	3.48	0.82	0.44	0.64
302	0.6:0.0	3.3	3.04	0	0	0.26
	0.5:0.1	3.47	3.11	0.17	0.07	0.36
	0.4:0.2	3.65	3.11	0.35	0.07	0.54
	0.3:0.3	4.01	3.13	0.71	0.09	0.88

Cyanex 272:D2EHPA molar ratio. One can attribute the selectivity of the mixture to the difference between the $pH_{0.5}$ values of the two metals. The data obtained for $pH_{0.5}$ and $\Delta pH_{0.5}$ of cobalt and nickel are listed in Table 1. This indicates that these mixtures caused a better separation of cobalt from nickel and that a mixture of D2EHPA/Cyanex 302 is slightly better than D2EHPA/Cyanex 272.

3.2. Extraction mechanism and thermodynamics of the process

Extraction curves of nickel, using 0.3 M D2EHPA and a 1:1 mixture of 0.3 M D2EHPA and Cyanex 302 are shown in Fig. 4. The extraction data obtained with the mixture of D2EHPA and Cyanex 302 coincide closely with that obtained for 0.3 M D2EHPA. Based on the results shown in Figs. 1 and 4, the extraction potential of the mixture is the same as that of D2EHPA. Thus in the range of $2<pH<5$, Cyanex 302 has no effect on the extraction of nickel. One can conclude similar results for the performance of Cyanex 272 mixed with D2EHPA in the extraction of nickel.

The extraction reaction of a divalent metal (M^{2+}) by a mixed organophosphorus acid can be represented by the following general equation:

$$M^{2+} + n\overline{(R/R')H} \leftrightarrow \overline{M(R/R')_2((R/R')H)}_{(n-2)} + 2H^+ \quad (1)$$

where R and R' stand for phosphoric and phosphinic acid extractant groups, respectively. The equilibrium

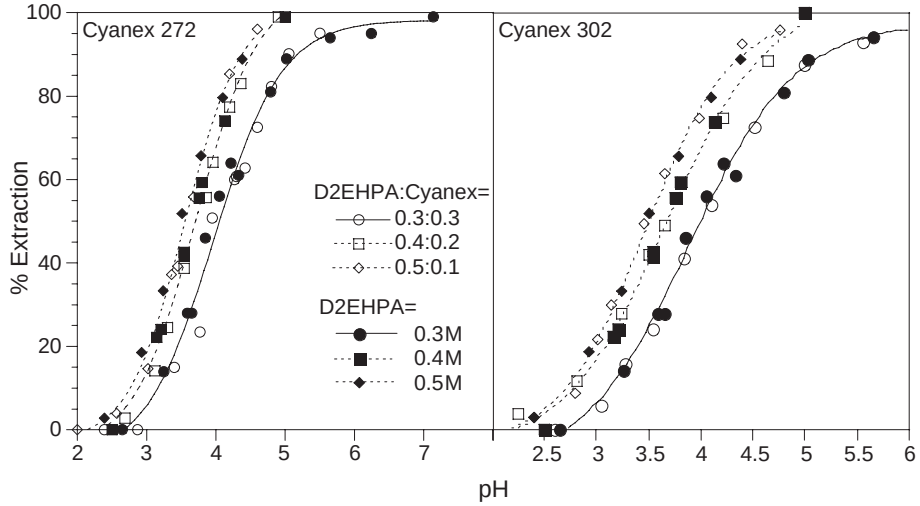

Fig. 4. Percent of nickel extracted by D2EHPA compared to D2EHPA–Cyanex mixtures at 25 °C.

concentration of the organic phase ($[(R/R')H]_{\text{equilibrium}}$) can be defined by the following general equation:

$$\left[\left(R/R^{'}\right)H\right]_{\text{equilibrium}} = \left[\left(R/R^{'}\right)H\right]_{\text{initial}} - n \times \left[\overline{\text{M}}\right]_{\text{Org}}. \quad (2)$$

The extraction constant is described as follows:

$$K = \frac{\left[\text{M}\overline{\left(R/R^{'}\right)_2\left(\left(R/R^{'}\right)H\right)}_{(n-2)}\right][H^+]^2}{[\text{M}^{2+}]\left[\left(\overline{R/R'}\right)H\right]^n_{\text{equilibrium}}}$$

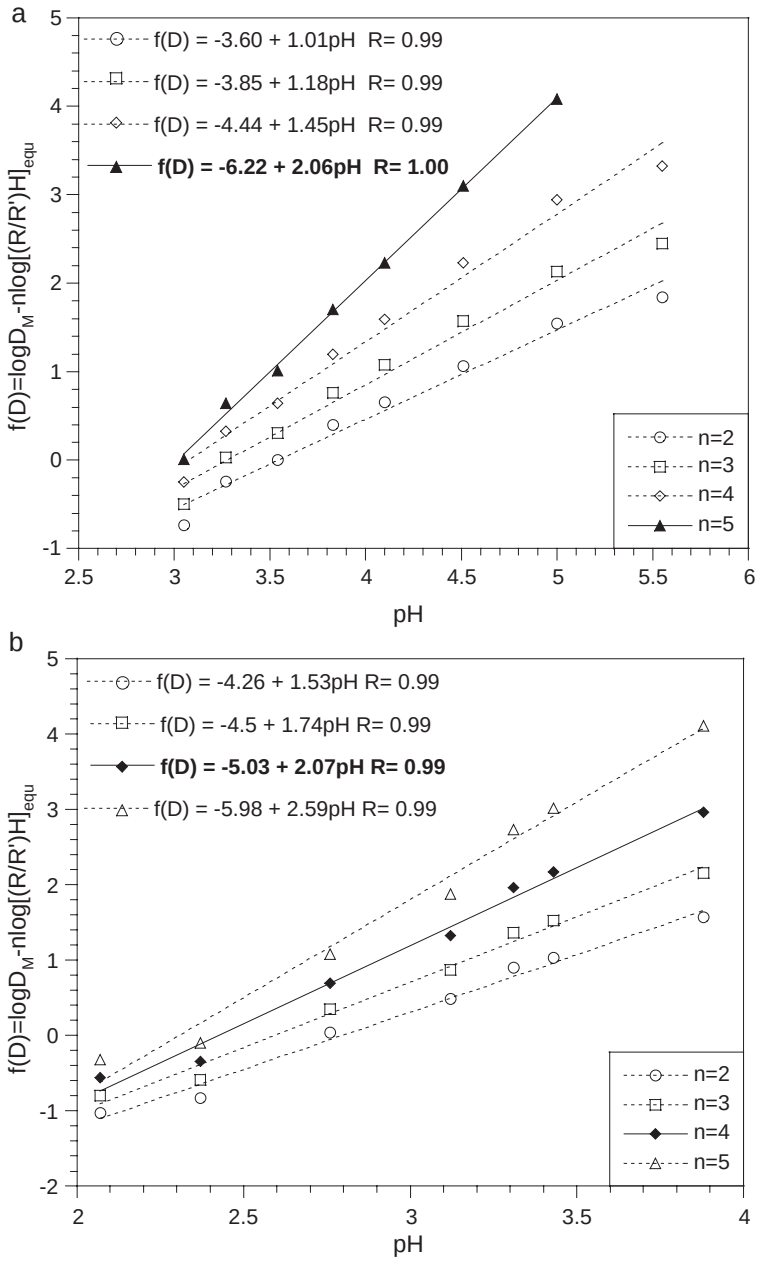

Fig. 5. Variation of $f(D) = \log D - n\log\left[\left(\overline{R/R^{'}}\right)H\right]_{\text{equilibrium}}$ versus pH, using mixture of D2EHPA and Cyanex 302 as extractant: (a) nickel and (b) cobalt.

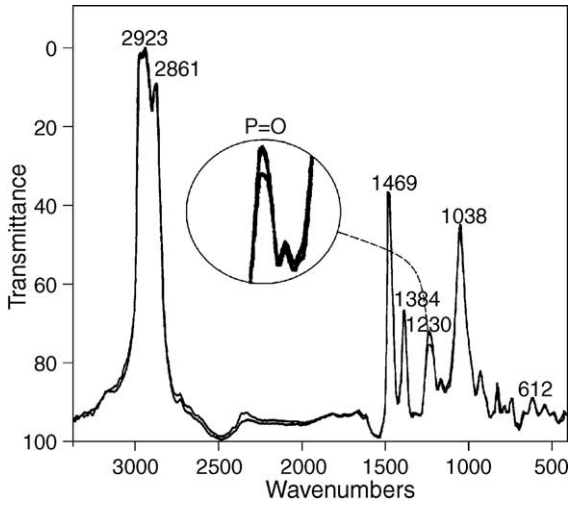

Fig. 6. FT-IR spectra of mixture of D2EHPA and Cyanex 302 at mole ratio of 0.3:0.3. Comparison between pure organic phase and loaded by nickel.

The distribution coefficient of M^{2+} may be written as:

$$D_M = \frac{\left[\overline{M(R/R')_2((R/R')H)_{(n-2)}}\right]}{[M^{2+}]}. \quad (4)$$

The following expression can thus be derived:

$$\log D_M = \log K + 2\mathrm{pH} + n\log\left[\overline{(R/R')H}\right]_{\text{equilibrium}} \quad (5)$$

and

$$\log K = \log D_M - 2\mathrm{pH} - n\log\left[\overline{(R/R')H}\right]_{\text{equilibrium}} = -\frac{\Delta H}{2.3\mathrm{RT}} + \frac{\Delta S}{2.3R}. \quad (6)$$

Fig. 5 shows the plots of $\log D_M - n\log[\overline{(R/R')H}]_{\text{equilibrium}}$ against pH plotted for various values of n. The line that most closely exhibits a slope equal to 2 is then selected. This slope is related to the stoichiometric coefficient of hydrogen ion (H^+) in the extraction Eq. (1). It should be noted that these results are valid when the concentration of metal in the organic phase is up to 0.08 M. According to FT-IR measurements, Manski et al. (2002) have shown that the formula of the complex in the organic phase does not change with the concentration up to 0.10 M.

A review of the previous work (Tait, 1993) shows that the stoichiometric coefficients for both cobalt and nickel are equal to 4 when using D2EHPA as a monomer extractant. Respective values, however, are 4 and 6 when using either Cyanex 272 (Tait, 1993) or Cyanex 302 (Preston, 1982) as the monomer extractant. This present investigation reveals a coefficient of 4 for cobalt when extracted with D2EHPA–Cyanex 302 mixture. This is consistent with the similar extraction behavior of the two mixtures used in the pH range of the experimentation. However, this coefficient is 5 for nickel extraction with the same mixed solution, but 4 for both cobalt and nickel when extracted with D2EHPA–Cyanex 272 solutions.

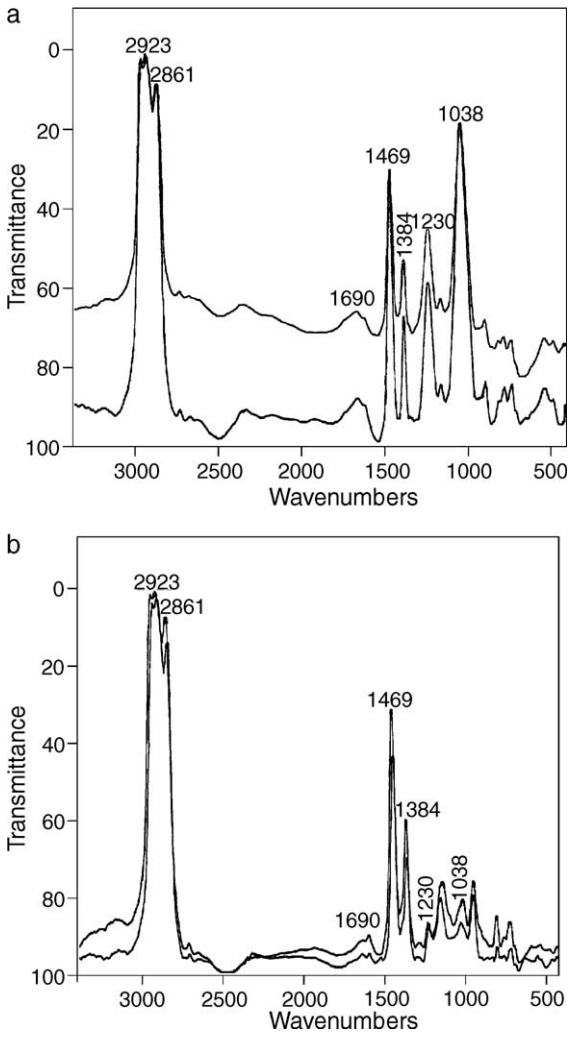

Fig. 7. FT-IR spectra of individual D2EHPA and Cyanex 272 (0.3 M). (a) Comparison between pure and loaded D2EHPA by nickel at pH=4. (b) Comparison between pure and loaded Cyanex 272 by nickel at pH=7.

3.3. FT-IR spectroscopy analysis

FT-IR measurements were carried out to assess the results obtained in the previous section. FT-IR analyses of the organic phases were carried out with a Unicam FT-IR Spectrometer (Mattson 1000 model) using NaCl Windows.

Some references on the application of FT-IR to the solvent extraction system reveal that phosphonic, phosphinic and phosphoric acids can be identified from relevant vibrational characteristic bands. The FT-IR spectra of pure liquid D2EHPA, Cyanex 272 and Cyanex 302 have been analyzed and the results are quite similar to those found by other researchers (Morais and Mansur, 2004; Bgona Menoyo et al., 2002; Sainz-Diaz et al., 1996). Characteristic vibrational bands for D2EHPA and Cyanex 272, i.e., P=O, P–O–C or P–O–H and OH are similar but more intense for D2EHPA than for Cyanex 272 (Fig. 6). These characteristic vibrational bands are identified at 1230, 1034 and 1690 cm^{-1}, respectively. An important vibrational characteristic band of Cyanex 302 is P=S. According to Menoyo et al. (2002), this band occurs at 612 cm^{-1}. The bands corresponding to the C–H stretch occur at 2923 and 2861 cm^{-1}. The C–H deformation vibration band has frequencies of 1469 cm^{-1} and 1384 cm^{-1}. This is a multiple band that confirms the presence of more than one CH_3 group on a carbon atom.

3.3.1. FT-IR spectroscopy analysis of metal extraction with Cyanex 302

FT-IR analysis of a nickel loaded mixture of D2EHPA and Cyanex 302 at the molar ratio of 0.3:0.3 is shown in Fig. 6. Based on the results of FT-IR measurements, it can be seen that the interaction of nickel affects only the characteristic vibrational band of D2EHPA (P=O and O–H) and there is no variation on the characteristic vibrational band of Cyanex 302 (P=S). Based on the results by Menoyo et al. (2002) when D2EHPA was used, the number of extractant molecules that participate in the organo-metallic complex is 4. Hence, considering that no variation occurs at the P=S vibrational band, it can be concluded that only one of the five extractant molecules, which form the complex, is due to Cyanex 302. Similar experiments were carried out for cobalt but all the characteristic vibrational bands of D2EHPA and Cyanex 302 varied during cobalt extraction. It is, therefore, concluded that D2EHPA and Cyanex 302 have similar behavior, which confirms the results shown in Fig. 2. Based on the results obtained from the slope analyses and FT-IR measurements, the

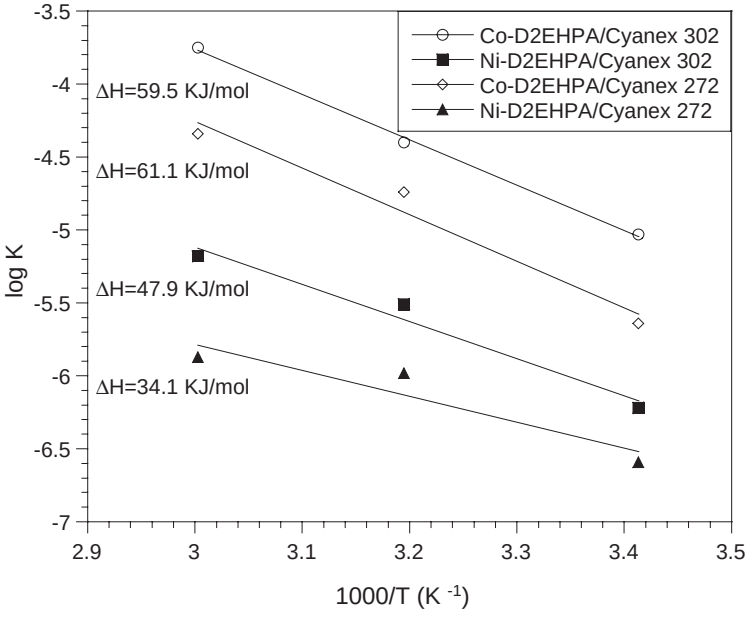

Fig. 8. Variation of log$K$ versus 1000/T, using mixture of D2EHPA/Cyanex 272 or Cyanex 302 as extractant at mole ratio of 0.3:0.3.

extraction of cobalt and nickel can be represented by the following equations:

$$Co^{2+} + 4\overline{(R/R')H} \leftrightarrow \overline{((R/R'))_2 Co((R/R')H)_2} + 2H^+ \quad (7)$$

$$Ni^{2+} + 5\overline{(R/R')H} \leftrightarrow \overline{(R)_2 Ni(RH)_2 (R'H)} + 2H^+. \quad (8)$$

3.3.2. FT-IR spectroscopy analysis of metal extraction with Cyanex 272

FT-IR analysis of a nickel loaded mixture of 0.3 M D2EHPA and Cyanex 272 is shown in Fig. 7. It can be seen that the nickel affects the 1230 and 1690 cm^{-1} vibrational bands of D2EHPA so that the transmittance of these bands increases. However, Fig. 7b shows that variation of vibrational bands of Cyanex 272 is not as noticeable as D2EHPA, in spite of carrying out this experiment at pH=7. Therefore, it can be concluded that at pH<5 only D2EHPA participates in the cation exchange of hydrogen with the metal coordinated bond. At pH>5, both D2EHPA and Cyanex 272 participate in cation exchange of hydrogen ion by metal ion.

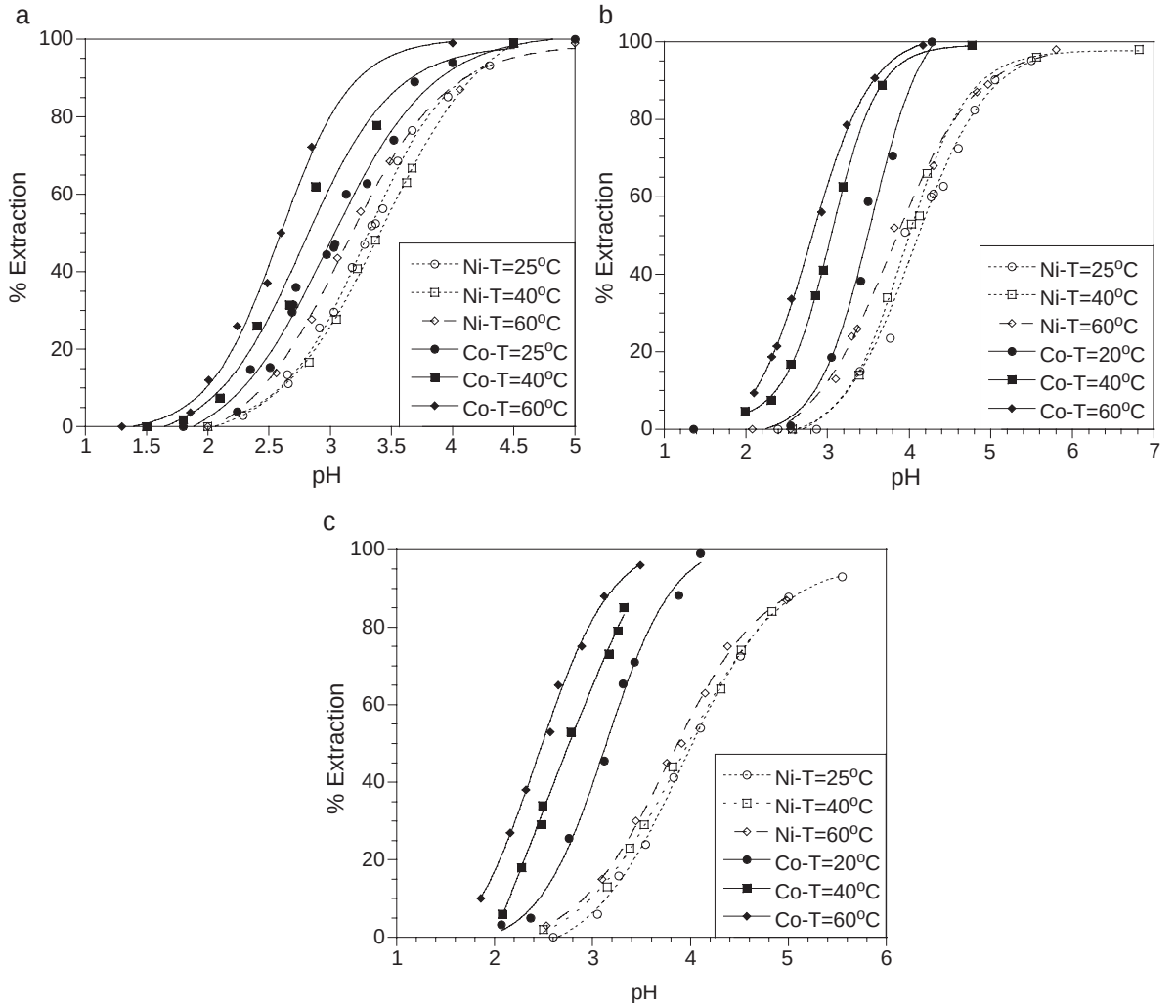

Fig. 9. Effect of pH on percent of extraction cobalt and nickel at different temperatures. (a) 0.6 M D2EHPA; (b) 0.3 M:0.3 M D2EHPA–Cyanex 272 and (c) 0.3 M:0.3 M D2EHPA–Cyanex 302.

Table 2
Effect of temperature on pH_{50}^{Ni}, pH_{50}^{Co} and $pH_{50(Ni-Co)}^{Co}$ for D2EHPA and D2EHPA–Cyanex mixtures

Temperature (°C)	Extractant (0.6 M)	pH_{50}		
		Ni	Co	Ni–Co
25	D2EHPA	3.30	3.04	0.26
	D2EHPA and Cyanex 272 (0.3–0.3)	4.12	3.48	0.64
	D2EHPA and Cyanex 302 (0.3–0.3)	4.01	3.13	0.88
40	D2EHPA	2.82	3.40	0.58
	D2EHPA and Cyanex 272 (0.3–0.3)	3.04	4.00	0.96
	D2EHPA and Cyanex 302 (0.3–0.3)	2.77	3.97	1.20
60	D2EHPA	2.59	3.18	0.59
	D2EHPA and Cyanex 272 (0.3–0.3)	2.81	3.86	1.05
	D2EHPA and Cyanex 302 (0.3–0.3)	2.49	3.86	1.47

3.4. Effect of temperature on extraction

To assess the effect of temperature on the extraction of cobalt and nickel, experiments were carried out at three different temperatures (25, 40 and 60 °C). The results obtained are shown in Fig. 8. Generally, cobalt and nickel extraction is endothermic. Values of enthalpy show that the effect of temperature on cobalt extraction is higher than that on nickel extraction. A temperature rise shifts the extraction curves of cobalt to the left to a larger extent than those of nickel (Fig. 9). Consequently, an increase in the temperature from 25 to 60 °C changes $pH_{0.5}$ and $\Delta pH_{50(Ni-Co)}$ for cobalt and nickel—as listed in Table 2. It is seen that the temperature rise from 25 to 60 °C results in an increase of 1.47 in $\Delta pH_{50(Ni-Co)}$ for D2EHPA–Cyanex 302 mixtures and 1.05 for D2EHPA–Cyanex 272 mixtures. Separation of cobalt and nickel is easier, therefore, at elevated temperatures than at the lower ones. Thus improved cobalt purification can be obtained at elevated temperatures with all mixtures.

3.5. Synergistic effect of Cyanex 272 and Cyanex 302

The separation factor (β) is a measure of selectivity in the extraction of cobalt and nickel. This factor is defined as:

$$\beta_{Co/Ni} = \frac{D_{Co}}{D_{Ni}}. \quad (9)$$

A lower nickel distribution factor gives a better separation of cobalt from nickel. This improves, of course, the selectivity of the solution. Increasing β eliminates the impurities from co-extraction with the required metal. It reduces, therefore, the number of

Table 3
Effect of temperature on distribution coefficient of Co and Ni and separation factor $\beta_{Co/Ni}$

Temperature (°C)	pH	D2EHPA=0.6			D2EHPA:Cyanex 272=0.3:0.3			D2EHPA:Cyanex 302=0.3:0.3		
		D_{Co}	D_{Ni}	$\beta_{Co/Ni}$	D_{Co}	D_{Ni}	$\beta_{Co/Ni}$	D_{Co}	D_{Ni}	$\beta_{Co/Ni}$
25	3.00	0.92	0.41	2.24	0.22	0.03	–	0.65	0.07	9.29
	3.20	1.59	0.75	2.12	0.41	0.06	6.83	1.19	0.13	9.15
	3.40	2.67	1.31	2.04	0.76	0.12	6.33	2.19	0.24	9.13
	3.60	4.49	2.28	1.97	1.46	0.22	6.64	4.22	0.39	10.82
	3.80	7.74	4.03	1.92	3.08	0.41	7.51	7.97	0.63	12.65
	4.00	12.89	6.61	1.95	7.15	0.72	9.93	18.12	0.97	18.68
40	3.00	1.63	0.35	4.66	0.79	0.05	–	1. 90	0.15	6.667
	3.20	2.78	0.59	4.71	1.59	0.10	15.85	3.28	0.24	13.67
	3.40	4.63	0.98	4.72	3.22	0.19	16.95	6.17	0.38	16.24
	3.60	7.69	1.66	4.63	6.00	0.33	18.18	10.04	0.58	17.31
	3.80	12.05	2.83	4.26	12.04	0.57	21.12	18.12	0.86	21.07
	4.00	18.12	5.10	3.55	21.08	1.01	20.87	30.85	1.30	23.73
60	3.00	4.00	0.63	6.35	1.68	0.10	16.80	4.98	0.17	29.04
	3.20	7.97	1.06	7.52	2.93	0.17	17.24	8.57	0.28	30.61
	3.40	15.89	1.73	9.18	5.38	0.26	20.69	15.86	0.42	37.09
	3.60	30.85	2.83	10.90	9.63	0.41	23.49	30.85	0.64	48.21
	3.80	70.94	4.41	16.09	19.49	0.62	31.44	50.55	1.01	50.26
	4.00	94.24	7.20	13.09	46.62	0.90	51.80	284.7	1.47	193.2

operational stages required for achievement of a highly concentrated metallic phase.

The values of cobalt–nickel separation factor $\beta_{Co/Ni}$ indicated in Table 3 show a mixture of D2EHPA with Cyanex 302 improves the selectivity of cobalt over nickel as compared to the pure D2EHPA. Under similar conditions, cobalt–nickel separation improves by increasing of both pH and temperature in the following order:

D2EHPA<D2EHPA − Cyanex 272
<D2EHPA − Cyanex 302.

It can be concluded that D2EHPA mixed in Cyanex 272 and D2EHPA mixed in Cyanex 302 have synergistic effects on the co-extraction of cobalt from nickel. These results are more prominent in the case of D2EHPA–Cyanex 302 than in the case of D2EHPA–Cyanex 272 mixtures. The value of $\beta_{Co/Ni}$ for extraction with D2EHPA at pH = 4.00 and $T = 60$ °C is 13. This value is 52 for the same conditions with a D2EHPA: Cyanex 272 mole ratio of 0.3: 0.3, and 193 for the same mole ratio of D2EHPA–Cyanex 302. These values are too different from those obtained with pure Cyanex 272 solution. Addition of both Cyanex 272 and Cyanex 302 to D2EHPA therefore clearly results in selectivity improvement of the cobalt/nickel extraction process. Further improvement is obtained if the temperature is increased above that of ambient.

4. Conclusions

Stoichiometric coefficients (n) of cobalt and nickel, defined by the extraction Eq. (2), were found to be 4 and 5, respectively, in all mixtures of D2EHPA and Cyanex 302 and 4 for all mixtures of D2EHPA and Cyanex 272. These coefficients were equal to 4 for both cobalt and nickel when D2EHPA was the only extractant. Slope analysis and FT-IR measurements showed that the mechanism of cobalt extraction by Cyanex 302 was similar to that by D2EHPA. However, no noticeable difference was observed for nickel extraction with the addition of Cyanex 302 to D2EHPA. Results showed that in the latter case, 5 extractant molecules participated in the organo-metallic complex.

Cobalt and nickel extraction reactions were both endothermic; with cobalt extraction more endothermic than that of nickel. With increasing the concentration of Cyanex 302, values of the apparent enthalpies increased also. The apparent enthalpy values for the extraction of cobalt and nickel with a D2EHPA:Cyanex 302 mole ratio 0.3:0.3 are 59.5 and 47.9 kJ/mol, respectively. The apparent enthalpy values for the extraction of cobalt and nickel with a D2EHPA:Cyanex 272 mole ratio 0.3:0.3 are 61.1 and 34.1 kJ/mol, respectively. Therefore, improved cobalt and nickel separation could be favored by elevating the temperature for all mixtures. By addition of Cyanex 272 or Cyanex 302 to D2EHPA and raising the temperature, the difference $\Delta pH_{50(Ni-Co)}$ increased. The calculated values of $\beta_{Co/Ni}$ show that this factor increases by temperature and pH in the following order:

D2EHPA<D2EHPA − Cyanex 272
<D2EHPA − Cyanex 302.

Further work on the extraction of other metals such as Zn, Cd and Mn by these mixtures is being carried out and will be reported later.

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