Adsorption (2008) 14: 31–36
DOI 10.1007/s10450-007-9043-3

Extraction of cobalt (II) and nickel (II) by a solvent impregnated resin containing bis(2,4,4-trimethylpentyl)monothiophosphinic acid

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Received: 6 May 2006 / Revised: 17 July 2007 / Accepted: 31 July 2007 / Published online: 20 September 2007
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Abstract In the present work, studies have been conducted on the equilibrium distribution of cobalt (II) and nickel (II) between aqueous hydrochloric solution and macromolecular resin impregnated with bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex302, HL). Effects of extraction time, pH values, metal ion concentration, and temperature were investigated. Analysis of the results shows that the extraction of the two metal ions can be explained assuming the formation of metal complexes in the resin phase with a general composition ML_2. An extraction reaction is proposed and the equilibrium constants of the complexes were determined. The Freundlich isotherm and thermodynamic quantities, i.e., ΔG, ΔH and ΔS were also obtained. Both of the extraction reactions of cobalt (II) and nickel (II) are endothermic ones. The efficiency of the resin in the separation of cobalt (II) and nickel (II) is provided according to the separation factors. Under the experimental conditions employed, pH_{50} values for cobalt (II) and nickel (II) are 3.76, 5.01, respectively. The logarithmic value of separation factor was calculated as 2.50.

Keywords Extraction · Cobalt · Nickel · Solvent impregnated resin · Bis(2,4,4-trimethylpentyl)monothiophosphinic acid

Abbreviations

D	Distribution ratio $D = \frac{V}{m} \cdot \frac{C_0 - C}{C}$ where V: volume of the aqueous phase (mL), m: mass of dry resin (g), C_0: initial total concentration of metal ions in aqueous phase, C: equilibrium concentration of metal ions in aqueous phase
K_{eq}	Stoichiometric equilibrium constant
D_c	Distribution ratio expressed as: $D_c = (C_0 - C)/C$ or $D_c = K_{eq}[HL]_{(r)}^{2+q}[H^+]^{-2}$ as shown in the text
β	Separation factor
pH_{50}	pH at which 50% of the metal ions are extracted
Q	Amount of M^{2+} adsorbed with impregnated resins
R	Mass of extraction resin
ΔG	Gibbs free energy change
ΔH	Enthalpy change
ΔS	Entropy change

1 Introduction

In the last decades, the study of solvent impregnated resins (SIR) has been a major field of research in separation science, and they could be considered as a link between solvent extraction and ion-exchange technologies (Cortina and Warshawsky 1997). The SIR concept is based on the incorporation of a solvent extraction reagent into a porous polymer by a physical impregnation technique (Warshawsky 1981). Nowadays, it is well developed and has a firmly established place in the extraction, separation, and preconcentration of metals, in both analytical and preconcentration procedures as stationary phases in extraction chromatography and technological applications (Jia et al. 2004; Wang et al. 1998).

Cobalt and nickel are ubiquitous trace metals that occur in soil, water, air, and in the biosphere. They are

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used for a wide variety of purposes in modern industry. Many methods such as solvent extraction, ion exchange, evaporation, and coprecipitation have been conducted for the separation or preconcentration of cobalt and nickel. Among these, solvent extraction with organophosphorus acids has attracted much attention. During the last 20 years, there has been a lot of research into cobalt and nickel solvent extraction separation by using organophosphorus acids, such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) (Ritcey et al. 1975; Sarangi et al. 1999; Preston 1982), bis(2-ethylhexyl)phosphinic acid (PIA-8) (Koladkar and Dhadke 2001), 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (PC-88A) (Sarangi et al. 1999; Dreisinger and Cooper 1984; Liranza et al. 1999), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) (Sarangi et al. 1999; Liranza et al. 1999; Tait 1993; Rickelton et al. 1984; Reichley-Yinger and Danesi 1985; Fu and Golding 1988; Feather and Cole 1996; Legault-Seguin et al. 2004; Tsakiridis and Agatzini-Leonardou 2004), and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex302) (Liranza et al. 1999; Tait 1993; Feather and Cole 1996; Legault-Seguin et al. 2004; Tsakiridis and Agatzini-Leonardou 2004). Preston (1982) investigated the extraction of cobalt and nickel by organophosphorus acids and obtained the stoichiometries of $Co(HA_2)_2$ and $Ni(HA_2)_2(H_2A_2)_x(H_2O)_{2-x}$ ($x = 0$, 1, or 2) for cobalt and nickel complexes, respectively. Cobalt is extracted at lower pH values than nickel; under comparable conditions, the cobalt-nickel separation increases in the order of phosphoric < phosphonic < phosphinic acids. Danesi et al. (1985) also reported that Co^{2+} and Ni^{2+} are extracted with various organophosphorus acids according to the following reaction:

$$M^{2+}_{(a)} + (2+x)H_2R_{2(o)} \rightleftharpoons MR_2 \cdot (2+2x)HR_{(o)} + 2H^{+}_{(a)} \tag{1}$$

where $x = 0$ for Co^{2+}, while $x = 1$ for Ni^{2+}, and H_2R_2 denotes the dimeric species of the extractant predominant in non-polar diluents.

Sorption and separation of Co(II) and Ni(II) with extraction resins containing organophosphorus acids have been studied extensively. For instance, Akita and Takeuchi (1992) conducted the adsorption of Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} by a macromolecular resin containing D2EHPA and PC-88A. Adsorption and separation of some divalent metals using 1-hexyl-4-ethyloctyl isopropylphosphonic acid (HEOPPA) impregnated resins were studied in our previous work (Jia et al. 2003). For the Cyanex extractants, Cyanex272, Cyanex302, and bis(2,4,4-trimethylpentyl)-dithiophosphinic acid (Cyanex301), Cyanex272 attracted the most attention (Huynh and Tanaka 2003; Yoshizuka et al. 1990; Inoue et al. 1987; Castilllo et al. 1999; Gonzalez et al. 2001). Gonzalez et al. (2001) studied the selective separation of Fe^{3+}, Cd^{2+}, and Ni^{2+} from dilute solutions using Cyanex272 and Cyanex302 solvent impregnated resins. Ensor et al. (2002) investigated the adsorption of Cd^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} by Cyanex302 and Cyanex301 impregnated on an inert polymeric substrate. In their work, the removal of these metals was determined from various concentrations of H_2SO_4 and H_3PO_4.

Since the separation of cobalt and nickel are of great importance and some SIR containing organophosphorus acids have been proved to be effective, the sorption and separation of these two metals with various SIR containing organophosphorus acids are very attractive. The investigation of cobalt and nickel extraction by solvent-impregnated resins containing Cyanex302 is the subject of this study. The present work is directed towards Cyanex302 resin impregnated on a mixture of styrene and divinylbenzene copolymers. The extracted complexes are suggested and the equilibrium constants of the extracted complexes are calculated. The Freundlich isotherm and thermodynamic quantities have also been determined.

2 Experimental

2.1 Reagents

Cyanex302 was kindly supplied by the CYTEC Canada, Inc. Solvent impregnated resin containing Cyanex302 with size of 0.07–0.15 mm was obtained from Beijing Institute of Chemical Engineering and Metallurgy, Ministry of Nuclear Industry. The resin was prepared by adding the extractant to the mixture of styrene and divinylbenzene copolymers (Li et al. 1993). It was washed with 3 mol/L HCl and water in order to eliminate inorganic impurities as well as monomeric materials. The content of Cyanex302 in the resin is determined to be 1.58 mmol/g by titrating with standard NaOH after shaking the resin in ethanol for 12 h.

Stock solutions of MCl_2 (M = cobalt, nickel) were prepared with AR Chemicals (Shenyang, China). The pH values of aqueous solutions were adjusted by the addition of a small amount of HCl or NaOH solution. All extraction experiments were performed at constant ionic strength (0.2 mol/L NaCl). The concentrations of Co(II) and Ni(II) were determined by a spectrophotometer using nitroso R salt (530 nm) and dimethylglyoxime (470 nm) photometric method, respectively. All the other reagents used in this study were of analytical reagent grade.

2.2 Apparatus

The pH values in the aqueous phase were measured by a pHS-3C digital pH meter made by Shanghai Rex Instruments Factory. A UV-VIS-NIR recording spectrophotometer of Model UV-365 made by Shimadzu Company (Kyoto, Japan) was employed for absorption measurements.

2.3 Methods

All the experiments of metal ions extraction were carried out batchwise at 303 ± 1 K except for the temperature experiments. Samples of resin containing Cyanex302 and 5 mL aqueous solution of Co(II) or Ni(II) were introduced into special glass-stoppered tubes and shaken to achieve equilibrium. After phase separation with a high-speed centrifuge the concentration of M(II) in the aqueous phase was analyzed by spectrophotometry. The amount of M(II) extracted on the resin was determined by material balance. The distribution ratio of metal ions was obtained as the following:

$$D = \frac{V}{m} \cdot \frac{C_0 - C}{C} \tag{2}$$

where V represents the volume of the aqueous phase (mL), m stands for the mass of dry resin (g), C_0 and C denote the initial total concentration and the equilibrium concentration of metal ions in aqueous phase respectively.

3 Results and discussion

3.1 Influence of shaking time

The time-dependent extraction of Co(II) and Ni(II) on Cyanex302 impregnated resin was studied at constant pH values, concentration of M(II) and mass of resin. The equilibration time was varied from 0 to 240 min and the results are shown in Fig. 1. It can be seen that 2 h is sufficient to reach equilibrium for both Co(II) and Ni(II). Therefore, a 2 h equilibration time was employed for all the subsequent experiments.

3.2 Extraction stoichiometry

In preliminary experiments, it was determined that Cl^- ions are not co-extracted by the resin phase, the extraction of Co^{2+} and Ni^{2+} with the resin can thus be expressed as the following general reaction (Cortina et al. 1996):

$$M^{2+} + (n+q)HL_{(r)} \rightleftharpoons ML_n(HL)_{q(r)} + nH^+ \tag{3}$$

where r denotes the resin phase; q and n denote unknown coefficients.

Figure 2 shows the metal distribution data from aqueous solutions of 0.2 mol/L (Na, H) Cl with Cyanex302 impregnated resin as log D versus pH. The distribution functions are straight lines with a slope of about 2 for both Co^{2+} and Ni^{2+}, indicating that 2 protons are released in the extraction reaction of metal ions by the resin phase. Equation (3) can thus be written as:

$$M^{2+} + (2+q)HL_{(r)} \rightleftharpoons ML_2(HL)_{q(r)} + 2H^+. \tag{4}$$

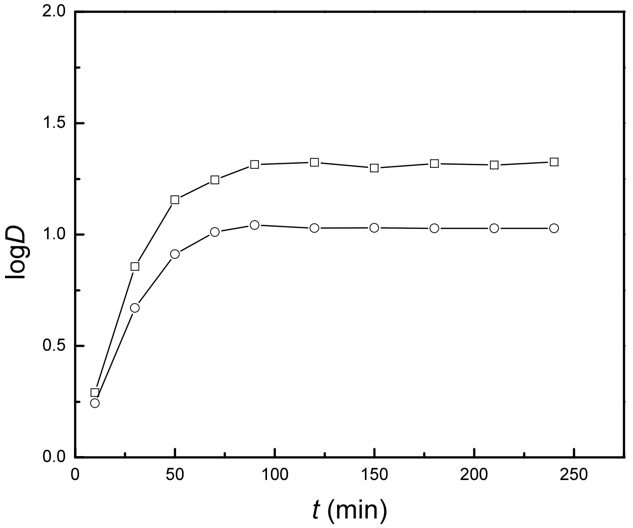

Fig. 1 Effect of time on the extraction of Co(II) and Ni(II) with Cyanex302 impregnated resin. $m_{\text{resin}} = 0.05$ g, $c_{\text{Cyanex302}} = 1.58$ mmol/g, $[M^{2+}] = 35.0$ µg/mL, [(Na,H)Cl] = 0.20 mol/L. (□) Co^{2+}, (○) Ni^{2+}

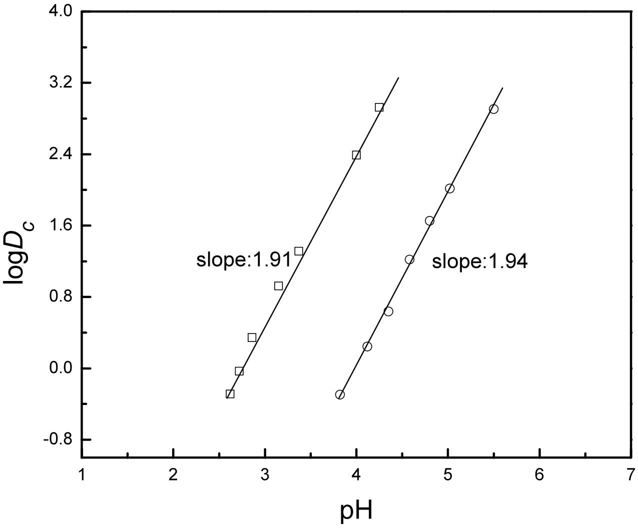

Fig. 2 Effect of equilibrium pH on the extraction of Co(II) and Ni(II) with Cyanex302 impregnated resin. $m_{\text{resin}} = 0.05$ g, $c_{\text{Cyanex302}} = 1.58$ mmol/g, $[M^{2+}] = 35.0$ µg/mL, [(Na,H)Cl] = 0.20 mol/L. (□) Co^{2+}, (○) Ni^{2+}

The stoichiometric equilibrium constant, K_{eq}, for the extraction can thus be expressed as:

$$K_{eq} = \frac{[ML_2(HL)_q]_{(r)}[H^+]^2}{[M^{2+}][HL]_{(r)}^{2+q}}. \tag{5}$$

The distribution ratio for M^{2+} becomes:

$$D_c = K_{eq}[HL]_{(r)}^{2+q}[H^+]^{-2}, \tag{6}$$

$$\log D_c - 2pH = (2+q)\log[HL]_{(r)} + \log K_{eq} \tag{7}$$

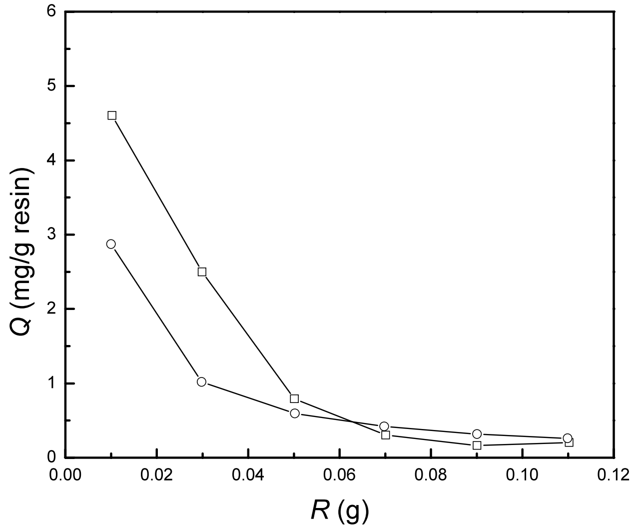

Fig. 3 Effect of resin amount on the extraction of Co(II) and Ni(II) with Cyanex302 impregnated resin. $c_{\text{Cyanex302}} = 1.58$ mmol/g, $[\text{M}^{2+}] = 35.0$ μg/mL, [(Na,H)Cl] = 0.20 mol/L. (□) Co^{2+}, (○) Ni^{2+}

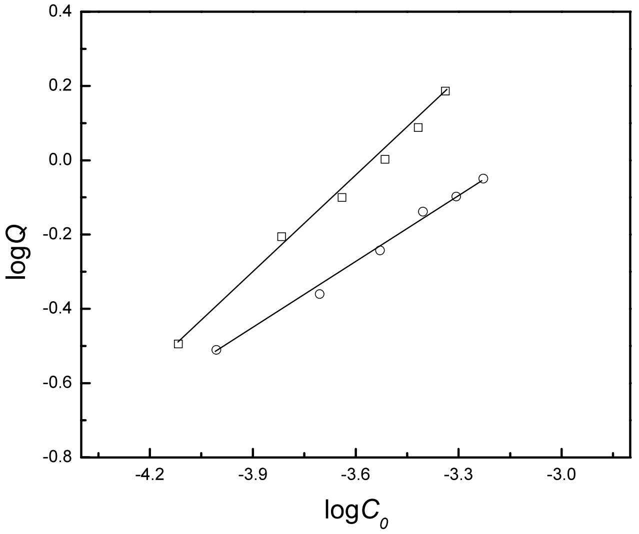

Fig. 4 Effect of M^{2+} concentration on the extraction of Co(II) and Ni(II) with Cyanex302 impregnated resin. $m_{\text{resin}} = 0.05$ g, $c_{\text{Cyanex302}} = 1.58$ mmol/g, [(Na,H)Cl] = 0.20 mol/L. (□) Co^{2+}, (○) Ni^{2+}

where $[\text{HL}]_{(r)}$ can be calculated according to $[\text{HL}]_{(r)} = [\text{HL}]_{(r),0} - (2+q)[\text{M}^{2+}]_{(r)}$; $[\text{HL}]_{(r),0}$ denotes the initial Cyanex302 content in the sorbent.

It can be also seen from Fig. 2 that Co(II) can be extracted at lower pH values than Ni(II), which is in accordance with previous results (Preston 1982). However, it is difficult to compare the extraction by Cyanex302 impregnated resin with that by Cyanex302 in solvent extraction. This is because studies concerning extraction of Co(II) and Ni(II) using Cyanex302 from chloride media are little as mentioned above.

The extraction order of the two metal ions can be considered for separating them. Whether the separation can be achieved is evaluated by the separation factor, (β), which is a useful indicator. The separation factor β and pH_{50} (pH at which 50% of the metal ions are extracted) have the following relation (Ni and Hong 1998):

$$\log\beta = 2\Delta pH_{50}. \tag{8}$$

As can be obtained from Fig. 2, pH_{50} values for Co(II) and Ni(II) are 3.76, 5.01, respectively. $\log\beta$ can thus be calculated as 2.50.

At constant values of M^{2+} concentration, acidity in aqueous phase and ionic strength, the effects of resin amounts on the amounts (Q, mg/g resin) of M^{2+} extracted with Cyanex302 impregnated resins are shown in Fig. 3. It can be seen that the Q values decrease with an increase in the mass of extraction resin (R). The total amount of Co^{2+} and Ni^{2+} extracted up to resin saturation is determined to be 0.787 mmol Co^{2+}/g resin and 0.789 mmol Ni^{2+}/g resin according to Wang et al.'s method (Wang et al. 1998). The molar ratio of Cyanex302 and M^{2+} can be calculated to be about 2. Therefore, the extraction reactions of Co^{2+} and Ni^{2+} from chloride medium with Cyanex302 impregnated resins can be described as:

$$M^{2+} + 2HL_{(r)} \rightleftharpoons ML_{2(r)} + 2H^{+} \tag{9}$$

which means that q in (7) is 0 for both Co^{2+} and Ni^{2+}.

According to (7), the equilibrium constant, K_{eq} of the complexes formed can be calculated as: $\log K_{eq} = -3.86 \pm 0.10$ and -6.38 ± 0.08 for Co^{2+} and Ni^{2+}, respectively.

3.3 Extraction isotherms

The concentration dependence of Co(II) and Ni(II) extraction on Cyanex302 impregnated resin was studied at a fixed pH value and amount of adsorbent. The data for the extraction has been analyzed in terms of the Freundlich isotherm. It was found that this equation was capable of describing the data over the entire range of concentration studied. The Freundlich isotherm can be expressed as (Suzuki 1990):

$$\log Q = \frac{1}{n} \cdot \log C_0 + \log K \tag{10}$$

where C_0 is the initial concentration of M^{2+}, K and $\frac{1}{n}$ stand for Freundlich constants. The values of $\log K$ and $\frac{1}{n}$ for M^{2+} can be determined according to the slope and intercept values in Fig. 4 and (10).

For Co(II): $\log Q = 0.84 \log C_0 + 2.97 \quad (R^2 = 0.9938)$,

For Ni(II): $\log Q = 0.61 \log C_0 + 1.91 \quad (R^2 = 0.9934)$.

The sorption data were also fitted to the Langmuir isotherm model:

$$C_r = \frac{C_m K C}{1 + KC}. \tag{11}$$

This equation can be rearranged to get the linear form:

$$\frac{1}{C_r} = \frac{1}{C_m K C} + \frac{1}{C_m} \tag{12}$$

where C_r is the equilibrium concentration of metal ions in the resin phase, C is the equilibrium concentration of metal ions in the aqueous phase, C_m is the monolayer sorption capacity, and K is a constant related to the energy of sorption. The fitted parameter values and values of the correlation coefficients are as the followings:

$$\text{For Co(II):}\quad \frac{1}{C_r} = \frac{0.018}{C} + 43.01 \quad (R^2 = 0.9588),$$

$$\text{For Ni(II):}\quad \frac{1}{C_r} = \frac{0.024}{C} + 116.40 \quad (R^2 = 0.9608).$$

It can be seen that the Langmuir isotherm is not as suitable as the Freundlich isotherm. The reason may be because the Langmuir model assumes that the surface of the sorbent can accommodate only a monolayer of the sorbate ions and no interaction between the sorbed species. Freundlich isotherm model, on the other hand, does not have any restriction on the sorption capacity of the sorbent, and is more appropriate in situations where the sorption sites possess a heterogeneous nature.

3.4 Effect of the experimental temperature

The effect of temperature on the extraction of Co(II) and Ni(II) by Cyanex302 impregnated resin was investigated at fixed concentrations of M(II), mass of the resin, ion strength and acidities in the aqueous phase. The temperature was varied from 20 °C to 50 °C. The change of the distribution coefficients with the temperature can be expressed by the equation:

$$\Delta \log D/\Delta(1/T) = -\Delta H/2.303R \tag{13}$$

which can be used to calculate the enthalpy change of the extraction reaction, ΔH.

The plots of log D versus $1/T \times 1000$ are illustrated in Fig. 5. The graphs are linear with slopes of -0.97 and -0.25 for Co(II) and Ni(II), respectively. ΔH for Co(II) and for Ni(II) were evaluated as $\Delta H_{\text{Co}} = 18.57$ kJ/mol and $\Delta H_{\text{Ni}} = 4.79$ kJ/mol. The free energy ΔG and entropy change ΔS were also calculated from (12) and (13), respectively.

$$\Delta G = -RT \ln K_{eq}. \tag{14}$$

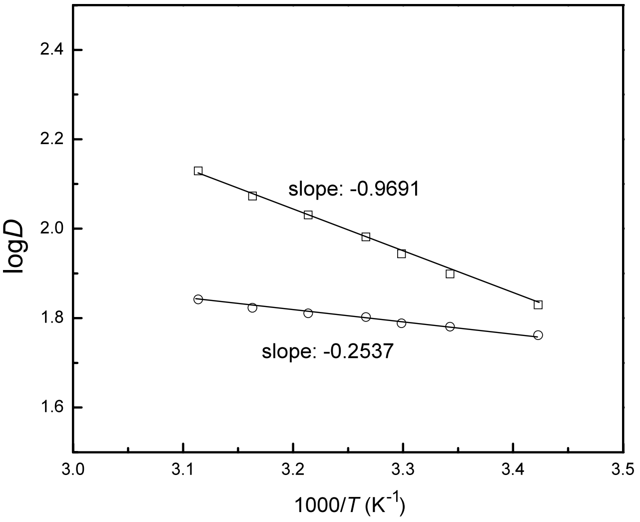

Fig. 5 Effect of experimental temperature on the extraction of Co(II) and Ni(II) with Cyanex302 impregnated resin. $m_{\text{resin}} = 0.05$ g, $c_{\text{Cyanex302}} = 1.58$ mmol/g, $[\text{M}^{2+}] = 35.0$ μg/mL, $[(\text{Na,H})\text{Cl}] = 0.20$ mol/L. (□) Co^{2+}, (○) Ni^{2+}

$$\Delta S = \frac{\Delta H - \Delta G}{T}. \tag{15}$$

$$\text{For Co(II):}\quad \Delta G = 22.40\ \text{kJ mol}^{-1},\quad \Delta S = 135.15\ \text{J K}^{-1}\,\text{mol}^{-1}.$$

$$\text{For Ni(II):}\quad \Delta G = 37.03\ \text{kJ mol}^{-1},\quad \Delta S = 137.94\ \text{J K}^{-1}\,\text{mol}^{-1}.$$

The positive value of enthalpy change (ΔH) confirms the endothermic extraction of Co(II) and Ni(II) on SIR containing Cyanex302. The positive value of entropy change (ΔS) suggests the increased randomness at the solid-solution interface during the extraction of Co(II) and Ni(II) on the resin.

4 Conclusions

Solvent impregnated resins containing Cyanex302 were used for the extraction and separation of cobalt (II) and nickel (II). The extraction stoichiometry is proposed and equilibrium constants of the extracted species are determined. A general composition, ML_2, is formed for both cobalt (II) and nickel (II). Cyanex302 contained in the resin behaves in the same extraction order as that in the organic diluents in solvent extraction, i.e. cobalt (II) is extracted at lower pH values than nickel (II). pH_{50} values for cobalt (II) and nickel (II) were determined as 3.76, 5.01, respectively, which provides the possibility to separate these two metal ions. Freundlich's isothermal equations have also been obtained. Furthermore, thermodynamic quantities, i.e.,

ΔG, ΔS and ΔH have been calculated for the system. According to temperature dependence experiments, the extraction reactions of cobalt (II) and nickel (II) are endothermic ones.

Because of the novelty of the impregnated resin in this paper, many questions still remain. The present work is currently in progress to study the extracted species, investigate the possibility to separate cobalt (II) and nickel (II). The long-term stability of the resin, and the stripping behavior are also under consideration.

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