EQUILIBRIA OF Co(II) AND Ni(II) EXTRACTION FROM SULPHATE SOLUTIONS WITH CYANEX 301

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ABSTRACT

The extraction equilibria of Co(II) and Ni(II) extraction from the sulphate solutions with di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) dissolved in an aliphatic kerosene have been studied. The obtained results prove that the stoichiometry of Co(II) and Ni(II) complexes extracted with Cyanex 301 (HA) corresponds to the following formulae $CoA_2(HA)_2$ and $NiA_2(HA)_4$, respectively.The logarithmic values of corresponding extractions constants (log $K_{ex,Co}$ and log $K_{ex,Ni}$) are equal to 2.47±0.03 and 4.73±0.02, respectively. The observed changes of electronic absorption spectra of the organic phases containing cobalt complexes have been attributed to the oxidation of Co(II) in contact with air.

Keywords: di(2,4,4-trimethylpentyl)dithiophosphinic acid, extraction equilibria, cobalt(II), nickel(II).

INTRODUCTION

Cyanex 301 is a trade name of di(2,4,4-trimethylpentyl) dithiophosphinic acid which has been developped for metal extraction, especially for zinc, from highly acidic solutions. Cyanex 301 is also effective for cobalt(II) and nickel(II) extraction, however, in such case it is practically impossible to separate these metals [1,2]. In contrast to di(2,4,4-methylpentyl)phosphinic acid (Cyanex 272), Cyanex 301 does not dimerize

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in the solutions in nonpolar organic solvents. The equilibria of Co(II) and Ni(II) extraction with Cyanex 301 have been studied by several authors [1,3-5], however, the reported results are not consistent and differ each other significantly when one compare the stoichiometry of extracted species and the values of corresponding extraction constants. In the present work the extraction equilibria in the system Co(II) – Ni(II) – 0.50 M (H$_2$SO$_4$, Na$_2$SO$_4$) – Cyanex 301 – aliphatic kerosene have been discussed in terms of stoichiometry of extracted Co(II) and Ni(II) complexes and their extraction constants. The electronic absorption spectra prove that the complexes of Co(II) with Cyanex 301 in the organic phase are easily oxidized with air to the complexes of Co(III).

THEORY

If the mononuclear complexes of Co(II) and Ni(II) are responsible for the extraction with Cyanex 301, the following extraction equilibrium could be written:

$$M_{(a)}^{2+} + xHA_{(o)} = MA_2(HA)_{x-2(o)} + 2H_{(a)}^{+} \qquad (1)$$
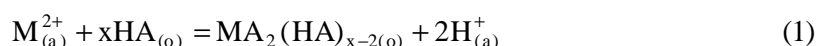
where indices a and o refer to the aqueous and organic phases, respectively, M stands for Co(II) or Ni(II) while HA and A denote the molecule of acidic extractant and its anion. The corresponding extraction constant, K_{ex}, is expressed as follows:

$$K_{ex} = D \cdot \frac{[H^+]_{(a)}^2}{[HA]_{(o)}^x} \qquad (2)$$

where D is a distribution ratio of Co(II) or Ni(II). From Eq. (2) it follows that

$$\log D - 2pH = \log K_{ex} + x \log[c_{HA(o)}^0 - x\, c_{M(o)}] \qquad (3)$$

where the equilibrium concentration of free Cyanex 301 in the organic phase is calculated from the formula:

$$c_{HA(o)}^0 - x\, c_{M(o)} = [HA]_{(o)} \qquad (4)$$

Eq. (3) permits to determine the stoichiometric coefficient x in Eq. (1) and then to evaluate the corresponding extraction constant.

EXPERIMENTAL

The initial aqueous phases have been prepared from chemically pure sulphates(VI) of Co(II) and Ni(II) dissolved in doubly distilled water to which the desired amounts of chemically pure sulphuric acid and sodium sulphate have been also added. All these reagents have been obtained from POCh (Poland). Cyanex 301 has been kindly supplied by Cytec (Canada). The initial organic phases have been obtained from the known quantity of Cyanex 301 dissolved in the aliphatic kerosene (POCh) containing mainly $C_{12} - C_{14}$ fraction of saturated hydrocarbons. The conical flasks containing equal volumes (10 cm^3) of both phases have been mechanically shaken at a constant temperature (25±1 ^{o}C). The phase contact time of 15 minutes has been found as sufficient to reach the equilibrium between both phases. The metal content in the aqueous phase has been determined by means of AAS Solaar 939 (Unicam) spectrophotometer while pH has been measured with CX-731 (Elmetron) pH-meter. The concentrations of metals in the organic phase have been calculated from the mass balance. The electronic absorption spectra of organic phases have been recorded with UV2 (ATI Unicam) spectrophotometer.

THE RESULTS AND DISCUSSION

The first series of experiments has been carried out to study the simultaneous extraction of Co(II) and Ni(II) from their binary 0.001 and 0.005 M solutions with 0.05 M Cyanex 301 solution at different pH of aqueous phase. Both metals have been also extracted with 0.05 M Cyanex from their individual 0.005 M solutions. The obtained results are presented in Fig. 1 and 2. Further experiments have been performed for 0.10 M Cyanex 301. The obtained results are presented in Fig. 3, 4 and 5.

The obtained results prove that Cyanex 301 cannot be used for separation of Co(II) and Ni(II) because the observed differences between their extraction depend both on metal and extractant concentrations. As can be seen (Figs. 1 and 2) the yield of Co(II) extraction with 0.050 M solution of Cyanex 301 is higher than that of Ni(II). However, at higher concentration of extractant (0.10 M) and lower concentrations of metals (0.001 and 0.002 M, respectively), the opposite relation occurs (Fig. 3), i.e. the yield of Ni(II) extraction is slightly higher than that of Ni(II), irrespective of the equilibrium pH. The picture is even more complicated when both metals are extracted with 0.10 M Cyanex 301 from their 0.005 M solutions (Figs. 4 and 5).
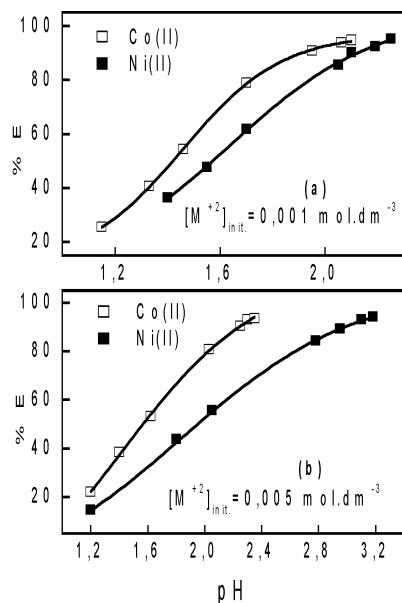
Fig. 1. Simultaneous extraction of Co(II) and Ni(II) from their (a) 0.001 M and (b) 0.005 M solutions with 0.050 M Cyanex 301.
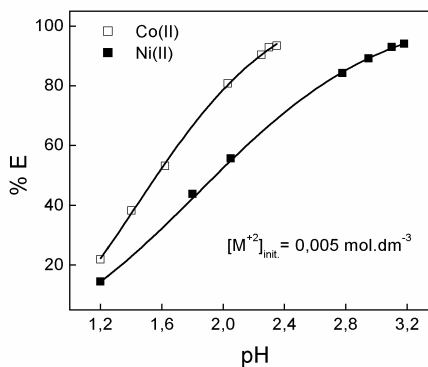
Fig. 2. Extraction of Co(II) and Ni(II) from sulphate solutions with 0.050 M Cyanex 301 in kerosene.
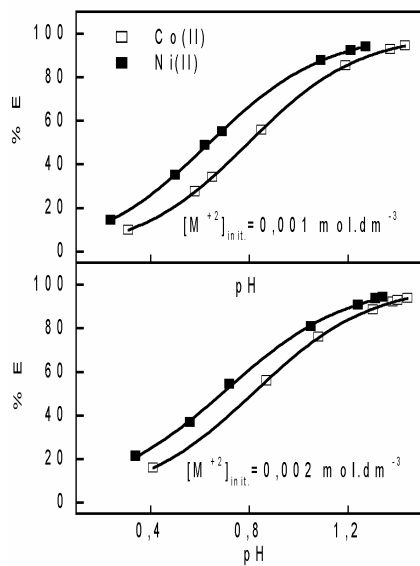

Fig. 3. Simultaneous extraction of Co(II) and Ni(II) from their 0.001 and 0.002 M solution with 0.10 M Cyanex 301.
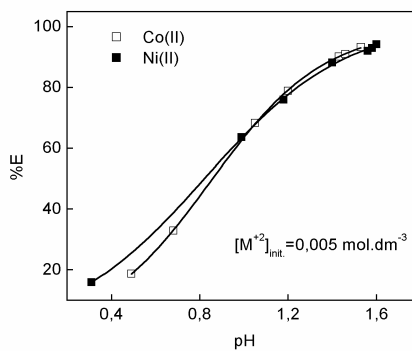
Fig. 4. Extraction of Co(II) and Ni(II) from sulphate solutions with 0.10 M Cyanex 301 in kerosene.

The obtained results have been used in the determination of stoichiometry of extracted species and evaluation of Co(II) and Ni(II) extraction constants. The extraction equilibria have been interpreted applying the nonlinear regression analysis, which leads to the following results:

$$Co(II): x = 4, R^2 = 0.9991, s.d. = 0.03, F = 26640;$$
$$Ni(II): x = 6, R^2 = 0.9997, s.d. = 0.02, F = 98030.$$

Therefore, the composition of extracted species can be expressed as $CoA_2(HA)_2$ and $NiA_2(HA)_4$, respectively. The logarithmic values of corresponding extraction constants are as follows: $\log K_{ex,Co} = 2.47 \pm 0.03$ and $\log K_{ex,Ni} = 4.73 \pm 0.02$. The plots of $(\log D - 2pH)$ vs. $\log[HA]_{(o)}$ obtained for both metals and all experimental points are presented in Fig. 6.
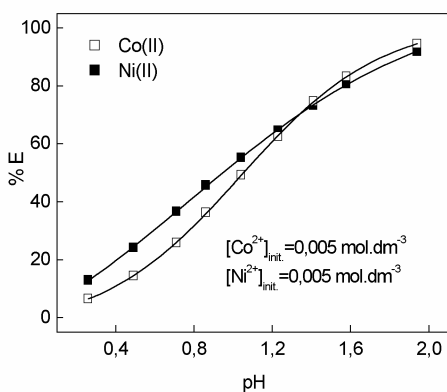

Fig. 5. Simultaneous extraction of Co(II) and Ni(II) from their 0.005 M solution with 0.10 M Cyanex 301.
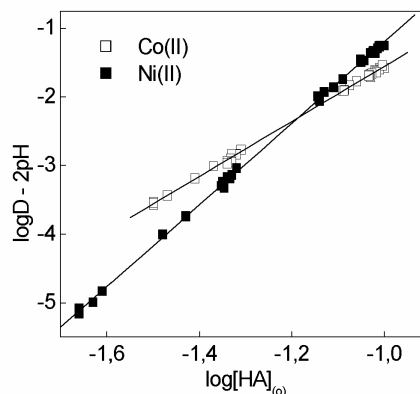
Fig. 6. Plots of $(\log D - 2\ pH)$ vs. log $[HA]_o$ for Co(II) and Ni(II) extraction with Cyanex 301.

The same stoichiometries of Co(II) and Ni(II) complexes extracted with Cyanex 301 solutions in xylene were determined by Sole and Hiskey [1]. It should be noted however, that the reported values of corresponding extraction constants seem to be erroneous since they were evaluated from the plots of pH of half extraction ($pH_{0.5}$) vs. log $[HA]_2$ [1]. As has been stated above, Cyanex 301 does not dimerize in nonpolar solvents like toluene and xylene [2,5]. Tait [5] found that the composition of mononuclear complexes of Co(II) and Ni(II) extracted from sulphate solutions with toluene solution of Cyanex 301 corresponds to the formulae CoA_2 and $NiA_2(H_2O)_2$, respectively. Menoyo and Elizalde [3] extracted Co(II) from chloride solutions with Cyanex 301 in toluene and distinguished two Co(II) complexes formed in the organic phase, namely CoA_2 and $CoClA$ with the logarithmic values of extraction constants 0.12 ± 0.01 and 0.20 ± 0.14, respectively. Singh and coworkers [4] found that Ni(II)

extraction from sulphate solutions with Cyanex 301 in toluene is followed with the formation of NiA_2 complex in the organic phase and logarithm of corresponding extraction constant is equal to 1.41. According to Sole and Hiskey [1] and Tait [2], Co(II) complexes with Cyanex 301 are tetrahedral whereas those of Ni(II) are octahedral.

It should be noted that the colour of organic phases containing complexes of Co(II) changes with the elapsed time. This observation is consistent with the remark of Facon and coworkers [2] who stated that such changes could be attributed to the oxidation of Co(II) complexes with Cyanex 301 affected by the contact of organic phase with air. The electronic absorption spectra of the organic phases recorded immediately after the separation of phases (Fig. 7) and after 24 hours (Fig. 8) indicate the increase of intensity of the band located at 400 nm. Therefore, this band can be identified as specifically responsible for the observed changes of color (from dark green to brown) of organic phases.
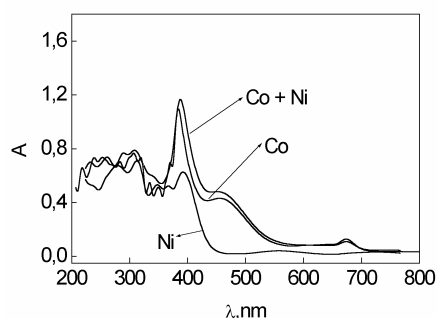

Fig.7. Electronic absorption spectra of organic phases containing cobalt and nickel(II) complexes extracted with 0.10 M Cyanex 301 from their 5.0 mM solutions in 0.50 M ($H_2SO_4+Na_2SO_4$). The spectra have been recorded immediately after the separation of phases.
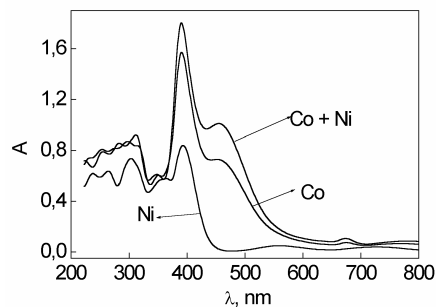
Fig.8. Electronic absorption spectra of organic phases containing cobalt and nickel(II) complexes extracted with 0.10 M Cyanex 301 from their 5.0 mM solutions in 0.50 M ($H_2SO_4+Na_2SO_4$). The organic phases have been aged 24 hours.

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