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THE EFFECT OF TRIBUTYL PHOSPHATE ON THE EXTRACTION OF NICKEL(II) AND COBALT(II) IONS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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The paper presents the results of studies on the extraction of nickel(II) and cobalt(II) ions from sulphate solutions with di(2-ethylhexyl)phosphoric acid (D2EHPA). As the modifier of extracting capacity, tributyl phosphate (TBP) was used. The obtained experimental results indicate that a high excess of TBP in relation to D2EHPA reduces the extracting capacity of the latter, whereas its small amount (in a proportion of 1:1) improves the extraction of nickel(II) ions, while not affecting the extraction of cobalt(II) ions.

Key words: extraction, phosphoric acid derivatives, metal ions

INTRODUCTION

The use of nickel and cobalt has distinctly increased in recent years. This can be indicated, on the one hand, by the increase in the world's production of these metals, and by the appearance of increasingly large amounts of various wastes containing them, on the other. Considering the fact that nickel and cobalt ions are toxic to the natural environment, this adds to the problem of their disposal. One of the feasible solutions is to apply liquid extraction in combination with chemical reaction.

As typical extractants for the extraction of nickel(II) and cobalt(II) ions from aqueous solutions, organic derivatives of phosphoric acid are used. In this group, both typical acid extractants, such as di(2-ethylhexyl)phosphoric acid (D2EHPA) or di(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), and Lewis bases can be distinguished, the most typical representatives of the latter being tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO).

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Phosphoorganic extractants, having functional groups with strongly electron-donor oxygen atoms, can form complexes of a diverse structure (Rydberg, et al., 2004). In addition, these extractants have an ability to interact with one another, creating various associated molecules (Marcus and Kertes, 1969). Acid phosphoorganic extractants in solvents used for the extraction of metal ions occur in a dimer form:

$$2HA_{org} = (HA)_{2,org}, \quad K_{\dim} = \frac{[(HA)_2]_{org}}{[HA]^2_{org}} \tag{1}$$

Data colleted in numerous publications indicate that the dimerization constant varies depending on the solvent used, for D2EHPA taking on the values of log (K_{dim}) ranging from 3.95 to 4.8 9 (Kolarik, 1982). Taking into account such large values of the dimerization constant, it can be assumed that, in the organic phase, about 98% of extractant occurs in a dimer form, where two strong hydrogen bond P(=O)OH…O=(OH)P is observed, with the single bond energy amounting to 4 – 5 kcal/mol (Figure 1).

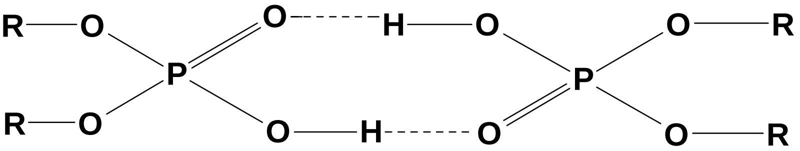

Fig. 1. Structure of the cyclic dimer of di(alkyl)phosphoric acid

On account of the dimerization of acid phosphoorganic extractants, it is adopted in scientific reports that in the formation of complexes with nickel(II) and cobalt(II) ions, these extractants take part in a monomer rather than dimer form (Swain, et al., 2006; Fu and Golding, 1987):

$$M^{2+}_{aq} + 2(HA)_{2,org} = M(HA_2)_{2,org} + 2H^+_{aq}, \quad K_{ex} = \frac{[M(HA_2)_2]_{org}[H^+]^2_{aq}}{[(HA)_2]^2_{org}[M^{2+}]_{aq}} \tag{2}$$

The complex formed in such reaction has a structure of an adduct, in which particular places in the coordination sphere of nickel(II) and cobalt(II) ions are occupied in total by four molecules of the extractant. At the same time, two of them, as acid anions, form polarized covalence bonds, and the other two, as non-dissociated molecules – coordinate bonds via the phosphoryl oxygen atom (Figure 2), (Marcus, and Kertes, 1969).

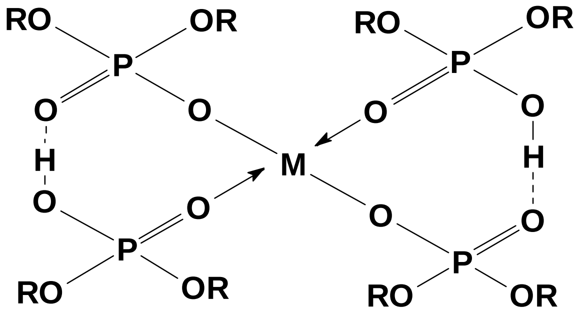

Fig. 2. Structure of the complex of the divalent metal ion with di(alkyl)phosphoric acid in the form of an $MA_2(HA)_2$ type adduct

The suggested structure of this complex is much more complicated than that of typical acid extractant complexes, which react with metal cations according to the reaction

$$M^{2+}_{aq} + 2HA_{org} = MA_{2,org} + 2H^{+}_{aq}, \quad K_{ex} = \frac{[MA_2]_{org}[H^+]^2_{aq}}{[HA]^2_{org}[M^{2+}]_{aq}} \tag{3}$$

to form chelate complexes, in which each extractant molecule occupies two coordinate places.

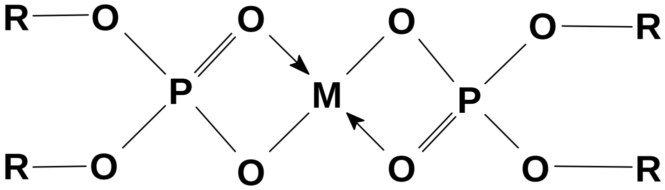

Fig. 3. Structure of the complex of the divalent metal ion with di(alkyl)phosphoric acid in the form of an MA_2 chelate complex

Complexes of nickel(II) and cobalt(II) ions, depending of loading have a face tetrahedral or octahedral structure (Sato and Nakamura, 1972; Van de Voorde et al. 2005). This means that, if the formation of a complex of the structure as shown in Figure (2) is assumed, the positioning of four large extractant molecules in the first coordination sphere should encounter problems associated with the spherical hindrance. Therefore, two of these molecules should be relatively easily exchanged for the molecules of another extractant of the properties of a Lewis base. Such an extractant, having a relatively smaller molecule and, at the same time, good extracting properties, is tributyl phosphate (TBP).

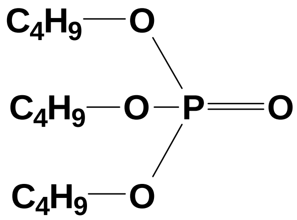

Fig. 4. Structure of tributyl phosphate (TBP)

TBP is often used in the extraction of metal ions as an additional solvating extractant, whose task is to form adducts with metal complexes existing in the solution. (Rydberg et al., 2004). The extraction process in this case can be written in the form of the equation:

$$MA_{2,org} + 2TBP_{org} = MA_{2,org}\cdot\left(TBP\right)_2, \quad K_{add} = \frac{\left[MA_{2,org}\cdot\left(TBP\right)_2\right]_{org}}{\left[TBP\right]^2_{org}\left[MA_2\right]_{org}} \;. \qquad (4)$$

The structure of adducts formed in this reaction is shown in Figure (5).

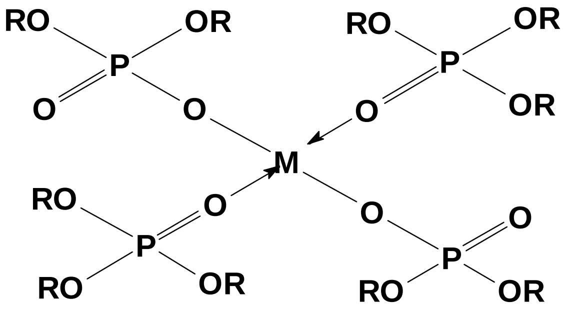

Figure 5. Structure of the complex of the divalent metal ion with di(alkyl)phosphoric acid and tributyl phosphate in the form of an $MA_2(HA)_2$ type adduct

The volume of the TBP molecule, as calculated from the van der Waals radii, is smaller than that of D2EHPA by about 50Å (Z. Kolarik, 1982) (Table 1). Therefore, it should easier replace D2EHPA molecules in the forming complex. The greater dipole moment of the molecule of this extractant (TBP), indicating its greater polarity, is also an argument for the formation of adducts shown in Figure (5). The smaller charge (in terms of its absolute value) on the phosphoryl oxygen atom in TBP, on the other hand, points out to D2EHPA as a more favoured in the formation of associated molecules.

On the other hand, the presence in the organic phase of an additional compound of strongly solvating properties can give rise to the formation of associated molecules between the molecules of di(2-ethylhexyl)phosphoric acid and tributyl phosphate.

$$HA_{org} + TBP = HA \cdot TBP_{org}, \quad K_{\dim} = \frac{[HA \cdot TBP]_{org}}{[HA]_{org}[TBP]_{org}} \tag{5}$$

Table 1. Physicochemical properties of di(2-ethylhexyl)phosphoric acid and tributyl phosphate. The volume calculated from the van der Waals radii

Extractant	Molecule volume, Å^3	Charge on the phosphoryl oxygen atom	Dipole moment, debye
D2EHPA	311.3	-0.873	2.74
TBP	263.7	-0.779	3.10

In such an associated molecule, the phosphoryl oxygen atom, owing to the two free electron pairs, form a hydrogen bond with the molecule of di(2-ethylhexyl)phosphoric acid (Figure 6).

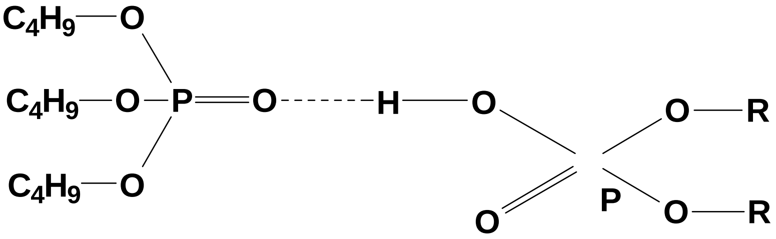

Fig. 6. Structure of the associated molecule of di(2-ethylhexyl)phosphoric acid with tributyl phosphate

As follows from the discussion above, the effect of a tributyl phosphate addition to the organic phase containing D2EHPA as an extractant is not unambiguous, because TBP can influence the extraction of nickel(II) and cobalt(II) ions either favourably or unfavourably.

The aim of the study is to examine the effect of TBP as a synergic addition in the extraction of nickel and cobalt with di(2-ethylhexyl)phosphoric acid from sulphate solutions.

REAGENTS

Hydrated sodium, nickel(II) and cobalt(II) sulphates(VI), as well as sodium hydroxide (supplied by POCh, Poland), were used for the tests. For the preparation of the organic phase solution, di(2-ethylhexyl)phosphoric acid (D2EHPA – 98 %, by Johnson Mathey GmbH, Germany), tributyl phosphate (TBP – 97%) and kerosene of a density of 0.85 g/dm^3 (by ALDRICH) were used.

EXPERIMENTAL

A sulphate(VI) solution containing 0.01 mol/dm^3 of nickel(II) and cobalt(II) ions, each, formed a blank. The ionic strength of the initial solution was set at 0.10 M by adding an appropriate amount of sodium sulphate(VI). The pH of the solution was varied by adding 1M NaOH. The organic phase was obtained by dissolving 0.05 M of the extractant (D2EHPA) in kerosene. As the modifier, TBP was added to the organic phase in a D2EHPA:TBP molar ratio of 1:1, 1:2 and 1:4, respectively. Flasks, each containing 10 cm^3 of the water phase and the organic phase, were shaken mechanically at a constant temperature of 21±1 ^{o}C for 15 minutes. After the separation of the phases, the concentration of metal ions in the water phase was assayed on an AAS Solaar 939 spectrophotometer (by Unicam), while pH was measured with a CX-731 pH meter (by Elmetron). The concentration of each sample was assayed three times, and the average value was taken for further consideration. The concentration of metal ions in the organic phase was calculated from the mass balance.

TESTING RESULTS AND DISCUSSION

Four series of experiments were carried out by testing the extraction of nickel(II) and cobalt(II) ions from sulphate solutions for different equilibrium pH values of the water phase. In the first series, D2EHPA in the concentration of 0.05 mol/dm^3 was used as the extractant. In subsequent series, TBP as the modifier of the extracting capacity of D2EHPA was added to the organic phase. TBP was added in the molar ratio to D2EHPA equal to 1:1, 1:2 and 1:4, respectively. The obtained results are shown in Figures 7 and 8.

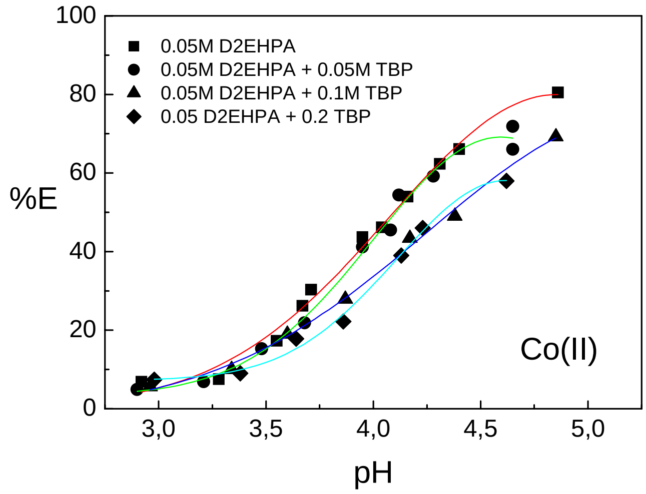

Fig. 7. Variations of the degree of extraction (%E) of cobalt(II) ions using D2EHPA as a function of pH for different amounts of TBP. Water phase – 0.01 mol/dm Co(II), organic phase – 0.05 mol/L D2EHPA, ■ - D2EHPA; ● - D2EHPA + 0.05 mol/L TBP; ▲ - D2EHPA + 0.1 mol/L TBP; ♦ - D2EHPA + 0.2 TBP

When comparing Figures 7 and 8 it can be noticed that the effect of TBP on extraction depends on the kind of metal being extracted. In the case of cobalt(II), the addition of TBP to the organic phase in the proportion of 1: 1 in relation to D2EHPA practically has no effect on the degree of extraction. A greater excess of TBP in relation to D2EHPA causes a decrease in the degree of extraction.

A different situation is observed for the extraction of nickel(II) ions. A small addition of TBP in the proportion of 1:1 in relation to D2EHPA in the organic phase causes an increase in the degree of extraction. Whereas, further increasing the amount of TBP in the solution results in its decrease.

The reduction of the degree of extraction for a high TBP excess in relation to D2EHPA suggests the formation of the associated molecules of TBP with D2EHPA (Figure 6). The formation of such associated molecules is possible, because the phosphoryl oxygen atom from the TBP molecule, having two free electron pairs, is able to form hydrogen bonds with D2EHPA molecules (Figure 6). Thus, the concentration of the monomer form of this extractant decreases (Equation 5), which causes the extraction equilibrium to shift to the right (Equations 2 and 3). This means the reduction of the degree of extraction of nickel(II) and cobalt(II) ions.

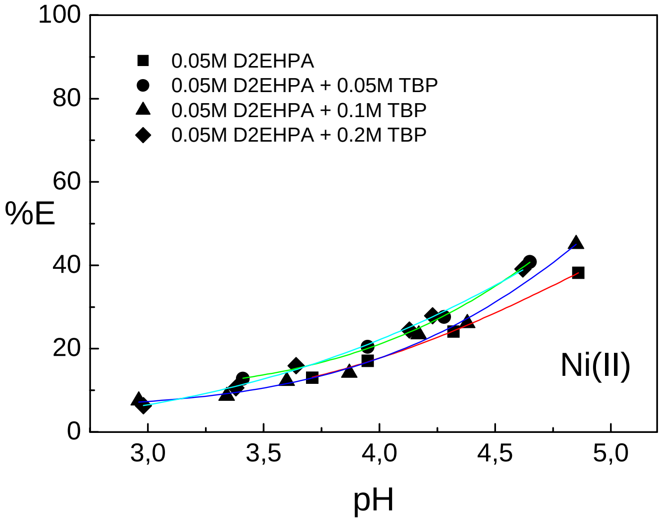

Fig. 8. Variations of the degree of extraction (%E) of nickel(II) ions using D2EHPA as a function of pH for different amounts of TBP. Water phase – 0.01 mol/dm Co(II), organic phase – 0.05 mol/L D2EHPA, ■ - D2EHPA; ● - D2EHPA + 0.05 mol/L TBP; ▲ - D2EHPA + 0.1 mol/L TBP; ♦ - D2EHPA + 0.2 TBP

A small TBP addition in the case of nickel(II) ions increases the extraction degree of nickel. This suggests a possibility of occurring adducts in the form of $NiA_2(TBP)_2$. In the case of cobalt(II) ion extraction, this effect is unnoticeable.

SUMMARY

The obtained experimental results show that a high excess of TBP in relation to D2EHPA reduces the extracting capacity of the latter towards nickel(II) and cobalt(II) ions, whereas its small amount (in the ratio of 1:1) improves the extraction of nickel(II) ions, while not affecting the extraction of cobalt(II) ions.

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W pracy zaprezentowano wyniki badań dotyczących ekstrakcji jonów niklu(II) i kobaltu(II) z roztworów siarczanowych za pomocą kwasu di(2-etyloheskylo) fosforowego. Jako modyfikatora zdolności ekstrakcyjnej użyto fosforanu tributylu. Otrzymane wynik badań wskazują, że duży nadmiar fosforanu tributylu w stosunku do kwasu di(2-etyloheskylo) fosforowego redukuje zdolności ekstrakcyjne kwasu di(2-etyloheskylo) fosforowego, podczas gdy jego małe ilości, w proporcji 1:1, zwiększają ekstrakcję jonów niklu(II), nie wpływając na ekstrakcję jonów kobaltu.