The role of β-diketones in the extraction of cobalt (II) and nickel (II) ions

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Abstract. β-diketones were used for Co(II) and Ni(II) separation from nitrate solutions by liquid-liquid extraction method. Pentane-2,4-dione (1), 3-methyl-pentane-2,4-dione (2) and 3-ethyl-pentane-2,4-dione (3), all in dichloromethane solution were extractants in this process. Potentiometric studies were used to determinate dissociation constants of investigated ligands. Stability constants of the created complexes were found by spectrophotometric methods and the increased in the order of $2 < 1 < 3$. Extraction was carried out from three types of aqueous phase: one-component Co(II) or Ni(II), and two-component Co(II)-Ni(II). It was proved that pentane-2,4-dione (1) is the most effective extractant.

1. Introduction
Recovery of non-ferrous metals from ores and metal bearing wastes is based either on pyrogenic or hydrometallurgical technologies. Selection of an appropriate manufacturing process depends on useful metal content. In a typical hydrometallurgical process, among the basic technologies (i.e. leaching, phase separation, extraction of metal ions from aqueous solutions), separation of the ions is of particular interest.

Removal of Co(II) and Ni(II) ions from aqueous solution usually takes place using precipitation methods, e.g. oxidative precipitation and sulphide precipitation [1].

The separation of Co(II) and Ni(II) ions from ammonia solution can be likewise conducted by hollow fiber supported liquid membranes (HFSLMs) with Alamine 300 (a water insoluble tri-n-octyl amine), which was a more effective extractant for Co(II) than for Ni(II) [2].

Sadyrbaeva [3] used liquid membranes which contain trialkylbenzylammonium chloride and tri-n-octylamine in 1,2-dichloroethane for electrodialytic separation of Co(II) and Ni(II) from 3–4 M HCl solutions into dilute solutions of various acids. In these conditions, the rate of the membrane transport of $\text{CoCl}_4^{2-}$ anions was increased with increasing density, acidity, and Co(II) concentration in the feed solution and only slightly was dependent on the Ni(II) concentration.

Both solvent sublation technique as well ion flotation were effectively applied for separation of Ni(II) and Co(II) ions from their solution after acidic leaching of chemical power sources [4]. Moreover, a method of microwave-assisted hydrothermal leaching and chemical deposition was proposed for extraction and separation of Co(II)-Ni(II) ions from saprolite laterite ore by Zhao et al.
It was shown that the extraction percentage of Ni(II) and Co(II) from the ore pre-roasted at 300°C for 5 h were 89.19% and 61.89%, respectively.

Solvent extraction can be also used for recovery Co(II) and Ni(II) ions. A different group of compounds can play the role of extractants in these processes. Mubarok and Hanif [6] used a combination of Versatic 10 (neodecanoic acid) and Cyanex 272 (bis-(2,4,4-trimethylpentyl)phosphinic acid). Their results showed that Cyanex 272 can be effectively used to separate Co(II) from Ni(II) in the solution with a low nitrate concentration at the absence of Fe(III) and Mg(II). Also Cyanex 302 (bis(2,4,4-trimethylpentyl)-monothiophosphinic acid) in solvent impregnated resins was proposed as extractant by Mu et al. [7].

A mixture of DEHPA (di-(2-ethylhexyl)phosphoric acid) and Cyanex 272 was used to determine extraction percentage of the Ni(II) and Co(II) from solution containing Mn(II), Mg(II), Ca(II) and Cu(II) ions [8]. The order for the separation of metal ions was: Cu(II) ≈ Mn(II) > Mg(II) > Co(II) and Cu(II) ≈ Mn(II) > Ca(II) > Co(II) ≈ Mg(II) using Cyanex 272 and DEHPA, respectively. The extraction of Ni(II) was lower than 50% [8].

Alkyl derivatives of imidazole were used for the extraction of Co(II) from nitrate aqueous solutions. The most effective extractants were hydrophobic derivatives containing more than 8 carbon atoms in the alkyl substituent [9-11].

1-Hexyl-2-methylimidazole was used to separate Co(II) from a mixture of Co(II)-Ni(II) at nearly neutral pH and the separation coefficient Co/Ni was 8.9 [12].

A non-equilibrium solvent extraction of Co(II)-Ni(II) from ammoniacal sulphate solution by distearyl acid phosphate (P303) in sulphonated kerosine used for fully separating Co(II) from Ni(II) at pH above 9.5 [13].

Also β-diketone derivatives are successfully used as extractants in solvent extraction. Ochromowicz et al. [14] and Kyuchoukov et al. [15] tested extraction of Cu(II) from ammoniacal solutions by LIX 54-100 (mixture of six isomers: 1-phenyldecane-1,3-diones, heptane-8,10-dione and 1,3-diphenylpropane-1,3-dione). Also Ni(II) can be extracted by LIX 54 at pH 9.0 [16].

In our previous papers we proved that the highest extraction percentage of Cu(II) takes place when 3-allyl-acetylacetone [17] or dibenzoylmethane [18] were used as extractants.

The aim of this work was to investigate complexation and extraction properties of β-diketones: pentane-2,4-dione (1), 3-methyl-pentane-2,4-dione (2) and 3-ethyl-pentane-2,4-dione (3). The extraction processes were conducted in ammonia solutions at 25°C. Methylene chloride was used as a solvent.

2. Experimental

2.1. Reagents
Pentane-2,4-dione (1) was purchased from Avantor (Gliwice, Poland), while 3-methyl-pentane-2,4-dione (2) and 3-ethyl-pentane-2,4-dione (3) were purchased from Sigma Aldrich (Poznan, Poland) (figure 1).

The standard solution of Co(II) and Ni(II) nitrates were purchased from Sigma Aldrich (Poznan, Poland). The potassium nitrate, nitric acid, both of analytical reagent grade, were purchased from Avantor (Gliwice, Poland). The concentration of potassium nitrate was determined gravimetrically like potassium sulphate. Ammonia buffer was prepared from ammonia and ammonium nitrate (both analytical reagent grade, Avantor, Gliwice, Poland). Carbonate-free potassium hydroxide (the titrant, Avantor, Gliwice, Poland) was prepared and standardised against a standard potassium hydrogenphthalate solution. Methylene chloride and methanol (analytical reagent grade, Avantor, Gliwice, Poland) were used as received. The pH-meter was calibrated using commercial buffer solutions (Avantor, Gliwice, Poland) having a pH of 7.00 ± 0.05, 9.21 ± 0.05 and 10.00 ± 0.05.

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2.2. Equipment

Potentiometric measurements were carried out using a pH-meter (pH meter, CX-731 Elmetron, Zabrze, Poland), with a combination pH electrode (ERH-126, Hydromet, Bytom, Poland). The atomic absorption spectrophotometer AAS 240FS (Agilent, Santa Clara, CA, USA) was used to determine Co(II) and Ni(II) concentration. A Cary 50 (Varian, Melbourne, Victoria, Australia) spectrophotometer was used for recording the absorption spectra of the Co(II) and Ni(II) complexes in the aqueous phase over the range of 200-800 nm.

2.3. Determination of dissociation constants (pK$_a$)

The dissociation constants (pK$_a$) of β-diketones (1-3) were determined by potentiometric titration. Measuring cell was thermostated at 25°C ± 0.5°C. Two water-methanol solutions were prepared. The first one (blank solution) contained nitric acid (1 mmol/dm$^3$), and a proper quantity of potassium nitrate to ensure a constant ionic strength (1 mol/dm$^3$). The second one contained nitric acid (1 mmol/dm$^3$), chosen β-diketone, and potassium nitrate (1 mol/dm$^3$). Measurements were taken for two β-diketone concentrations (60 mmol/dm$^3$ and 50 mmol/dm$^3$) in the second solution. A 50 cm$^3$ volume of the first solution was placed in the measuring cell, and the solution was titrated with standard solution of 5 mmol/dm$^3$ potassium hydroxide. Then, the second solution was titrated in the same way. Three series of measurements were made.

2.4. Determination of stability constants (log K$_i$)

Stability constants (log K$_i$) of complexes of β-diketones (1-3) with Co(II) and Ni(II) ions were determined based on absorption spectra and according to the previously described method [19].

2.5. Spectrophotometric studies of aqueous phase

UV-Vis spectra of the aqueous phase after extraction process were recorded in the wavelength range of 200 nm to 800 nm. Water solution of 0.5 mol/dm$^3$ potassium nitrate was used as a reference solution while testing the aqueous phase. The spectra of the samples were recorded with spectral slits of 1 nm and with 1 nm steps using curettes having 1 cm path lengths.

2.6. Extraction Procedure

The measurements were run at 25°C, at a fixed ionic strength (0.5 mol/dm$^3$) maintained in the aqueous phase with potassium nitrate. A constant pH was maintained using ammonia buffer (NH$_3$ + NH$_4$NO$_3$, 1:1).

Extraction was carried out from three types of aqueous phase:

- **Co(II) aqueous phase** consisting of: Co(II), NH$_3$ + NH$_4$NO$_3$, KNO$_3$
• **Ni(II) aqueous phase** consisting of: Ni(II), NH$_3$ + NH$_4$NO$_3$, KNO$_3$

• **Co(II)-Ni(II) aqueous phase** consisting of: Co(II), Ni(II), NH$_3$ + NH$_4$NO$_3$, KNO$_3$.

Before the extraction, concentrations of Co(II) and Ni(II) ions in the aqueous phases were held constant (10 mmol/dm$^3$) whereas the ligand ($1$-$3$) concentrations in organic phase (methylene chloride) were varied (from 20 to 50 mmol/dm$^3$). A volume of 5 cm$^3$ of the aqueous phase was placed in a graduated test tube and an equal volume of β-diketones ($1$-$3$) solution in the organic solvent was added. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes; however, never longer than 30 min. Afterwards, it was checked if any changes in the phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured. The concentration of Co(II) and Ni(II) ions in the aqueous phase was determined by atomic absorption spectrophotometry.

### 3. Results and discussion

#### 3.1. Dissociation constants of β-diketones

β-Diketones dissociate according to the following reaction:

$$\beta\text{-diketone} \rightleftharpoons \beta\text{-diketone}^-$$

Dissociation constants ($pK_a$) of investigated extractants ($1$-$3$) were determined by potentiometric method using equilibrium constant of the above reaction:

$$K_a = \frac{[H_3O^+][\beta - \text{diketone}^-]}{[\beta - \text{diketone}]}$$

where: ($H_3O^+$), ($\beta$-diketone$^-$), and ($\beta$-diketone) are equilibrium concentrations of the oxonium ion, the extractant anion and its undissociated form, respectively.

In table 1, the $pK_a$ values of studied β-diketones are summarised.

| β-diketone                  | $pK_a$ | ref.  |
|-----------------------------|--------|-------|
| pentane-2,4-dione           | 9.65   | [20]  |
| 3-methyl-pentane-2,4-dione  | 9.66   | [this work] |
| 3-ethyl-pentane-2,4-dione   | 9.62   | [this work] |

The given values of the carry ±0.01 tolerance

Results in table 1 are similar and indicate that 3-ethyl-pentane-2,4-dione (3) has the strongest acid properties among the investigated extractants. Pentane-2,4-dione 1 and 3-methyl-pentane-2,4-dione 2 have similar acid-base properties, but they are stronger base than 3-ethyl-pentane-2,4-dione (3).

#### 3.2. Stability constants of β-diketone complexes with cobalt(II) and nickel(II) ions

The absorption spectra were measured in the range of 200–400 nm wavelengths and at various β-diketone concentration ($1$-$3$) versus metal ions mole ratios (figure 2). In figure 1, the Ni(II)/(pentane-2,4-dione) complexes are formed in the studied systems. Vanishing of the band due to pentane-2,4-dione (1) ligand (280 nm) and the appearance of new bands (309 nm) together with the isosbestic points at 248 and 295 nm were also recorded.
Figure 2. Absorption spectra of Ni(II) complexes with 1 in various pentane-2,4-dione concentration versus Ni(II) mole ratios: 1 : 0 (line 1); 1 : 0.125 (line 2); 1 : 0.25 (line 3); 1 : 0.375 (line 4); 1 : 0.5 (line 5); 1 : 0.625 (line 6); 1 : 0.75 (line 7); 1 : 0.875 (line 8); 1 : 1 (line 9).

Based on such spectra the values of stability constants of β-diketone complexes with Co(II) and Ni(II) ions were calculated and were summarised in table 2.

A methyl derivative of β-diketone (2) forms the most stable complexes. The methyl substituent located in the third position of pentane-2,4-dione increases the affinity of the metal for the ligand.

| β-diketone                        | $\log K_i$ Co(II) | $\log K_i$ Ni(II) |
|-----------------------------------|-------------------|-------------------|
| 1 pentane-2,4-dione               | 5.40              | 4.96              |
| 2 3-methyl-pentane-2,4-dione      | 5.56              | 4.99              |
| 3 3-ethyl-pentane-2,4-dione       | 5.03              | 4.97              |

The given values of the carry ±0.01 tolerance

Table 2 shows that stability constants of Co(II) complexes are higher than constants of Ni(II) complexes. The reason for this phenomenon may be that Co(II) complexes have the ability to change the shape of a coordination polyhedron from an octahedron to a tetrahedron [9-11].
\[
(M(H_2O)_b)^{2+} + nL \leftrightarrow (M(H_2O)_{b-n}L_n)^{2+} + nH_2O \quad (3)
\]
\[
(M(H_2O)_b)^{2+} + nL \leftrightarrow (M(H_2O)_{4-n}L_n)^{2+} + (n+2)H_2O \quad (4)
\]
where L denotes the extractant molecule.

The reactions described by equation (4) involving a change in the coordination number, are typical for Co(II). In such cases, configuration equilibria are established (equation 5) between \( ML_n \) complexes, which have different coordination sphere structures, for instance:

\[
(M(H_2O)_2L_4)^{2+} \leftrightarrow (ML_4)^{2+} + 2H_2O \quad (5)
\]

The occurrence of configuration equilibria will lead to higher values of its corresponding stability constant, \( K \) (table 2), because it is the sum of the stability constant of the tetrahedral complex, \( K_t \), and the octahedral complex \( K_o \) (\( K = K_t + K_o \)) \[10,11\].

### 3.3. Spectrophotometric studies

The following figures show exemplary spectra of the Ni(II) aqueous phase after extraction using extractants (pentane-2,4-dione (1), 3-methyl-pentane-2,4-dione (2) and 3-ethyl-pentane-2,4-dione (3)) in different concentrations thereof in organic phase.

Above spectra clearly show that extraction process of investigated metal ions from aqueous phase is closely related to the concentration of extractant in organic phase and is the most effective when pentane-2,4-dione (1) is used (figure 3). Concentration of Ni(II) ions in aqueous phase decreases together with an increase in the concentration of pentane-2,4-dione (1) in organic phase (figure 3A). These changes are caused by the complexation reaction with pentane-2,4-dione (1), which takes place at the interface of aqueous and organic phase. At this moment in organic phase complexes of Co(II) and Ni(II) ions with pentane-2,4-dione (1) are formed.

The extractants: 3-methyl-pentane-2,4-dione (2) (figure 3B) and 3-ethyl-pentane-2,4-dione (3) (figure 3C), are significantly less effective in comparison with unsubstituted pentane-2,4-dione (1), even at their high concentration in organic phase. This phenomenon may be caused by the formation of sterical hindrance in the molecules.

Similar results were received during extraction from Co(II) and Co(II)-Ni(II) mixture in the aqueous phase.
Figure 3. Absorption spectra of Ni(II) aqueous phase after extraction using A. pentane-2,4-dione, B. 3-methyl-pentane-2,4-dione and C. 3-ethyl-pentane-2,4-dione depending on extractant concentration: 0 mmol/dm$^3$ (line 0), 20 mmol/dm$^3$ (line 1), 30 mmol/dm$^3$ (line 2), 40 mmol/dm$^3$ (line 3), 50 mmol/dm$^3$ (line 4).
3.4. Extraction processes

Amount of metal ions extracted from aqueous phase (E%) is described by equation 6:

\[
E\% = \frac{C_0 - C_E}{C_0} \cdot 100\%
\]

(6)

where: \(C_0\) – initial concentration of metal ions in aqueous phase, \(C_E\) – concentration of metal ions in aqueous phase after extraction.

Figure 4 shows dependences between the extraction percentage of Co(II) and Ni(II) ions for one-component aqueous phase depending on pH after extraction equilibrium was achieved.

Results presented in figure 4 confirmed that both extraction percentages of Co(II) and Ni(II) had the highest values when pentane-2,4-dione (1) was used as an extractant and they were increased with the increase in pH of aqueous phase.

The pentane-2,4-dione (1) was the most efficient extractant for two-component Co(II)-Ni(II) aqueous phase (figure 5). Extraction percentage increased with the increase in pH of aqueous phase.
Absence of substitution in the position 3 and high basic properties (table 1) caused 1 to be the best extractant in comparison with 2 and 3.

Table 3. The values of extraction percentage depending of extractant concentration in organic phase.

| extractant | concentration of extractant in organic phase (mmol/dm³) | E% Co(II) aq. phase | E% Ni(II) aq. phase | E% Co(II)-Ni(II) aq. phase/Co(II) extraction | E% Co(II)-Ni(II) aq. phase/Ni(II) extraction |
|------------|------------------------------------------------------|----------------------|---------------------|-----------------------------------------------|-----------------------------------------------|
| 1          | 20.0                                                 | 69.58                | 71.33               | 66.31                                         | 71.33                                         |
|            | 30.0                                                 | 73.74                | 79.18               | 76.26                                         | 84.41                                         |
|            | 40.0                                                 | 74.64                | 84.46               | 77.64                                         | 88.70                                         |
|            | 50.0                                                 | 82.85                | 86.41               | 80.74                                         | 90.75                                         |
| 2          | 20.0                                                 | 4.75                 | 7.79                | 9.73                                          | 11.74                                         |
|            | 30.0                                                 | 6.00                 | 7.83                | 9.70                                          | 12.30                                         |
|            | 40.0                                                 | 7.00                 | 7.86                | 9.86                                          | 12.77                                         |
|            | 50.0                                                 | 7.13                 | 10.73               | 9.86                                          | 13.20                                         |
| 3          | 20.0                                                 | 6.56                 | 8.01                | 10.17                                         | 17.43                                         |
|            | 30.0                                                 | 7.09                 | 8.69                | 11.31                                         | 17.64                                         |
|            | 40.0                                                 | 7.94                 | 9.18                | 11.57                                         | 18.05                                         |
|            | 50.0                                                 | 7.94                 | 9.41                | 12.65                                         | 18.06                                         |

The given values of the carry ±0.01 tolerance
Table 3 presents data of extraction percentage vs. concentration of extractant in organic phase made for three different aqueous phases: one-component Co(II) or Ni(II) and two-component Co(II)-Ni(II) solution.

Results summarised in table 3 proved that extraction percentage of both metal ions depends on extractant concentration in the organic phase. The highest percentage value was achieved for 50.0 mmol/dm$^3$ of each extractant.

Extraction percentage of Ni(II) ions was higher than that of Co(II), either in one-component or two-component solutions, but separation coefficient Ni(II)/Co(II) decreased. Separation coefficient for Co(II)-Ni(II) in two-component solution was equal to 1.12, 1.34, and 1.43 using extractant 1, 2, 3, respectively.

Extraction of metal ions from two-component aqueous phases using 2 and 3 is more efficient than from one-component solution. Although the stability of Co(II) complexes is higher than that of Ni(II) complexes (table 2), table 3 shows that Ni(II) ions in comparison with Co(II) ions can be removed more effectively from aqueous solution using all investigated β-diketones as extractants. These differences are the result of differences in the process of the complex formation of Co(II) or Ni(II) with extractant molecules.

4. Conclusion
A process of Co(II) and Ni(II) extraction was studied from one-component and two-component solutions using pentane-2,4-dione (1), 3-methyl-pentane-2,4-dione (2), and 3-ethyl-pentane-2,4-dione (3) in dichloromethane. The pentane-2,4-dione (1) was the most efficient extractant in all studied aqueous phases, maybe because there is no substituent in position 3 in its molecule.

Extraction depends on concentration of extractant in organic phase and pH of aqueous phase. The highest percentage values were achieved for 50.0 mmol/dm$^3$ of each extractant and pH around 9.8. In these conditions for one-component solutions the extraction percentage of Co(II) and Ni(II) were equal to 83% and 86%, respectively. For two-component solutions the extraction percentage were equal to 81% and 91% for Co(II) and Ni(II), respectively.

The Ni(II) ions can be removed from aqueous solution more effectively than Co(II) ions, although the stability constants of Co(II) complexes with investigated β-diketones are higher than the stability constants of Ni(II) complexes with the same extractants.

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References
[1] Flett D S 2004 Chem. Sustainable Develop. 12 p 81
[2] Leepipatpiboon N, Pancharoen U and Ramakul P 2013 Korean J. Chem. Eng. 30(1) p 194
[3] Sadyrbaieva T Zh 2013 Russian Journal of Applied Chemistry 86(2) p 186
[4] Sobianowska K, Grzesiak A, Wierzbicka W and Sobianowska-Turek A 2016 Chem. Environ. Biotechnol. 19 p 13
[5] Zhao Y, Gao J-M, Yue Y, Peng B, Que Z-Q, Guo M and Zhang M 2013 Int. J. Min. Met. Mater. 20(7) p 612
[6] Mubarok M Z and Hanif L I 2016 Procedia Chem. 19 p 743
[7] Mu F T, Jia Q, Tian Y M and Shang Q K 2008 Adsorption 14 p 31
[8] Santanillal A J M, Tenório J A S and Espinosa D C R 2014 Annual Meeting Supplemental Proceedings TMS (The Minerals, Metals & Materials Society) p 1157
[9] Radzyminska-Lenarcik E and Witt K 2015 Sep. Sci. Technol. 50(5) p 676
[10] Radzymińska-Lenarcik E 2008 Polish J. Chem. Technol. 10 p 73
[11] Lenarcik B and Ojczenas P 2004 Sep. Sci. Technol. 39 p 199
[12] Radzyminska-Lenarcik E and Wasilewska A 2015 Challenges of Modern Technology 6(3) p 20
[13] Wang K-Y, Niu C-W, Qian D, Liu J-H, Chen X-Y and Lai D-Y 2001 J. Cent. South Univ. Technol. 8(1) p 50
[14] Ochromowicz K, Jeziorek M and Wejman K 2014 Physicochem. Probl. Miner. Process. 50(1) p 327
[15] Kyuchoukov G, Bogacki M B and Szymanowski J 1998 Ind. Eng. Chem. Res. 37(10) p 4084
[16] Alguacil F J and Cobo A 1998 Hydrometallurgy 48 p 291
[17] Radzyminska-Lenarcik E and Witt K 2018 Sep. Sci. Technol. 53 p 1223
[18] Witt K and Radzyminska-Lenarcik E 2017 E3S Web of Conferences 18 01016
[19] Lis S, Pawlicki G, Staniszewski B, Urbaniak W and Witt K 2011 Chem. Pap. 65(2) p 221
[20] Witt K, Radzyminska-Lenarcik E and Urbaniak W 2016 Sep. Sci. Technol. 51(15-16) p 2620
[21] Borduin W G, Guter G A and Hammond G S 1959 J. Am. Chem. Soc. 81 p 4682