Liquid-liquid extraction of cobalt(II), nickel(II) and copper(II) from basic medium using some $\beta$-diketones

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Abstract. The solvent extraction of cobalt(II), nickel(II) and copper(II) using 2,4-pent-dione (Hacac) and 4-phenyl-2,4-but-dione (Hbzac) is carried out by varying the reagent concentration and pH of the aqueous phase. Each of these metals is quantitatively separated (~98%) from their binary mixtures with monovalent (Ag), divalent (Mn, Zn, Cd, Hg, Mg, Sn, Pb) and trivalent (Cr, Fe) metals. The extraction constants are calculated from the metal distribution data using linear regression analysis. The extracted species is MA$_2$ in each case. A most significant result is separation of copper(II) from iron(III) which otherwise interferes when extracted from the acidic medium.

Keywords. Liquid-liquid extraction of metals; $\beta$-diketones; extraction of cobalt, nickel and copper; metals in basic media.

1. Introduction

The solvent extraction chemistry of metals occupies an important area of applied chemistry demanding increasing interest in its development (Nicol et al 1987). The $\beta$-diketones and tertiary phosphine chalcogenides are some of the important extractants widely used in literature (De et al 1970; Lobana 1992). The simplest reagent, acetylacetone (Hacac) shows poor extraction of cobalt(II) and nickel(II) from the acidic medium, while copper(II) is extracted quantitatively (Stary and Hladky 1963; Lobana et al 1989). The fluorinated $\beta$-diketones, however, are efficient extractants for these metals from the acidic medium (Kingdon and Mellon 1956; Zolotov and Alemarin 1962; Koshimura and Okubo 1983).

This paper reports extraction chemistry of cobalt(II), nickel(II) and copper(II) from the basic medium using 2,4-pent-dione (Hacac) and 4-phenyl-2,4-but-dione (Hbzac).

2. Experimental

The stock solutions of 0·1 M cobalt as CoCl$_2$$\cdot$6H$_2$O (LR), nickel as Ni(NO$_3$)$_2$$\cdot$6H$_2$O (LR) and copper as Cu(OOCCH$_3$)$_2$$\cdot$H$_2$O(LR) were prepared in the distilled water. Similarly, stock solutions of 0·2 M Hacac and 0·2 M Hbzac (Sisco) were prepared in chloroform. For basic media, 7 M ammonia solution was used. The metal salt solutions used were standardised using 0·01 M disodium salt of H$_4$EDTA with xyleneol

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orange as the indicator (Bassette et al. 1978) or spectrophotometrically using Shimadzu-UV-visible UV-240 spectrometer (Lacoste et al. 1951; Lobana and Bhatia 1991).

The extraction procedure consists of equilibrating a metal salt solution (2 ml) with 5 ml of Hacac or Hbzac in chloroform for 25–30 minutes. To the aqueous phase 8 ml of 7 M ammonia solution was initially added for keeping pH of the aqueous phase as 10.0 (only 0.5 ml of conc. ammonia solution was added in case of copper). The contents were allowed to stand for 15 minutes in a separating funnel. The metal was transferred to the aqueous phase after stripping the loaded organic layer with 5 ml of 5 M HCl solution and volume of the aqueous phase made to 25 ml using distilled water. The metal was estimated from this solution and the former aqueous phase using sodium diethyldithiocarbamate reagent (Lacoste et al. 1951; Lobana and Bhatia 1991). For studying the effect of possible interference, 2 ml of a 0.1 M metal salt solution was added in addition to the other contents as described above. Rest of the procedure was same as before. The metals added were studied by EDTA method or KSCN method (Bassette et al. 1978), while Co, Ni and Cu were monitored by spectrophotometric methods.
3. Results and discussion

The extraction of cobalt(II), nickel(II) and copper(II) may be represented by

\[ M^{2+} (aq) + mX(aq) + nHA(org) \rightleftharpoons MX_{m-n} \cdot A_n(org) + nHX, \]  

(1)

where \( M = \text{Co, Ni, Cu} \); \( X = \text{Cl, NO}_3, \text{CH}_3\text{COO} \); \( HA = \text{Hacac, Hbzac} \).

The amount of each metal extracted increases with the increase in the concentration of Hacac (0.02–0.2 M) or Hbzac (0.01–0.15 M) and becomes quantitative at 0.2 M Hacac or 0.15 M Hbzac (figure 1, a–c). The plots of \( \log D \) versus \( \log [\text{reagent}] \) reveal the slope of the line 2 in the reagent concentration range (0.07–0.2 M). For Cu(II), the slope was 2.8 in case of Hbzac. Hence the metals are extracted as \( MA_2 \) (HA = Hacac or Hbzac) and for Cu(II)–Hbzac system, as \( \text{Cu(bzac)}_2 \). The Hbzac species is inferred. From (1) using the distribution ratio

\[ D = K_{HA}[HA]^2, \]  

(2)

and linear regression analysis (Daniel 1956), the extraction constants calculated are given in table 1. From this table, it is concluded that Hbzac shows higher extraction than shown by Hacac for all the three metals.

Cobalt(II) and nickel(II) do not show any measurable extraction in the pH range 2–6; however, the extraction increases to 55–60% at pH 8–9 and becomes maximum (about 98%) at pH 10. And for copper(II), there is no extraction at pH 2–4, but the extraction becomes about 98% at pH 4–10. The anions, \( \text{NO}_3^- \), \( \text{CH}_3\text{COO}^- \), \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) caused no interference. Table 2 gives a list of binary mixtures from which each of the metals under study was separated. A most significant separation is that of

<table>
<thead>
<tr>
<th>Metal extracted</th>
<th>Interference, if any</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>Ni(II)/Cu(II)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Co(II)/Cu(II)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Co(II)/Ni(II)</td>
</tr>
</tbody>
</table>

**Table 1. Extraction constants for the species extracted.**

<table>
<thead>
<tr>
<th>Species</th>
<th>( K_{ex} \times 10^3 )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(acac)(_2)</td>
<td>0.99</td>
<td>1.458</td>
</tr>
<tr>
<td>Co(bzac)(_2)</td>
<td>2.72</td>
<td>8.920</td>
</tr>
<tr>
<td>Ni(acac)(_2)</td>
<td>1.03</td>
<td>4.974</td>
</tr>
<tr>
<td>Ni(bzac)(_2)</td>
<td>1.99</td>
<td>4.400</td>
</tr>
<tr>
<td>Cu(acac)(_2)</td>
<td>1.72</td>
<td>9.488</td>
</tr>
<tr>
<td>Cu(bzac)(_2)</td>
<td>7.32</td>
<td>4.870</td>
</tr>
</tbody>
</table>

**Table 2. Separation of Co(II), Ni(II) and Cu(II) from binary mixtures.**

Metal salts added were CrCl\(_3\)·6H\(_2\)O, MnSO\(_4\)·6H\(_2\)O, FeCl\(_3\), ZnSO\(_4\)·7H\(_2\)O, MnSO\(_4\)·7H\(_2\)O, Mg(NO\(_3\))\(_2\)·6H\(_2\)O, MgCl\(_2\)·6H\(_2\)O, HgCl\(_2\), Ag(NO\(_3\))\(_3\), Pb(NO\(_3\))\(_2\) and CdCl\(_2\) in each case.
copper(II) from iron(II) which otherwise interferes in the acidic medium (Lobana and Bhatia 1992).

Acknowledgement

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