

EXTRACTION OF COBALT AND NICKEL BY  
ORGANIC COMPLEXING AGENTS

By  
Amal Abou Bakr Khedr  
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Approved

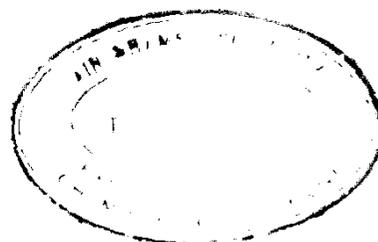
Dr. N.E. Milad .....

Dr. Sh.A. Sherif .....

Prof. F.G. Baddar



Head of Chemistry Department





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A.A. Khedr

N O T E

The candidate has attended postgraduate courses for two years in Inorganic and Physical Chemistry covering the following topics :-

- 1- Advanced surface chemistry.
- 2- Solid state chemistry.
- 3- Structural inorganic chemistry.
- 4- Electrochemistry.
- 5- Techniques of inorganic chemistry.

She has successfully passed a written examination in these courses.

Prof. F.G. Baddar



Head of Chemistry Department

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calculated by the two methods of Nyberg and Bjerrum. The data may also be used for the calculation of the stepwise and overall hydrolysis constants of nickel(II) and cobalt(II).

## 7- ANALYTICAL

### A- SOLVENT EXTRACTION

During the last few years a large number of papers has been published on the use of solvent extraction and its application for separation of a great number of inorganic and organic materials.

Extraction with non-aqueous solvents is very widely used in solving various problems in different aspects of chemistry and chemical technology. Many investigators (1-8) however, have evanced interest in the study of extraction processes which serve in, the separation of elements with closely similar properties, the purification and isolation of micro and ultra-micro concentrations of metals and the clear separation and identification of difficultly separable organic substances (9-13). The solubility of both inner complexes and of a number of other complex species of metals with organic ligands in various organic solvents makes it possible to utilize distribution methods as a reliable means of studying the composition and many other physicochemical characteristics of complex compounds.

Liquid-liquid extraction is simply achieved by shaking an aqueous solution with an organic solvent essentially

immiscible liquids; a process which brings about the transfer of one or more solutes into the organic solvent. Application of solvent extraction technique for analysis is simple and convenient since it requires no more than separating funnels.

### 1- Fundamental extraction principles

A) The distribution law :

The distribution of a substance between two immiscible liquids A and B at equilibrium can be expressed by the equation :

$$\frac{a_{iA}}{a_{iB}} = k \dots\dots\dots (1.1)$$

where  $a_{iA}$  and  $a_{iB}$  are the activities of "i" in the liquids A and B respectively. Activities may be replaced by concentrations in dilute solutions, thus :

$$\frac{a_{iA}}{a_{iB}} = \frac{c_{iA}}{c_{iB}} = k_d \dots\dots\dots (1.2)$$

This solute concentration ratio is shown to be in many cases invariant i.e., independent of the total concentration.

The distribution law was first formulated by distribution by Jungfleisch (14) and elaborated by Nernst (15) in 1891. This ratio remains constant so long as the substance do not change its molecular formula. If on the other hand the total concentration in each liquid phase is considered, the previous ratio named by the distribution ratio is represented by  $q$ . The distribution ratio  $q$  is the ratio of the solute between <sup>two</sup> immiscible solvents usually water and an organic one, provided the metal ions does not undergo hydrolysis in water. In cases where metal ions hydrolyse in water, two immiscible organic solvents may be used e.g., the recent application of acetonitrile-isoamylether as a solvent pair in the separation of the metal zirconium and hafnium (16). The value of  $q$  can be determined from the following equation :

$$q = \frac{A_o}{A_w} \dots\dots\dots(1.3)$$

where  $A_o$  represents the concentration of the solute in the organic solvent and  $A_w$  is its concentration in water. If the total number of solute molecules is equal to  $M_R$  and the volumes of the organic and aqueous phases are  $V_o$  and  $V$  respectively then

$$M_R = A_o V_o + A_w V \dots\dots\dots(1.4)$$

$$q = \frac{\frac{M_R}{A_W} - V}{V_0} \quad \text{or} \quad = \frac{V}{\frac{M_R}{A_0} - V_0} \dots\dots\dots(1.5)$$

if  $V_0$  and  $V$  are equal and  $A_i = A_0 + A_W$

where  $A_i$  is the original concentration of the solute A, the distribution ratio  $q$  can be represented by the following :

$$q = \frac{A_i - A_W}{A_W} = \frac{A_0}{A_i - A_0} = \frac{A_0}{A_W} \dots\dots\dots(1.6)$$

Using equation (1.6) the value of  $q$  can be practically determined by knowing the value of  $A$  and/or  $A_W$ . It is clear that the determination of  $q$  requires that the two immiscible layers to be in a pure form. The separation of the two liquids is usually easy but sometimes a temporary emulsion is formed and in this case the system should be centrifuged at a high speed.

Several methods are widely used for the determination of solute concentration. Among these methods the volumetric, colorimetric, radiometric, flame photometric, and direct photometric if the solution is colored are the most important.

and the percent extraction  $E$  which is related to  $q$  by the following equation :

$$E = \frac{100[A_o] V_o}{[A_o] V_o + [A_w] V_w} = \frac{100 q}{q + \frac{V_w}{V_o}} \dots\dots\dots(1.7)$$

from this equation it is shown that the percent extraction  $E$  varies with variation of  $q$  as well as the variation of the volume ratio of the two solvents.

The separation factor:

Since solvent extraction is used as a method of separation it becomes necessary to introduce a term, called separation factor, which describes the effectiveness of separation of two solutes. The separation factor  $\beta$  is related to the individual distribution ratios by the relation

$$\beta = \frac{[A]_o [B]_o}{[A]_w [B]_w} = \frac{[A]_o [A]_w}{[B]_o [B]_w} = \frac{D_A}{D_B} \dots\dots\dots(1.8)$$

where A and B represent the respective solutes. It is shown from equation (1.8) that when the distribution ratio of

one solute to the other and that of the other to the first. Large, complete separation can be quickly and easily achieved. An interesting example can be illustrated by the separation of zirconium and hafnium using solution of TTA in benzene (17).

In the process of the extraction the choice of the solvent is very important (18,19).

- 1- It should be immiscible with water.
- 2- It should not decompose the solute.
- 3- In case of the separation, the separation factor  $\beta$  should not be less than 3, if it is less repeated extraction would be necessary.
- 4- The two liquids should separate easily and should not form permanent emulsion.
- 5- The substance should be extracted easily from the solvent.

#### B- Extraction process

The process of extraction involves three essential steps which are shared by almost all extraction systems :

- 1- Chemical interaction in the aqueous phase.

A major point of differentiation between extraction of organic and inorganic materials is found in the