STUDIES IN EXTRACTION POLAROGRAPHY

(Resacetophenoneoxime as chelating agent in the
determination of first transition metals)

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P. RAMASWAMY, M Sc.,

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PREFACE

The application of liquid-liquid extraction in inorganic analysis is known for the past one hundred years. However, a new era is opened up with the introduction of the very versatile organic reagent dithizone by Helmut Fischer in 1929. In contrast to solvent extraction technique involving ion-association complexes extractions employing metal chelate systems are receiving importance since the complex species will be neutral and less hydrophilic. Further, the systems involving metal chelates are more ideal in the thermodynamic sense since the partition equilibria can be expressed by relatively simple equations. It is also possible for an analytical chemist to devise separation procedures on a sound theoretical basis. It is not a surprise to say that a wide range of organic reagents have been employed in recent times besides the well known chelating agents such as dithizone, oxine, cupferron, thenceyltrifluoroacetone and dialkylammonium carbarates. With the advent of the introduction of oximes of carbonyl compounds by Ephraim as analytical chelating agents, momentum was gained in the solvent extraction studies. Analytical determination following selective solvent extraction is often based on colorimetric methods. These methods are time consuming and sufficiently selective extraction cannot be
obtained ever with accurate pH control or the use of masking agent. Moreover colorimetric method of determination led's in sequential analysis in the true sense. Many of the drawbacks mentioned above are successfully overcome by replacing colorimetric analysis by polarographic method of analysis. Extraction polarography has thus become important in the recent times in the analysis of small amounts of metal ions.

The different types of practical methods, classical and instrumental developed for various metal ions in our laboratories revealed the versatility of resacetophenoxine (3,4-dihydroxy-acetophenone oxine) as a chelating agent. The author has therefore taken up the study on the use of the oxine as a chelating agent in the extraction polarographic determination of some metal ions of the first transition series. n-Butanol is chosen as the extracting liquid since an alcohol offers several advantages as a polarographic solvent unlike the hydrocarbons and the halocarbons generally employed as extracting liquids. Polarographic analysis of the organic layer is usually carried out in non-aqueous conditions after adding methanolic solution of the supporting electrolyte to the organic layer. This procedure has many limitations especially when the technique is used as a tool in industrial analysis. The author has therefore introduced in the present investigations a ternary system, n-butanol-methanol-aqueous supporting electrolyte for polarographic analysis.
The results obtained in the extraction polarographic studies carried out with resacetoephenoquezine as chelating agent in the analysis of titanium, vanadium, chromium, manganese, iron and cobalt are presented in this thesis. The entire thesis is divided into three parts. Part I is intended to serve as a general introduction and divided into four chapters. Part II consists of two chapters and deals with the general experimental section of the work. Part III describes the results obtained in the extraction polarographic studies. This part comprises of eight chapters.

Chapter 1 of part I deals with the general principles of solvent extraction and the various factors influencing the extraction equilibrium. A brief account of the principle of polarography and the nature and characteristics of different polarographic reduction processes with the relevant current-voltage relationships is presented in chapter 2 of this part. The work reported in the literature on extraction polarographic analysis employing different chelating agents is briefly reviewed in chapter 3. The last chapter of part I summarizes the analytical work carried out on resacetoephenoquezine in these laboratories or elsewhere. The objectives of the present investigations are also presented at the end of the chapter.

Chapter 1 of part II deals with the preparation of the oxime and the solutions employed in the present investigations.
A brief account of the instruments used and the general procedures adopted in solvent extraction and polarographic analysis are presented in chapter 2.

Part II of the thesis deals with the results obtained in the present investigations on extraction polarographic determination of titanium(IV), vanadium(IV), vanadium(V), chromium(III), manganese(II), iron(III) and cobalt(II).

Chapter 1 describes the investigations on titanium(IV). Nasaolephenoneoxime reacted with titanium sulfate in acid buffers giving an yellow soluble complex. The same is extracted at pH 5 completely into n-butanol. The extract gave a polarographic reduction wave with an half-wave potential -1.22 V vs mercury pool. The wave height is found proportional to concentration of titanium. The polarographic characteristics of the wave indicated a diffusion controlled reduction. The results in respect of interference of iron(III), nickel(II) and zinc(II) in the determination of the metal are presented at the end of this chapter.

Chapters 2 and 3 contain the results obtained in the studies on vanadium(IV) and vanadium(V) respectively. Vanadium(IV) reacted with the reagent in weakly acidic buffers yielding an yellow soluble complex. The same however is not extracted into n-butanol. Addition of iso-tri-nonylamine resulted in the complete extraction. The extract gave a
diffusion controlled reduction wave with $E_i = -0.29$ V and whose height is proportional to concentration of the metal ions. The interference of iron, zinc and nickel is discussed. Vanadium(V) gave with the oxime in dilute HCl solution an yellowish orange soluble complex which is extracted only partially into n-butanol. Addition of 8-hydroxyquinoline improved the results satisfactorily. The organic layer gave a polarogram with half-wave potential $-0.87$ volts versus mercury pool and the height of the wave is found proportional to the concentration of the metal. The results obtained in respect of interference of other metal ions and the nature of the polarographic reduction are discussed.

The results of the investigations on chromium(III) oximate complex are presented in chapter 4. Unlike the other metal ions investigated chromium(III) reacted with the oxime only slowly at room temperature. At 70°C the complex formation is sufficiently rapid and a dark red brown complex is formed. It is extracted into n-butanol completely at low concentrations of chromium(III) in presence of magnesium sulphate. The organic layer gave a diffusion controlled wave with half-wave potential $-1.52$ V vs mercury pool. The limiting current is proportional to the concentration. The results relating to interference studies are also discussed.

Chapter 5 summarizes the results in respect of manganese(II) (II). The metal gave with the reagent in alkaline buffers a
dark brown complex. The complex is partially extracted at pH 9.2. A double extraction or a single extraction in presence of pyridine gave satisfactory results. The nature of the polarographic wave suggested the formation of manganese(III) complex. The polarogram in presence of pyridine contained two waves while that obtained in the double extraction is a three wave polarogram. The nature of the electroactive species giving these waves is discussed in the light of the wave nature.

Investigations relating to ferric iron are described in chapter 6. Iron reacted with the oxime in weakly acidic solutions giving a purple colour reaction. This purple complex is extracted partially into n-butanol when iron is present in large concentrations. Addition of pyridine improved the extraction satisfactorily. The organic layer however gave a reduction wave in sodium perchlorate which is found not useful for the determination of iron. The wave obtained in presence of potassium chloride is well defined and a linear calibration curve is obtained.

Chapter 7 deals with the determination of cobalt(II). As in the case of manganese, cobalt also gave brown complex in ammoniacal medium. It is noticed that the addition of pyridine is necessary to effect complete extraction. Addition of a strong solution of magnesium sulphate helped to get a
clear separation of the aqueous and non-aqueous layers. The nature of polarographic reduction and the interference of metal ions are discussed at the end of the chapter.

A summary of the results obtained in the different investigations carried out is given in chapter 8.
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Sri Venkateswarapuram
NAPTAPUR

July 1976

P. RAMASWAMY
DECLARATION

I declare that the work is original and has not been submitted in part or full for the award of any degree or diploma.

P Rama Swamy

19/3/1976

(L. Rama Swamy)
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