STUDIES IN SOLVENT EXTRACTION CHEMISTRY AND ION-SELECTIVE ELECTRODES

Robert Walter Cattrall B.Sc.(Hons), Ph.D, F.R.A.C.I.

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PREFACE

(a) General comments on the published scientific work submitted for the Degree of Doctor of Science

My published scientific work contained in this thesis consists of contributions to two main areas of research, solvent extraction chemistry and ion-selective electrodes. These two fields of my work have strong connections and the ion-selective electrode research has evolved out of my interests in solvent extraction. Certain types of reagents which I have used for making ion-selective electrodes are important in solvent extraction and my knowledge of solvent extraction chemistry has assisted me in developing and understanding the ion-selective electrode systems. Where possible, correlations have been drawn between extraction behaviour and electrode selectivity.

My solvent extraction work has been primarily concerned with the extraction of metal ions from aqueous solutions by high molecular weight quaternary ammonium salts. This work started in 1961 during my Ph.D. candidature and at that time very little was known about the physical chemistry of these systems and certainly nothing about the mechanism of extraction. My initial work elucidated the nature of the complex extracted into the organic phase in the extraction of iron(III) by bis(3,5,5-trimethylhexyl)amine from sulfate media. This work also provided some of the first data on aggregation phenomena and the interfacial activity of the amine salts.

Subsequent work on solvent extraction has been directed towards improving the methods and procedures for studying the extraction of metals. Slope analysis procedures to study the nature of the extracted complexes were first improved by including terms for the aggregation of the reagents and complexes. Finally, computing techniques have been developed which allow the experimental data to be fitted to mathematical models and provide values for the extraction equilibrium constants of the organic phase complexes.

The experimental techniques have also been improved by replacing the batch-wise extraction method by a two-phase titration procedure. This is a faster method for obtaining many data points with considerably better precision.

Most recently, mechanistic studies have been carried out and for this the single drop technique has been employed. This work has confirmed the interfacial mechanism originally proposed for extraction by high molecular weight quaternary ammonium salts. A comparison has also been made between extraction equilibrium constants obtained from two-phase titration and values calculated from forward and back extraction rate studies. The excellent agreement further confirms the proposed interfacial mechanism.

My research in the field of ion-selective electrodes is concerned primarily with the invention, development and application of polymer membrane coated-wire electrodes. Extensive work has been carried out on electrodes sensitive towards calcium. Another major thrust of the work is the application of electrodes based on halo-metal complexes to the analysis of metals. Electrodes have been produced which respond to anionic halo-complexes of mercury, cadmium, zinc, iron(III), copper and cobalt. The polymer membranes in these electrodes consist of the appropriate salts of the reagent Aliquat 336, prepared by solvent extraction and immobilized in poly(vinyl chloride). Aliquat 336 is one of the quaternary ammonium salts which I have studied extensively in solvent extraction and the selectivity properties of these electrodes have been related to solvent extraction parameters.

In both the solvent extraction and ion-selective electrode studies there is a considerable emphasis on analytical chemistry. Methods have been developed using atomic absorption spectroscopy, U.V.-visible spectrophotometry and radioisotope tracer techniques for analysing the extract phases. Computer methods have been used extensively. In the ion-selective electrode work standard addition methods as well as calibration graph methods have been employed. One important study has involved the characterization of Aliquat 336 using gas chromatography and mass spectrometry.

(b) Statement concerning the authorship of papers submitted for the Degree of Doctor of Science

(i) In the fields of solvent extraction chemistry and ion-selective electrodes

1. Many of my papers have been produced in conjunction with my graduate students both in the field of solvent extraction chemistry and in my research on ion-selective electrodes. In each case I produced the original ideas for the work, directed the research including teaching the relevant techniques and advising on the interpretation of the results and wrote the paper. The papers concerned are nos. 5, 7-11, 13, 15, 21, 22, 24, 25, 27-35, 39, 42, 43, 46-52.

2. Certain papers produced in conjunction with my graduate students have additional authors. These are co-supervisors or collaborators for certain sections of the work. However, I was the senior investigator and produced the original ideas for the work and had a major role in writing the paper. The papers concerned are nos. 16-20, 23, 26, 45, 53, 59.

3. Three papers on solvent extraction chemistry arose out of my employment as a research chemist with the Australian Mineral Development Laboratories (1958-1960). These are nos. 36-38 of which paper 38 is under joint authorship and for which I carried out all the experimental work.

4. Papers 1-4, 12, 14 arose out of work in my Ph.D. thesis (University of Adelaide, 1965). I carried out all the experimental work for these and, in addition, because of my previous experience in solvent extraction chemistry, I produced many of the ideas for the work including suggesting the initial problem. None of these papers had been written at the time the thesis was presented.

5. In 1971 I spent a sabbatical leave at the University of Arizona working with Professor Henry Freiser. During this time I conceived the idea of the coated-wire electrode which Freiser and I published (paper 40). This initial study, for which I did all the experimental work, involved the calcium sensitive electrode which was subsequently expanded into additional systems by other workers in Freiser's laboratory and made the substance for the patent (publication 41).

(ii) In the general field of Inorganic Chemistry

6. One publication arose out of post-doctoral work undertaken at University College London (paper 56). I carried out all the experimental work for this.

7. In certain other publications I would consider my contribution to be less than 50% and consisted mainly of producing some of the initial ideas for the work and providing information concerning the interpretation of the results with a minor role in writing the paper. These are publications nos. 6, 44, 55, 57, 58.

CONTENTS

Papers published in the scientific literature and submitted for the Degree of Doctor of Science

SECTION A: Extraction from sulfate media by high molecular weight amines

1. The Extraction of Iron(III) from Aqueous Sulphate Solutions by Di(3,5,5-trimethylhexyl)amine, Part I.
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The published papers presented for the degree of Doctor of Science have not been presented for the award of a degree in any University or Institution by the candidate except where indicated and have not been published in any journal other than those stated. I declare the statements I have made concerning the contribution to my papers by others to be true and accurate.

I consent to this thesis being made available for photocopying and loan if accepted for the award of the degree.

R.W. CATTRALL

SECTION A: Extraction from sulfate media by high molecular weight amines

Papers in this section are primarily concerned with the extraction of iron(III) from acidified aqueous sulfate solutions by di(3,5,5-trimethylhexyl)amine in various diluents and the extension of this study to include primary amines. Also the extraction of scandium(III) and sulfuric acid have been studied.

In papers 1 and 2 it is shown that the red iron(III) complex extracted into benzene and chloroform has the stoichiometric formula $(R_2NH_2)_2FeOH(SO_4)_2$ which is formed by the extraction of the species $FeOHSO_4$ and $(FeOHSO_4)_2$ from the aqueous phase. This was established by equilibrium studies and by isolation and characterization of the complex. Previous work[1,2] does not elucidate the nature of the complex and, in fact, the paper by Good *et al.*[1] postulates an incorrect result. Molecular weight studies of the complex in benzene and acetone show association and structures are proposed based on hydroxy-bridging which is supported by magnetochemical measurements.

This work demonstrates the effect of aggregation of the amine salts on the equilibrium behavior and the severe non-ideality displayed in benzene is shown by light scattering studies to be due to the association of 48 molecular units into micelles. It is also shown that, even though the organic phase contains a mixture of both the amine sulfate and bisulfate salts, it is the amine sulfate salt which reacts with the iron(III) species from the aqueous phase.

An Additional study (paper 3) shows that the extraction of iron(III) is dependent on the nature of the diluent and that the degree of aggregation of the amine salt is greatest in diluents of low dielectric constant and low hydrogen bonding ability. The aggregation studies were carried out by light scattering measurements, the isopiestic method and viscometry. In this study measurements of the interfacial tension using the drop number technique are also reported and it is demonstrated that those diluents in which the greatest lowering of interfacial tension is produced are the most efficient diluents for iron(III) extraction.

This led to the postulation of an interfacial mechanism for the extraction which had been suggested only once previously for the extraction of uranium[3]. As is discussed in later sections this mechanism is now generally accepted for extraction systems involving high molecular weight amines.

In paper 4 infrared spectroscopic studies are described of the salts and the iron(III) complex of di(3,5,5-trimethylhexyl)amine and the shift in the position of the N-H stretching band is interpretted in terms of the strength of the cation-anion interaction. This is also correlated with the ability of the salts to aggregate in non-polar solvents. The lower degree of association found in the iron(III) complex is due to reduced cation-anion interaction.

Paper 5 describes the extension of the iron(III) extraction work to include primary amines and reports the isolation of dark red complexes of stoichiometric formula $(RNH_3)_2FeOH(SO_4)_2$ with 3,5,5-trimethylhexylamine and n-dodecylamine. These were found to crystallise from methanol or ethanol without change in composition except for the addition of a mole of alcohol. Temperature variable magnetic susceptibility studies (carried out by K.S. Murray) on these compounds and on $FeOHSO_4$ itself (paper 6) led to the conclusion that the basic unit in the adducts is most likely a trinuclear cluster (isosceles triangle) of interacting iron(III) ions which are bridged through hydroxy-groups and not through oxy-linkages.

Prados and Good[4] measured the Mössbauer spectra of the iron(III) complexes (supplied by myself) and obtained results consistent with the proposed equilateral triangular trimer.

Paper 7 describes the extraction of scandium(III) from sulfate solutions by di(3,5,5-trimethylhexyl)amine in chloroform to yield a complex of stoichiometric formula $(R_2NH_2)_4ScOH(SO_4)_3$. This complex contains two molecules of the amine sulfate compared with only one in the iron(III) case. Also the scandium complex is monomeric in chloroform as determined by vapor phase osmometry in contrast to the iron(III) complex which associates. This paper points out the dangers associated with relying on slope analysis studies to determine the complex stoichiometry without having a knowledge of such factors as the extent of association of the reagent and complex in the organic phase. It was observed that the exponential dependence of the distribution ratio on the stoichiometric amine sulfate concentration was close to one which could lead to the conclusion that one amine sulfate molecule is bound per scandium in contradiction to the results of preparative studies. The answer lies in the fact that the amine sulfate in chloroform is not monomeric but conforms to a monomer-dimer-trimer behaviour. On using monomer concentrations in the treatment of the extraction data the expected second order dependence is observed.

This work highlights the need to have reliable data on the aggregation of all species in the organic phase and thus extensive use has been made of vapor phase osmometry along with computer fitting procedures, a theme which has continued and been expanded in my solvent extraction studies. Paper 8 describes the first of these detailed aggregation studies for bis(3,5,5-trimethylhexyl)ammonium sulfate and bisulfate in chloroform.

Some unpublished work was carried out on the extraction of yttrium and europium from sulfate solutions by di(3,5,5-trimethylhexyl)amine which showed very poor extraction of these elements, however, this necessitated the development of new analytical methods (papers 9 and 10).

The work on the extraction of metals from sulfate solutions by high molecular weight amines is contained in a review I was invited to write for Coordination Chemistry Reviews (paper 11).

Some work on the extraction of sulfuric acid has arisen out of the metal extraction work (papers 12, 13, 14) and also shows the effect of aggregation of organic phase species. In isoamyl alcohol, where aggregation is absent, extraction by di- and tri(3,5,5-trimethylhexyl)-amines follows the mass action law. In chloroform, on the other hand, the behaviour is more complicated and systematic trends in the values of the extraction equilibrium constants for the formation of the sulfate and bisulfate salts are observed.

One other study (paper 15) which arose out of the iron(III) extraction work led to the preparation of the phosphate salts of 3,5,5-trimethylhexylamine and di(3,5,5-trimethylhexyl)amine and the isolation of the iron(III) complex extracted from phosphate solutions. This was shown for the primary amine to have the stoichiometric formula $RNH_3.H_2PO_4.FePO_4$.

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SECTION B: Extraction from chloride media by high molecular weight amines

Papers in this section are concerned with the extraction of niobium(V) and iron(III) from chloride solutions by high molecular weight amines. As discussed in Section A a knowledge of the aggregation phenomena of the amine salts is an essential part of the study. In this section equilibrium studies are linked with studies of the extraction mechanism and are based on interfacial processes of the type postulated in Section A.

Papers 16, 17 and 18 describe kinetic studies of the extraction of niobium(V) from 10.8 M hydrochloric acid by bis(3,5,5-trimethylhexyl)amine in chloroform, carbon tetrachloride and benzene. For this work the single drop technique was used and is an adaptation and extension of the method used by R.J. Whewell, M.A. Hughes and C. Hanson[1]. The work in these papers forms the basis of the extensive kinetic studies carried out with the other systems discussed in this thesis, in particular, those using Aliquat 336. In the initial studies drops were formed under the influence of a mercury filled plunger, however, this was replaced in later studies by a peristaltic pump which provided much better control of drop formation. In all studies metal transfer was from the disperse to the continuous phase which ensured initial rate theory to be applicable. Also an extensive study was made of the hydrodynamics of the drops to show that they were rapidly mixing internally thus eliminating diffusion from being rate determining. Thus, the systems were assumed to be operating under a kinetic regime with chemical reactions being rate determining.

Papers 16, 17 and 18 also include studies by vapor phase osmometry of the aggregation of bis(3,5,5-trimethylhexyl)ammonium chloride in the solvents used which was necessary to fully evaluate the kinetics results.

The kinetic studies in these papers provide forward and back extraction rate constants from which estimates of the extraction equilibrium constants can be obtained. These are compared with some success with values obtained from equilibrium studies in paper 19. The results in these papers confirm the ideas concerning interfacial processes postulated in Section A for systems involving high molecular weight amines.

As indicated above, aggregation studies of the amine salts in the organic phase are again a feature of the work in this section and one study (paper 20) describes the aggregation of the chloride, bromide and iodide salts of dilaurylamine in chloroform from distribution data obtained using the two-phase titration technique of Högfeldt and Fredlund.[2,3] This work shows the presence of a monomer-dimer equilibrium in chloroform and a model for the dimer is proposed. In this model strong cation-anion interaction is suggested and confirmed by infrared spectroscopy.

The above work using the two-phase titration technique led to an improved method for obtaining distribution data for metal extraction and this is described in paper 21 for the extraction of iron(III) from 6 M hydrochloric acid by tri-n-octylammonium chloride in chloroform. The method, which allows the fast collection of a large number of reliable data points, is two-phase titration with fast stirring of the phases. This method is now used routinely in my work for collecting equilibrium distribution data.

The work in paper 21 describes the application of the graphical method of Sillén[4] as described in detail by Högfeldt[2] for determining the average numbers of amine hydrochloride ($\bar{q}$) and metal ($\bar{p}$) moities per complex. These values are used to make guesses concerning the stoichiometries of the extracted complexes. Once a model for the system is chosen the extraction equilibrium constants can be evaluated graphically according to Muhammed *et al.*[5] or alternatively by computer fitting. This is the procedure which I now use in the treatment of all of my data from equilibrium studies.

The work on the extraction of iron(III) from 6 M hydrochloric acid has been extended to include other amines in chloroform solution as described in paper 22. The results demonstrate the strong tendency to form heterogeneous aggregates in these systems. The results also identify the importance of the reagent monomer in the extraction process, a point which has been verified in the kinetic study of the systems (paper 23). The aggregation study of the amine salts, necessary for the interpretation of the extraction data, is described in paper 24. The tertiary amine salts are monomeric in chloroform and the secondary amine salts show a monomer-dimer behaviour. The primary amine salt studied, n-dodecylammonium chloride, is more highly aggregated with tetramers and possibly higher oligomers being present.

The study of the mechanism of the extraction of iron(III) from 6 M hydrochloric acid by long chain amines in paper 23 is interpretted in terms of the formation of a (1,1) complex at the interface by fast ion-exchange followed by replacement of the complex at the interface by one molecule of reagent monomer from the bulk organic phase. Additional heterogeneous aggregates are then formed in the organic phase. For this model the assumption is made that the interface is saturated with reagent monomer. Support for this mechanism is obtained through the excellent agreement between the extraction equilibrium constants calculated from the rate data and the values obtained by two phase titration (papers 21, 22).

One novel study (paper 25) describes the extraction of copper(II) from methanolic lithium chloride solutions by bis(3,5,5-trimethylhexyl)-ammonium chloride in benzene. This follows from a study by Florence and

Farrar[6,7] who made use of essentially non-aqueous media for the extraction of metals such as Ni(II) and Mn(II) which would otherwise not form extractable anionic chloro-complexes in aqueous solutions. Paper 25 describes the elucidation of the stoichiometry of the extracted copper(II) complex as well as describing the distribution of the amine chloride salt itself between the methanol phase and benzene and its aggregation in benzene.

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SECTION C: Extraction from chloride media by Aliquat 336

Aliquat 336 is a commercial solvent extraction reagent produced by the Henkel Corporation (formerly General Mills Chemicals, Inc.). This section contains papers dealing with the extraction of mercury(II), copper(II), zinc(II), cadmium(II) and cobalt(II) from chloride solutions by Aliquat 336 in chloroform.

Most papers in the literature on Aliquat 336 make the assumption that it consists of several quaternary ammonium chlorides with a mixture of C_8 and C_{10} carbon chains, with the C_8 compound, methyltrioctylammonium chloride, predominating. One paper[1] reports a detailed analysis of Aliquat 336 by gas chromatography and mass spectrometry but is based on a statistical approach which relates the amounts of the various tertiary amines formed in the gas chromatography to factors such as the tendency to split off particular alkyl groups and the number of common alkyl groups present in the quaternary ammonium chloride. Because of the assumptions made in this approach, the amounts of the quaternary ammonium chlorides estimated may be in considerable error.

Paper 26 describes an improved method for the quantitative analysis of Aliquat 336 using gas chromatography and is based on the use of an internal standard. The individual components of Aliquat 336 were identified initially using mass spectrometry by analysis of the peaks in the gas chromatogram. The major component was identified as methyldioctyldecylammonium chloride with up to four other quaternary ammonium chlorides present together with small amounts of 1-octanol, 1-decanol and water. Analysis of two separate batches of the material revealed small differences in composition, however, subsequent work (paper 30) showed that this was not a significant factor in determining the solvent extraction behaviour. As expected some discrepancy with Paatero's results was observed but the validity of the method was confirmed by the analysis of a known mixture of quaternary ammonium chlorides.

In Section F it is shown that Aliquat 336, as well as being an important commercial solvent extraction reagent, has uses in the construction of ion-selective electrode membranes. It is demonstrated in Section F that successful electrodes can be made which respond to anionic halometal complexes of mercury(II), copper(II), zinc(II), cadmium(II) and cobalt(II). These electrodes show interesting selectivity properties, for example, the mercury electrodes respond preferentially towards monovalent complex anions whereas the electrodes for the other metals respond generally towards divalent complexes. The zinc and cadmium electrodes show some monovalent anion response in strong hydrochloric acid.

It is generally accepted that, for particular reagents, there is a correlation between extraction behaviour and ion-selective electrode selectivity. This arises through the similarity in the ion-exchange processes occurring at the interface in a solvent extraction system and at the surface of an ion-selective electrode membrane. Thus, one reason for studying the solvent extraction systems described in this section was to see if correlations with the ion-selective electrode behaviour could be observed. Another reason, of course, for studying extraction with Aliquat 336 was to extend the application of the graphical and computer fitting methods discussed in Section B to other systems. Aliquat 336 in chloroform is ideal for this since its components are generally not highly aggregated which makes the data treatment less complicated.

Paper 27 reports an equilibrium study of the extraction of mercury(II) from hydrochloric acid solutions by Aliquat 336 in chloroform. The species extracted are shown to be $HgCl_3^-$ and $HgCl_4^{2-}$ with the monovalent species being preferentially extracted. This result correlates well with the observed ion-selective electrode behaviour (paper 49). The extraction equilibrium constants have been evaluated for various concentrations of hydrochloric acid.

Paper 28 is an extension of the work to include the extraction of mercury(II) from potassium iodide solutions and copper(II), zinc(II) and cadmium(II) from hydrochloric acid. In each case the curve fitting procedures have been used to evaluate the extraction equilibrium constants. It is shown that for mercury the monovalent species is again preferentially extracted and that for zinc and cadmium at low acid concentrations the divalent anion is preferentially extracted. This is in keeping with the ion-selective electrode behaviour. At high acid concentrations, however, for zinc and cadmium, there is a preference for the extraction of a monovalent species. This is explained as being due to the presence of the protonated species $HMCl_4^-$ in strong acid.

This latter point has been verified by studying the extraction of zinc and cadmium from lithium chloride solutions (paper 29) which shows a preferential extraction of the divalent anion at high chloride concentrations. This is also in keeping with the observed electrode behaviour.

The work described in paper 26 on the analysis of Aliquat 336 required the synthesis of two of the pure components of the material, methyltrioctylammonium and methyltridecylammonium chlorides. This allowed a study to be carried out on the solvent extraction behaviour of these two components and a comparison to be made with Aliquat 336 itself.

This is described in paper 30 and the work contains, in addition to the equilibrium study, a study of the aggregation behaviour of these two quaternary ammonium salts in chloroform and certain other diluents. The aggregation study shows very weak dimerization in chloroform and validates the assumption that aggregation can be neglected in the treatment of the equilibrium data. The extent of aggregation in certain other low-polarity solvents such as o-xylene and cyclohexane is more extensive.

The equilibrium studies show only small differences between the extraction behaviours of the two pure components and Aliquat 336 itself and these are suggested to be due to steric and thermodynamic effects resulting from different numbers of carbon atoms in the chains of the quaternary ammonium ions, as well as being due to the presence of long-chain alcohols. The conclusion is also drawn that small differences in composition for different batches of Aliquat 336 will not affect, significantly, the extraction behaviour or efficiency.

Various models for extraction systems have been reviewed by Danesi and Chiarizia[2] who describe the kinetic behaviour expected in each case including the saturated interface model. A study of the mechanism of the extraction of zinc(II) from chloride solutions by one of the components of Aliquat 336, methyltrioctylammonium chloride, in chloroform is described in paper 31 and shows behaviour consistent with the saturated interface model. Support for this is also seen in the results of a study of the interfacial tension in this system. The rate data for forward and back extraction has been tested against the rate equations derived on the basis of the saturated interface model and show excellent agreement. Excellent agreement is also seen between the extraction equilibrium constants calculated from the rate data and those obtained from the two-phase titration equilibrium studies.

Papers 32 and 33 describe the extraction of cobalt(II) from lithium chloride and hydrochloric acid solutions by Aliquat 336 in chloroform. Both equilibrium studies and kinetic studies are reported and again the saturated interface model is used for the mechanistic studies. The results show that the species $CoCl_4^{2-}$ and $CoCl_3^-$ are extracted from lithium chloride solutions with the divalent anion being the predominant one. This is also in keeping with the behaviour of the ion-selective electrode based on the chlorocobaltate(II) salts of Aliquat 336 which shows selectivity towards the divalent anion. Paper 33 shows that the protonated species $HCoCl_4^-$ is extracted from hydrochloric acid solutions and this is verified by analysis of the loaded organic phase.

References:

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SECTION D: Extraction by high molecular weight carboxylic acids and organophosphorus compounds

Paper 34 describes the extraction of iron(III) from nitrate solutions by the high molecular weight carboxylic acids, n-octanoic, n-nonanoic, n-decanoic, 2-ethylhexanoic, 3,5,5-trimethylhexanoic and phenylacetic acids in benzene and other diluents. The work elucidates the nature of the extracted complex as well as illustrating the effect of the structure of the carboxylic acid on the extraction. It is shown that complexes of the type FeR_3 and $FeR_3.HR$ are extracted in the lower pH region and partially hydrolysed complexes such as $FeOHR_2$ and $Fe(OH)_2R.HR$ are extracted at high pH. Slope analysis methods have been used to treat the experimental data in this paper. The strongest extractant for iron(III) is phenylacetic acid and this is used in an analytical procedure for the determination of iron(III) (Paper 35). In this determination colorimetric detection is used together with the amplification procedure provided by solvent extraction of having a large aqueous to organic phase ratio. This enables iron(III) concentrations of less than 1 μg/ml to be easily determined.

The extraction of beryllium and aluminium from aqueous sulfate solutions by di(2-ethylhexyl)phosphoric acid in kerosene is discussed in paper 36. The extraction equations are derived from the experimental data and it is shown that it is feasible to separate these two metals by pH adjustment of the aqueous phase. In fact, this paper forms the basis of a process developed by the South Australian Department of Mines (now the Australian Mineral Development Laboratories) for the recovery of high purity beryllium oxide from beryl ore. The earlier work which describes the treatment of the ore to produce a solution containing the beryllium and aluminium sulfates is contained in paper 37.

The extraction of thorium from nitrate solutions by a neutral organophosphorus reagent, dibutylbutylphosphonate, in kerosene is reported in paper 38. It is suggested, by slope analysis studies of the equilibrium data, that thorium is extracted as the trisolvate, $Th(NO_3)_4.3DBP$. It is also shown that this reagent extracts thorium more strongly than the traditional reagent, tri-n-butylphosphate.

Paper 39 reports a survey of a number of trialkylmonothiophosphates and trialkylphosphine sulfides for their ability to extract copper(II), gold(III), silver(I) and mercury(II). The paper also describes the attempted use of these reagents in polymer membrane coated-wire ion-selective electrodes. Even though they proved to be efficient plasticizers for poly(vinyl chloride) they were found to be unsuitable as ion-sensors.

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SECTION E: Ion-selective electrodes sensitive towards calcium and potassium

My research in the field of ion-selective electrodes commenced in 1971 when I conceived the idea of applying a poly(vinyl chloride) based calcium sensitive membrane to the surface of a platinum wire to produce an ion-selective electrode without an inner aqueous reference system. This idea was prompted by a paper by Hirata and Date[1] in which they described the application of silicone rubber membranes containing metal sulfides to the surface of a platinum wire to produce electrodes of the Pungor type. This initial work is contained in paper 40 in which the electrode is first called the "coated-wire" electrode. There are now numerous examples of useful coated-wire electrodes in the literature.

Paper 40 describes the response characteristics of the calcium sensitive coated-wire electrode based on a commercial liquid exchanger (Orion Research 92-20-01) immobilized in poly(vinyl chloride). This electrode shows very similar characteristics to the commercial liquid membrane electrode except for some differences in selectivity and a slightly larger response range.

This initial discovery led to a patent on coated-wire electrodes being secured in the United States, Great Britain, Canada, West Germany and Japan. Paper 41 is a copy of the British patent and describes coated-wire electrodes in a more general sense covering many types of systems with specific examples referring to the calcium electrode and a number of anion sensitive electrodes. My contribution to the patent is the work on the calcium electrode.

A number of commercially available phosphoric acid esters have been investigated in an attempt to find reagents suitable as calcium ion sensors in coated-wire electrodes. This work is contained in papers 42 and 43.

The work describes the preparation of the electrodes and the investigation of the response characteristics and selectivities. One reagent di(octylphenyl)phosphoric acid was separated from a mixture of mono- and di-esters obtained from Mobil Chemical Co. and proved to be a very selective reagent for calcium. Initially, this reagent was thought to be the n-octylphenyl derivative from information supplied by the manufacturer but subsequent work including the crystal structure (carried out by M.F. Mackay) showed the compound to be the 1,1,3,3-tetramethylbutyl derivative. The structural determination is contained in paper 44. One particularly interesting result from the structural determination is that the calcium ions are not chelated by the phosphate groups and it is suggested that this may, in fact, facilitate ion-exchange reactions involving the phosphate salt.

A potassium selective coated-wire electrode is reported in paper 45 and is based on the well-known neutral carrier reagent, valinomycin. With di-n-decylphthalate as the plasticizer this electrode responds with Nernstian behaviour in the region 10^{-1} to 10^{-5} M. It is demonstrated that this electrode can be used for the analysis of whole blood and sea water without significant interference from sodium.

Paper 46 describes the application of the potassium and calcium coated-wire electrodes to the analysis of human and sheep blood serum in a flow-through cell using differential potentiometry. In this technique two identical coated-wire electrodes are used with one in contact with a reference stream and the other in contact with the sample. Electrodes with a conventional reference system are also described. This technique produces the precision obtained with conventional methods but without the need for continual restandardization.

References:

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SECTION F: Ion-selective electrodes sensitive towards anionic halometal complexes

The papers in this section describe the most important contribution I have made to the field of ion-selective electrodes and are based on my original ideas, although an earlier paper by Scibona, Mantella and Danesi[1] studied liquid membrane electrodes based on similar principles for zinc(II) and palladium(II) and posed the question as to whether the approach could be applied to iron(III). The invention of the coated-wire electrode provided the practical means for making electrodes sensitive to anionic halometal complexes since it avoided the problems associated with providing a suitable inner aqueous reference system.

It is recognised that ion-selective electrodes are not suitable for the determination of ions of charge greater than two because of the low slope of the Nernst plot and the consequent low sensitivity. Thus, an electrode which responds to Fe^{3+} is not of particular advantage, however, if the iron(III) can be sensed as a complexed species of lower charge, such as the tetrachloroferrate(III) ion, the sensitivity associated with a monovalent ion is achieved. These ideas for the development of a coated-wire electrode for the determination of iron(III) are described in paper 47. Use is made of the extraction reagent Aliquat 336 for preparing a poly(vinyl chloride) membrane containing the tetrachloroferrate(III) ion which is coated onto a platinum wire. This coated-wire electrode shows near Nernstian behaviour in the iron(III) concentration range of 10^{-1} to 10^{-4} M in solutions containing 6 M chloride. High selectivity towards the tetrachloroferrate(III) ion is observed which enables analysis for iron(III) in ore samples.

Paper 48 demonstrates that the tetrachloroferrate(III) ion-selective electrode can be used in the determination of iron(III) in mineral samples by titration with EDTA. It is shown that because of the high stability of the iron(III)-EDTA complex it is possible to titrate iron(III) in strongly acid solutions using the electrode to sense the end-point. This is, of course, not possible using conventional EDTA titrations because the metallochromic indicators will not function in strong acid.

These ideas and techniques have been extended to other halometal complexes and paper 49 describes electrodes for the determination of mercury(II) which are based on response to the iodomercurate(II) and chloromercurate(II) ions. For a divalent ion like mercury(II) response towards two anions is possible, the monovalent trihalomercurate(II) ion and the divalent tetrahalomercurate(II) ion, and it is shown that the electrodes respond preferentially to the monovalent anion for both iodide and chloride. This is correlated with the solvent extraction behaviour of Aliquat 336 in Section C where the preferential extraction of the monovalent anion is discussed.

The preferential response of the halomercurate(II) electrodes towards the monovalent anion has considerable advantages in increasing the sensitivity particularly for potentiometric titrations in the chloride system and this point is discussed in paper 49.

Paper 50 reports a coated-wire electrode for the determination of zinc(II) as the tetrachlorozincate(II) ion which has been used for the analysis of zinc oxide and some zinc concentrates. Electrodes responsive to chlorocadmate(II) ions and to chlorocuprate(II) ions are described in paper 51 and paper 52 respectively.

Paper 53 describes electrodes responsive to chlorocobaltate(II) ions of the coated-wire type and with a conventional internal reference system.

The latter electrode gave more reliable results for this system and reasons for this are discussed in the paper.

In these papers concerned with the use of Aliquat 336 complexes in polymer membranes a novel method has been developed for the preparation of the electroactive reagents. This makes use of the solubility of the chloride salt of Aliquat 336 in n-hexane and the general insolubility of the other salts and complexes in this diluent. The consequence of this is the formation of a third oil phase in the preparation by solvent extraction which consists exclusively of the desired Aliquat 336 complex. The oil is compatible with poly(vinyl chloride) which also removes the need for a secondary plasticizer.

Paper 54 is an invited review chapter for Ion-Selective Electrode Methodology (CRC Press, Inc., Editor, A.K. Covington) and contains a discussion of much of my work on coated-wire electrodes as well as a general review of the literature on heterogeneous membrane, carbon support and coated-wire ion-selective electrodes.

References:

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SECTION G: Papers in the general field of inorganic chemistry

Papers in this section are in the general area of inorganic chemistry and involve the preparation and physico-chemical study of coordination and organometallic compounds.