THE LIQUID-LIQUID EXTRACTION OF GERMANIUM WITH THE 7-ALKYLATED 8-HYDROXYQUINOLINE DERIVATIVE - KELEX 100

by

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1990

PREFACE

This thesis presents work carried out by the author and has not been submitted in part, or in whole, to any other university. Where use has been made of the work of others it has been duly acknowledged in the text.

This work described in this thesis was performed in the Department of Chemistry and Applied Chemistry, University of Natal, King George V Avenue, Durban, 4001, from February 1989 to October 1990 under the supervision of Prof. L.F. Salter.

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ABSTRACT

Germanium can be extracted from aqueous solutions by KELEX 100 dissolved in an appropriate diluent. KELEX 100 is a commercially available chelating extractant containing the active constituent 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline. Previous work in the solvent extraction of germanium with this reagent has shown that germanium is extracted most efficiently at low pH. When the germanium is present in sulphuric acid solutions at pH less than 2, the extracted complex is $GeL_3^+HSO_4^-$, however at pH 3 to 8, the metal is extracted as $GeL_2(OH)_2$ (where HL = KELEX 100).

In this work, the extraction kinetics and equilibrium extraction of germanium in the Ge-KELEX 100 solvent extraction system is examined by AKUFVE and shaking assemblies, which both employ rapid mixing of the organic and aqueous phases, and by a quiescent interface Lewis Cell.

The AKUFVE is a Swedish designed apparatus for solvent extraction, its performance and suitability for solvent extraction studies is evaluated using the extraction experiments carried out on the Ge-KELEX 100 solvent extraction system.

Experiments conducted using an experimental set-up with a large interfacial area to phase volume ratio reveal that the extraction of germanium occurs in two distinct kinetic regimes. The first regime occurs in the first few minutes of an extraction experiment and is fast relative to the second kinetic regime which follows this fast initial extraction period and occurs until the extraction of germanium attains the equilibrium value. In this work an extraction mechanism involving interfacial reaction of germanium and extractant is proposed to explain this kinetic behaviour.

An increase in ionic strength is shown to reduce the rate of germanium extraction in the Ge-KELEX 100 solvent extraction system. Modifiers, such as organic alcohols, are shown to greatly improve extraction kinetics.

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CHAPTER ONE

INTRODUCTION

Liquid-liquid extraction, also known as solvent extraction, refers to a process wherein a substance in one liquid phase is transferred to another liquid phase. The two different phases should be immiscible because they are usually in contact during the process of solvent extraction.

Most liquid-liquid extraction systems, including the system studied in this work, involve an aqueous phase and an organic phase. To improve the extraction of a substance from one phase to another, usually from the aqueous phase to the organic phase, an extractant may be dissolved in one of the phases which reacts with the substance being extracted and promotes its extraction into the desired phase.

In solvent extraction processes of industrial importance the substance used as an extractant is usually dissolved in the organic phase and has a low solubility in the aqueous phase. By reaction with the substance that is being extracted, usually a metal ion, (via a chelation, solvation, ion-pair reaction etc.) the extractant renders the extracted substance soluble in the organic phase because of the extractant's solubility in the organic phase.

The reaction between the extractant and the extracting substance usually is a multi-step reaction, involving diffusion to the reaction site of the reactants, one or more reaction steps between the extractant and the extracted substance, then diffusion of the products of the reactions at the reaction site away from the reaction site into the bulk organic or aqueous phase.

The site of the reaction or reactions between the extracted species and the extractant has provided a topic for speculation. Some researchers propose that the reaction between the extractant and the extracted substance occurs in the bulk of either of the two phases[1-3], while others propose that the site of the reaction occurs at the interface between the two immiscible phases[4-6] e.g. for systems where the substance to be extracted has very low solubility in the phase that it is to be extracted into and where the extractant has very low solubility in the phase in which the substance to be extracted is originally present. The solution to the argument may lie in the fact that some solvent extraction processes involve reaction of the extractant and extracted substance in the bulk of either phase, some processes proceed via an interfacial mechanism and some processes proceed via a combination of both pathways.

Substances used as extractants usually have long-chain alkyl substituents to solubilise them in the organic phase as well as a moiety which has an affinity for the extracted substance.

This work is concerned with the solvent extraction of germanium. Its price is approximately $ 4000 / kg[7]. Ge was discovered in 1886 by Winkler.

Elemental germanium is a grey-white metalloid and is crystalline and brittle when pure. An important property of germanium is that it is a semi-conducting material. The use of germanium as a semi-conducting material (doped with arsenic, gallium and other elements) accounts for most of the commercial usage of germanium.

Germanium and germanium dioxide are also used in infra-red spectroscopes and other optical applications because of their transparency to infra-red radiation. Germanium dioxide also has a high refractive index and thus is useful as a component of glasses in wide angle camera lenses and microscope objectives.

Newer applications of germanium include its uses as an alloying agent, as a phosphor in fluorescent lamps and as a catalyst and, because of their low

toxicity to mammals, some organometallic germanium compounds are attracting interest as chemotherapeutic agents.

Germanium is considered a strategic material in first world countries[8] i.e. a disruption in supply would constitute a national and industrial emergency.

In Southern Africa there are large reserves of germanium located in Namibia e.g. at Tsumeb germanium is mined as a minor constituent of zinc-, iron-, lead- and copper-bearing ores. Germanium is also present in small quantities in Namibia's coal reserves.

A number of patents exist for the use of solvent extraction for the selective extraction of germanium from acidic solutions containing other ions e.g. European Patent No. 0 313 201 A1, which describes the separation of germanium from acidic solutions containing zinc, arsenic, cadmium, indium, copper and iron. Solvent extraction may also be ideal for the small volume reclamation of germanium from coal ash.

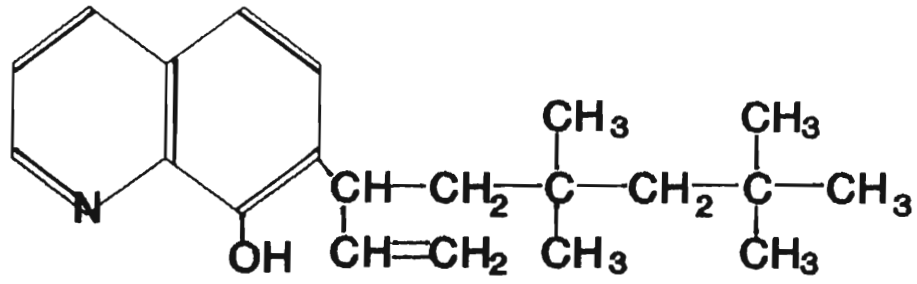
The extractant examined in this study is KELEX 100. From 1972 to 1976 the active constituent of

KELEX 100 was 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline (shown in Figure 1.) Work by Ashbrook[9] in 1975 showed the active constituent of KELEX 100 to be present in approximately 77.7 % purity. This compound is referred to throughout this study as "pre-1976" KELEX 100. In 1976 the manufacturing process for KELEX 100 was changed to produce a new active component, 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (shown in Figure 1). This compound was identified as the active component in "post-1976" KELEX 100 by Demopoulos and Distin[10] in 1983 and was present in 82 % purity in commercial KELEX 100. More recent work by Gareil et al.[11] in 1989 reports a purity of above 86 % for the active constituent in KELEX 100. The KELEX 100 used in this study is of comparable purity to that used in the two last mentioned studies.

Figure 2 outlines the process used for the synthesis of KELEX 100[11].

KELEX 100 was developed for use as an extractant for copper[12]. Copper is extracted from an aqueous phase at a pH of approximately 4.0 and the extracted copper-KELEX 100 complex stripped from the organic phase by contacting it with a strongly acidic solution. This commercial use of KELEX 100 was never successful primarily because the extractant causes

"pre-1976" KELEX 100



"post-1976" KELEX 100

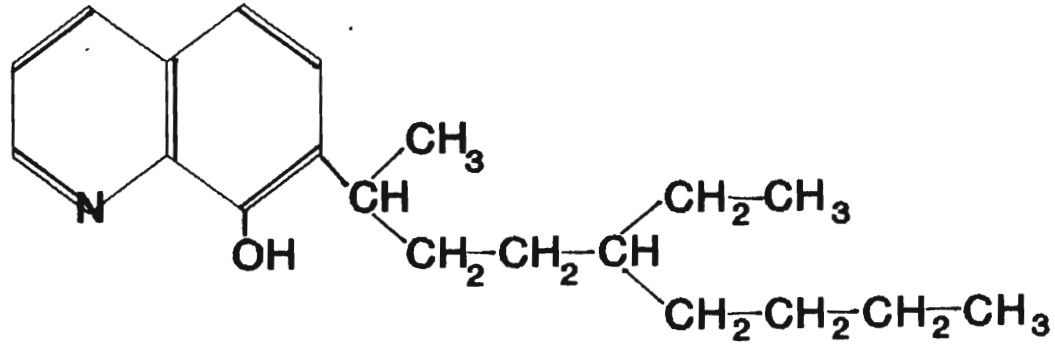


Figure 1

The synthesis of KELEX 100

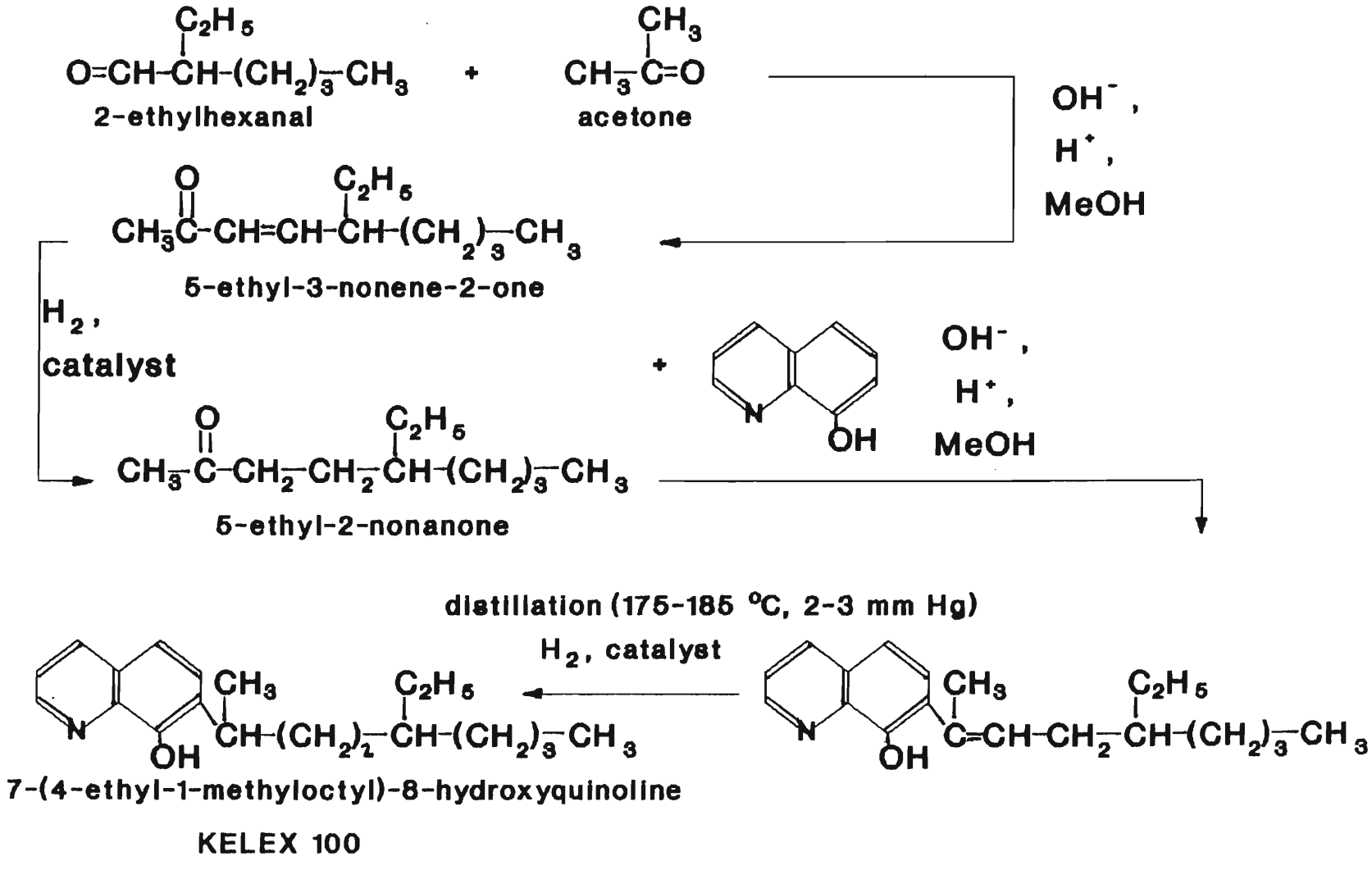


Figure 2

acid to be extracted into the organic phase when the copper is stripped from the organic phase. The unsuitable nature of KELEX 100 for the liquid-liquid extraction of copper prompted researchers to examine other metal ions which could be successfully extracted by KELEX 100, e.g. gallium[13] and germanium[14,15].

This investigation focuses on the liquid-liquid extraction mechanism of germanium (as Ge^{4+}) with KELEX 100. Prior work on this topic[14,15], although published in 1979 and 1980, has made use of "pre-1976" KELEX 100, but the general conclusions of Marchon, Cote & Bauer[14] and Cote & Bauer[15] concerning the mechanism of the extraction of germanium with "pre-1976" KELEX 100 are expected to be applicable to the extraction of germanium with "post-1976" KELEX 100. This work does check the applicability of some of the conclusions of these earlier studies.

Cote and Bauer[15] report a survey of ten commercially available extractants concerning their efficiency for germanium (as Ge^{4+}) extraction. Of these ten extractants, "pre-1976" KELEX 100 is by far the best.

Marchon et al.[14] and Cote and Bauer[15] report that

germanium (as Ge^{4+}) is extracted most efficiently from aqueous solutions into "pre-1976" KELEX 100-containing organic solutions at extremely low pH (<0). Below pH 2, germanium is extracted from sulphuric acid solutions by "pre-1976" KELEX 100-containing organic solutions as $GeL_3^+HSO_4^-$ (where HL = "pre-1976" KELEX 100), between pH 3 and 8 extraction occurs as $GeL_2(OH)_2$. The extraction reaction of germanium is completely reversible and when equilibrated with an aqueous phase above pH 12, complete back extraction of germanium from the organic phase to the aqueous phase occurs. However, this process is slow and could cause some problems with the commercial applications of KELEX 100 as an extractant. Work presented here will not be concerned with the reverse extraction of germanium from KELEX 100-containing solutions to alkaline solutions.

Earlier in the Introduction the site of the reaction between the extracting species (in this study germanium) and the organic extractant (in this study KELEX 100) was discussed. Cote and Bauer[15] believe the reaction mechanism is interfacial because of the observation that the extractant is practically insoluble in the aqueous phase and the species to be extracted (Ge^{4+}) is practically insoluble in the organic phase. Bag and Freiser[16] have measured the

distribution coefficient of "pre-1976" KELEX 100 (between a chloroform solution containing KELEX 100 and an aqueous phase at ionic strength 0.1 M and pH 5.5 - 6.2) as $10^{5.52}$. Although this value is not for "post-1976" KELEX 100 and not for acidic pH, the distribution coefficient for KELEX 100 under any conditions is likely to be of similar order. This value of the distribution coefficient obtained by Bag and Freiser represents an aqueous solubility of KELEX 100 of below 10^{-3} g/l for any organic KELEX 100 concentration used in this study. This extremely low aqueous phase solubility of KELEX 100 effectively rules out a mechanism in which the reaction between germanium and the KELEX 100 occurs in the bulk aqueous phase. Thus the interfacial region between the organic and aqueous phase is believed to be the site of the formation of the extracted germanium species.

Cote and Bauer[15] demonstrate the practicality and feasibility of the use of liquid-liquid extraction with "pre-1976" KELEX 100 to separate small quantities of germanium from aqueous acid solutions containing large amounts of zinc by outlining a procedure which has been tested on a small scale. However, it is not the intention of this study to develop a procedure to purify germanium that could be used on an industrial scale, but to study the

kinetics and mechanism of the extraction of germanium from aqueous to organic solutions containing KELEX 100.

CHAPTER TWO

EXPERIMENTAL

This chapter is divided into five sections. The first section lists the materials used and the names and addresses of the various chemical suppliers. The second section describes the development of the technique used to analyse for germanium in this project and the various germanium solutions used in this investigation. The third section describes experiments conducted to examine the constituents of KELEX 100 and the various organic solutions containing KELEX 100 that were used. The fourth section contains a brief description of LIX 26, a 7-alkylated 8-hydroxyquinoline derivative similar in structure to KELEX 100 that was also briefly studied. The fifth section is divided into three parts and describes the three experimental set-ups (viz. AKUFVE, Lewis Cell and shaking experiments) used to obtain kinetic data for the germanium-KELEX 100 system. Each part of the fifth section contains a full description of the experimental technique used as well as descriptions of the various experiments carried out using the technique described.

2.1 MATERIALS

The materials used are summarised below and

catalogued in the order: name, chemical grade, supplier and assay.

2.1.1 Extraction with AKUFVE apparatus

Absolute Ethanol, Lab, SAARCHEM, assay 99 %

Toluene, AR, Kleber Chemicals, assay 99,4 %

Sulphuric Acid, Lab, SAARCHEM, assay 98 %

Germanium Dioxide, Electronic Grade, Aldrich, assay 99,999%

KELEX 100, Schering, assay 82-84 %[17]

Nitric Acid, HOLPPRO, assay 55 %

LIX 26, HENKEL, assay 72 %[18]

Sodium Hydroxide, AR, Kleber Chemicals, assay 98 %

2.1.2 Extraction with Lewis Cell

Toluene, AR, Kleber Chemicals, assay 99,4 %

Sulphuric Acid, Lab, SAARCHEM, assay 98 %

Germanium Dioxide, Electronic Grade, Aldrich, assay 99,999%

Sodium Hydroxide, AR, Kleber Chemicals, assay 98 %

KELEX 100, Schering, assay 82-84 %[17]

2.1.3 Shaking Experiments

Toluene, AR, Kleber Chemicals, assay 99,4 %

Sulphuric Acid, Lab, SAARCHEM, assay 98 %

Germanium Dioxide, Electronic Grade, Aldrich, assay 99,999%

KELEX 100, Schering, assay 82-84 %[17]

8-Hydroxyquinoline, Riedel-de Haën, assay 99 %

Sodium Hydroxide, AR, Kleber Chemicals, assay 98 %

Sodium Chloride, Lab, SAARCHEM, assay 99,5 %

2.1.4 Chemicals for Buffers

Potassium Chloride, Lab, BDH, assay 99,5 %

Hydrochloric Acid, Lab, SAARCHEM, assay 32 %

Potassium Hydrogen Phthalate, AR, BDH, assay 99,9 %

Sodium Hydroxide, AR, Kleber Chemicals, assay 98 %

Sodium Citrate, AR, SAARCHEM, assay 99 %

Citric Acid, chem. pure, Riedel de-Haën, assay 99 %

Potassium Dihydrogen Phosphate, AR, BDH,
assay 99.5 %

2.1.5 Chemicals for Infra-Red, UV - visible Spectrophotometry and GC - Mass Spectrometry

KELEX 100, Schering, assay 82-84 %[17]

Carbon tetrachloride, AR, BDH, assay 99,5 %

2.1.6 Chemicals for Viscosity and Interfacial Tension Measurements

KELEX 100, Schering, assay 82-84 %[17]

Toluene, AR, Kleber Chemicals, assay 99,4 %

2.1.7 Water Used in This Investigation

The results obtained with Millipore Water (water which has been passed through a Milli-Q system, this comprised of a carbon pre-filter, a reverse osmosis

membrane, a cationic and an anionic exchange resin filter) were compared to results obtained with laboratory deionised water (whenever water was required in the experiments conducted in this investigation). In all instances the purity of deionised water was found to be adequate and all further experiments were therefore conducted with deionised water.

2.1.8 Names and Addresses of Chemical Suppliers

BDH Chemicals Ltd
Broom Road
Poole, Dorset, BH12 4NN
England

Kleber Chemicals
P. O. Box 12018
Jacobs, 4026
South Africa

Saarchem (Pty) Ltd
P.O. Box 144
Muldersdrift, 1747
South Africa

Waters (Division of
Millipore): Agent
P.O. Box 2268
Pinetown, 3600

Riedel de Haën AG
Sielze
Hanover
West Germany

Schering
Industrie-Chemikalien
Waldstraße 14
Postfach 1540
West Germany

Aldrich
P.O. Box 355
Milwaukee
Wisconsin 53201

Henkel Corporation
Suite 104
1844 West Grant Rd
Tucson AZ 85745-1273

2.2 GERMANIUM

2.2.1 Germanium Determination

Many different methods for the determination of germanium are described in the literature, including atomic absorption[19-22], uv-visible absorption[23-30] and gravimetric methods[30]. In this study a method had to be found that was reproducible and suitable for the analysis of large numbers of samples on a daily basis. The following sections (Section 2.2.1.1, Section 2.2.1.2 and Section 2.2.1.3) discuss the various methods which were investigated and the final method chosen.

2.2.1.1 **Germanium Determination by Atomic Absorption Spectrometry**

Atomic Absorption Spectrometry has been a principal technique for germanium analysis since the 1960's[19,20] and is an obvious starting point when examining techniques that would be suitable for the purposes of this investigation. A number of methods are available in the literature and these are briefly discussed below.

Manning[19,20] describes a method using a nitrous oxide-acetylene flame and although this reported

method has adequate sensitivity the reproducibility is not given in the report. However, mention is made of the fact that for analytical purposes a high temperature flame is required.

Johnson et al.[21] observed that the Atomic Absorption Spectrometric determination of germanium is subject to poor sensitivity and reproducibility because germanium produces a highly stable oxide species which does not efficiently produce Ge atoms. Germanium is also lost as volatile GeO which forms at 1000 ^{0}C in the presence of carbon. Ge atoms are only produced at 3000 ^{0}C and this is a large source of potential error. Johnson et al.[21] approached this problem by using a graphite tube atomizer to increase the residence time of the atomized Ge in the high temperature environment and thus allowed the GeO to reach the temperature required to break the Ge-O bond.

Sohrin et al.[22], using a graphite furnace, suggested that GeO loss can be minimized by adding an oxidizing acid or alkali to suppress the premature reduction of GeO_2 to GeO by carbon. A tantalum treated furnace also suppresses the premature GeO formation because the tantalum carbide layer in the graphite furnace prevents the analyte from

contacting the graphite[22].

More recent techniques, such as the formation of germanium hydride before atomization in a palladium coated graphite tube by Doidge et al.[31] and work published by the Council for Mineral Technology[32] using electrothermal atomization in atomic absorption spectrometry, have obtained better sensitivity and reproducibility than earlier atomic absorption spectrometry methods. However, equipment and financial considerations precluded the use of the two techniques referred to above.

Work in this laboratory[33] using a Varian Atomic Absorption spectrometer with an acetylene-nitrous oxide gas mixture showed the atomic absorption technique to be unreliable for accurate Ge determination at low concentration with an error of 25 to 33 % for Ge samples ranging from 300 to 700 ppm. Equipment was not available to develop the more sophisticated approaches referred to above and hence Atomic Absorption analysis was rejected as an appropriate technique. Attention was therefore turned to classical colourimetric methods.

2.2.1.2 **Germanium Determination with Mannitol**

The mannitol titration technique reported by

Nazarenko[29] was tried in this laboratory[34]. The method involves acidifying an alkaline solution of germanium dioxide (10 ml, 1-50 mg Ge). The solution is then boiled to expel CO_2 , neutralized with NaOH and 0.5-0.7 g of mannitol added. The monobasic acid formed by the addition of the polyol[29] is titrated with 0.1 M NaOH till the appearance of a rose colour. More mannitol is added and if the solution is decolourized, the titration is continued to the same endpoint. This method was discarded due to the difficulty in judging the endpoint as several colour changes of the mannitol occur near the endpoint. In addition the method is unsuitable for the purposes of this work due to the length of time required to carry out a single determination.

2.2.1.3 Spectrophotometric Determination of Germanium - The Phenylfluorone Method

The technique finally decided upon for germanium analysis was a complexiometric technique in which a germanium-phenylfluorone complex is formed and the absorbance at 510 nm measured. The germanium concentration is then read off a previously prepared calibration curve. Many variations of the method have been described[23-25,27,29], and the chosen method is that described in two publications by the Council for Mineral Technology[35,36].

Germanium complexes with phenylfluorone in the ratio Ge : phenylfluorone = 1 : 2 [29]. Phenylfluorone (Figure 3) is a hydroxy carbonyl derivative of a xanthene and complexes with Ge as $GeL_2(OH)_2$ with the phenylfluorone losing a hydrogen from the 2-hydroxy group then, together with the electron lone pair on the 1-oxygen, bonding to the Ge[29].

The method is rapid, reproducible and suitable for the analysis of large numbers of samples. Thus it is adequate for the purposes of this investigation.

2.2.1.3.1 Method of Spectrophotometric Determination of Ge Using Phenylfluorone

In addition to the sample containing the analyte, the following solutions are required for the phenylfluorone procedure:

(a) Sulphuric Acid - 1 : 1

A 50 % (v/v) H_2SO_4-in-water solution was made up by adding 250 ml of H_2SO_4 (sp. gr. 1.84) to an equal volume of water and then cooling to room temperature.

(b) Gelatin - 5.0 g/l

The gelatin solution was made by dissolving 0.50 g of gelatin in about 30 ml of water with gentle

Structure of phenylfluorone
(2,6,7-trihydroxy-9-phenyl-3-H-xanthen-3-one)

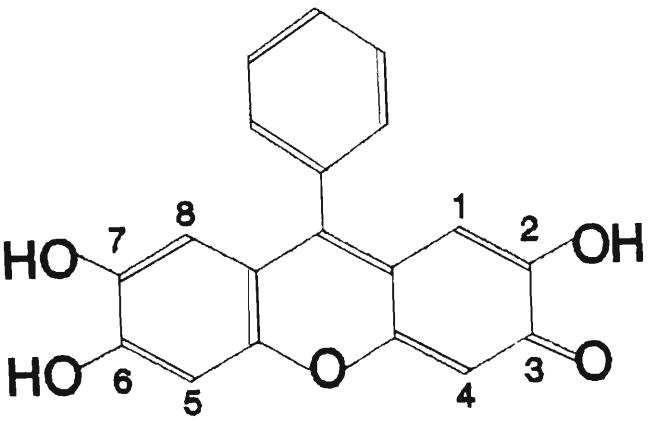


Figure 3

Ge - phenylfluorone calibration curve

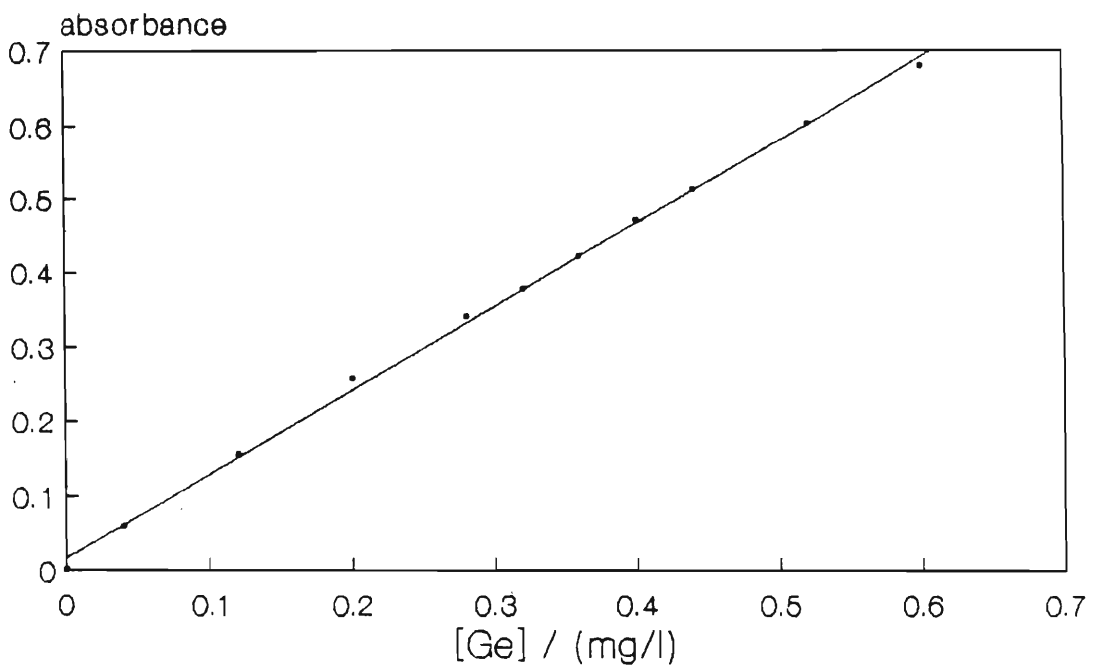


Figure 4

boiling. The solution was then cooled and diluted to 100 ml in a volumetric flask.

(c) Phenylfluorone - 1.0 g/l

The phenylfluorone (0.050 g) was dissolved in 75.0 ml ethanol and 5.0 ml 2.5 M H_2SO_4 by warming gently. The solution was cooled and diluted to 500 ml with ethanol in a volumetric flask.

(d) Standard Germanium Solution - 1.00 µg/l

Germanium Dioxide (0.1441 g) was dissolved in 100 ml hot water made slightly basic with a few drops of saturated NaOH. This solution was cooled and diluted to 500.00 ml, 5.00 ml of this solution was diluted to one litre in a volumetric flask to give a standard Ge solution of concentration 1.00 µg/l.

The procedure for making up the solutions to be used for absorbance measurements is outlined below:-

(1) Between 0 and 15 µg of Ge was transferred into a 25 ml volumetric flask.

(2) 1.40 ml of the 1 : 1 H_2SO_4 solution, 1.0 ml of gelatin and 5.0 ml phenylfluorone were buretted into the 25 ml flask from (1) with mixing after each addition. The solution was diluted to 25.00 ml with water and thoroughly mixed.

(3) The solution was allowed to stand for 90 minutes. A 1.00 cm pathlength glass cuvette was then filled with the solution and the absorbance read off against a similarly prepared blank (i.e. no germanium) at 510 nm in a Varian DMS 300 double beam uv-visible spectrophotometer.

The calibration curve was prepared by carrying out the above steps {(1) to (3)} on 1.00 to 15.00 ml of a 1.00 µg/l Ge stock solution and the absorbance plotted against germanium concentration.

Figure 4 shows a typical calibration curve. The curve in Figure 4 is linear with a correlation coefficient of 0.9994.

2.2.1.3.2 Use of Micropipette in Ge Determination

Because of the high concentrations of germanium in solutions used in the solvent extraction experiments, a technique was required to extract small quantities of Ge in precisely known volumes for the phenylfluorone analysis. Initially, successive dilutions with volumetric glassware was employed, but this method was discarded because of the size of the sample required initially (at least 1 ml) and the laborious nature of the procedure. To ensure accuracy when using successive dilutions, a

reasonably large initial volume of sample was required because available glass pipettes are inaccurate at low volumes. This was a drawback because the removal of a large number of large volume samples would significantly alter the phase ratio in an experiment involving the reaction of two phases; this may alter the reaction kinetics and thus was undesirable.

A micropipette was found to meet all the requirements for sample dilution in that accurate small aliquots of Ge-containing solution can be extracted and directly pipetted into 25 ml flasks for analysis. The micropipettes used throughout this investigation were a 20-200 µl Volac High Precision Micropipette and a 100-1000 µl Volac High Precision Micropipette.

The accuracy of one of the micropipettes used was checked by weighing (with a Mettler balance) aliquots of water pipetted into a 10 ml sample vial and calculating the volume of each aliquot from the density of water at the temperature of the water pipetted. For a 250 µl aliquot the average volume pipetted for 10 repetitions was 253.4 µl with a standard deviation of 0.48 µl. This inaccuracy in aliquots was acceptable for the germanium determination.

2.2.1.3.3 Accuracy of the Phenylfluorone Technique

Work done in this laboratory[33] using the phenylfluorone technique to determine the Ge concentration of a 0.6000 g/l Ge solution gave a result of 0.584 g/l for 10 determinations giving a relative standard deviation of 0.0070 for the 10 determinations, compared to the relative standard deviation of 0.039 obtained by Marshall[32] using atomic absorption spectrophotometry with electrothermal atomization.

In evaluating extractant performance the precision of results is more important than their accuracy since evaluation of extractant performance usually involves comparison of changes in percent extraction of Ge by the extractant under the experimental conditions and not the absolute values of Ge concentration. Thus a precise technique is more important than an accurate one. The phenylfluorone technique adopted in this laboratory for Ge analysis meets the requirement of precision.

2.2.2 Preparation of Germanium Solutions for Kinetic and Equilibrium Extraction Experiments

In this section, the preparation of the aqueous germanium solutions used throughout the investigation is discussed.

All germanium solutions used in this investigation were prepared from GeO_2. GeO_2 exists in four forms[29]: the hexagonal "soluble" form (α-GeO_2), the tetragonal "insoluble" form (β-GeO_2), the cubic form (β-cristobalite) and the amorphous vitreous form. The GeO_2 used in this investigation was the soluble α-GeO_2.

A standard concentration of 0.200 g/l (2.76×10^{-3} M) of germanium was employed throughout this investigation for the aqueous germanium solutions.

Listed below are the germanium-sulphuric acid solutions that were used and the methods of preparation.

(1) 0.200 g/l Ge in 2.00M, 1.00M, 0.50M, 0.25M and 0.10M Sulphuric Acid

A one litre 1.000 g/l Ge solution in water was prepared by dissolving 1.441 g of GeO_2 in 600 ml

slightly basic (a few drops saturated NaOH were added) hot water. The solution was cooled and diluted to one litre in a volumetric flask.

A one litre 4.00 M H_2SO_4 aqueous solution was prepared by adding 217.6 ml H_2SO_4 (98 % sp. gr. 1.84) slowly, with cooling to 500 ml water. The cooled solution was then diluted to one litre in a volumetric flask.

50.00 ml of the 1.000 g/l Ge solution was pipetted into 5 x 250 ml volumetric flasks, 125.00, 62.50, 31.25, 15.63 and 6.25 ml of the 4.00 M H_2SO_4 solution was also added from a burette into the flasks and the flasks filled to the mark.

(2) 0.200 g/l Ge in 1.50 M Sulphuric Acid

GeO_2 (0.2882 g/l) was dissolved in 200 ml slightly basic hot water (few drops saturated NaOH solution). 81.7 ml of H_2SO_4 (98 % sp. gr. 1.84) was added slowly with cooling to 500 ml water. The GeO_2 solution was added to the acid solution in a one litre volumetric flask and cooled, then diluted to one litre.

Table 1 (a) - Composition of buffers used for Ge solutions - Reference 37 (*see Reference 38)

KHP - Potassium hydrogen phthalate

total volume of solutions: 250 ml

approximate pH required	1.0	1.5	2.0	2.5	3.0	3.0*	3.5
measured pH	1.35	1.73	2.30	2.93	3.35	3.07	3.89
Vol. 0.400M HCl (ml)	83.75	25.88	8.13				
Vol. 0.200M KCl (ml)	62.50	62.50	62.50				
Vol. 0.200M KHP (ml)				62.50	62.50		62.50
Vol. 0.100M citric acid (ml)						113.75	
Vol. 0.100M tri-sodium citrate (ml)						11.25	
Vol. 0.100M HCl (ml)				97.00	55.75		

Table 1(b) - Composition of Buffers used for Ge solutions - Reference 37 (*Reference 38)

KHP - Potassium hydrogen phthalate

KDP - Potassium dihydrogen phosphate

total volumes of solution: 250 ml

approximate pH required	4.0	4.0*	4.5	5.0	6.0	7.0
measured pH	4.23	4.10	4.70	5.20	6.05	7.05
Vol. 0.200M KHP (ml)			62.50	62.50		
Vol. 0.100M NaOH (ml)			21.75	56.50	14.00	72.75
Vol. 0.100M citric acid		81.25				
Vol. 0.100M tri-sodium citrate (ml)		43.75				
Vol. 0.100M HCl (ml)	0.25					
Vol. 0.200M KDP (ml)					62.50	62.50

(3) 0.200 g/l Ge Buffered Solutions at Constant Ionic Strength

A 1.000 g/l Ge in water solution was prepared as for (1). Solutions were prepared by adding to a series of 250 ml volumetric flasks the volumes of reagent listed in Table 1 (a) & (b). The total ionic strength was adjusted to 0.500 M with NaCl. 50.00 ml of the 1.000 g/l Ge solution was pipetted into each volumetric flask and the flasks made up to volume.

(4) 0.200 g/l Ge in 1.50 M Sulphuric Acid and 8-hydroxyquinoline

A 1.000 g/l Ge in water solution was prepared as for (1). A 20.00 ml aliquot of this solution was pipetted into 5 x 100 ml volumetric flasks. Masses of 0.10, 0.50, 1.00, 1.50 and 2.00 g 8-hydroxyquinoline were weighed into each flask and 37.50 ml 4 M H_2SO_4 was added to each flask from a burette to give five solutions with 1.0, 5.0, 10.0, 15.0 and 20.0 g/l 8-hydroxyquinoline and 0.200 g/l Ge in 1.50 M H_2SO_4.

(5) 0.200 g/l Ge in 0.50 M Sulphuric Acid with Differing Concentrations Sodium Sulphate

A 1.000 g/l Ge in water solution was prepared as for (1), 20.00 ml of this solution was pipetted into 5 x 100 ml volumetric flasks, 0.025, 0.050, 0.150 and 0.200 moles of Na_2SO_4 was weighed into the volumetric

flasks. 12.50 ml of 4.00 M H_2SO_4 solution was added to each flask to give solutions containing 0.200 g/l Ge in 0.50 M H_2SO_4 and 0.25 M, 0.50 M, 1.00 M, 1.50 M and 2.00 M in Na_2SO_4.

2.3 KELEX 100

This section describes the major extractant used in this liquid-liquid extraction study. The composition of the commercial product is considered and the preparation of the organic solutions containing KELEX 100 is described.

The KELEX 100 used was obtained from Schering Aktiengesellschaft, batch No. Q788. All experiments described in this investigation were carried out using the same batch of KELEX 100.

KELEX 100 has as major component 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline[10] (Figure 5).

To date little work has been published discussing the constituents of KELEX 100. Two papers[10,11] that have been published highlight the fact that although the active constituent of KELEX 100 has remained the same since 1976 (prior to 1976 the active constituent was 7-(1-vinyl-3,3,5,5,tetramethyl hexyl)-8-hydroxyquinoline) the commercial product has been altered in make-up over the years.

2.3.1 Purity of KELEX 100 used

Gareil et al.[11] have identified 10 impurities in

KELEX 100

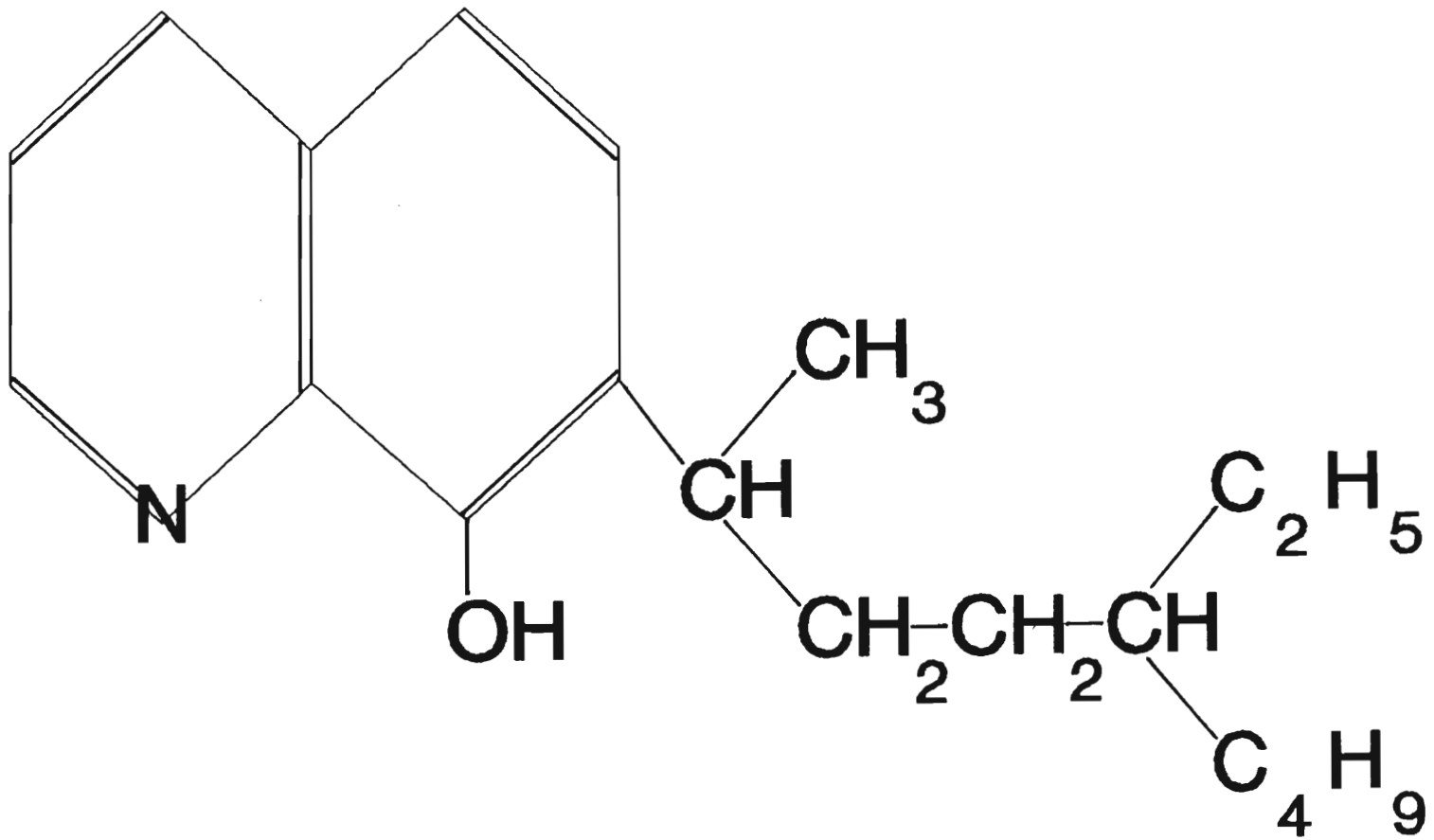
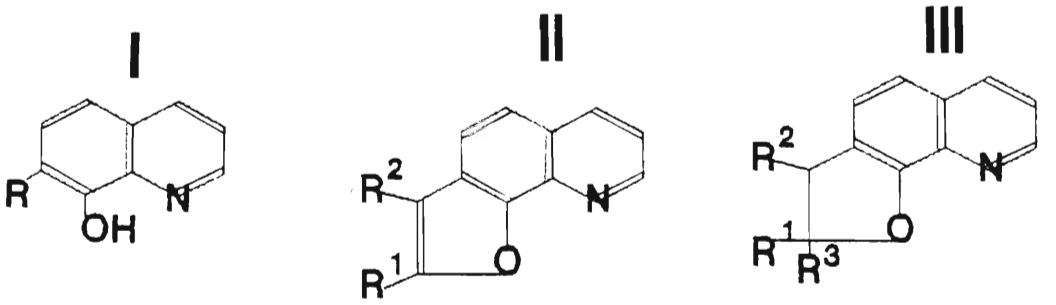


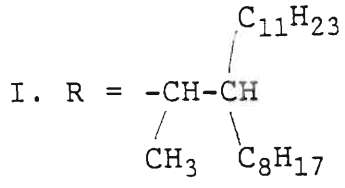
Figure 5

Table 2 - Components of KELEX 100 determined by Gareil et al.[11]



Molecular Weight	Structure	
324*	$C_{11}H_{23}$ CH-C=O C_8H_{17} CH_3	
145	I. R = -H	8-hydroxyquinoline
172*	OH CH_3-CH-CH_2-C_8H_{17}	
257	I. R = $-CH_2-CH(C_2H_5)(C_4H_9)$ = $-C_8H_{17}$	
297	I. R = $-C(CH_3)=CH-CH_2-CH(C_2H_5)(C_4H_9)$	
299	I. R = $-CH(CH_3)-(CH_2)_2-CH(C_2H_5)(C_4H_9)$ = $-C_{11}H_{23}$	KELEX 100

453



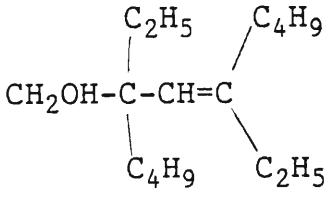
295 II. $R_1 = -C_8H_{17}$ 3-methyl-2-octyl

$R_2 = -CH_3$ furoquinoline

195* II. $R_1 = -H$

$R_2 = -CH{=}CH_2$

240*



451* III. $R_1 = -C_8H_{17}$ 3-hydro-3-methyl-2-octyl undecenyl

$R_2 = -CH_3$ furoquinoline

$R_3 = -C_{11}H_{23}$

* Compounds not identified in the Demopolous and Distin study[10].

Table 3 - Percentage KELEX 100 and Major Impurity in Four Batches of Commercial Grade KELEX 100.[11]

Batch	A	B	C	D
% KELEX 100	86.2	86.6	91.0	92.7
% major impurity	11.2	11.0	7.7	7.1

KELEX 100 using liquid chromatography and mass spectrometry. Their results are given in Table 2. Using liquid chromatography (with a 2 mM copper sulphate in methanol - acetic acid (99 : 1 - v/v) mobile phase and a Spherisorb-phenyl 5 μm stationary phase) and area normalisation of the peaks obtained, percentages of total area for each component were calculated. Table 3 shows the average percentage active component in four different batches of commercial grade KELEX 100 as well as the percentages of the major impurity (the 295 molecular weight compound in Table 2).

Earlier work by Demopoulos and Distin[10] detected some of the impurities found by Gareil et al.[11] and some that they did not, notably a compound of molecular weight 197. Demopoulos and Distin identified this compound as the major impurity in the KELEX 100 sample that they studied. The compound has structure

II in Table 2 with R_1 = -H and R_2 = $-C_2H_5$.

Gareil et al.[11] remark that their inability to detect what was in 1983 a major impurity is a reflection of the improved synthesis procedure for KELEX 100.

Demopoulos and Distin[10] identified all of the components in Table 2 except the ones marked with an asterisk. They calculated the percentage of active component as 82 % with 3.7 % 8-hydroxyquinoline.

A sample of the KELEX 100 used in this study was dissolved in CCl_4 (0.2 g/l) and analyzed by gc-ms on a 5988 A mass spectrometer with 70 eV ionizing energy at ion source temperature 250 ^{0}C and 5890 A Hulett Packard gc. Figure 6 shows the gc chromatogram for a sample of commercial grade KELEX 100. Three components have been detected and Tables 4, 5 and 6 show the mass to charge ratio and percent abundance for each of the three components.

The major peak at 8.687 minutes is the KELEX 100. This can be seen from a large peak at m/z = 299.35, (the molecular mass of KELEX 100 is 299.46). The fragmentation pattern for this peak has been worked out in Table 7.

The peak at 8.179 minutes corresponds to the 324

Gas Chromatogram for KELEX 100

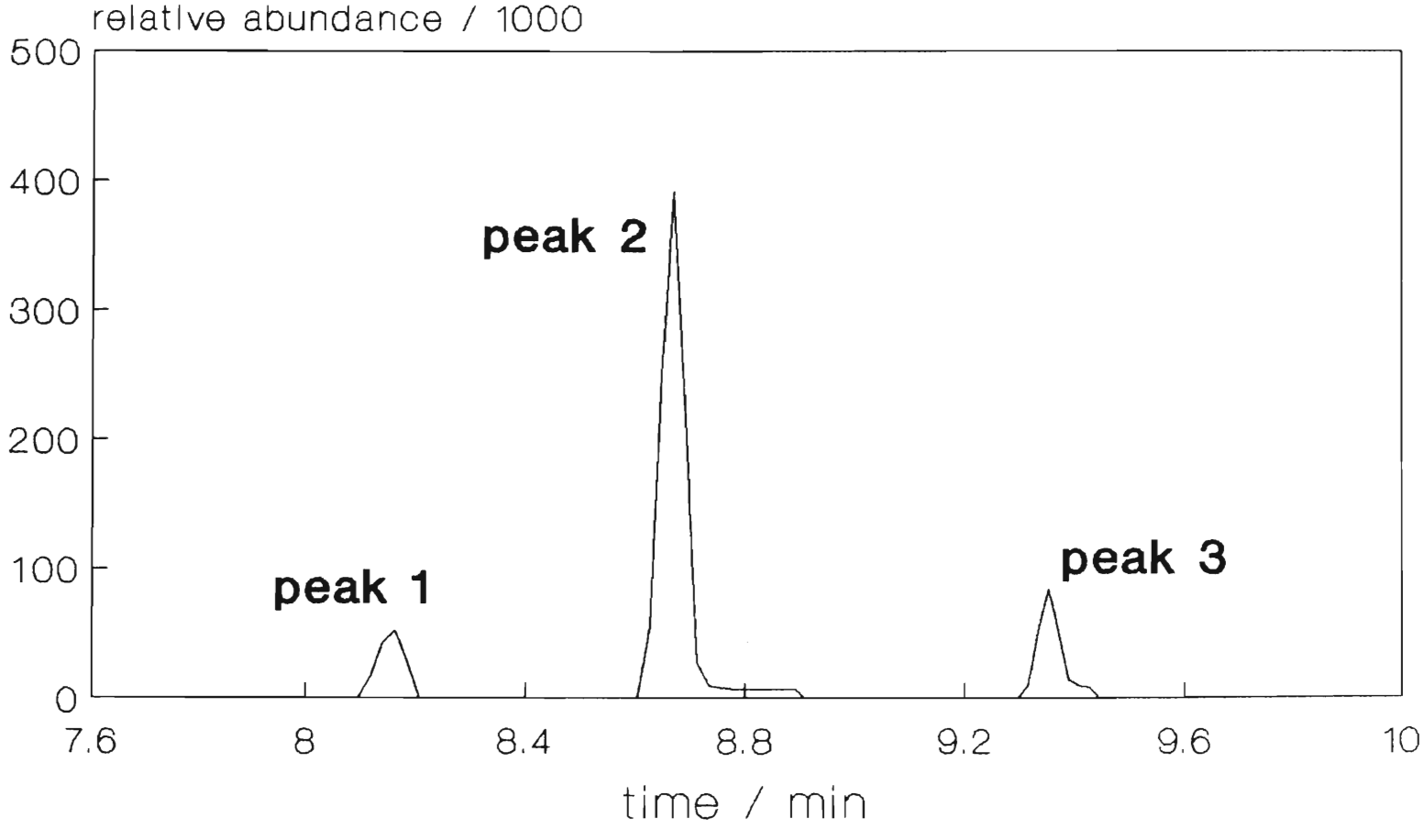


Figure 6

Table 4 - Relative Abundance and Mass to Charge Ratio for Peak 2 in Figure 6.

m/z	abun	m/z	abun	m/z	abun	m/z	abun
41.05	6293	92.20	180	153.25	816	196.35	767
42.05	772	92.40	177	154.25	3485	197.35	216
43.10	3882	101.10	505	155.15	744	198.35	1430
44.10	235	102.10	524	156.25	971	199.25	426
51.00	489	103.10	436	158.15	20632	200.35	11713
52.20	162	104.10	335	159.25	10592	201.35	3648
53.10	649	113.20	239	160.15	1290	202.35	545
54.10	187	114.00	402	166.25	663	212.10	187
55.00	3211	115.10	2529	167.15	1241	228.10	534
56.00	324	116.10	1460	168.25	556	240.10	392
57.10	4114	117.10	2814	170.25	13158	242.20	2643
63.10	446	118.10	640	171.15	2180	243.10	361
64.20	197	126.15	673	172.25	61024	256.20	1875
65.00	389	127.15	1772	173.25	105928	257.20	876
67.10	367	128.15	1834	174.25	11769	270.20	2162
69.10	1058	129.25	777	175.35	806	271.10	519
71.20	312	130.15	2013	178.25	103	282.20	1132
71.70	146	140.15	517	180.25	411	283.20	26
76.10	402	141.25	1652	182.25	767	284.30	1273
77.00	1034	142.25	3434	183.25	1048	285.30	214
78.00	384	143.25	3440	184.25	7861	297.25	528
79.00	291	144.25	3161	185.25	1085	298.25	919
83.10	276	145.25	2456	186.25	17512	299.35	9965
89.00	1188	146.25	4361	187.25	12131	300.35	1957
90.10	432	147.25	572	188.25	1577	301.35	291
91.00	501	152.25	472				

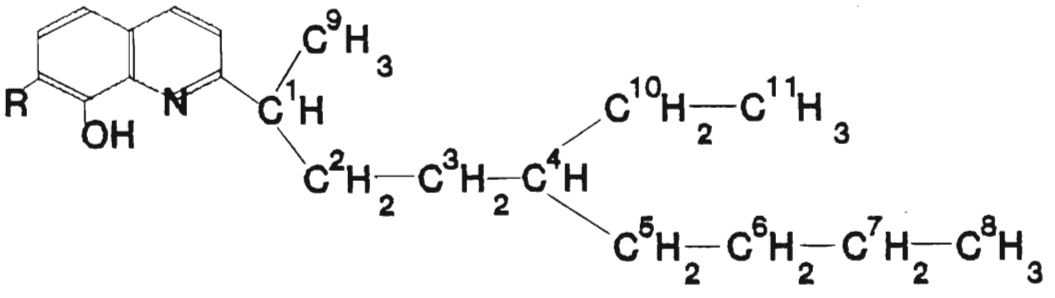
Table 5 - Relative Abundance and Mass to Charge Ratio for Peak 1 in Figure 6.

m/z	abun.	m/z	abun.	m/z	abun.	m/z	abun.
41.05	2385	70.10	1371	99.20	384	171.35	1128
42.05	594	71.10	2439	108.30	131	172.35	202
43.10	2912	72.10	391	109.20	567	179.45	458
53.10	274	79.10	207	110.00	350	183.45	268
53.90	126	81.10	965	111.10	309	194.45	155
55.00	2495	82.00	276	112.10	3308	197.35	3750
56.00	597	83.10	915	113.10	807	198.45	531
57.10	4814	84.00	335	114.20	127	211.20	555
58.00	958	85.10	3329	123.20	679	212.10	205
59.20	297	86.10	276	137.25	608	213.20	698
64.80	123	95.10	898	152.35	1851	225.20	415
67.10	488	96.20	313	153.35	460	239.30	143
68.10	254	97.20	844	154.35	882	295.35	621
69.10	2097	98.10	598	155.35	1171	324.35	430

Table 6 - Relative Abundance and Mass to Charge Ratio for Peak 3 in Figure 6.

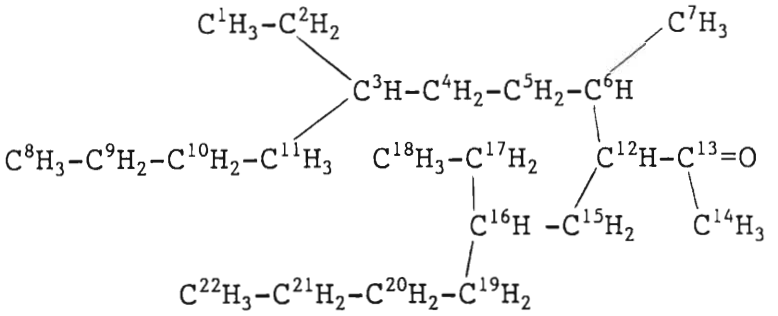
m/z	abun.	m/z	abun.	m/z	abun.	m/z	abun.
41.05	3407	114.10	211	158.25	301	195.25	1237
43.10	1961	115.20	685	166.15	719	196.35	31176
50.30	117	116.20	219	167.25	3349	197.35	10421
51.10	366	117.00	372	168.25	972	198.35	1408
53.10	498	127.15	270	170.35	357	200.35	1665
55.00	859	128.15	230	172.25	378	201.35	304
56.00	223	129.25	119	173.25	220	208.00	516
57.10	1948	139.25	724	177.25	301	210.10	194
63.00	383	140.15	643	178.25	300	222.10	385
65.00	245	141.15	393	180.25	373	238.10	298
69.10	194	142.25	318	182.25	589	240.10	130
77.00	349	145.25	120	183.35	506	266.20	752
78.00	122	151.15	297	184.25	704	295.25	4230
89.00	255	152.25	339	185.35	115	296.25	975
90.00	155	153.15	375	191.25	225	299.35	1528
98.40	105	154.15	485	194.25	768	300.35	285
99.10	136	155.25	226				

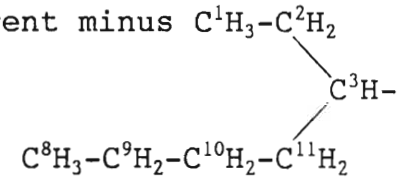
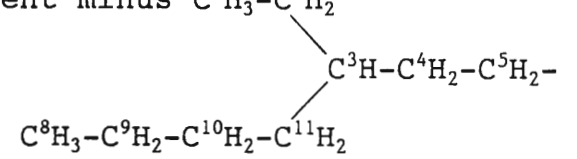
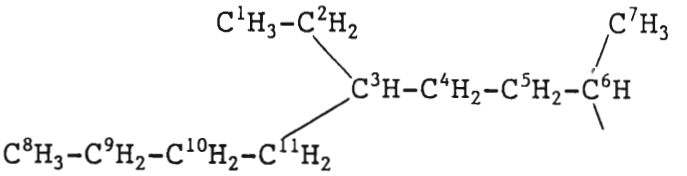
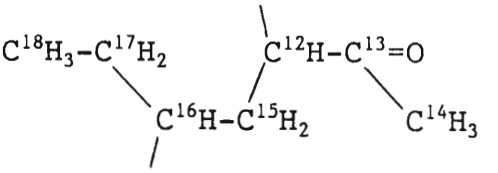
Table 7 - Fragmentation Pattern of KELEX 100 (major constituent)



m/z	Group lost
284.30	$-C^{8}H_{3}$
270.20	$-C^{7}H_{2}-$
256.20	$-C^{6}H_{2}-$
242.20	$-C^{5}H_{2}-$
200.35	$-C^{11}H_{3}-C^{10}H_{2}-C^{4}H$
186.25	$-C^{3}H_{2}-$
173.25	$-C^{2}H_{2}-$
158.15	$-C^{9}H_{3}$
145.25	$-C^{1}H$

Table 8 - Fragmentation Pattern of 324 molecular weight compound



m/z	fragment
295.35	parent minus $C^1H_3-C^2H_2-$
225.20	parent minus 
197.35	parent minus 
155.35	
112.10	
70.10	$C^8H_3-C^9H_2-C^{10}H_2-C^{11}H_2-C^3H-$

57.10 $C^{8}H_3-C^{9}H_2-C^{10}H_2-C^{11}H_2-$

or

$C^{22}H_3-C^{21}H_2-C^{20}H_2-C^{19}H_2-$

43.10

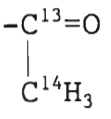
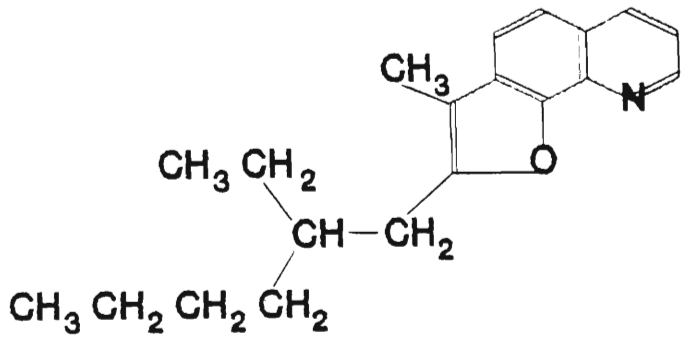


Table 9 - Fragmentation Pattern of 3-methyl-2-octyl furoquinoline



m/z	fragment
196.35	parent minus CH_3-CH_2
167.25	parent minus CH_3- and CH_3-CH_2
57.10	$CH_3-CH_2-CH_2-CH_2-$

molecular weight compound as found by Gareil et al.[11] as can be deduced from the peak at m/z = 324.35 and the splitting pattern in Table 8. The peak at 9.371 minutes corresponds to 3-methyl-2-octyl furoquinoline. The splitting pattern is shown in Table 9. The order in which the peaks are eluted in this work corresponds to the order which Gareil et al.[11] obtained using semi-preparative column chromatography, although the relative peak areas are not in the same ratio. Gareil et al.[11] obtained 3-methyl-2-octyl furoquinoline as the major impurity. These results indicate the sample of KELEX 100 used in this study also has 3-methyl-2-octyl furoquinoline as the major impurity.

The KELEX 100 used in this study does have differences from the KELEX 100 used in Demopoulos and Distin's[10] and Gareil et al.'s[11] studies. If the first peak in the gc chromatogram is entirely attributable to the 324 molecular weight compound, the KELEX 100 used in this study contains more of this impurity than the KELEX 100 analyzed by Gareil and co-workers. The KELEX 100 studied by Gareil et al.[11] contained an average of 0.3 % of this 324 molecular weight compound, the gas chromatogram obtained in this work indicates a concentration in excess of 0.3 %, however, absolute percentages have not been calculated for Figure 6.

The KELEX 100 used in this study has a minimum purity of 84 %, a minimum Cu loading of 90 g/kg and a maximum 8-hydroxyquinoline content of 1.5 %[17]. Percent purity has thus been taken as 84 %.

The difference in product make-up from the 1983 publication by Demopoulos and Distin[10] is not surprising, but the slight difference between the KELEX 100 used in the Gareil et al.[11] study and this study is unexpected and the reason for this can only be attributed to the fact that batch variations in KELEX 100 can affect impurities present in the final product. It is not expected that these batch-to-batch variations will affect the conclusions of this work significantly.

2.3.2 Preparation up of KELEX 100 Solutions

The choice of diluent for the organic phase containing the organic extractant is important since in a variety of liquid-liquid extractant systems the diluent can affect the rate of extraction as well as the percent extraction at equilibrium[15,39,40]. An industrial extraction operation usually uses a kerosene-type organic phase to dissolve the extractant but for the purposes of this study, to ensure reproducibility of the work performed, a pure (reproducible) organic compound had to be chosen.

Previous work in the field of liquid-liquid extraction of germanium from acid solutions[14,15] with KELEX 100 has been done with AR grade toluene, taking the lead from this work the majority of the experiments reported here were performed with this diluent only.

Much work has been done in this laboratory[33,41] attempting to purify KELEX 100. Some of the literature on KELEX 100[42-44] suggests that purification of KELEX 100 is easily accomplished by a few acid washes with dilute sulphuric acid. Work in this laboratory using thin layer chromatography to separate KELEX 100 from its impurities (mobile phase CCl_4, silica gel plates {supplier - Merck} stationary phase) has showed that even after 60 acid washes (1 M H_2SO_4), KELEX 100 still contained some impurities.

The major impurities identified in the KELEX 100 used in this study are unable to extract germanium since one is a branch-chained hydrocarbon and the other is a furoquinoline dervative. Both molecules do not have the required chelating sites (the furoquinoline derivative cannot lose a hydrogen on the oxygen in the furan ring because the oxygen atom has no hydrogen). The only effect these components would thus have on extraction would be similar to

that of introducing small amounts of foreign inactive diluent causing changes in the dielectric strength, viscosity of the medium and interfacial blocking if they are interfacially active, as well as other indirect factors which may influence extraction. These effects are not expected to be of major significance to the conclusions of this work.

One of the starting materials for the synthesis of KELEX 100 is, of course, 8-hydroxyquinoline and unreacted 8-hydroxyquinoline is another minor impurity in commercial grade KELEX 100. 8-Hydroxyquinoline has been shown to complex certain metal ions[42,45-47]. However work presented in this thesis shows that the presence of 8-hydroxyquinoline does not affect the rate or position of equilibrium for germanium extraction under the conditions of the extraction study.

Limited success has been obtained with silica gel column chromatography in isolating the active component of LIX 26 in this laboratory[33] (LIX 26 is a 7-alkylated 8-hydroxyquinoline derivative). But the amounts of "pure" product obtained were very small (± 0.1 g) and this technique would be therefore impractical for purifying large amounts of KELEX 100 required for the experiments described in this work.

With these factors in mind it was decided to prepare all KELEX 100 solutions from the material as supplied and use the percentage purity to estimate actual extractant concentrations where necessary. This practice has the advantage that results obtained are more informative regarding extractant performance in an industrial environment since the experiments have been conducted with the extractant in the form in which it is most likely to be commercially used.

2.3.2.1 KELEX 100 in Toluene Solutions

Solutions of KELEX 100 were made up as required by dissolving the appropriate mass of KELEX 100 in toluene (masses measured to two decimal points). The maximum concentration of extractant used was 300 g/l of KELEX 100 and this amount easily dissolved in the toluene.

2.3.2.2 KELEX 100 in Toluene Solutions Containing Alcohol Modifiers

A series of experiments were conducted with KELEX 100 dissolved in toluene containing an alcohol modifier. In each case 10.00 g KELEX 100 was placed in a 100 ml volumetric flask then 10.00 ml of the alcohol to be studied was added to the flask, the

solution was then made up to volume with toluene. The effect of benzyl alcohol, octanol, pentanol, butanol and propanol on rate of extraction was studied.

2.3.3 Properties of KELEX 100

A series of experiments were conducted to examine the behaviour of KELEX 100 under certain conditions with a view to providing information that would be useful in proposing a mechanism for extraction of germanium and for using a computer program to attempt a kinetic simulation of the mechanism proposed. These experiments are discussed below and the implications of these experiments are discussed later.

2.3.3.1 **Infra-Red Spectra of KELEX 100**

A series of KELEX 100 solutions in CCl_4 were prepared. The infra-red spectra of approximately 1, 4, 10, 20, 50, 100 and 200 g/l solutions (actual masses measured to two decimal points) were measured on a Pye Unicam SP-3-300 Infra-Red Spectrophotometer in a cell with NaCl windows and 0.10 mm thickness over the range 4000 cm^{-1} to 2000 cm^{-1}. By examining the validity of Beer's law for the absorbance of the hydroxy and methyl/methylene peaks this experiment

would provide information about extractant self-association at high extractant concentration.

2.3.3.2 Ultra-violet spectra of KELEX 100

KELEX 100 was dissolved in hexane to give a series of solutions of approximately 10, 20, 40, 70 and 100 g/l (masses measured to two decimal places). The absorbances of the solutions at 400 and 450 nm were measured versus a hexane blank on a double beam Varian DMS 300 uv-visible spectrophotometer. The examination of the validity of Beer's law for the absorbances at 400 nm and 450 nm would reveal if extractant dimerization or further self-association occurred.

2.3.3.3 Viscosity Measurements - KELEX 100 in Toluene

The viscosities of pure toluene and solutions containing approximately 50, 75, 100, 125, 125, 150, 200 and 300 g/l KELEX 100 in toluene were determined using a Ubbelohde viscometer. The viscosities of the solutions were then calculated using Poiseuille's Equation. The possibility that viscosity had some effect on the interfacial area of a rapidly mixing two phase system was considered. Although the precise nature of the effect on interfacial area is not known, the existence of large changes in organic

phase viscosity could contribute to decreased reaction rates as extractant concentration increases.

2.3.3.4 Interfacial Tension Measurements for the KELEX 100 in Toluene / 1.50 M Sulphuric Acid System

The following solutions of KELEX 100 in toluene were prepared: 0.10, 0.20, 0.50, 1.00, 2.00, 4.00 and 10.00 g/l. The interfacial tension of 20 ml of each solution was measured against 20 ml 1.50 M H_2SO_4 using a Torsion Balance manufactured by White Electrical Co. LTD, Worcestershire, England. The instrument uses a platinum ring of exactly 1 cm diameter and measures the force required to pull the ring away from a surface. The force required to pull the ring away from this surface is proportional to the surface tension or the interfacial tension associated with the surfaces. The instrument is calibrated in units of interfacial/surface tension (N/m).

To ensure the accuracy of each measurement, the platinum ring was cleaned with chromic acid (made by dissolving 5 g $K_2Cr_2O_7$ in 200 ml H_2SO_4), rinsed with water, then with acetone then dried. The accuracy of the instrument was checked regularly by measuring the surface tension of deionized water.

For each reading the ring was suspended inside a dish supplied with the instrument. The ring was carefully covered with the acid phase then the organic phase carefully poured above the acid phase. The two phases were equilibrated for ten minutes before each reading was taken.

For comparison the interfacial tensions were measured for the above organic solutions versus an acid phase containing 0.200 g/l Ge in 1.50 M H_2SO_4. These measurements were made to check if the germanium in the aqueous phase had any effect on the surface activity of the KELEX 100 in the two phase system.

2.4 LIX 26

LIX 26 was used as an extractant to allow a comparison to be made with similar experiments carried out using KELEX 100 as the extractant. The use of LIX 26 comprised a minor portion of the study presented here as its extractant behaviour in germanium extraction is the subject of another investigation performed in this laboratory[33].

LIX 26 is a commercially available 7-alkylated 8-hydroxyquinoline derivative. It differs from KELEX 100 in the alkyl side group. Rao and Ramesh[60] have published some preliminary experiments using this extractant to extract a series of metal ions.

The structure of LIX 26 has not been published, but is believed to be the structure indicated in Figure 7[33].

The LIX 26 used in this investigation was used as supplied and is approximately 76 % pure[18].

LIX 26

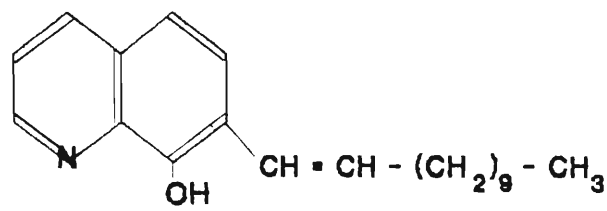


Figure 7

2.5 KINETIC EXPERIMENTS

Three different experimental approaches were used to study the germanium-KELEX 100 liquid-liquid extraction system. In this section these three approaches are analysed and discussed. The kinetic experiments performed using each experimental technique are described in each section.

2.5.1 The AKUFVE

The AKUFVE is a device described in a number of publications that appeared in the late '60's and early '70's[48-55]. The apparatus was first described in 1967 by Reinhardt and Rydberg[48]. The word AKUFVE is a Swedish acronym for "apparatus for continuous measurement of distribution factors in solvent extraction". The original purpose of the instrument was thus to provide a reliable, fast method of determining distribution curves for an analyte of choice between an organic and an aqueous phase. The general flow diagram for the AKUFVE is shown in Figure 8.

The apparatus consists of a mixer (one litre capacity) and a centrifuge (140 ml capacity) with the appropriate valves, flow meters, detector loops, heat exchangers and connections (directing fluid

General flow diagram for AKUFVE

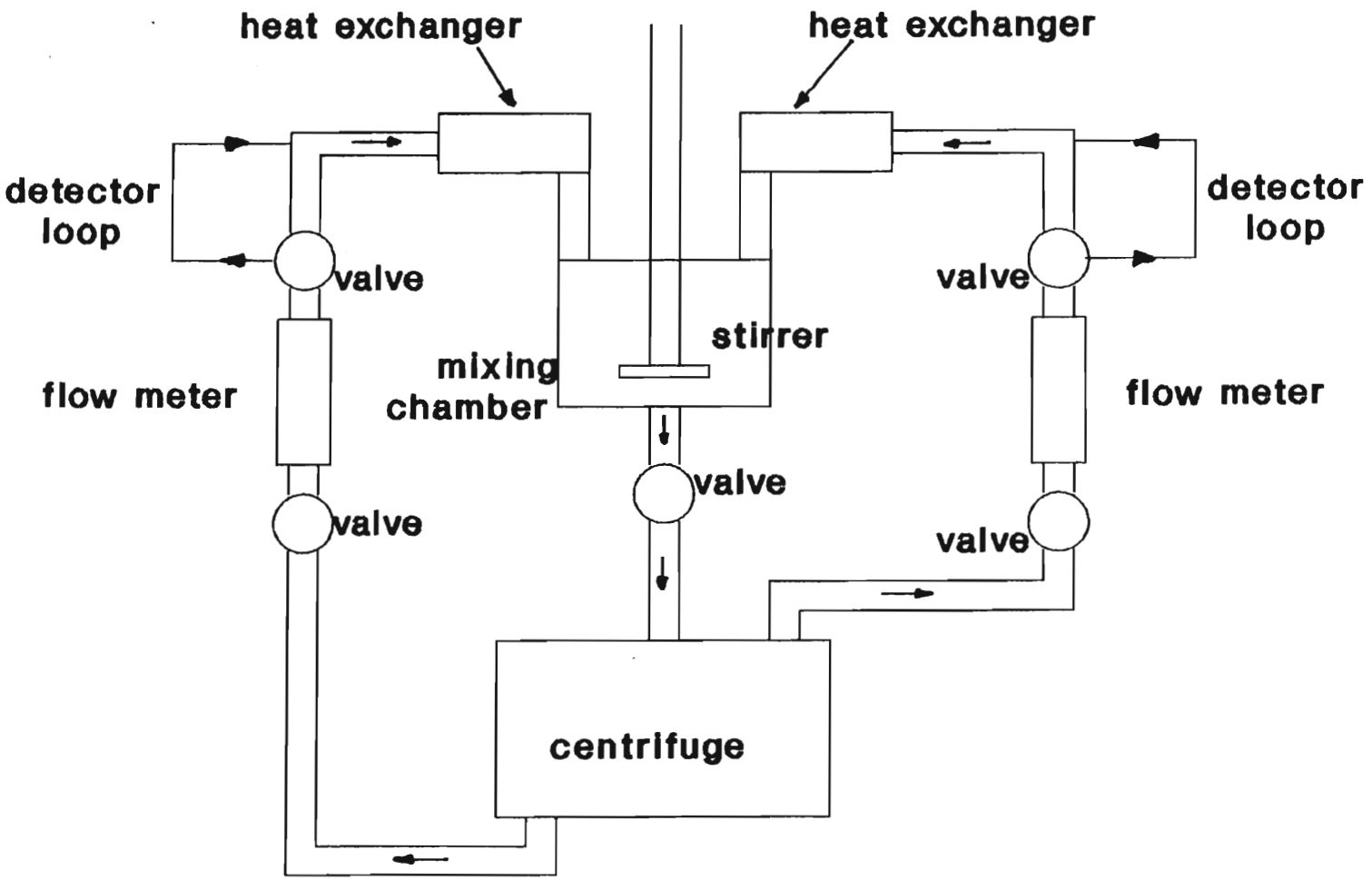


Figure 8

flow between the various components) making the apparatus a working unit. The organic and aqueous phases are mixed thoroughly in the mixer. They run down into the centrifuge which separates the organic and aqueous phases. The analyte of interest can now be detected in either phase with an appropriate technique. The two phases are then passed through a heat exchanger (i.e. thermostat) then returned to the mixer. The mixer also has openings in its lid to allow additions of any required reagent to the mixing phases during the course of an experiment.

2.5.1.1 The Perfect AKUFVE

In a subsequent and more comprehensive publication[49] describing the AKUFVE, Rydberg describes the "perfect AKUFVE" and using the description of this ideal instrument, Rydberg assesses the limitations of the real AKUFVE.

The "perfect" AKUFVE has:-

(i) instant mixing of the phases and instant phase separation,

(ii) the ability to vary mixing time and the time from mixing to separation from zero upwards,

(iii) no time lag between separation and detection,

(iv) absolute phase separation,

(v) the ability to use a large variety of detection

systems - eg. radiometric, spectrophotometric, refractive index, pH,

(vi) small liquid volumes (for dangerous and/or expensive substances).

Criteria (v) and (vi) are easily met with the AKUFVE apparatus. Criterion (iv) is usually met with the correct adjustments to the centrifuge speed and/or flow rates of the aqueous or organic phases leaving the centrifuge. Criteria (i) to (iii) are not met with the real AKUFVE but with correct design the limitations introduced by the deviations from the ideal are usually acceptable.

Physical two phase equilibrium in a vigorously stirred system is achieved in less than 1 second[49]. These conditions apply in the AKUFVE. Rydberg[49] shows by calculation that separation time for absolute phase separation is heavily dependent on droplet size, the smaller the droplets, the longer the time taken for phase separation. Actual separation time is of the order of a few seconds and depends on droplet size. Thus criterion (i) is not met fully by the real AKUFVE. For criterion (ii), separation time can only be varied from the minimum actual separation time upwards and not from zero.

The time lag from phase separation to detection

depends on the flow rate of the liquid stream leaving the centrifuge and the length of the connection from the centrifuge to the detection system. This time lag is of the order of a few seconds. Criterion (iii) is thus not fully met.

Absolute phase separation (i.e. no droplets of one phase present in the other - no phase contains more of the other phase than solubility permits) is a desirable feature of the AKUFVE because many detection devices require clear phases, for instance droplets of a foreign phase seriously alter optical densitometry and refractometry.

2.5.1.2 The H - Centrifuge

To meet the requirements of the AKUFVE design objective, an efficient means of phase separation had to be found or developed. Outlined in this sub-section is the description of the phase separation set-up used in the AKUFVE.

A consideration by Rydberg[49] of available phase separation techniques showed only the liquid flow type centrifuge could meet all the requirements of the AKUFVE. Reinhardt and Rydberg[50] trace the development of the centrifuge used in the AKUFVE in their 1969 publication. Figure 9 shows a schematic

of liquid phase separation in a rotating bowl.

The distance the inflow liquid has to travel before phase separation is achieved is dependent on the mechanical arrangement of the centrifuge and the operating conditions of the centrifuge (flow rate, centrifuge speed, temperature etc.). Tests conducted on commercially available centrifuges highlighted the need to design a new type of centrifuge to meet the demands of the AKUFVE. A centrifuge was designed which was named the H - centrifuge for use in the AKUFVE[50]. The centrifuge is depicted in Figure 10.

The mixture enters the centrifuge bowl and is accelerated at (1). Separation occurs in the separation chamber (2). The separation chamber contains eight individual chambers separate from each other. The liquid flows in a zig-zag manner through the chambers with the light phase collecting above and the heavy phase below. The light phase goes to the collecting chamber (3) and a (dynamic pressure) turbine pump wheel at (3) pumps the light phase to the detector, then the mixer. The heavy phase goes to the collecting chamber (4) where a (potential pressure) pump pumps the heavy phase up to the detector system then back to the mixer.

The centrifuge system develops heat from friction of

Schematic of liquid phase separation in a rotating bowl (reference 50)

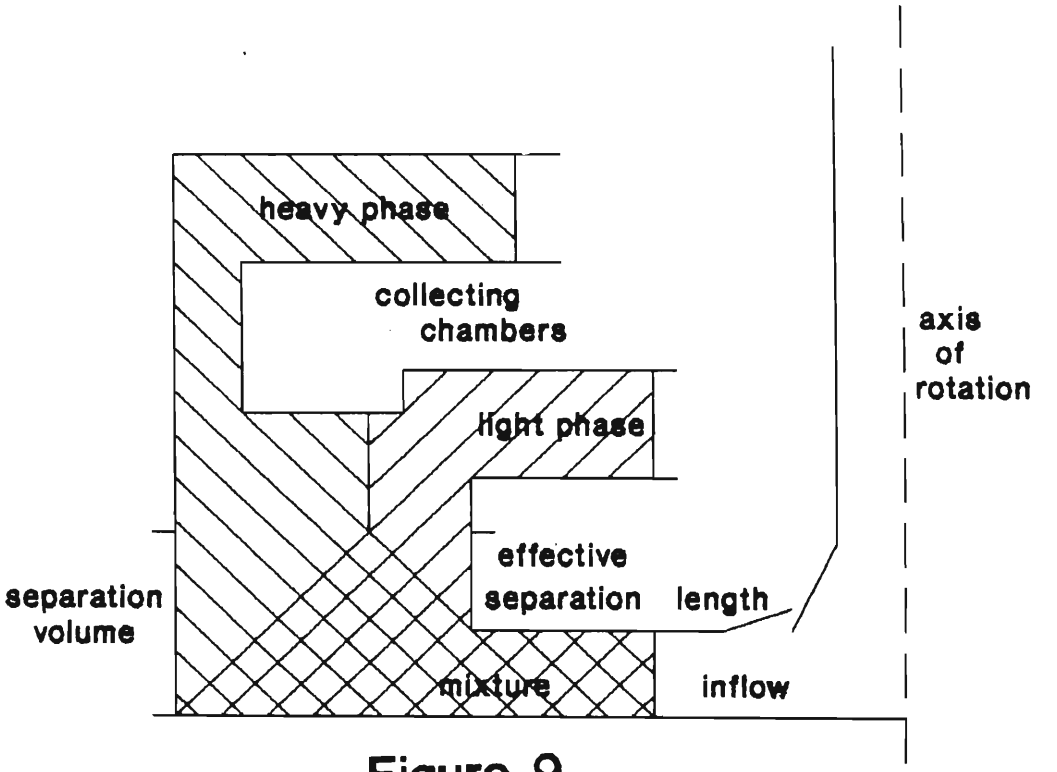


Figure 9

The H - centrifuge (reference 50)

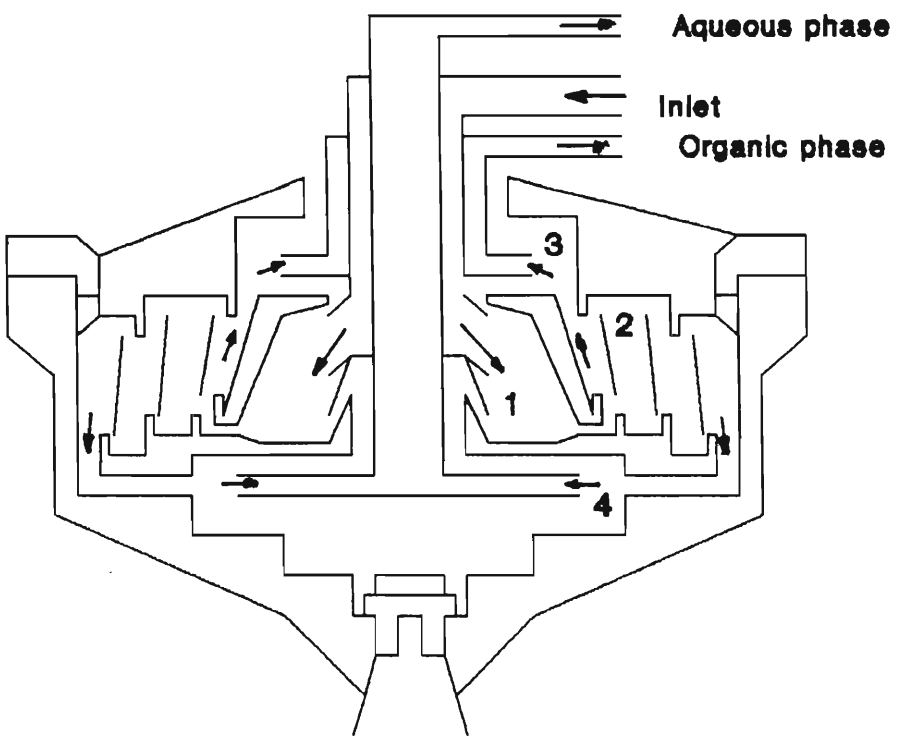


Figure 10

the liquid during acceleration and retardation, necessitating the introduction of a heat exchanger system to cool the separated phases before returning to the mixer.

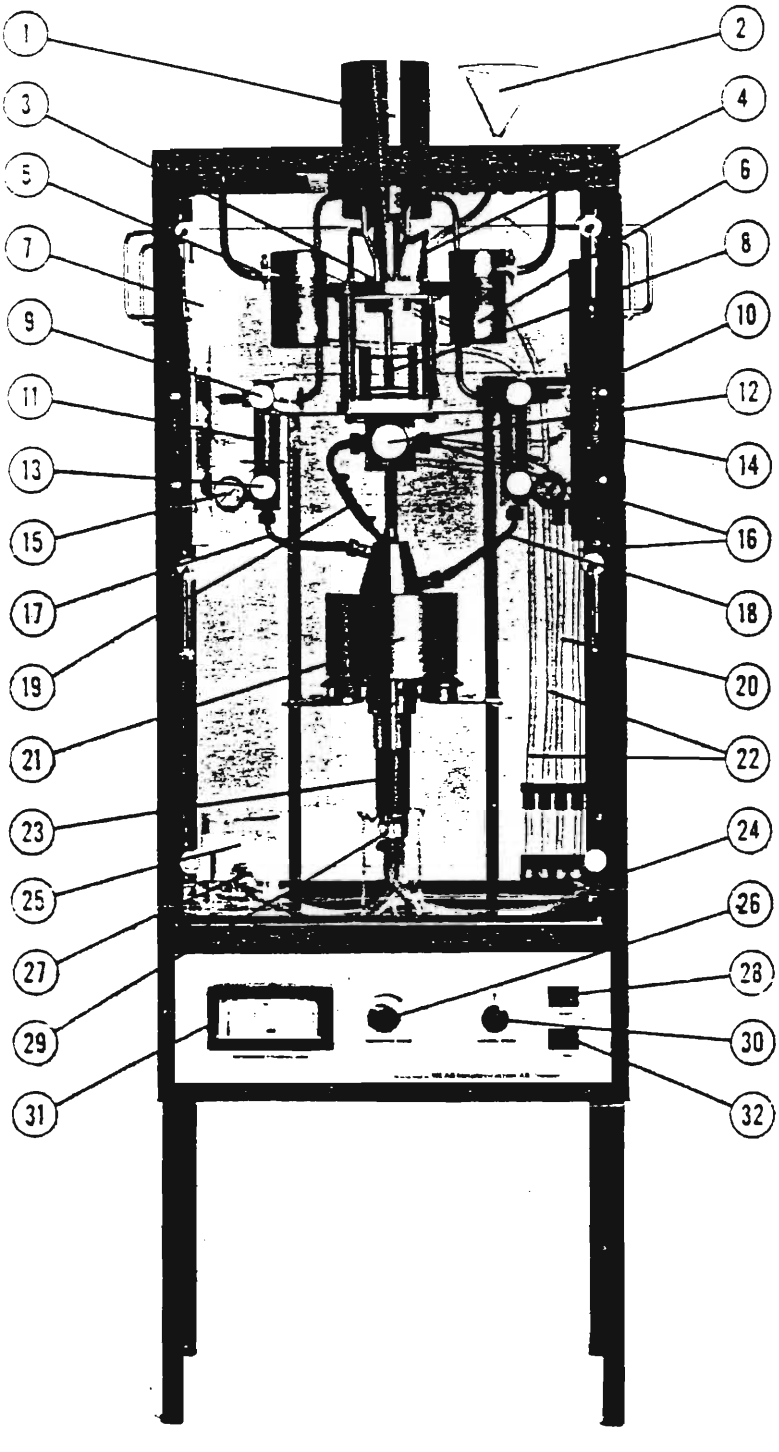
Often as the centrifuge starts operating complete separation of one or both phases is not achieved but by increasing the hold-up time of one or both phases in the centrifuges by slightly closing the appropriate valves [indicated (13) in Figure 11] phase separation can be achieved.

The H - centrifuge can achieve a hold-up time of five seconds for a centrifuge volume of 150 ml and a rotation speed of 10 000 r.p.m.

2.5.1.3 **Approach to Mixing Equilibrium**

The AKUFVE has a laminar volume (in the pipes connecting the centrifuge to the mixer and in a portion of the centrifuge) and a turbulent volume (mainly in the mixer). If a change is made in the chemical composition in the mixing chamber e.g. if more ligand or more metal ion is added, it will take a period of time for mixing equilibrium to be established in the entire liquid volume. In the AKUFVE used in this investigation, this time is about 20 seconds[58]. This fact is important if

The AKUFVE (reference 58)



1. Stirrer motor
2. Main feed inlet
3. Burette inlets
4. Connection to thermistor
5. Sampling valve
6. Heat exchanger
7. Lamp
8. Mixer
9. Directing valve DETECTOR - MIXER
10. Glass cell
11. Flow meter
12. Directing and regulating valve CENTRIFUGE - CLOSED - DRAIN
13. Throttling valve
14. Detector outlet
15. Pressure gauge
16. Connection to drain

17. Centrifuge outlet, heavy phase
18. Centrifuge outlet, light phase
19. Centrifuge inlet
20. Once-through inlet
21. Centrifuge
22. Connections for heat exchangers
23. Centrifuge motor
24. Compressed air for centrifuge
25. Silencer
26. Throttling valve
27. Inlet silencer
28. Mixer switch
29. Centrifuge drain
30. Control potentiometer, stirrer speed
31. Pressure gauge, pressure air motor
32. Illumination switch
16. Connection to drain

Figure 11

reaction kinetics are studied by adding a reagent (e.g. a concentrated metal ion solution) to an already circulating aqueous and organic phase in the AKUFVE and then by monitoring the changes in concentration of the reagent in one of the phases. It must be recognised that because of the 20 seconds pre-equilibration period reactions with fast extraction kinetics will be incorrectly monitored using the AKUFVE.

2.5.1.4 Detection of Analyte in an AKUFVE Experiment

A feature of the AKUFVE is the facility for on line detection of an analyte of interest in the aqueous or organic phase. For this feature to be used to its maximum potential, methods of detection should be used that involve no pre-analysis sample preparation and that can be performed on a flowing stream of solution containing the analyte. Techniques that can be used include spectrophotometry, conductivity, refractive index measurement and scintillation counting of a radioactive isotope of the analyte (particularly in the case of some metal ion under investigation).

To date, some of the methods used in published results obtained using an AKUFVE with on line detection include scintillation counting (of a

radioactive isotope)[48,51,52,54,57] ion selective electrode potentiometry[56] and spectrophotometry[53]. The collection of vast amounts of data in the form of various analyte concentrations at various times is facilitated by the use of computer data logging with an appropriate program to make data processing easier. This has been done with some success[55,57]. Such datalogging was not available for this work because: (a) the funding was not available, (b) a suitable computer set-up was not available, and (c) the rate of data collection required for the kinetic process examined in this project was not rapid enough to warrant a computer aid in data processing.

As well as the constraints (a), (b) and (c) above, the system studied in this project was unsuitable for on-line detection of germanium. The use of radiometry not possible due to the lack of a source of a radioactive isotope of germanium. No other suitable on-line method of germanium analysis in the aqueous phase was found. Germanium analysis in the organic phase was also impractical for the same reasons. Thus an important advantage of the AKUFVE could not be used.

2.5.1.5 Specifications of the AKUFVE used in this Work[58]

The AKUFVE used in this investigation was a model 110, manufactured by Metallextraktion AB, Sweden, designed at the Chalmers University of Technology, Sweden. All parts of the device in contact with the solutions studied were made of glass, teflon or palladium passivated titanium. The instrument was thus suitable for the study of a large variety of liquids. The apparatus consisted of (1) a mixer (volume 1.0 dm^3) (2) a centrifuge (volume 140 ml) (3) a variety of flow paths, flow meters, valves and heat exchangers as indicated in Figure 11.

The AKUFVE required 220 V, 50 Hz, 500 W ac current to provide power for the illumination lights and the stirrer motor. The centrifuge was powered by a pneumatic motor designed to operate with air supplied at a pressure of 6 to 7 kg/cm^2 (6 to 7 atmospheres) giving a maximum rotation speed of 18 000 r.p.m. The pneumatic motor was lubricated with an automatic oil fog lubricator placed between the compressed air source and the inlet to the pneumatic motor.

2.5.1.6 Repair of the AKUFVE

The AKUFVE used in this project was loaned to the University by the Institute for Mineral Technology and when the instrument was first received it was non-functioning.

The variable resistor controlling the speed of the stirrer motor in the mixer had several breaks in its copper windings. A comparison of the electronic circuitry inside the AKUFVE with the circuit diagram supplied in the AKUFVE Manual for Operation and Maintenance[58] showed several inconsistencies. The stirrer motor had a break in its copper circuit. The three way valve at the bottom of the mixer [(12) in Figure 11] was blocked with previous solutions that had not been washed out properly.

Once these faults were detected and rectified, the AKUFVE was operational.

2.5.1.7 Air Supply for the AKUFVE

Initially the centrifuge was run at a pressure of 3.5 bar with air from a compressed air cylinder (approximate capacity 50 dm^3 at 17 MPa). The lifetime of the air in the cylinder was approximately 30 minutes. Although the centrifuge is

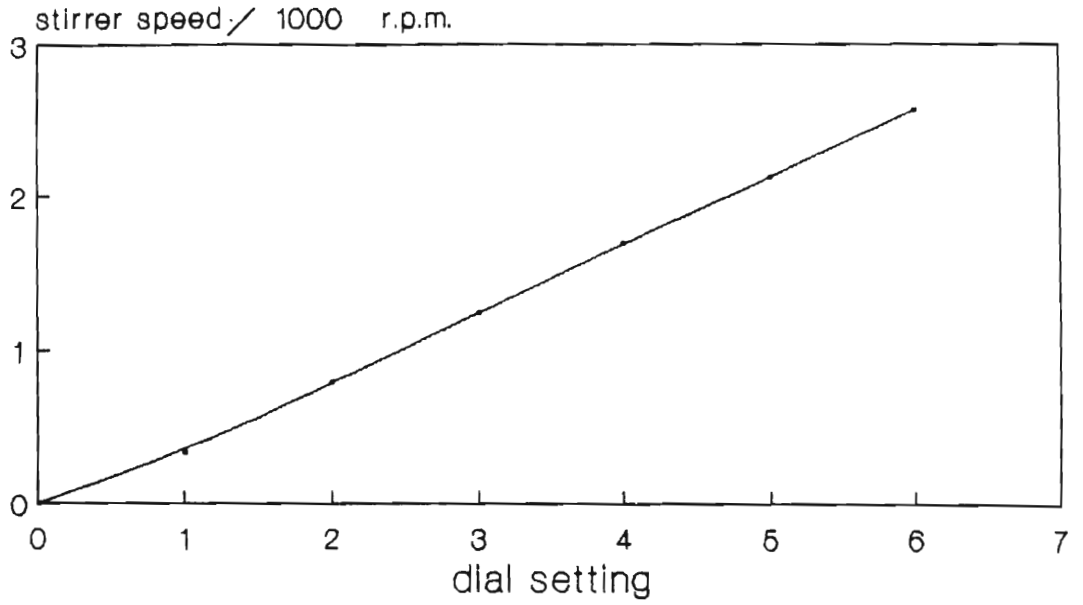
designed to operate with 6-7 bar compressed air, a pressure of 3.5 bar (350 kPa) was sufficient to yield a completely pure aqueous phase. Since analyses of germanium were performed on aqueous phase samples, this pressure of compressed air was satisfactory.

The short length of time available for experiments (± 30 minutes) using compressed air cylinders necessitated the use of a better and longer running source of air. This requirement was met with the purchase of a 50 l tank capacity, 1.5 Kilowatt air compressor (supplier - Balma S.A). This compressor could supply air at the required flow rate and 350 kPa for any specified time period.

2.5.1.8 **Experiments performed using the AKUFVE**

Figure 12 shows the stirrer speed in r.p.m. versus dial setting on the variable resistor controlling stirring speed. The stirrer speed was determined with an EE-2 SHIMPO Hand Digital Tachometer. All AKUFVE runs were carried out at stirring setting 3 after an initial investigation of extraction rate dependence on stirrer speed showed that at the operating stirrer speed (dial setting 3 in Figure 12) the extraction rate was independent of stirrer speed.

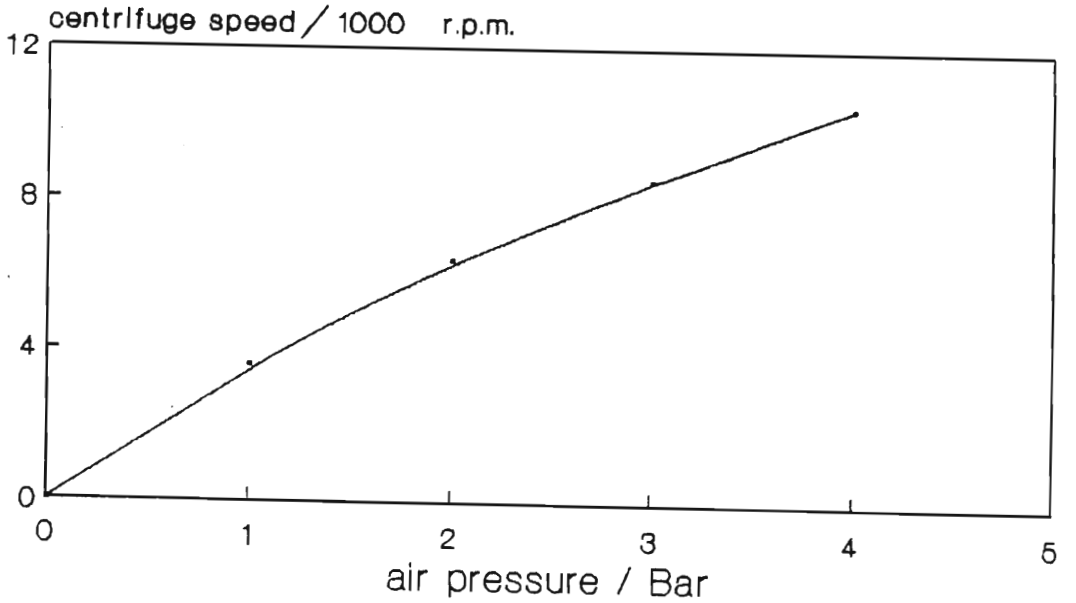
Stirrer speed versus dial setting for AKUFVE mixer



Stirrer speeds measured with appropriate fluid volume in mixer .

Figure 12

AKUFVE centrifuge speed versus air pressure



Balma VD2 50 Litre Air Compressor

Figure 13

Figure 13 shows the centrifuge rotation speed (while empty) in r.p.m. versus applied air pressure. Centrifuge speed was determined with an EE-2 SHIMPO Hand Digital Tachometer. All AKUFVE experiments were conducted with air at a pressure of 350 kPa flowing into the centrifuge pneumatic motor.

Before each and every extraction experiment, the apparatus had to be cleaned and dried out. This was done according to the following procedure:[58]

(1) The AKUFVE was drained of any remaining solution by turning the three way valve at the bottom of the mixer to DRAIN (valve 12 in Figure 11).

(2) Approximately 800 ml water was poured into the mixer and with the stirrer on, the water was cycled through the centrifuge by turning the three way valve (valve 12 in Figure 11) to CENTRIFUGE.

(3) After a period of 30 seconds the water was drained, step (2) was repeated until the water cycling through the AKUFVE had a clear appearance.

(4) The apparatus was then washed three times with 400 ml alcohol as for step (2). This step removed all traces of organic matter in the system.

(5) The centrifuge and mixer were then switched off and the centrifuge dismantled. This dismantling was essential because the centrifuge always retained some of the solution that was last circulating in the AKUFVE, this solution had to be removed so that it did not contaminate the next experiment.

(6) The dismantled centrifuge, the mixing unit and the flow system were then dried with compressed air. The apparatus was then reassembled for the next experiment.

Care must be taken when dismantling and reassembling the centrifuge. The entry and exit streams of liquid in the centrifuge are sealed from each other by means of Viton O-rings. These O-rings were easily damaged and damage to these O-rings was often the cause of leakages and therefore material loss in an experiment conducted using the AKUFVE.

Measurements of distribution of analyte (e.g. Ge) versus pH, ligand concentration, ionic strength etc. were not performed using the AKUFVE because of the length of time required for the Ge/H_2SO_4 // KELEX 100 /toluene system to reach equilibrium. Because this could take hours in some cases the use of a more conventional shaking technique whereby organic and aqueous solutions are equilibrated by shaking them

together in a wrist action shaker was more efficient. Only kinetic experiments were performed using the AKUFVE.

The AKUFVE was used to study the kinetics of germanium extraction for the following solutions shown in Table 10.

Table 10 - Solutions used for kinetic studies in AKUFVE

Aqueous phase	Organic phase
0.200 g/l Ge in 1.50 M H_2SO_4	25.00 g/l 35.00 g/l 50.00 g/l KELEX 100 75.00 g/l and 100.00 g/l LIX 26 150.00 g/l in toluene 200.00 g/l

Kinetic experiments were conducted by allowing the centrifuge to build up to maximum speed with 350 kPa of compressed air driving the pneumatic motor. The aqueous Ge solution was poured into the mixing chamber, then the organic solution was added as quickly as possible. The stirrer was switched on (at the correct stirring rate) and the valve to the centrifuge was opened simultaneously as the kinetic run was started. Adjustments to the valves [(13) in

Figure 11] were made to provide a clear aqueous phase as quickly as possible.

Samples of the aqueous germanium solution were withdrawn at appropriate time intervals from the aqueous germanium exiting the centrifuge. The aid of a "detector loop" in which aqueous sample continuously passed was required. Liquid flow through the loop could be stopped using a valve on the aqueous outflow circuit so that a small aliquot (70.0 µl) of aqueous solution could be withdrawn for analysis via the phenylfluorone technique.

A concentration of 0.200 g/l Ge was chosen for the aqueous germanium solutions because at this concentration of germanium (0.00276 M), the lowest concentration of ligand (25.00 g/l - 0.08360 M) is in a 30-fold excess over the Ge concentration. This is sufficient for the concentration of extractant to be considered constant during the extractant runs using the lowest ligand concentrations.

Phase volumes of 300 ml organic and 300 ml aqueous phase were chosen for all experiments. All experiments were conducted with the reactants thermostatted to 25 ^{0}C ± 1 ^{0}C.

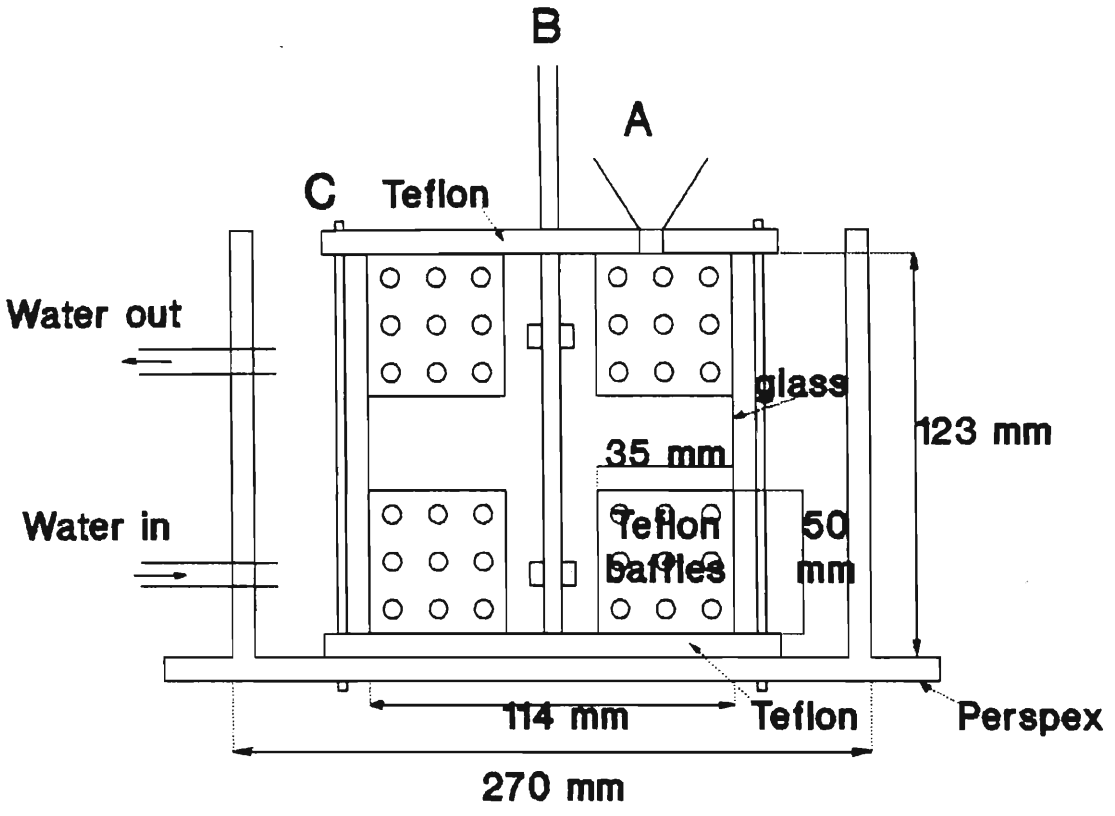
2.5.2 The Lewis Cell

A series of extraction experiments were conducted in a quiescent interface cell. These types of experiments were originally described by Lewis[59] in 1953. The cell (named after its innovator) is designed to examine a solvent extraction process under conditions where the interfacial area is constant and measurable. This enables mass transfer coefficients across the interface to be calculated. Because of the relatively low surface area available for mass transfer from organic to aqueous phases and vice versus, reaction rates are slow. Because of the long times required to reach equilibrium (t~3 days for 75.00 g/l KELEX 100 in the organic phase) the apparatus is obviously unsuitable for equilibrium extraction studies and only reaction kinetic parameters are suitable for examination.

2.5.2.1 **Description of Lewis Cell**

A diagram of the Lewis Cell used in this investigation is shown in Figure 14. The cell consists of a glass tube of 114 mm diameter inside a perspex container. The perspex container had a teflon base and the glass tube was bolted onto the base with a teflon covering sealing the glass tube and forming a cell with an opening for a stirrer and

Diagram of the Lewis Cell



A - opening for solution addition

B - overhead stirrer

C - bolts sealing glass tube into teflon top and bottom

Figure 14

openings for solution addition in the top teflon covering. The glass tube was bolted between the teflon top and bottom with four bolts. The teflon bottom was held in place in the perspex container by the same four bolts. The holes made in the bottom of the perspex container to accommodate the bolts were sealed with a silicone rubber polymer, this prevented the thermostatting water surrounding the cell from leaking out of the perspex container.

The cell also contained four perforated teflon baffles, two baffles in the top half of the cell and two in the bottom half. The function of the baffles was to reduce eddy currents in the organic and aqueous phases during an extraction experiment.

The Lewis Cell's inner glass compartment can be thermostatted to a constant temperature by surrounding the cell with water at the required temperature, as shown in Figure 14. Also present in the cell was a teflon stirrer. This stirrer was powered by an overhead motor with variable speed control. The stirrer had two impellers, the upper one for stirring the organic and the lower one for stirring the aqueous phase.

2.5.2.2 Experimental Conditions used in the Cell

All extraction experiments were performed with the contents of the cell thermostatted to 25 ^{0}C ± 1 ^{0}C. The geometry of the cell produced an organic-aqueous interfacial area of 103.9 cm^2 when 630.0 ml of aqueous phase and 550.0 ml of organic phase were placed in the cell. The stirrer rotation speed was 80 ± 1 r.p.m. This speed was used for all extraction experiments. Results in this laboratory[33] with the same Lewis Cell showed that at 80 r.p.m. the extraction rate was independent of stirrer rotation speed.

2.5.2.3 Experiments Conducted in the Lewis Cell

For each extraction experiment, 630.0 ml of aqueous phase was carefully poured into the cell. 550.0 ml of organic phase was then carefully poured on top of the aqueous phase. The extraction experiment was started as the stirrer was switched on immediately after the organic phase was added. The interface was approximately midway between the upper and lower baffles, and no perturbations, ripples etc. were observed at the interface during an extraction experiment. At appropriate time intervals, samples of the aqueous phase were withdrawn by placing a pipette into the aqueous phase through a hole in the

top teflon covering and removing approximately 0.2 ml of sample. Over the course of the extraction run (two to five days) the volume change would be negligible.

Table 11 shows the composition of organic and aqueous solutions examined during kinetic experiments using the Lewis Cell.

Table 11 - Solutions used for kinetic studies in the Lewis Cell

Aqueous phase	0.200 g/l Ge in 1.50 M H_2SO_4
Organic phase	25.00 g/l KELEX 100 in toluene 35.00 g/l " 50.00 g/l " 75.00 g/l " 100.00 g/l " 150.00 g/l " 200.00 g/l "

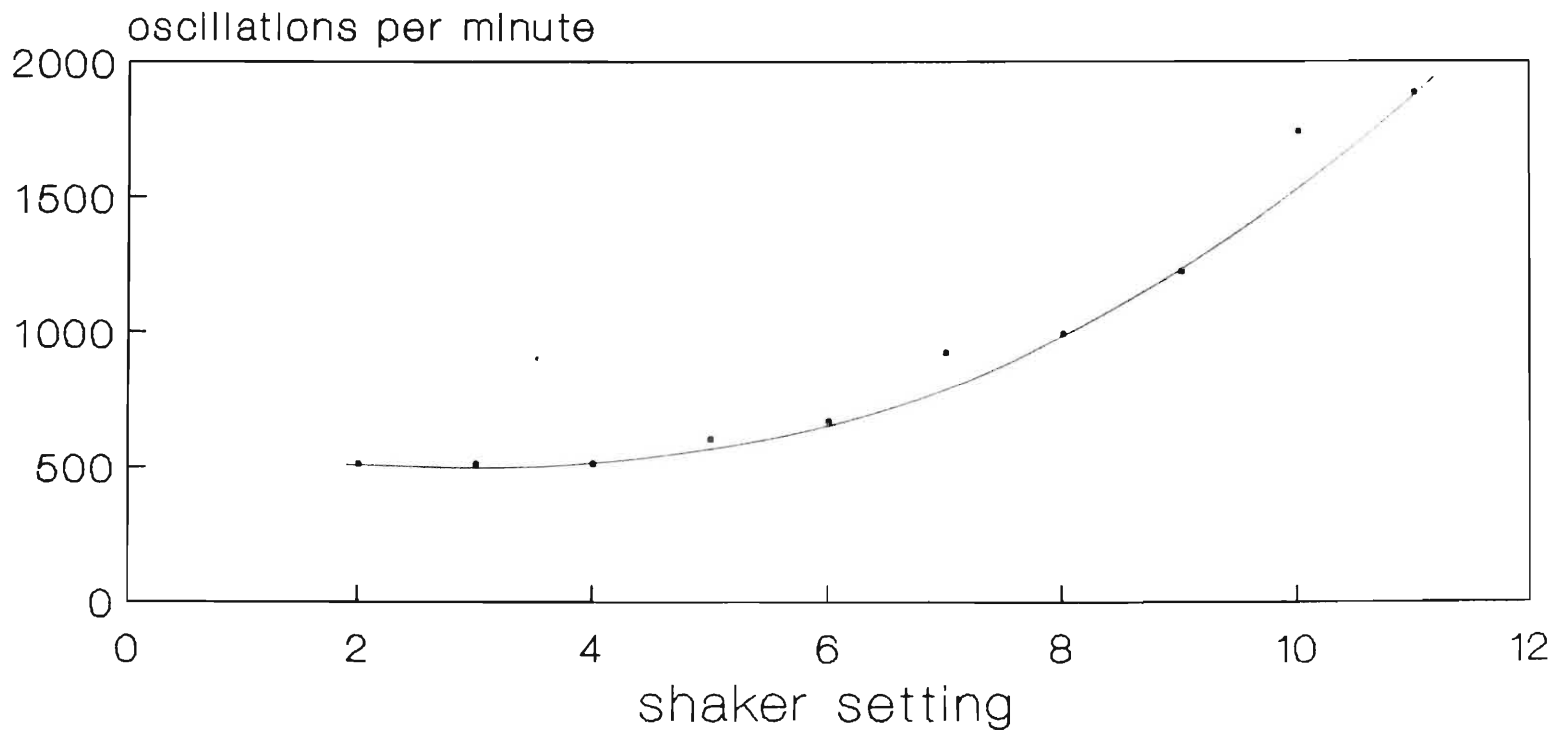
2.5.3 Shaking Experiments

Previous investigations[14,15,61] have made use of shaking experiments to collect equilibrium and kinetic data concerning the solvent extraction of metal ions. In spite of the unsophisticated and primitive nature of experiments using a wrist action shaker to study the reaction kinetics of a heterogeneous system, the method does have the advantage that of the variety of methods available to the solvent extraction chemist (AKUFVE, stirred cell[2,77,79-81], Lewis cell, rising or descending drop experiments[82,83]) it is representative of a likely industrial technique for solvent extraction. Work presented here does show the technique used to study solvent extraction with a wrist action shaker is capable of producing reproducible results.

2.5.3.1 **Experimental Set-up of Shaking Experiments**

All the kinetic and equilibrium data presented in this thesis using a shaking regime were obtained by using two solutions of 100 ml of each phase (aqueous and organic) in two 500 ml pear-shaped flasks placed diagonally opposite each other in a Gallenkamp wrist action flask shaker, shaking at the maximum shaking speed the shaker could attain.

Number of oscillations per minute for the wrist-action Gallenkamp flask shaker



(Two flasks each containing 200 ml)

Figure 15

Figure 15 shows a plot of up and down strokes per minute versus the dial setting on the shaking apparatus. Experiments conducted in this laboratory[33] showed that even at half of the maximum speed setting on the shaker, the extraction rate was unchanged. All shaking runs were carried out with the shaker shaking at maximum oscillation.

Samples of the aqueous phase in each shaking run were extracted by stopping the shaker, removing the stopper from the flask then withdrawing approximately 0.3 ml of sample with a small pipette. The stopper was then replaced and the shaking resumed. For samples in which the organic and aqueous phases did not separate quickly ($t < 15$ s), the sample was centrifuged in a high speed centrifuge (Helletich Mikroliter, supplier - Natalab) (at 15 000 r.p.m.) for 1 minute. This usually gave good phase separation. The concentration of germanium was only analysed in the aqueous phase and for this purpose the small aqueous phase aliquot required was removed from the aqueous phase as quickly as possible after removal from the shaking kinetic experiment to prevent further extraction of the germanium into any organic material withdrawn with the sample.

The technique described above does introduce a

certain degree of experimental error. Sources of error are:

(a) The period of stoppage of the shaker to withdraw the sample for analysis. This period is usually less than 15 seconds and is more serious for experiments where extraction is rapid (e.g. for 90 % extraction in 10 minutes or less). For experiments where extraction is relatively slow (e.g. 50 % extraction in 1 hour) the error is insignificant. In the absence of a better method of sample extraction, the error is unavoidable.

(b) Usually during the course of an experiment, more aqueous phase is withdrawn than organic phase, this changes the phase ratio somewhat in favour of the organic phase and could affect the results. However during a typical run, about 13 aqueous phase samples of 0.3 ml are withdrawn, representing a loss of 4.0 ml. This is thought to be a tolerable change for a system where the aqueous phase has a starting volume of 100 ml.

(c) The time taken for the aliquot to be removed from the sample for analysis represents a period where additional mass transfer of germanium to the organic phase can take place. Considering that the sample is not shaken during this time period the extraction

would thus be minimized in this small system compared to the shaking experiment. This small potential error is acceptable and is not expected to influence any results obtained significantly.

Bearing in mind the errors described above, the shaking technique does represent a simple and elementary method of obtaining kinetic data for a liquid-liquid extraction system.

2.5.3.2 Experiments Performed with the Shaking Technique

2.5.3.2.1 The Effect of Ligand Concentration on Rate of Extraction

The kinetics of extraction of germanium from a 0.200 g/l Ge in 1.50 M H_2SO_4 aqueous phase into organic phases of 25.00 g/l, 35.00 g/l, 50.00 g/l, 75.00 g/l, 100.00 g/l, 150.00 g/l and 200.00 g/l of KELEX 100 in toluene was examined.

2.5.3.2.2 The Effect of pH on Rate of Extraction

Buffered solutions prepared according to Section 2.2.2.1.1. (3) were reacted with 100.00 g/l KELEX 100 in toluene solutions and the rate of extraction examined. The percent extraction at equilibrium was also obtained for these buffered solutions versus

35.00 g/l KELEX 100 in toluene solutions.

2.5.3.2.3 The Effect of a Modifier on the Rate of Extraction

The kinetics of germanium extraction from aqueous solutions of 0.200 g/l Ge in 0.50 M H_2SO_4 into organic solutions containing 100.00 g/l KELEX 100 in 10 % (v/v) alcohol modifier in toluene (see Section 2.3.2.2) was examined.

2.5.3.2.4 The Effect of 8-Hydroxyquinoline on Rate of Extraction

The rate of extraction of germanium from the germanium solutions prepared in Section 2.2.2.1.1 (4) containing 8-hydroxyquinoline into an organic phase containing 50.00 g/l KELEX 100 in toluene was examined.

2.5.3.2.5 The Effect of Ionic Strength on Rate of Extraction

The germanium extraction kinetics of the aqueous solutions prepared in Section 2.2.2.1.1 (5) containing varying amounts of Na_2SO_4 into 100.00 g/l KELEX 100 in toluene was examined.

2.5.3.2.6 The Effect of Sulphuric Acid Concentration on the Rate of Extraction

The rates of germanium extraction from aqueous solutions of Ge containing varying amounts of H_2SO_4 prepared in 2.2.2.1.1 (1) into 100.00 g/l KELEX 100 in toluene solutions was examined. In addition the equilibrium extraction of samples of the above germanium solutions by 35.00 g/l KELEX 100 in toluene was examined.

2.5.3.2.7 The Effect of Organic Phase Pre-equilibration with Acid Phase on Extraction Rate

8.20 ml of sulphuric acid was added to 50 ml water, cooled, then diluted to 80.0 ml. This solution was shaken with 100.0 ml of 50.00 g/l KELEX 100 in toluene for 30 minutes. 20.0 ml of a 1.000 g/l Ge in water solution was then pipetted into the mixture and the aqueous germanium concentration monitored versus time.

This experiment was carried out to see if pre-equilibration of the organic phase with the acid in the aqueous phase had any effect on the rate of extraction of the germanium in the aqueous phase.

2.5.3.2.8 The Extraction of Sulphuric Acid by KELEX 100 in Toluene Solutions

The extraction of sulphuric acid by a series of

organic solutions of 25.00, 35.00, 50.00, 75.00, 100.00, 150.00 and 200.00 g/l KELEX 100 in toluene during equilibration with equal volumes of 1.50 M sulphuric acid aqueous solutions was determined by shaking the organic solutions mentioned above with 1.50 M sulphuric acid for 30 minutes. The amount of sulphuric acid remaining in the aqueous phase was determined by titrating an aliquot of the aqueous phase with 0.2000 M standardised NaOH to a phenolphthalein endpoint. The amount of sulphuric acid extracted by the KELEX 100 solutions could thus be calculated.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 KELEX 100 - CHEMICAL AND PHYSICAL PROPERTIES

This section discusses experiments conducted to examine the behaviour of KELEX 100 in organic solutions. Ligand self-association is examined as well as the viscosities of KELEX 100 containing toluene solutions. Interfacial tension data is also examined with a view to obtaining an indication of the availability of KELEX 100 at the aqueous/organic interface. The discussion of the data presented in this section is not confined to Section 3.1 and is expanded in subsequent sections.

3.1.1 Dimerization of ligand

Many commercial extractants are known to associate in organic solutions[62-65], usually this association only occurs between two species and can thus be referred to as dimerization. There is no literature suggesting that 7-alkylated 8-hydroxyquinoline extractants, such as KELEX 100, self-associate to any degree in organic solutions. Dimerization of extractant molecules would be an important consideration in any attempted kinetic simulation of the extraction process since dimerized and monomerized ligand would have different kinetic and

Infra-red spectra of KELEX 100
in carbon tetrachloride

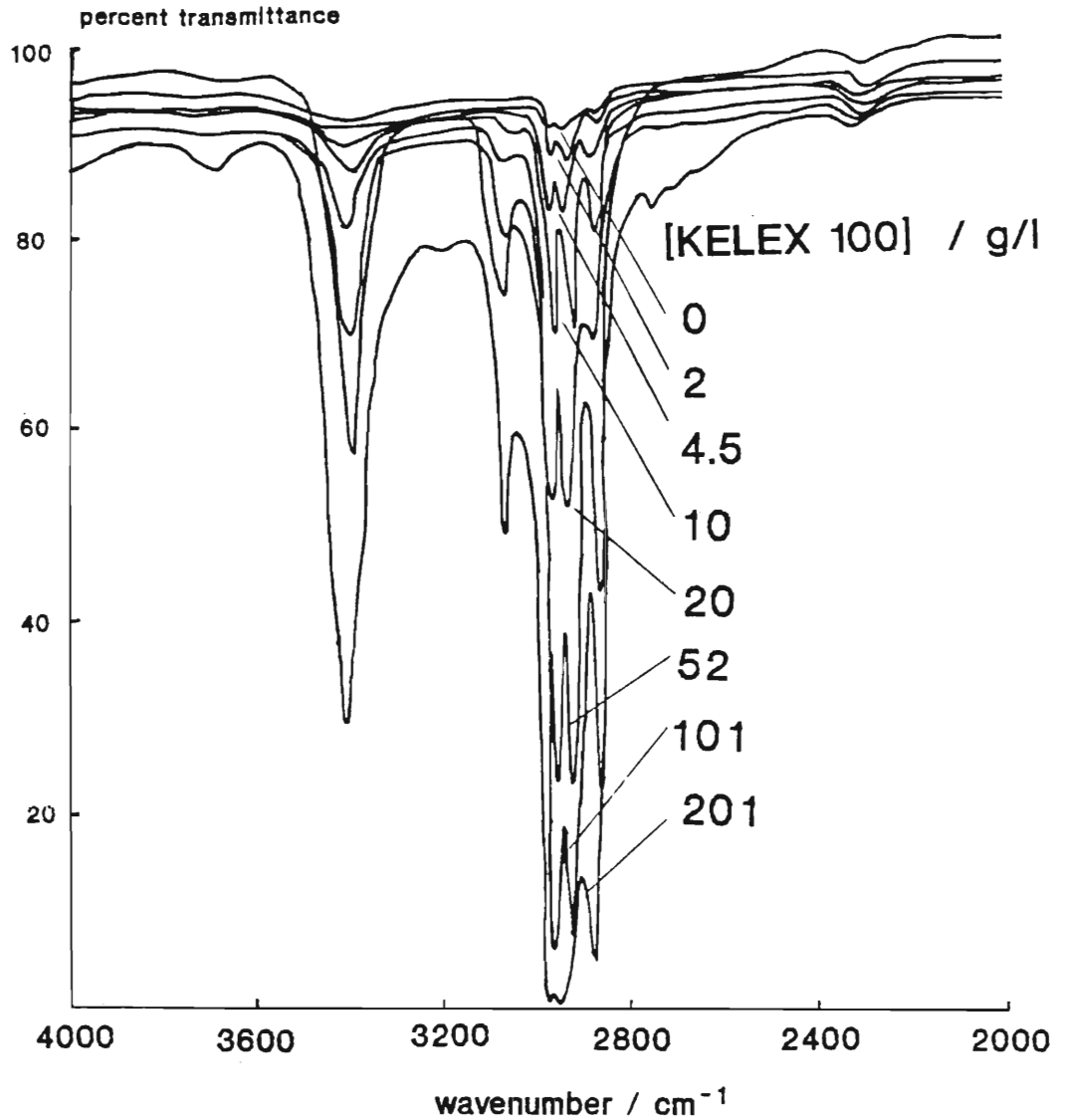
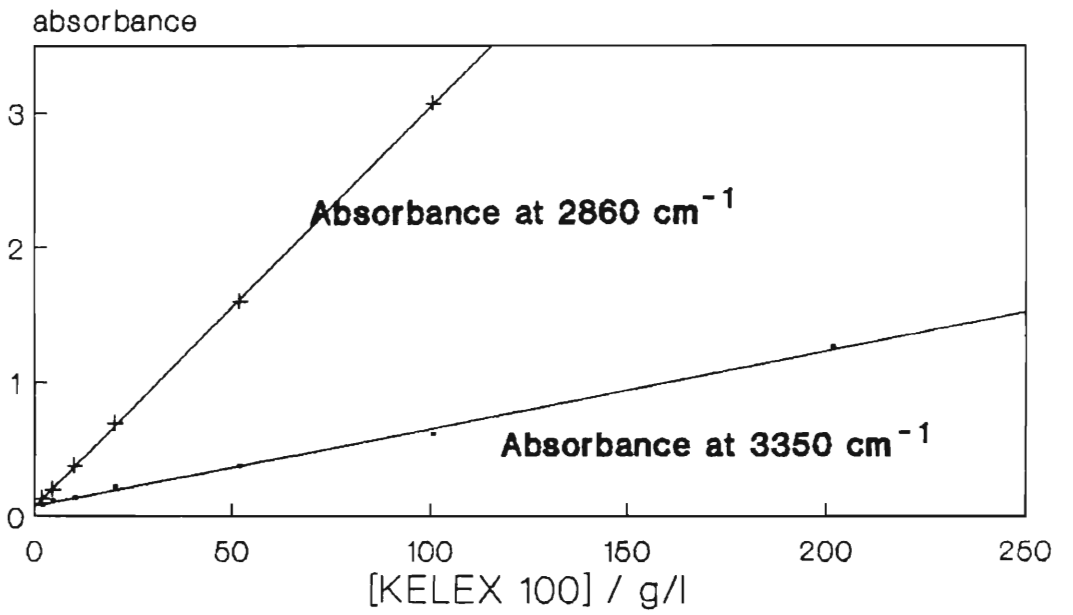


Figure 16

Absorbance as a function of KELEX 100 concentration



physical properties. In this work infra-red and uv-spectroscopy have been used to investigate whether KELEX 100 associates in the organic phase.

3.1.1.1 Infra-red Examination of Extractant

Infra-red spectra have been used in previous publications to examine self-association of commercial extractants in liquid-liquid extraction[62,66]. A consideration of the structure of KELEX 100 reveals that any dimerization or self-association of KELEX 100 would affect the hydroxyl group in some manner. A useful method of examining any changes in the nature of the hydroxyl group (especially examining hydrogen bonding involving the hydrogen or oxygen atoms of the hydroxyl group) is to examine the change in intensity of the hydroxyl peak (approx. 3300 cm^{-1})[66]. Figure 16 shows the infra-red spectra (described in Section 2.3.3.1) of 1 g/l, 4 g/l, 10 g/l, 20 g/l, 50 g/l, 100 g/l and 200 g/l solutions of KELEX 100 in CCl_4, from 4000 cm^{-1} to 2000 cm^{-1}. The -OH peak is at 3350 cm^{-1} and the methyl and methylene group peaks at just below 3000 cm^{-1}. Figure 17 shows the Beer's law plot of the absorbances of the peaks at 3350 cm^{-1} and 2860 cm^{-1}. The absorbance was calculated from:-

$$A = - \ln \frac{(\%\ transmittance)}{100} \quad (1)$$

Both plots are linear indicating that no change in chemical environment around the -OH and the methyl/methylene groups on KELEX 100 occurs. This can be taken as evidence that in CCl_4, KELEX 100 exists only as monomer. Self-association in other organic solvents, such as toluene, is also not expected to occur.

3.1.1.2 U.V. Examination of KELEX 100

If self-association of KELEX 100 occurred, it is unlikely that for a particular u.v. wavelength the molar absorptivity of the dimer would be precisely double the molar absorptivity of the monomer. Thus if Beer's law is obeyed by organic solutions of ligand for a particular u.v. wavelength, this would be evidence that dimerization or further self-association did not occur.

The absorbance of a series of KELEX 100 solutions in hexane (Section 2.3.3.2) were measured at 450 nm and at 400 nm. Hexane was chosen as a diluent because it has very little absorbance from 400 nm to 450 nm.

Figure 18 shows a plot of absorbance versus

Absorbance as a function of KELEX 100 concentration

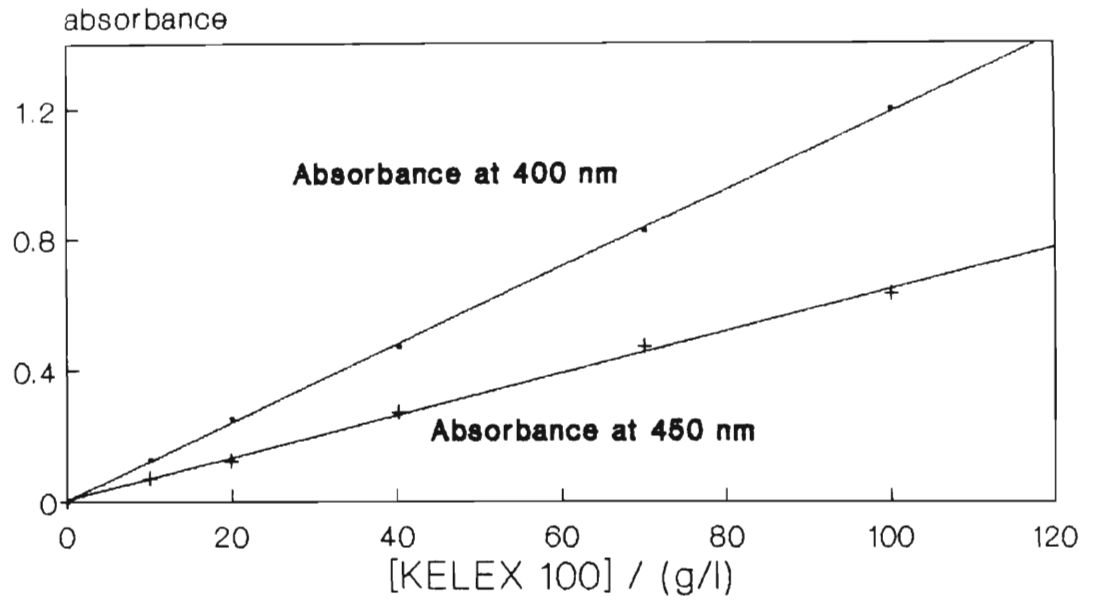


Figure 18

Viscosity as a function of ligand concentration in toluene

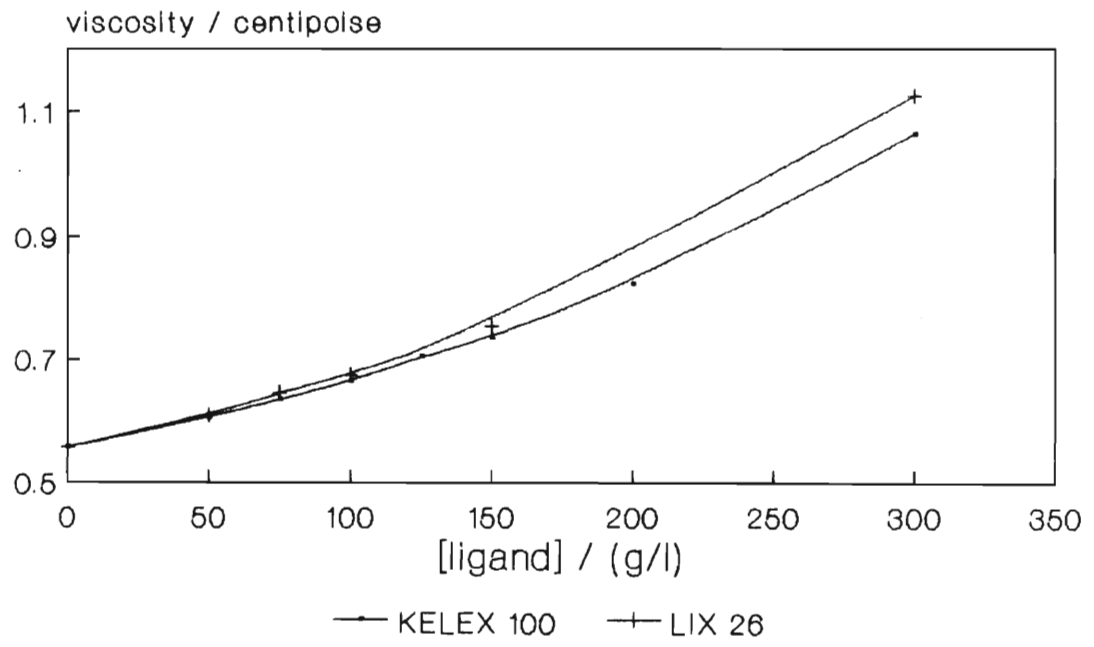


Figure 19

concentration of KELEX 100 in hexane. The points are linear, passing through the origin indicating that Beer's law is obeyed and no association of extractant molecules has occurred.

3.1.2 Viscosity of Extractant Solutions

The viscosity of a series of KELEX 100 solutions in toluene were measured because of the likelihood that the viscosity of the organic phase in a vigorously stirred or shaken two phase system would have some effect on the surface area generated between the two solutions. A high viscosity organic phase may generate a different interfacial area than a low viscosity organic phase when vigorously mixed with an aqueous phase of similar composition as the rate of production and coalescence of droplets in a rapidly mixed two-phase system may change if the viscosity of one of the mixing phases changes.

Figure 19 shows a plot of viscosity versus ligand concentration in a toluene solvent. The viscosities of a similar series of LIX 26 in toluene solutions are also shown on the same axes[33]. The plot shows that the concentration of KELEX 100 in the organic phase has a considerable effect on viscosity. Although the relationships between viscosity of the organic phase and interfacial area for the AKUFVE

and shaking systems are not known, a comprehensive simulation of the Ge-KELEX 100 extraction system would have to include such an effect.

3.1.3 Measurements of Interfacial Tension

Some researchers[67] have made use of interfacial tension measurements to examine the amount of extractant available for the reaction at the interface under various conditions (e.g shaking or Lewis Cell experiments). By calculating the surface excess (described later in this section) an indication of the surface concentration of ligand can be obtained for various bulk ligand concentrations. For this reason the interfacial tensions of a series of KELEX 100 in toluene solutions (Section 2.3.3.4) versus 1.50 M H_2SO_4 and also versus 0.200 g/l Ge in 1.50 M H_2SO_4 were measured. 1.50 M H_2SO_4 was chosen as the aqueous phase in these experiments because kinetic experiments examining the order of reaction with respect to ligand were conducted using a concentration of 1.50 M H_2SO_4 in the aqueous phase.

Figure 20 shows a plot of interfacial pressure (Π = interfacial tension of pure toluene and aqueous phase minus interfacial tension of KELEX 100 in toluene and aqueous phase) versus ligand

Interfacial pressure as a function of KELEX 100 concentration

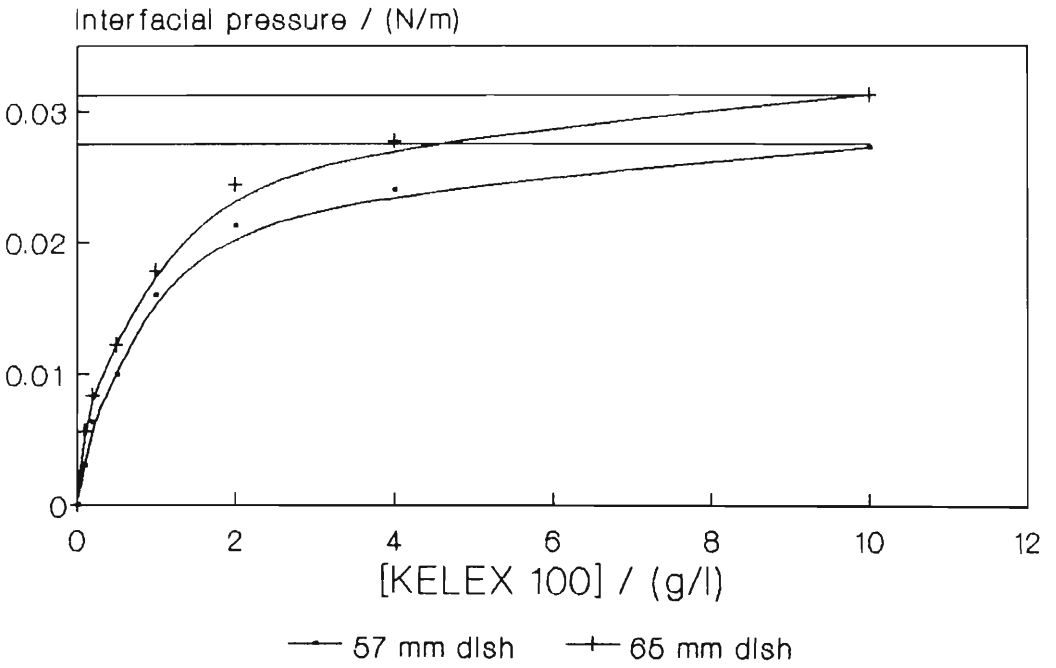


Figure 20

Interfacial tension as a function of l n [KELEX 100]

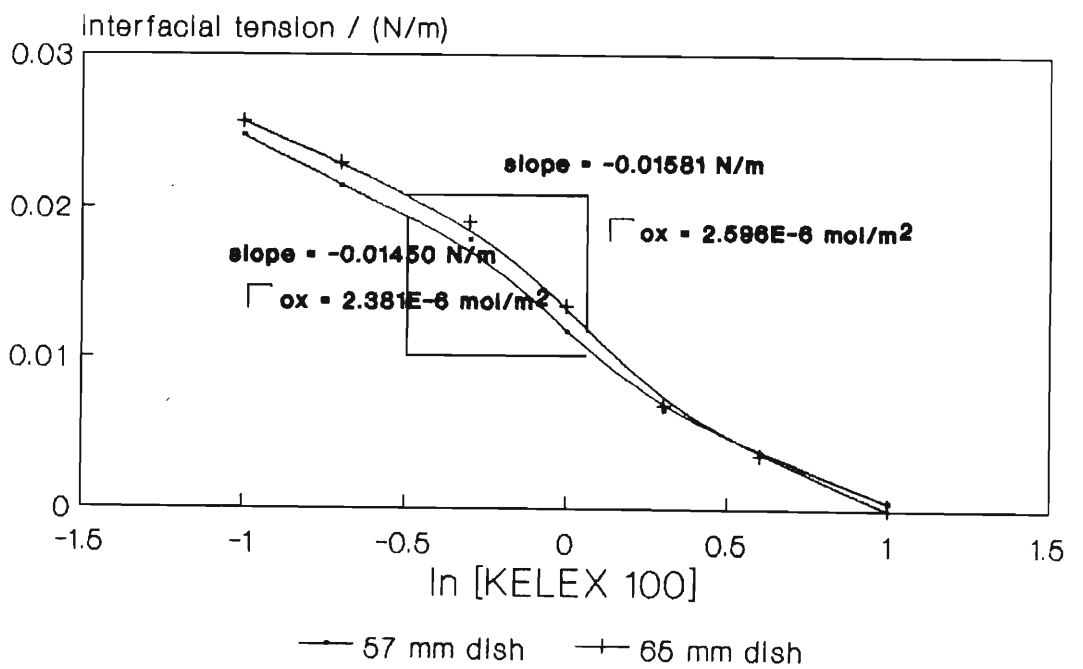


Figure 21

concentration (Section 2.3.3.4). Two different diameter dishes were used to examine the effect of container size on interfacial excess. The results have not been corrected as suggested by Hawkins and Jordan[68] and Freud and Freud[84]. The correction factor suggested to change interfacial tension readings is very close to unity and does not alter the results obtained.

The two parallel lines in Figure 20 represent the value of interfacial tension for pure toluene versus an aqueous solution of 1.50 M H_2SO_4. At 10 g/l KELEX 100 in the organic phase, Π is equal to the interfacial tension of the pure toluene / 1.50 M H_2SO_4 solution. This is because at concentrations of extractant greater than 10 g/l the interfacial tension between the organic solution and acid phase is too small to measure using the experimental set-up described in Section 2.3.3.4. This result indicates that at concentrations of KELEX 100 in toluene greater than 10 g/l under the conditions described in Section 2.3.3.4, the organic/aqueous interface is saturated with extractant molecules.

Figure 21 shows a plot of interfacial tension versus the logarithm of KELEX 100 concentration. The slope of this plot can be used to calculate the surface excess (Γ_{ox}) according to the Gibb's isotherm[67].

$$\Gamma_{ox} = - \frac{1}{RT\,2.303} \left(\frac{\delta\gamma}{\delta \log a} \right)_T \quad (2)$$

where a is the activity of the solute, which under the conditions used here can be taken as approximately equal to the concentration of the solute,

$(\frac{\delta\gamma}{\delta \log a})_T$ is the slope of the linear region of the curves in Figure 21 (the middle portion of the curve).

Table 12 shows the interfacial excesses and surface areas per molecule of KELEX 100 calculated from the interfacial excesses for KELEX 100 in the two different diameter dishes.

Table 12 - Interfacial excess and surface area of KELEX 100

Diameter of Dish (mm)	Interfacial Excess Γ_{ox} (mol / m^2)	Surface area (Å^2 / molecule)
57.0	2.38×10^{-6}	69.7
65.0	2.60×10^{-6}	64.9

The significance of this information will be fully discussed in Section 3.3.1.1 in an examination of the dependence of available ligand at the interface

on bulk organic phase ligand concentration.

However a noteworthy feature of these results is that the use of a slightly different size dish to determine interfacial tensions causes a significant change in the values of interfacial tension and interfacial excess obtained using identical solutions.

3.2 REACTION KINETICS

The results from three different types of experiments were used to study the reaction kinetics of germanium extraction from aqueous into organic solutions using KELEX 100 (i.e. Lewis Cell, AKUFVE and shaking experiments). These results are presented and discussed separately in this section with comparisons being made where appropriate between the results obtained with the various experimental approaches. A kinetic model to explain all results as fully as possible is proposed in Section 3.3.2 after the implications of all the results obtained concerning reaction kinetics have been fully discussed in this section.

3.2.1 The AKUFVE

The initial aim of the project was to study the Ge-KELEX 100 liquid-liquid extraction system as fully as possible with the AKUFVE. Preliminary results obtained indicated that a study of the Ge-KELEX 100 system could only be thoroughly undertaken if other techniques (e.g Lewis Cell and shaking experiments) were also used to examine the same system from different perspectives. The reasons for the broadening of the study to include Lewis Cell and shaking experiments are fully discussed later in

this section. Briefly, unexpected information concerning the order of extraction rate with respect to ligand necessitated the use of a different technique to see if the information supplied by AKUFVE experiments would be confirmed by other experiments.

3.2.1.1 The Effect of Ligand Concentration on the Rate of Extraction

Initial studies on germanium extraction with "pre-1976" KELEX 100[14,15] showed that for KELEX 100 to be useful in extracting germanium, the aqueous phase needed a high concentration of acid. Following the lead of Cote and Bauer[15], sulphuric acid was used throughout this study where high acid concentrations were required.

Unlike the case of copper extraction where good extraction rates are achieved with relatively low organic KELEX 100 concentrations (approx. 10 g/l)[69], in the case of germanium extraction, for reasonable extraction rates, relatively high concentrations of extractant in the organic phase must be used (> 25 g/l) when using an aqueous germanium solution containing 1.50 M H_2SO_4. Even at 25.00 g/l KELEX 100 in the organic phase, only 20 % extraction of germanium from a 1.50 M H_2SO_4 aqueous phase is

achieved in two hours. It is unlikely that germanium extraction using KELEX 100 would ever be commercially useful with such a slow rate of extraction and so in this work the extraction kinetics were studied only at concentrations of KELEX 100 in the organic phase higher than 25 g/l.

Figures 22 and 23 show plots of percent extraction versus time for various concentrations of KELEX 100 in toluene (described in Section 2.3.2.1). As can be seen from Figures 22 and 23, extractant performance improves drastically as more ligand is added to the organic phase. To evaluate extractant performance more quantitatively it is useful to determine the forward rate constant for the extraction reaction.

$$Ge_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ge_{org} \quad (3)$$

k_f = forward rate constant

k_b = reverse rate constant

aq = aqueous phase

org = organic phase

The forward rate constant k_f can be determined from a derived equation obtained by using a similar analysis to that outlined by Liljenzin et al.[71]:

Percentage extraction versus time AKUFVE experiments with KELEX 100

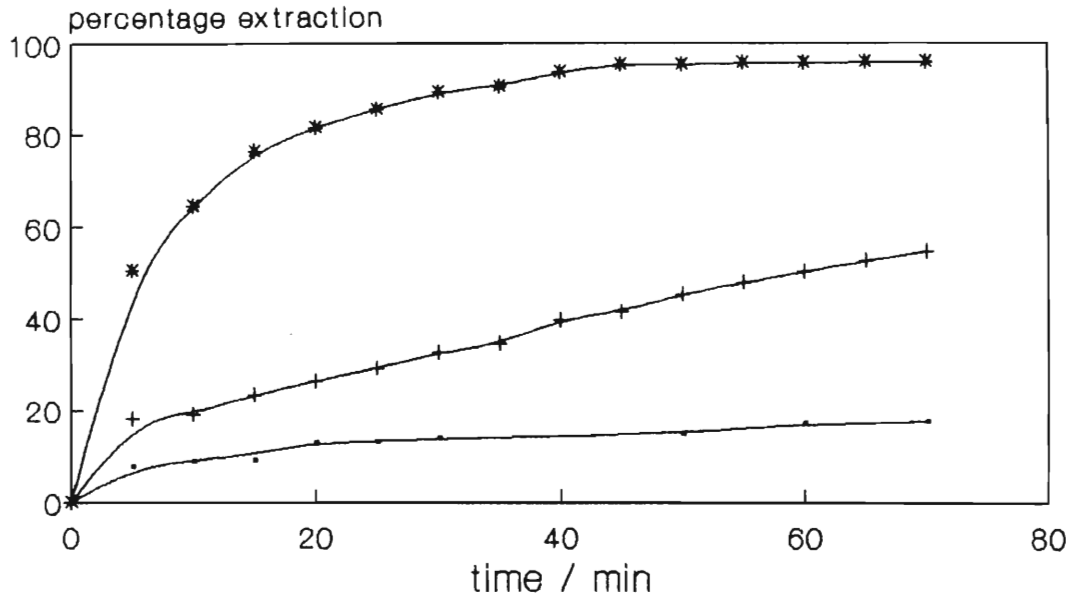


Figure 22

Percentage extraction versus time AKUFVE experiments with KELEX 100

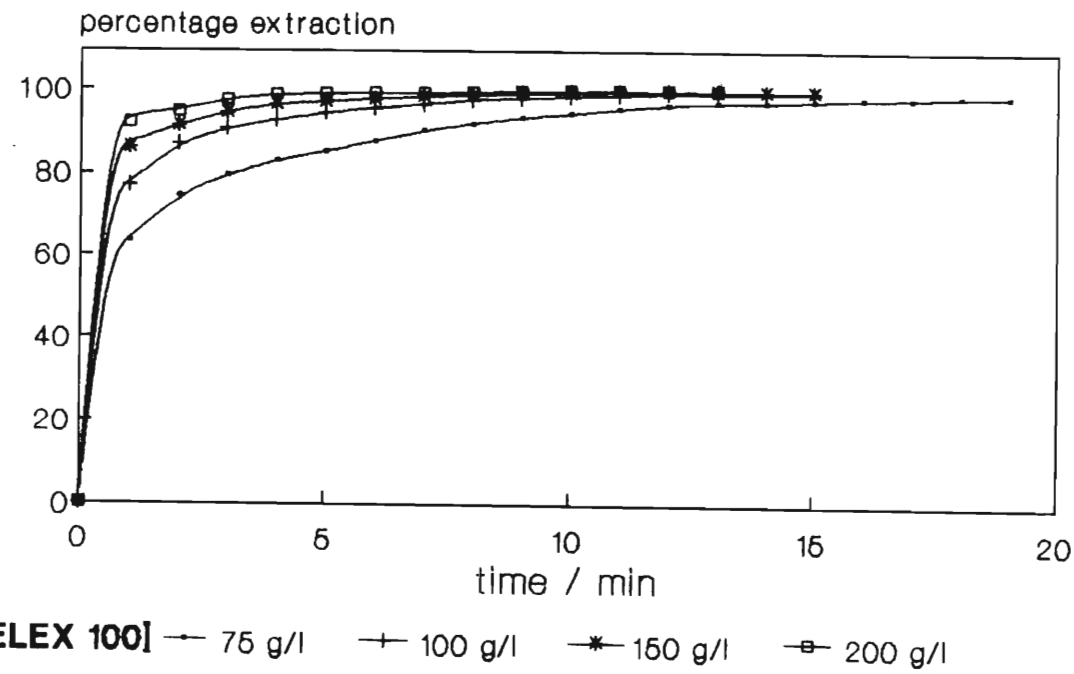


Figure 23

$$F(a) = k_f t = \frac{a_o - a_e}{a_o} \ln\left(\frac{a_o - a_e}{a_t - a_e}\right) \quad (4)$$

where a_o = concentration of Ge in aqueous phase at time = 0

a_e = equilibrium aqueous concentration of Ge

a_t = concentration of Ge in aqueous phase at time = t

Figure 24 shows a typical plot of the above function versus time for 35.00 g/l KELEX 100 in toluene, thus the slope in the linear region of the curve in Figure 24 is equivalent to the first order rate constant for germanium extraction from the aqueous to the organic phase.

The balanced reaction for germanium extraction by KELEX 100 may be represented as[15]:

$$Ge(OH)_{i\,aq}^{(4-i)+} + 3\ HL_{org} + HSO_{4\,aq}^{-} \rightleftharpoons GeL_3^+\ HSO_{4\,org}^{-} + i\ H_2O + (3 - i)\ H_{aq}^{+} \quad (5)$$

where i = number of hydroxyl groups bonded to each aqueous germanium atom

In this series of AKUFVE runs, KELEX 100 is in an excess of at least 10-fold (taking into account the 3-fold stoichiometry), $HSO_4^-{}_{aq}$ and $H^+{}_{aq}$ are in excess

AKUFVE kinetic experiment
F(a) versus time

organic phase: 35 g/l KELEX 100 in toluene

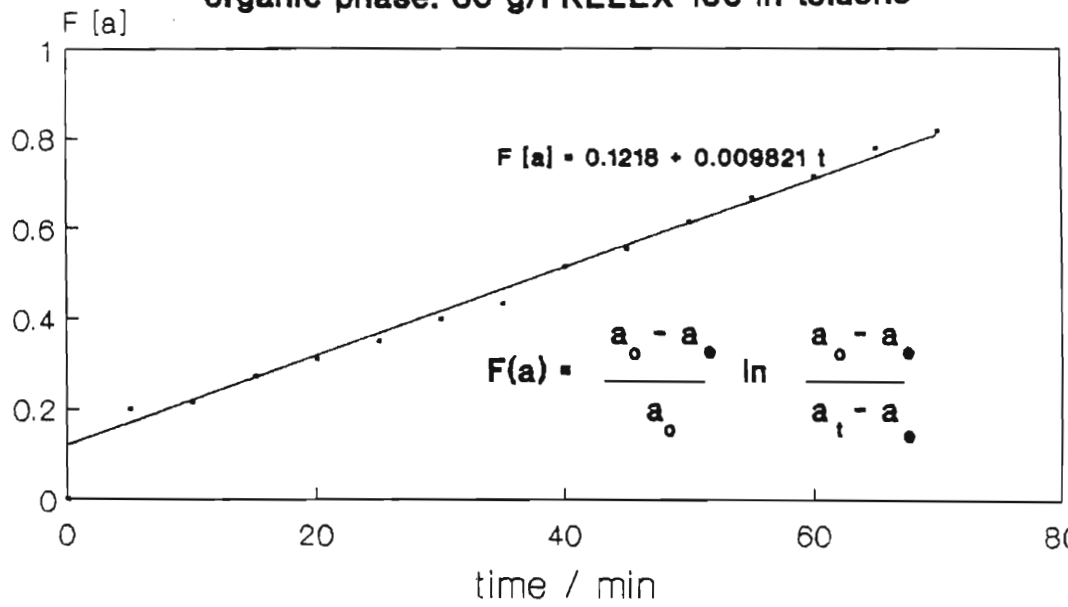


Figure 24

ln k_f as a function of ln [KELEX 100]

k_f = pseudo-first order forward rate constant for germanium extraction

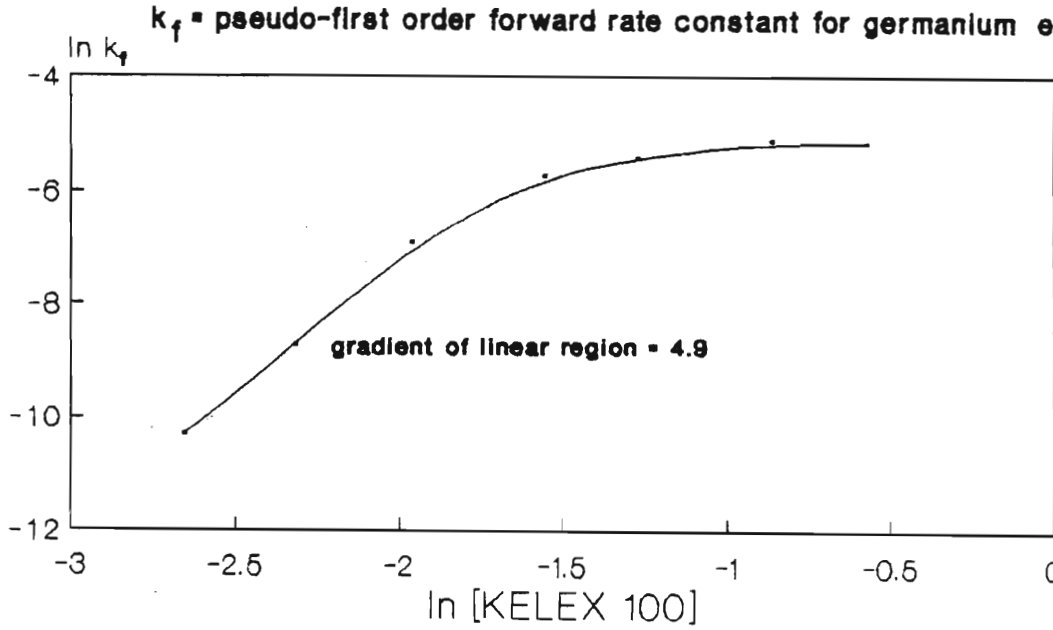


Figure 25

because 1.50 M H_2SO_4 was present originally in the aqueous phase. H_2O is obviously in excess. Considering these factors, the reaction kinetics of the extraction run shown in Figure 24 should be first order in germanium i.e. a straight line passing through the origin. The straight line obtained (using linear regression analysis) for the points on the curve (excluding the first point) has a slope of 9.821×10^{-3}. This indicates that after an initial period (of less than 5 minutes) the reaction follows kinetics which are first order in germanium.

This is a surprising result considering that for other systems, such as Cu-KELEX 100 liquid-liquid extraction[69], the first order plots pass directly through the origin. This deviation from expected behaviour for the Ge-KELEX 100 system occurs for all of the ligand concentrations (and all of the 7-alkylated 8-hydroxyquinoline derivatives used in this laboratory[33]) in these AKUFVE experiments. The fast initial rate followed by a slower rate presents some experimental difficulties as it accounts for a large proportion of the percent germanium extracted (up to 90 % at higher KELEX 100 concentrations) while it is not possible to sample the aqueous phase at small enough time intervals to obtain a full picture of the extraction kinetics in the initial fast extraction period.

An initial suggestion to explain the reason for this anomalous behaviour could be that it is a feature of the AKUFVE, however shaking experiments disproved this idea.

Figure 25 shows a plot of ln k_f (where k_f = slope of the linear region {in s^{-1}} of the F(a) versus time curves) versus ln [KELEX 100] (ligand concentrations in M (mol dm^{-3}) - corrected for purity). The plot has an initial slope of 4.9. This is an unexpected result since it indicates that the order of the extraction reaction in the second extraction period with respect to ligand is 4.9 .

Previously the general equation for the extraction of germanium by KELEX 100 proposed by Cote and Bauer[15] was considered to be as below:

$$Ge(OH)_{i\,aq}^{(4-i)+} + 3\ HL_{org} + HSO_{4\,aq}^{-} \underset{k_{b_i}'}{\overset{k_{f_i}'}{\rightleftharpoons}} GeL_3^{+}\ HSO_{4\,org}^{-} + i\ H_2O + (3 - i)\ H_{aq}^{+} \quad (6)$$

For the Ge^{4+} species (predominant at an aqueous phase sulphuric acid concentration of 1.50 M)[29] the general equation becomes:

$$Ge^{4+}_{aq} + 3\ HL_{org} + HSO_4^-{}_{aq} \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} GeL_3^+\ HSO_4^-{}_{org} + 3\ H^+_{aq} \quad (7)$$

The reaction obviously does not occur in one step, but a series of steps, the nature of which will be discussed in Section 3.3.2. For the purposes of the explanation of the order of the extraction reaction with respect to ligand, the mechanism is simplified by treating it as a one-step reaction.

Thus,

$$-\frac{d[Ge^{4+}_{aq}]}{dt} = k_f'[Ge^{4}_{aq}+]\ [HL_{org}]^3\ [HSO_4^-{}_{aq}] - k_b'[GeL_3^+HSO_4^-{}_{org}]\ [H^+_{aq}]^3 \quad (8)$$

For an extraction reaction that is far from equilibrium or where [HL] is large, the second term (i.e. $k_b'[GeL_3^+HSO_4^-{}_{org}][H^+]^3$ can be ignored because the concentration of $[GeL_3^+HSO_4^-{}_{org}]$ is low. This yields the following equation:

$$-\frac{d[Ge^{4+}]}{dt} = k_f'[Ge^{4+}_{aq}]\ [HL_{org}]^3\ [HSO_4^-{}_{aq}] \quad (9)$$

This equation is valid if all the aqueous germanium is present as Ge^{4+}. It can be shown, however that

$$-\frac{d[Ge_{aq}]}{dt} = k_f''[Ge_{aq}][HL_{org}]^3[HSO_4^-{}_{aq}] \quad (10)$$

$$where \quad [Ge_{aq}] = \sum_{i=0}^{4} Ge(OH)_i^{(4-i)+} \quad (11)$$

$$k_f'' = (k_{f1}\,a + k_{f2}\,b + k_{f3}\,c + k_{f4}\,d + k_{f5}\,e) \quad (12)$$

k_{fi} = forward rate constant for extraction of i th aqueous phase species

a = $[Ge^{4+}]$ / $[Ge_{aq}]$

b = $[Ge(OH)^{3+}]$ / $[Ge_{aq}]$

c = $[Ge(OH)_2{}^{2+}]$ / $[Ge_{aq}]$

d = $[Ge(OH)_3{}^{+}]$ / $[Ge_{aq}]$

e = $[Ge(OH)_4]$ / $[Ge_{aq}]$

a, b, c, d and e are assumed to be constant, the validity of this assumption will be discussed in Section 3.2.2.1.1 when it will be argued that the equilibrium reactions between the various aqueous germanium species occur at a rate far more rapid than the overall extraction reaction. Equation (10) can now be expressed as:

$$\frac{d[Ge_{aq}]}{dt} = k_f'''[Ge_{aq}] \quad (13)$$

$$where \quad k_f''' = k_f''[HL_{org}]^3[HSO_{aq}^-] \quad (14)$$

As previously mentioned $[HL_{org}]$ and $[HSO_4^-{}_{aq}]$ are constant for these experiments.

If this mechanism is correct then a plot of ln k_f versus ln $[HL_{org}]$ would be expected to be a straight line of slope three.

A similar plot for the Cu-LIX 63 system using the AKUFVE where Cu^{2+} is extracted as CuR_2 yielded an initial slope of two[56]. The slope of 4.9 obtained for the initial region of the curve shown in Figure 25 indicates that the kinetic analysis shown here does not hold under these experimental conditions.

Thus the "order" of 4.9 with respect to KELEX 100 is not easily explained and the explanation of this phenomenon will be left till a later section. The levelling off of Figure 25 is not unexpected and is caused by a maximum interfacial population of the available interface by the ligand molecules. The interface can be thought of as a surface with a fixed number of sites available for the ligand, once all of these sites have been populated, further increases of ligand concentration in the organic phase will thus not be able to populate the interface to a higher degree.

To investigate this unexpected order of 4.9 for the

extraction rate with respect to KELEX 100 concentration, the experiments conducted in the AKUFVE with KELEX 100 were repeated using LIX 26. Figures 26 and 27 show plots of percent extraction versus time obtained under similar conditions (using LIX 26) to the extraction curves in Figures 22 and 23. From these plots similar F(a) (defined in Equation (5)) versus time plots were used to calculate the first order rate constant for the slower kinetic region of the extraction reaction. Figure 28 shows an example of an F(a) (defined in Equation (5)) versus time plot for 35.00 g/l LIX 26 in toluene as organic phase.

Figure 29 shows the plots of ln k_f for KELEX 100 and LIX 26 versus concentration (corrected for purity) of KELEX 100 and LIX 26.

Figure 29 shows that the "order" of extraction rate with respect to KELEX 100 and LIX 26 is not the same in the initial region of the plots. The variance of these two plots was contrary to expectations since LIX 26 and KELEX 100 are essentially similar in structure. The ultimate goal of an investigation such as this is to propose a kinetic model consistent with all the kinetic data obtained. The difference in behaviour between similar ligands under similar conditions served as an indication

Percentage extraction versus time AKUFVE experiments with LIX 26

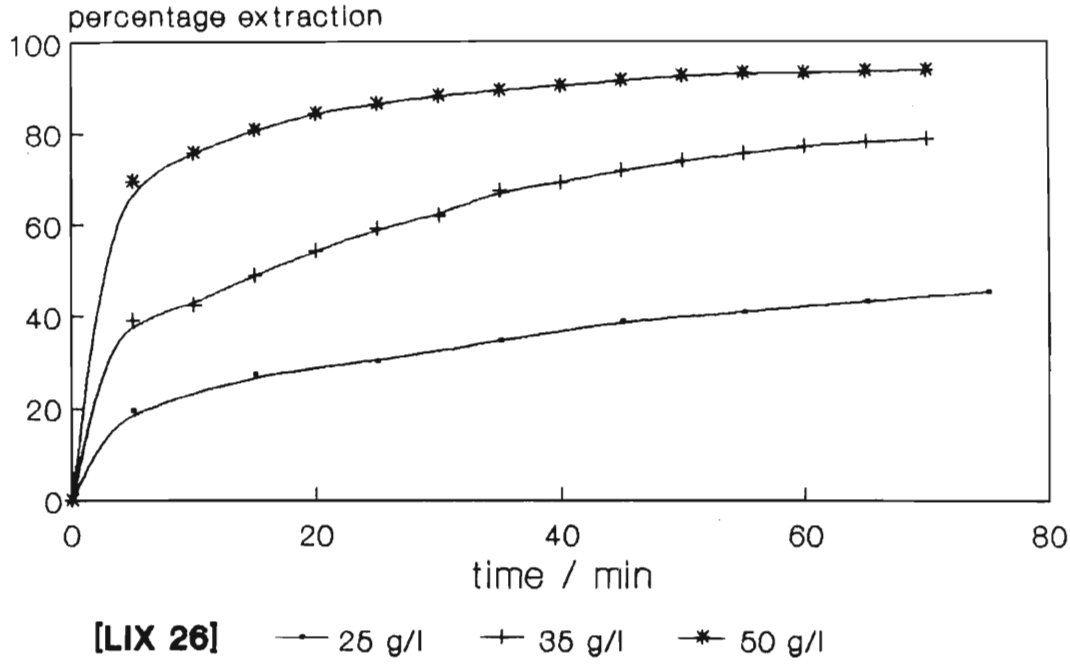


Figure 26

Percentage extraction versus time AKUFVE experiments with LIX 26

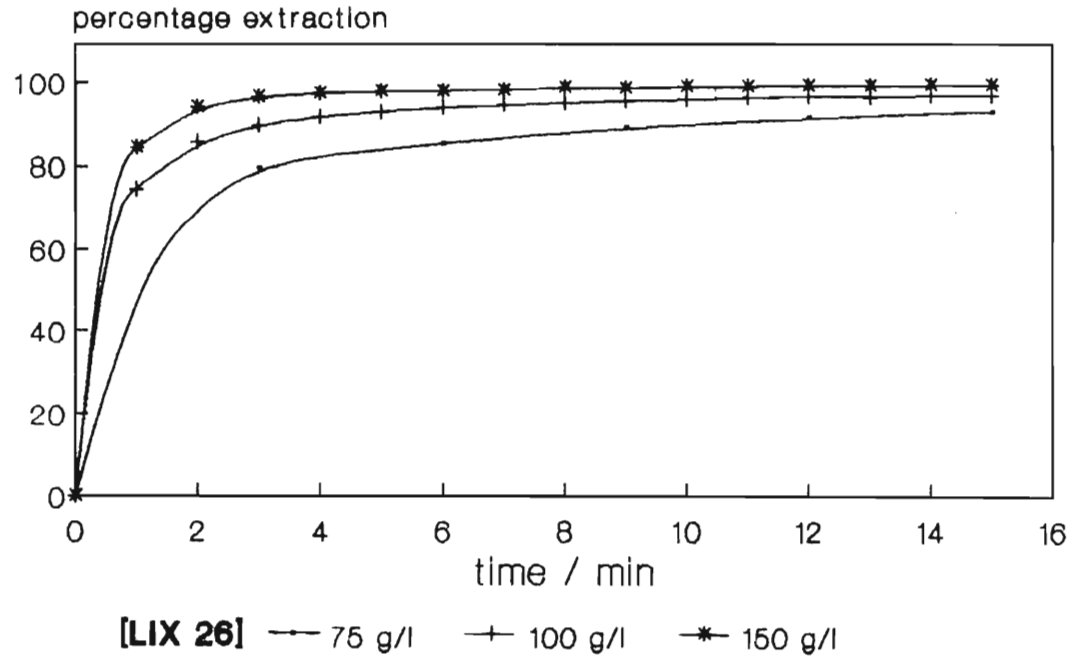


Figure 27

AKUFVE kinetic experiment
F(a) versus time

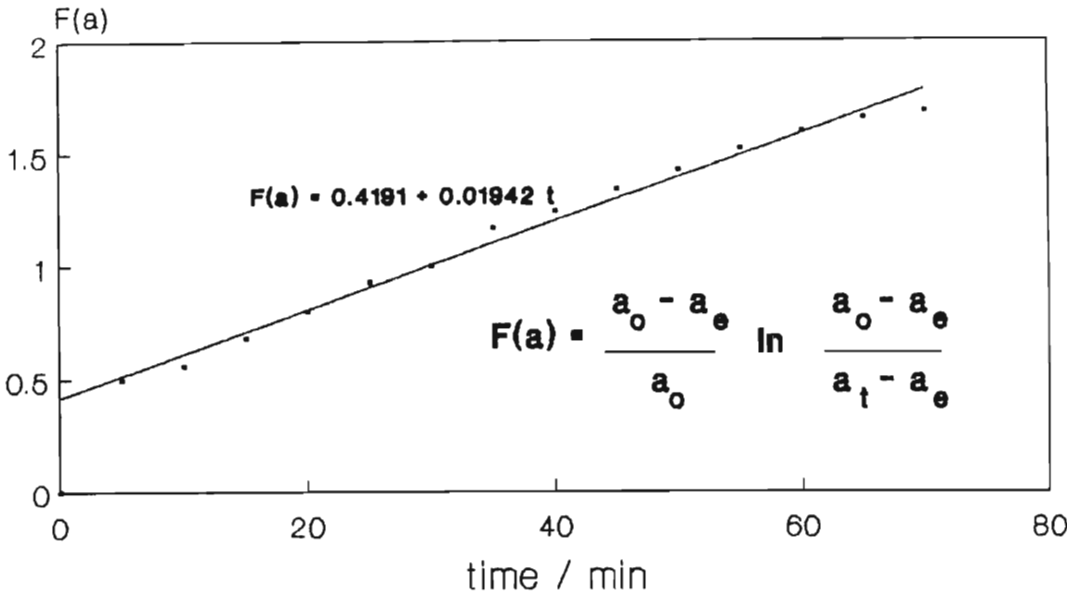


Figure 28

I n k_f as a function of I n [Ligand]
Comparison of KELEX 100 and LIX 26

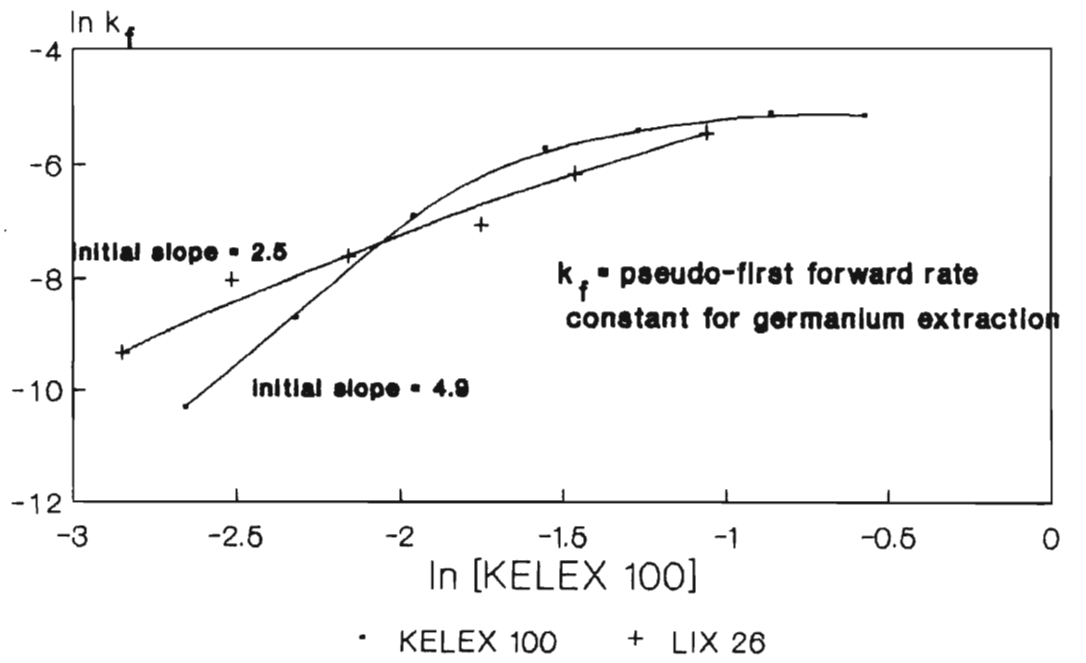


Figure 29

that the final proposed model would be complex.

The shortcomings of the AKUFVE technique for obtaining kinetic data for liquid-liquid extraction are discussed in Section 3.2.1.2. Because of these shortcomings it was decided that an attempt to formulate a kinetic model from AKUFVE data alone would be premature, and that more kinetic information was required.

An explanation for anomalous reaction orders could lie in the fact that the reported extraction reaction mechanism[14,15] using "pre-1976" KELEX 100 was not applicable for the KELEX 100 used in this study. In order to examine this possibility further, the reported stoichiometry of the extracted Ge-KELEX 100 complex at low pH (<2) was checked using the following argument:

From the data in Table 13, a plot of log D ($D = [Ge_{org}] / [Ge_{aq}]$ at equilibrium) versus log [KELEX 100] can be made. This has been done in Figure 30. If the extraction reaction for Ge is written as:

$$Ge^{4+} + n\,HL \leftrightarrows GeL_n^{(4-n)+} + nH^+ \quad (15)$$

where HL = KELEX 100 and n = number of ligand molecules reacting with each Ge ion extracted

Table 13 - Equilibrium percentage extraction versus concentration of ligand

organic concentration of KELEX 100 (g/l)	% Ge extraction (after 48 hours)
25.00	88.3
35.00	93.9
50.00	97.7
75.00	99.3
100.00	100
150.00	100
200.00	100

The equilibrium constant (K) for the reaction can be written:

$$K = \frac{[GeL_n^{(4-n)+}]\,[H^+]^n}{[Ge^{4+}]\,[HL]^n} \quad (16)$$

$$\frac{[GeL_n^{(4-n)+}]}{[Ge^{4+}]} = \frac{K\,[HL]^n}{[H^+]^n} = D \quad (17)$$

$$\log D = \log K + n\log[HL] - n\log[H^+] \quad (18)$$

Thus a plot of log D versus log [HL] will have a

log D as a function of log [KELEX 100]

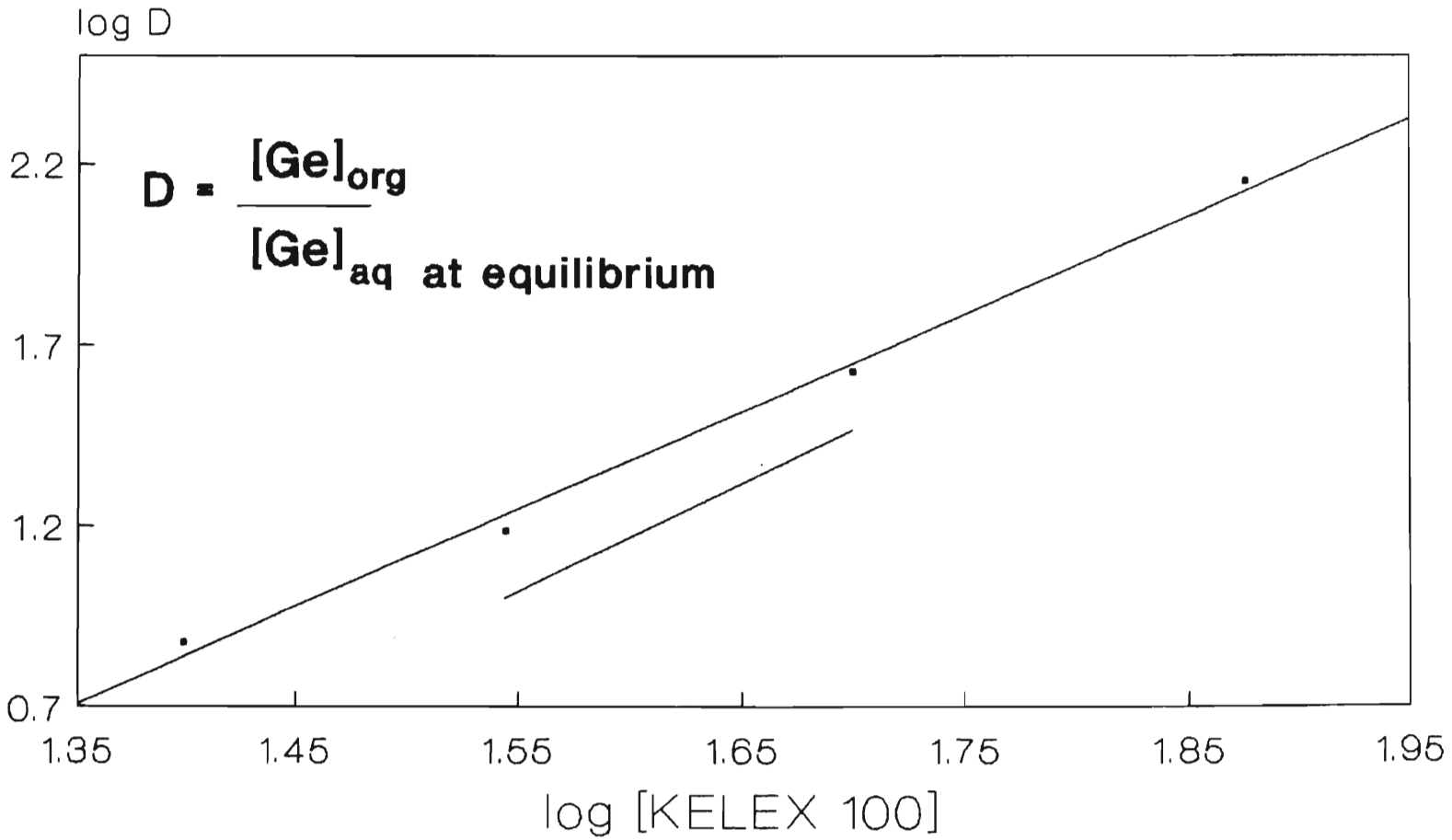


Figure 30

slope of n. Figure 30 shows the best fit straight line for KELEX 100 concentrations 25.00 g/l, 35.00 g/l, 50.00 g/l and 75.00 g/l. The slope of the line is 2.7, below the best fit line is a line of slope 3, this line shows the result could be interpreted as indicating that n = 3, which would confirm the work of Cote and Bauer[15] which reports that at low pH (<2) Ge extracts from sulphuric solutions as $GeL_3^+HSO_4^-$ with a 7-alkylated 8-hydroxyquinoline extractant.

On the basis of this result no further work was done examining the stoichiometry of the germanium : KELEX 100 extracted species and the conclusions reported by Cote and Bauer[15] concerning the extracted Ge-KELEX 100 complex taken as reliable.

3.2.1.2 **Reproducibility of AKUFVE data**

Table 14 shows the values of k_f determined for a series of repeat AKUFVE kinetic experiments.

The results show that good reproducibility is obtainable when measuring rate constants with the AKUFVE.

Table 14 - k_f values (the forward rate constant for germanium extraction as defined in Section 3.2.1.1) and corresponding KELEX 100 concentrations for a series of repeat AKUFVE kinetic experiments.

[KELEX 100] / g/l	k_f / s^{-1}	ln k_f
25	3.327×10^{-5}	-10.31
25	2.627×10^{-5}	-10.55
35	1.637×10^{-4}	-8.72
35	1.623×10^{-4}	-8.73
35	1.593×10^{-4}	-8.75

3.2.1.3 **Shortcomings of the AKUFVE**

As mentioned above, there were several difficulties associated with the use of the AKUFVE apparatus. The AKUFVE has been used previously to study a number of aspects of solvent extraction. A typical study[51] reports the distribution ratio (D) for the metal ion under examination (usually copper) as a function of pH, ligand concentration, ionic strength, temperature etc. and uses both log D versus pH and the log D versus log [ligand] as a basis for proposing an extraction mechanism.

Aside from collecting equilibrium data for determination of distribution ratios, some authors have reported kinetic studies using the AKUFVE[71], however, it is noticeable that equilibrium studies are more popular with AKUFVE users than kinetic studies. In the first papers describing the AKUFVE, a major attribute of the AKUFVE was that its design enabled it to be used to study reactions with half-lifes down to ten seconds[50], but subsequent to this early work the lack of kinetic studies using the AKUFVE suggests that the instrument was not as well suited to examining the kinetics of liquid-liquid extraction as the designers had hoped.

In the course of this study, experiments using the AKUFVE were compared with experiments using different approaches and some insight was gained into the reasons for the lack kinetic studies done using the AKUFVE. A number of shortcomings of the AKUFVE technique for kinetic studies were identified and these are listed below.

(1) The most obvious problem is that in the AKUFVE there is no control over the surface area available for mass transfer. This fact has been observed by Rydberg[50], one of the developers of the AKUFVE. For an extraction reaction which has a rate proportional to interfacial area (such as the reaction studied in

this investigation - this interfacial reaction mechanism has been argued in the Introduction), this factor is important since any changes in interfacial area as an AKUFVE is being run will be impossible to take account of when data is to be analysed. For instance, the additional surface area created in the centrifuge because of a longer time taken to separate the organic/aqueous mixture would greatly complicate the analysis of data.

Compared to other techniques involving the rapid mixing of two phases (such as the shaking technique or the rapid stirring of the two phases) this drawback is not serious as surface area is also difficult to determine for these systems. The determination of interfacial area in rapidly mixing systems is a relatively new development in solvent extractant and only a few studies are reported in the literature[77,78].

(2) A major drawback of the AKUFVE technique for kinetic analysis of reaction rates is related to the problem of the approach to mixing equilibrium discussed in Section 2.5.1.3. For a rapid extraction reaction the degree of reaction of the organic and aqueous phases entering the AKUFVE after leaving the centrifuge will be different from the contents of the mixing chamber. This difference will not be as great for a

slow reaction as for a fast reaction but the net effect will be to present a system where not all elements of organic and aqueous phase are at the same stage of reaction. This could contribute to distortions in the observed kinetics.

(3) The AKUFVE is more expensive to operate than a small wrist action shaking device as operation involves the purchase of the instrument as well as a compressor to supply air to the centrifuge motor. The apparatus has to be washed with absolute ethanol (1200 ml) before each experiment, this washing procedure is more laborious and more expensive than washing a 500 ml pear-shaped flask.

(4) A further consideration in AKUFVE experiments is the fate of interfacially adsorbed species which enter the centrifuge. Once entering the centrifuge, the liquid-liquid interface is effectively destroyed. Any interfacially adsorbed reaction intermediates either pass into the organic or the aqueous phase, this process is not part of the "normal" extraction reaction scheme and the ultimate effect of this process on extraction kinetics is not quantifiable. This effect is not likely to effect results greatly because interfacially adsorbed reaction intermediates are shortlived due to the dispersed elements of organic and aqueous phase being unlikely

to form a discrete interfacial region for any reasonable time interval in a rapidly stirring system. However, without the experimental means to test the effect described, any possible influences on extraction rate cannot be dismissed.

(5) The final disadvantage or flaw in using the AKUFVE technique for kinetic analysis is that fresh unreacted solutions of aqueous and organic phases are required for each kinetic experiment, this involves preparing (in the case of these experiments) 400 ml of each solution. A similar shaking experiment requires only 100 ml of each solution. The AKUFVE technique is thus not economical for kinetic experiments and does not possess any inherent advantages over the use of similar shaking experiments.

3.2.1.4 General Appraisal of AKUFVE

The AKUFVE is unsuitable for examining the kinetics of liquid-liquid extraction. It is an expensive method of examining a process which could be examined using a similar, simpler technique (eg. shaking experiments or a rapidly stirred cell). The use of the AKUFVE to examine reaction kinetics only serves to complicate an already complex system. In the examination of the shaking technique (Section

3.2.2.1), kinetic experiments similar to kinetic experiments conducted with the AKUFVE are presented. These results show differences to the data obtained with the AKUFVE and highlight the fact that data obtained using the AKUFVE is specific to the AKUFVE.

As mentioned earlier, the majority of literature studies using the AKUFVE report only distribution ratios as a function of various parameters (eg. ligand concentration, pH). Rydberg[50] in his 1969 publication announces that the AKUFVE is 10-100 times faster than the test tube procedure for obtaining distribution ratios as a function of ligand concentration, pH etc. The test tube procedure referred to is a procedure in which similar solutions of organic and aqueous phase are shaken to equilibrium and by varying one parameter, the effect of that parameter on the distribution ratio can be studied.

As an example, if the effect of pH on the distribution ratio of a metal ion of interest were to be examined using a specific concentration of a certain organic extractant, then a known volume of an aqueous solution of the ion of interest would be equilibrated in the AKUFVE with an equal volume of an organic solution of known extractant

concentration. The aqueous or organic concentration of the ion of interest would be measured at equilibrium then small aliquots of base (or acid) added to the solutions in the AKUFVE and the system allowed to equilibrate each time before the aqueous or organic metal ion concentration was determined. A pH meter would be required to monitor the pH of the aqueous phase exiting the centrifuge.

Thus in the manner described above a distribution ratio curve versus any variable could be obtained provided there was some means of measuring the analyte of interest in either phase and the method of analysis was rapid enough to follow the approach of the analyte of interest to equilibrium to ensure that the distribution ratios obtained were equilibrium distribution ratios.

Another pre-requisite for using the AKUFVE to determine distribution ratios is that the reaction studied should have a rapid reaction rate. For extraction processes that may take hours or days to reach equilibrium, the convenience of obtaining rapid results would be lost. For the liquid-liquid extraction of germanium with KELEX 100 in toluene, only at extremely high sulphuric acid concentration (> 1 M) and extremely high ligand concentration (> 100 g/l) does the time taken for the extraction

reaction to reach equilibrium take less than one hour, even one hour is too long to allow the AKUFVE to be conveniently used for the determination of distribution ratios.

To take full advantage of the AKUFVE to determine distribution ratios as the function of some variable, it is essential that a rapid on line technique for the analysis of the analyte of interest, (in the case of this study - germanium), is obtained. Reported studies using the AKUFVE suggest that the best on line technique is the use of a radioactive isotope of the metal ion of interest. Published studies available using the scintillation counting of a metal ion to monitor extraction include extraction of copper[51,52,71], zinc[52,54], cobalt[57] and neptunium[72]. No comparable literature exists for germanium.

The scintillation counting of a radioactive isotope of germanium to monitor germanium extraction was not employed in this study because this university did not possess the required facilities to produce and detect radioactive isotopes.

No other method of on-line detection of germanium was found. Thus without a means to follow the approach of the mixing system to equilibrium it

would not be possible to rapidly determine if the mixing liquids had reached equilibrium.

For the reasons described above, the AKUFVE was not used to determine distribution ratios under any conditions. The efficient and effective use of the AKUFVE to determine distribution ratios as a function of any variable would require:

(1) The system to rapidly equilibrate after any changes in composition (i.e. within 5 to 10 minutes).
(2) An on-line system of metal ion detection (eg. scintillation counting of a particular metal ion).
(3) An on-line pH meter.

In addition to the shortcomings of the AKUFVE discussed above, Rydberg[50] draws attention to a further limitation that may be experienced with the AKUFVE. If an emulsion is easily produced by the solvent-solute system, the AKUFVE may not be able to break up the emulsion and thus would not enable the solvent extraction system that formed the emulsion to be studied. This was observed in some of the kinetic experiments (not described here) conducted with the AKUFVE.

3.2.1.5 Consequences of AKUFVE Experiments

The initial AKUFVE experiments provided more questions than answers. Explanation of AKUFVE results has not been attempted in this section because the AKUFVE experimental system for obtaining kinetic data lacks clarity as a kinetic system and observed kinetic effects may be mistaken as extraction phenomena when in fact the effects are attributes of the AKUFVE set-up. To place the AKUFVE results in perspective and understand their significance, it was decided to use a shaking regime to repeat the AKUFVE experiments and compare the results obtained with the AKUFVE results.

3.2.2 Shaking Experiments

Initially, the desire to clarify seemingly anomalous data obtained from AKUFVE experiments was the motivation for shaking experiments, however once the convenience of the shaking experiments to obtain kinetic data was established, the bulk of the kinetic experiments performed to complete this investigation were performed using a shaking regime.

3.2.2.1 **The Effect of Ligand Concentration on Extraction Rate**

These experiments were carried out to enable a comparison of the AKUFVE data with data obtained using a similar set-up of rapid phase mixing.

Figures 31 and 32 show the rate of extraction of germanium from a 1.50 M H_2SO_4 aqueous phase into a similar series of KELEX 100 in toluene solutions (described in Section 2.5.3.2.1) to those used in the AKUFVE runs. A similar plot of the function

$$F(a) = \frac{(a_o - a_e)}{a_o} \ln\left(\frac{a_o - a_e}{a_t - a_e}\right) \quad (4)$$

(where the symbols have the same meaning as in

Percentage extraction versus time shaking experiments with KELEX 100

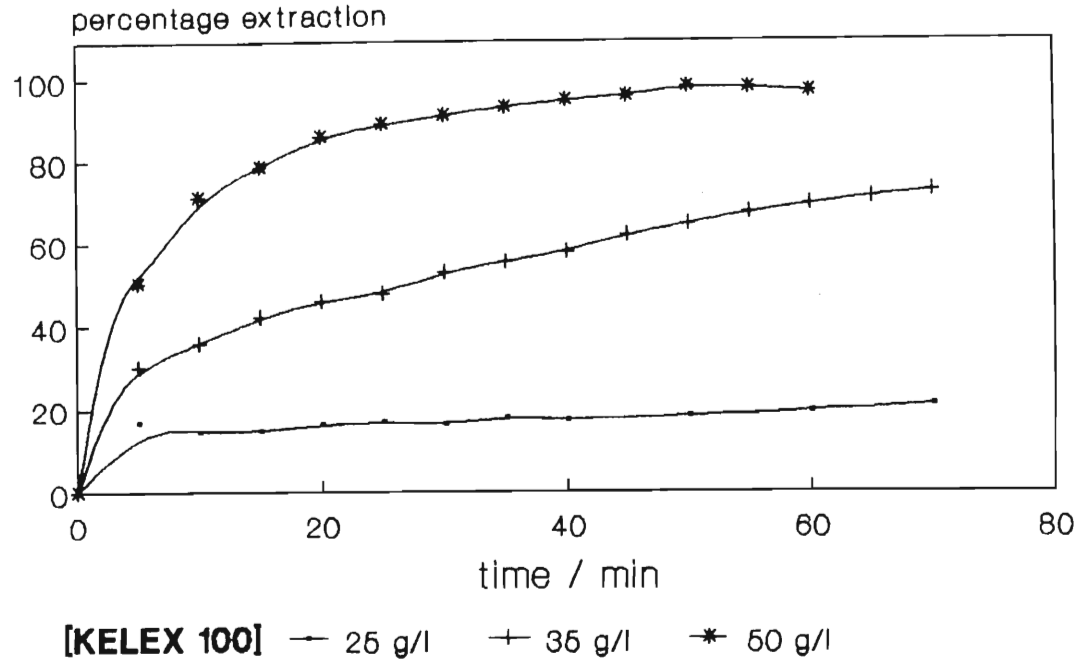


Figure 31

Percentage extraction versus time shaking experiments with KELEX 100

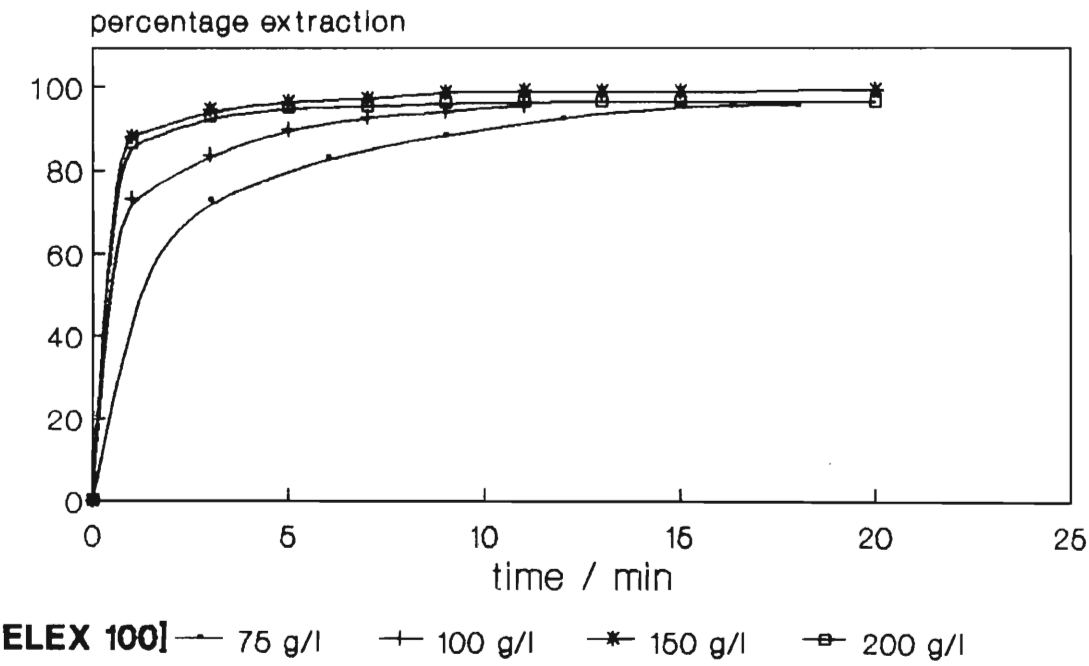


Figure 32

Section 3.2.1.1) versus time yields a straight line that does not pass through the origin. Figure 33 shows a plot of F(a) (Equation(5) versus time for 35.00 g/l KELEX 100 in toluene. All of the F(a) versus time plots for the shaking experiments using KELEX 100 are similar in that they yield a straight line which does not pass through the origin but somewhat above the origin. This indicates that the extraction reaction has two kinetic regions, a fast initial region, then a slower region which obeys first order kinetics with respect to germanium until close to equilibrium. As seen in the AKUFVE experiments, the initial fast reaction is over the first few minutes of the reaction and accounts for a significant proportion of the germanium extracted in an extraction reaction. The observation of this phenomenon in shaking experiments shows that it is not caused by the AKUFVE technique but is a genuine kinetic result.

Figure 34 shows a plot of ln k_f (the slope of the linear region of the F(a) versus time plots) versus ln [KELEX 100]. The slope of the initial region of the graph is 6.6 indicating an apparent reaction order of 6.6 with respect to ligand. In terms of reaction stoichiometry, this order is impossible, as one Ge atom does not have enough space to allow the chelation of 6 (or 7) ligand molecules. The addition

Shaking experiment : F[a] vs time
KELEX 100 - 35 g/l

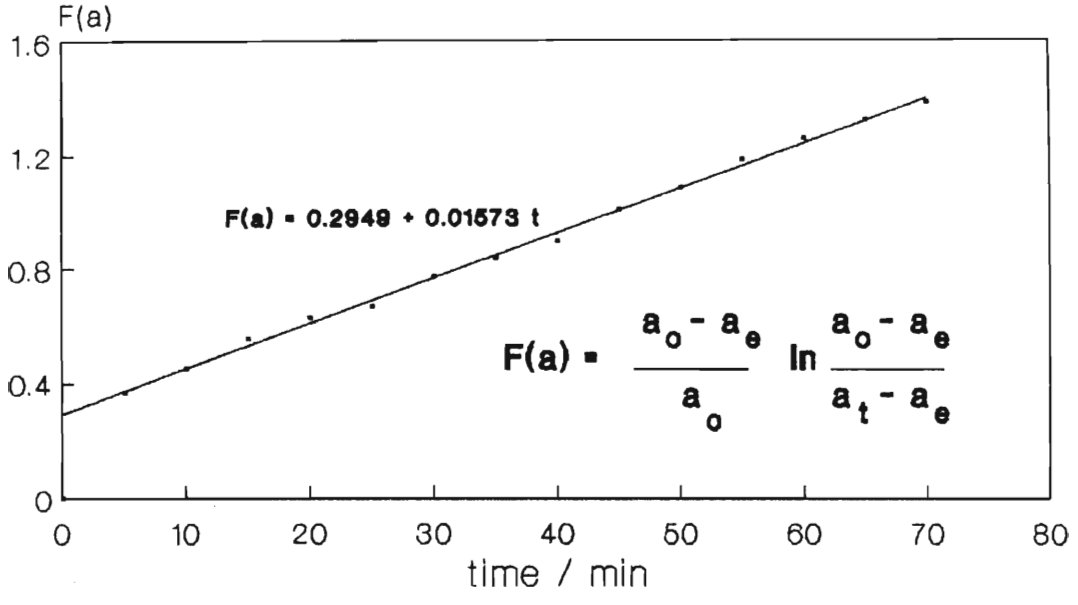


Figure 33

ln k_f as a function of ln [KELEX 100]

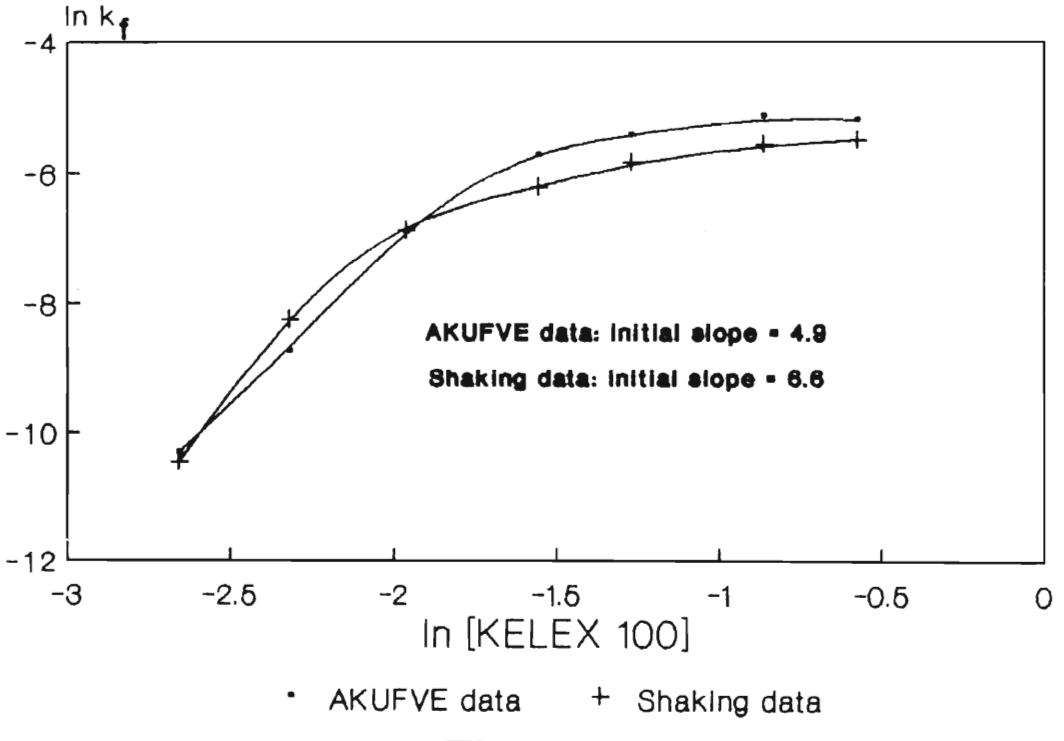


Figure 34

of 6 ligands to germanium, if it were possible, would produce a compound with 22 electrons in its outer valence shell which is certainly improbable. Some effect, physical or chemical is responsible for this anomalous reaction order.

The first possibility is that an implicit assumption made in the derivation of Equations (13) and (14) (Section 3.2.1.1) is incorrect. In the derivation of Equations (13) and (14), the heterogeneous two phase system was treated as a homogeneous system for the purposes of the kinetic analysis. Thus for this analysis to hold, the concentrations of the reactants at the reaction site (i.e. interface) must be proportional to the bulk reactant concentrations. For the reactants involved in the extraction process, particularly the interfacially active ligand, there is no guarantee that this is the case. However even the failure of this assumption cannot be responsible for such a large deviation from expected reaction order. An explanation for the large reaction order with respect to ligand must lie elsewhere and a possible explanation will be presented in the next sub-section.

3.2.2.1.1 The Fast Initial Extraction Period - Possible Causes

This sub-section presents a consideration of

possible causes of the change in extraction kinetics from an initial extremely fast rate to a slower rate.

Before causes for the fast initial extraction rate can be considered, the phenomenon of the fast initial extraction rate will be more fully examined.

Figure 35 shows a plot of [Ge] versus time for the 35.00 g/l KELEX 100 in toluene shaking run shown in Figure 31. The slope of a tangent to the curve at t = 0 is equal to the initial rate of extraction of germanium into the organic phase. Using the following analysis, the order of the extraction reaction in the initial region with respect to KELEX 100 can be determined.

$$-\frac{d[Ge]}{dt} = k'[Ge]\,[HL]^x \quad (19)$$

where k′ = a rate constant including parameters such as $[H^+]$ which are assumed to be constant throughout the extraction reaction

x = order of extraction reaction with respect [HL]

A plot of ln {-d[Ge]/dt} versus ln [HL] will have a slope of x if [Ge] is constant. If the initial slopes of all the Ge versus percentage extraction

Concentration of germanium in the aqueous phase (1.5 M sulphuric acid) versus time

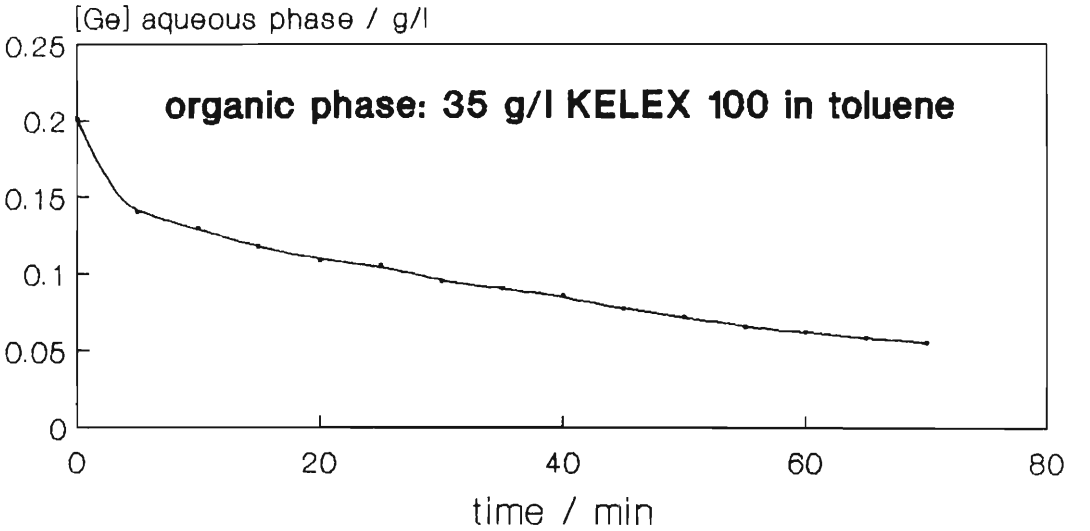


Figure 35

l n (initial rate) versus l n [KELEX 100]

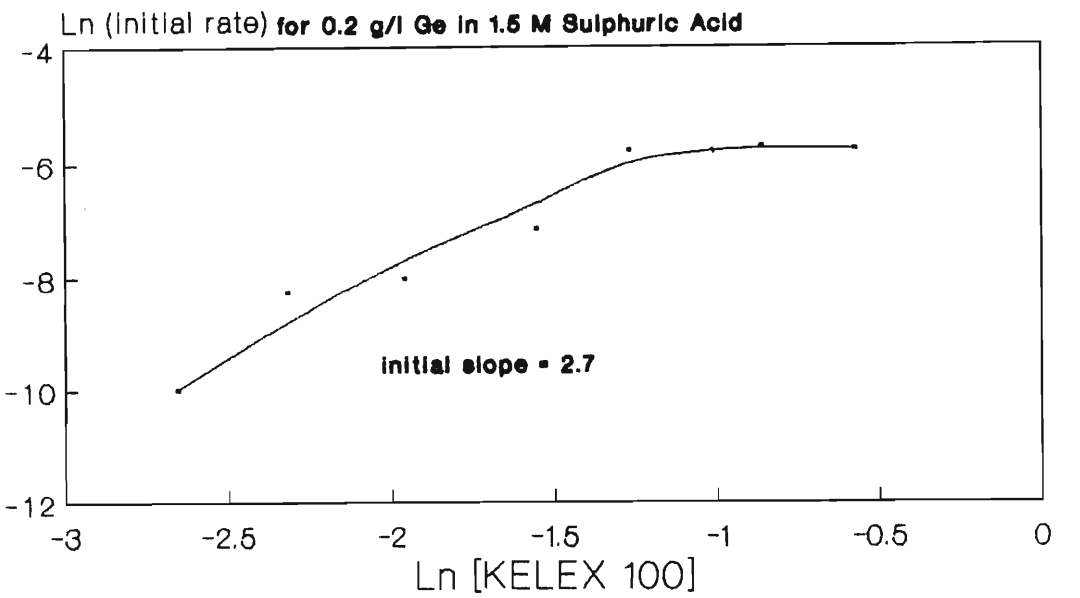


Figure 36

curves are measured and the natural logarithm of this extraction rate is plotted versus ln [KELEX 100] the slope will yield the value of x. Figure 36 shows such a plot with initial slope = 2.7 indicating that initially:

$$-\frac{d[Ge]}{dt} = k' [Ge] [HL]^{2.7} \quad (20)$$

From the analysis presented in Section 3.2.1.1, this order of 2.7 with respect to ligand is not a surprising result since considering the inaccuracies of measuring initial rate, the slope of 2.7 may be rationalised as representing a reaction order of 3.

In the course of this investigation, four possible hypotheses were considered for the change from fast extraction rate to slower extraction rate. Each hypothesis is considered below.

Hypothesis One: The first hypothesis considered was the possibility that the presence of different species of germanium in the aqueous phase were responsible for the fast, then slower initial extraction period. Germanium is present predominantly as Ge^{4+}, $Ge(OH)^{3+}$ and $Ge(OH)_2^{2+}$ at the pH experienced in 1.50 M H_2SO_4. In Section 3.2.2.2 it is argued that Ge^{4+} extracts faster than $Ge(OH)^{3+}$ and

the other Ge species in solution and that this fact is partly responsible for the better rates of extraction of germanium at lower pH's than at higher pH's.

The possibility was considered that if the initial stage was due to the Ge^{4+} extracting rapidly, the slow stage would thus be a combination of the remaining germanium species extracting slower than Ge^{4+} and also forming Ge^{4+} which then extracts into the organic phase. This explanation for the fast rate was rejected for three reasons.

An indication of the amount of germanium extracted into the organic phase can be obtained by calculating the concentration of germanium required (i.e. a value of a_t) to give a value of $\{(a_o-a_e)/a_o\}$ ln $\{(a_o-a_e)/(a_t-a_e)\}$ equal to the y-intercept for the straight lines obtained for the series of F(a) versus time plots (eg. for 35 g/l - Figure 33). This "value" for a_t at t = 0 is subtracted from the total germanium concentration in the aqueous phase at t = 0 to give an amount of germanium that is an indication of the amount of germanium extraction in each experiment due to the fast initial step. The reasoning behind this analysis is that if all extraction were due to the second "first order" reaction then the plot of

$\{(a_o-a_e)/a_o\}$ ln $\{(a_o-a_e)/(a_t-a_e)\}$ would pass through the origin. Thus the amount of germanium extracted by the fast initial step can be calculated from the y-intercept.

Figure 37 shows the percent germanium extracted by the initial fast step versus the concentration of KELEX 100. The plot shows that as the concentration of KELEX 100 is increased, the percentage of extraction due to the initial fast step increases. If the initial fast step was due to the preferential extraction of Ge^{4+} over the other germanium species, then the amount of germanium extracted by the initial fast step would be expected to remain constant and correspond to the amount of Ge^{4+} present in the aqueous in 1.50 M H_2SO_4 i.e. about 63 % of the total germanium concentration.

Reason two is that the order of extraction with respect to KELEX 100 in the second slower step cannot be rationalised in terms of Ge^{4+}, $Ge(OH)^{3+}$ and $Ge(OH)_2^{2+}$ redistribution and extraction as $GeL_3^+HSO_4^-$. Any rationalisation predicts a reaction order from zero (in the case of $Ge(OH)^{3+} \rightarrow Ge^{4+}$ being the rate determining step) to three (in the case of $Ge(OH)^{3+} + 3\ HL \rightarrow GeL_3^+ + 2\ H^+ + H_2O$ or $Ge(OH)_2^{2+} + 3\ HL \rightarrow GeL_3^+ + H^+ + 2\ H_2O$ being the rate

Percentage germanium extracted by initial fast step versus [KELEX 100]

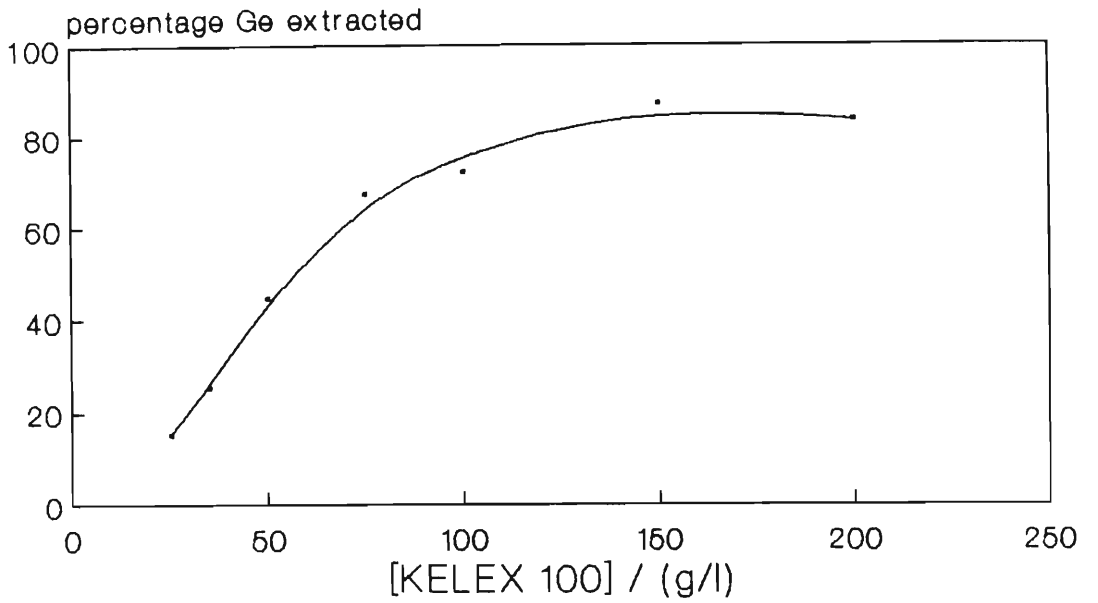


Figure 37

Concentration sulphuric acid in the organic phase as a function of KELEX 100 concentration in the organic phase

1.5 M Sulphuric Acid in the aqueous phase

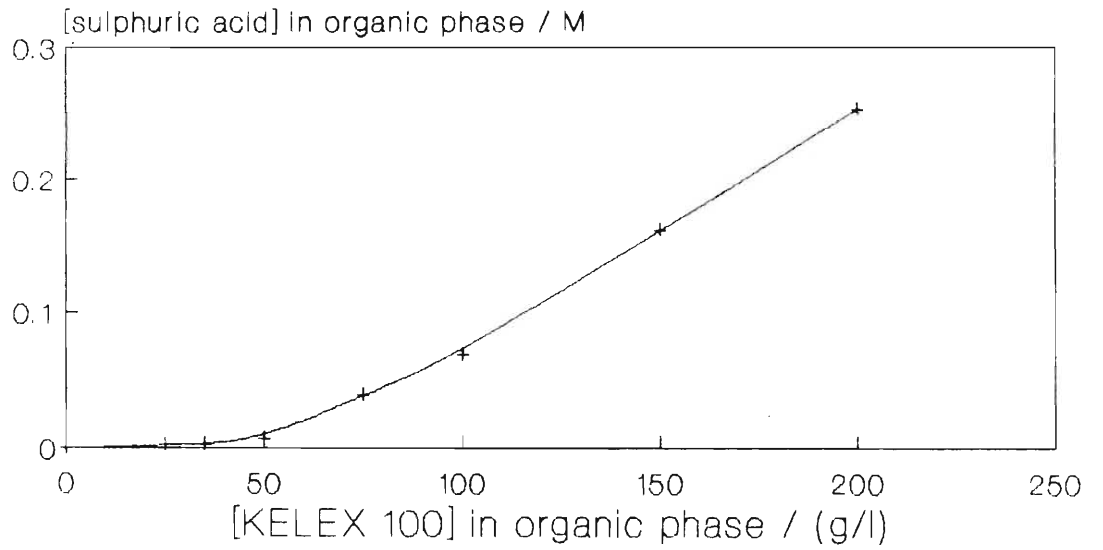


Figure 38

determining steps). Thus a reaction order of 6.6 is inexplicable in terms of this hypothesis.

The final reason for rejecting this hypothesis is that if the reactions for the interconversion of the various aqueous germanium species in the 1.50 M H_2SO_4 i.e.

$$Ge^{4+} + H_2O \leftrightarrows Ge(OH)^{3+} + H^+$$
$$Ge(OH)^{3+} + H_2O \leftrightarrows Ge(OH)_2^{2+} + H^+ \quad (21)$$

are assumed to be diffusion controlled, they will have reaction rate constants of the order 10^9 to 10^{10} $dm^3\ mol^{-1}\ s^{-1}$ [76]. Since the measured observed rate constants for the fastest extraction reaction in Figure 31 and 32 are of the order $10^0\ s^{-1}$, it is impossible that the interconversion reaction rates of the various germanium aqueous species will have any influence on extraction rates.

Hypothesis Two: Organic solutions of 7-alkylated 8-hydroxyquinoline derivatives absorb sulphuric acid[15,72]. This is also true for KELEX 100. Figure 38 shows a plot of concentration of sulphuric acid absorbed by the organic phase for solutions of KELEX 100 in toluene that have been equilibrated with an equal volume of 1.5 M H_2SO_4 for 30 minutes (Section

2.5.3.2.8). The absorbance of H_2SO_4 is reported[15] to occur via the following reaction:

$$HL_{org} + H^+_{aq} + HSO_4^-{}_{aq} \leftrightarrows \{H_2L^+HSO_4^-\}_{org} \quad (22)$$

Figure 38 shows that at high [KELEX 100], the amount of sulphuric acid extracted from the aqueous phase is considerable and represents a corresponding drop in the sulphuric acid concentration in the aqueous phase. Data presented in Section 3.2.2.2 shows that the extraction rate improves dramatically as the aqueous phase contains more sulphuric acid.

For the extraction experiments shown in Figures 31 and 32, the possibility was investigated that the two distinct extraction rates (i.e. the fast initial and slower second rate) were caused by the change in pH that would occur due to extraction of sulphuric acid by the organic phase. In the fast initial stage, germanium extraction is fast but after a period, the organic phase has extracted the sulphuric acid the pH drops to a lower value which then yields a slower extraction rate.

This explanation was rejected for a number of reasons. These are given below:

Percentage extraction versus time shaking experiments KELEX 100 - 50 g/l

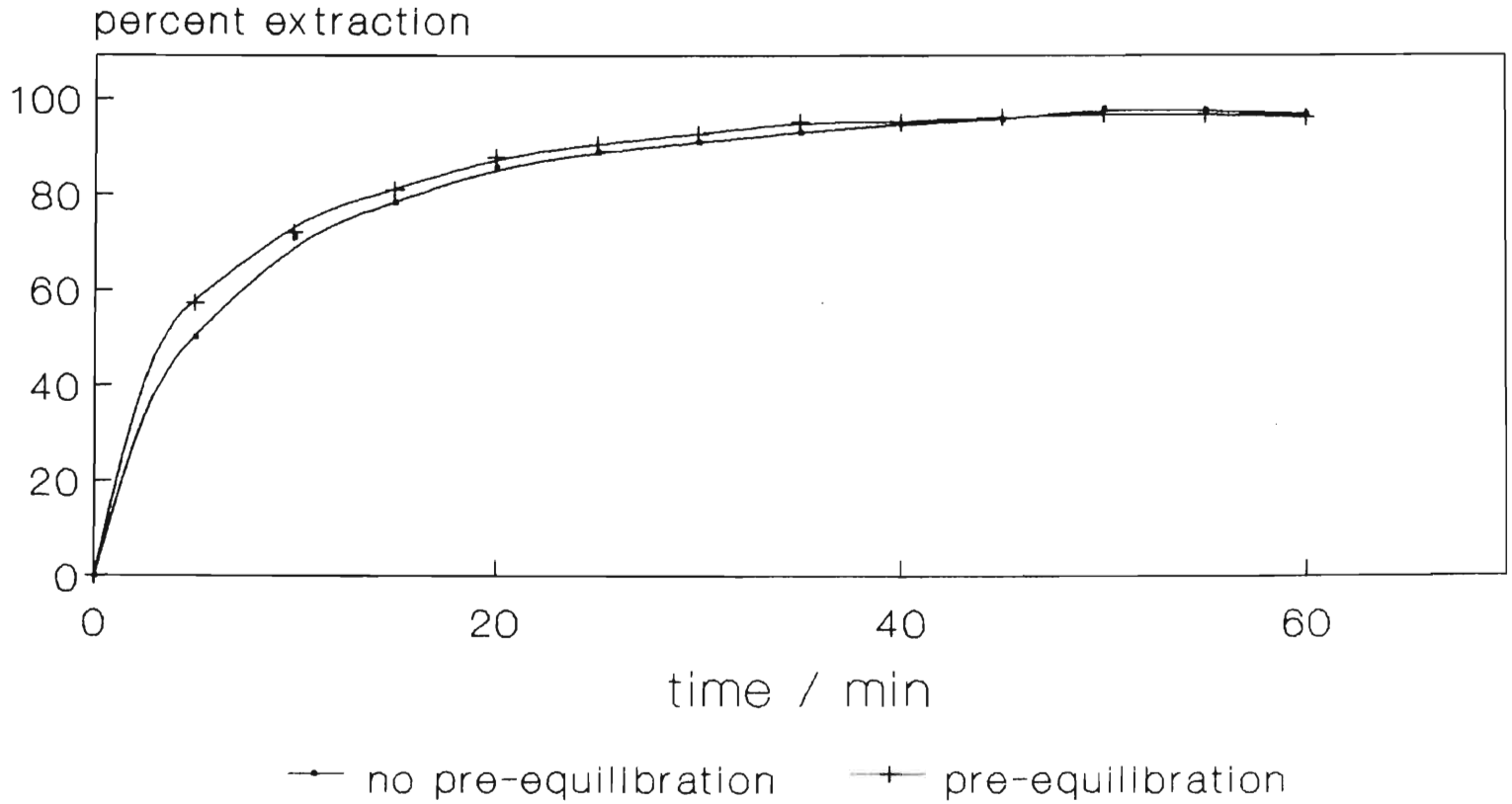


Figure 39

Figure 39 shows two plots of percentage extraction versus time for an aqueous phase of 0.200 g/l germanium in 1.50 M H_2SO_4 shaken with an equal volume of 50.00 g/l KELEX 100 in toluene. One of the plots was obtained in the usual way (i.e. mixing fresh solutions of aqueous and organic phases and withdrawing samples of the aqueous phase at the indicated time intervals). This plot is marked "no pre-equilibration" on the diagram. The procedure used to obtain plot two is described in Section 2.5.3.2.7. The second plot indicates the percentage extraction versus time curve for an organic phase that has been pre-equilibrated with the acid that is present in the aqueous phase during a kinetic run.

The two curves in Figure 39 show that, within the confines of experimental error, there is no difference in extraction rate for the conditions set down in each experiment.

The second reason for the rejection of the above explanation is that at low KELEX 100 concentration, the amount of sulphuric acid extracted into the organic phase is too low to significantly alter the pH of the aqueous phase, only at high [KELEX 100] (> 100 g/l) is the amount of H_2SO_4 extracted significant, thus although reduction in pH may have some effect in the extraction runs for high

concentration of ligand, it certainly has no effect at low ligand concentration where the fast initial rate is still a dominant feature of extraction kinetics.

Because of the high interfacial activity of the ligand and the fast nature of acid-base reactions, it is expected that the extraction of sulphuric acid by KELEX 100 in toluene would be a rapid process and occur almost immediately in a kinetic extraction experiment so that fast then slow kinetics caused by a pH change would not be observed as the pH change would occur very rapidly at the beginning of the experiment.

An effect of the pH drop caused by sulphuric acid extraction would be to cause slower extraction kinetics as the [KELEX 100] in the organic phase increased, this effect would oppose the improved extraction rate caused by higher organic ligand concentrations. This factor could contribute to the levelling off of extraction rate (and even decrease in extraction rate) observed as [KELEX 100] is increased.

The final reason for the rejection of Hypothesis Two is that it cannot, like Hypothesis One, explain why the order of the extraction reaction with respect to

ligand changes from 2.7 in the initial extraction period to 6.6 in the second extraction period. Such an explanation would predict similar reaction orders in both kinetic regions as the rate determining step is the same, only the concentrations of germanium species in the aqueous phase are different.

Hypothesis Three: This hypothesis is also related to the extraction of sulphuric acid by the extractant-containing organic phase. It was proposed that the initial fast extraction represented the extraction of germanium as GeL_3^+ until all the sulphuric acid originally extracted into the organic phase has reacted with the extracted GeL_3^+. The slower second step was a result of the fact that insufficient HSO_4^- was present in the organic phase to complex the GeL_3^+ forming and thus reaction kinetics were slower because the rate determining step became the rate at which sulphuric acid could be taken up into the organic phase.

This explanation was rejected first of all because of the fact that a reaction order of 6.6 does not correlate with the rate determining step being the rate at which sulphuric acid is extracted into the organic phase. Below is the equation representing the forward reaction for the uptake of sulphuric acid into the organic phase.

$$HL_{org} + H^{+}_{aq} + HSO_4^{-}{}_{aq} \xrightarrow{k'} \{H_2L^{+}HSO_4^{-}\}_{org} \quad (23)$$

$$thus, \; -\frac{d[H_2SO_4\,aq}{dt} = k'[H_2SO_4\,_{aq}]\,[HL_{org}] \quad (24)$$

The order of the forward reaction with respect to ligand would be expected to be one.

Second, Figure 40 shows a plot of the concentration of germanium extracted by the fast initial step versus the concentration of sulphuric acid in the organic phase. If the fast initial step was due to germanium extracting until all of the sulphuric acid had reacted with the GeL_3^{+} formed, then the concentration of germanium extracted in the initial fast period would be expected to correspond to the amount of sulphuric acid in the organic phase (i.e. a plot of [Ge] extracted in initial period versus $[H_2SO_4]$ in the organic phase would be linear with a slope of one). From Figure 40, this not the case. Thus Hypothesis Three was rejected.

<u>Hypothesis Four:</u> This hypothesis is thought to be the most likely explanation for the fast initial rate followed by a slower pseudo-first order rate in all the extraction experiments shown in Figures 31 and 32.

Concentration of germanium extracted by the initial fast step as a function of organic sulphuric acid concentration

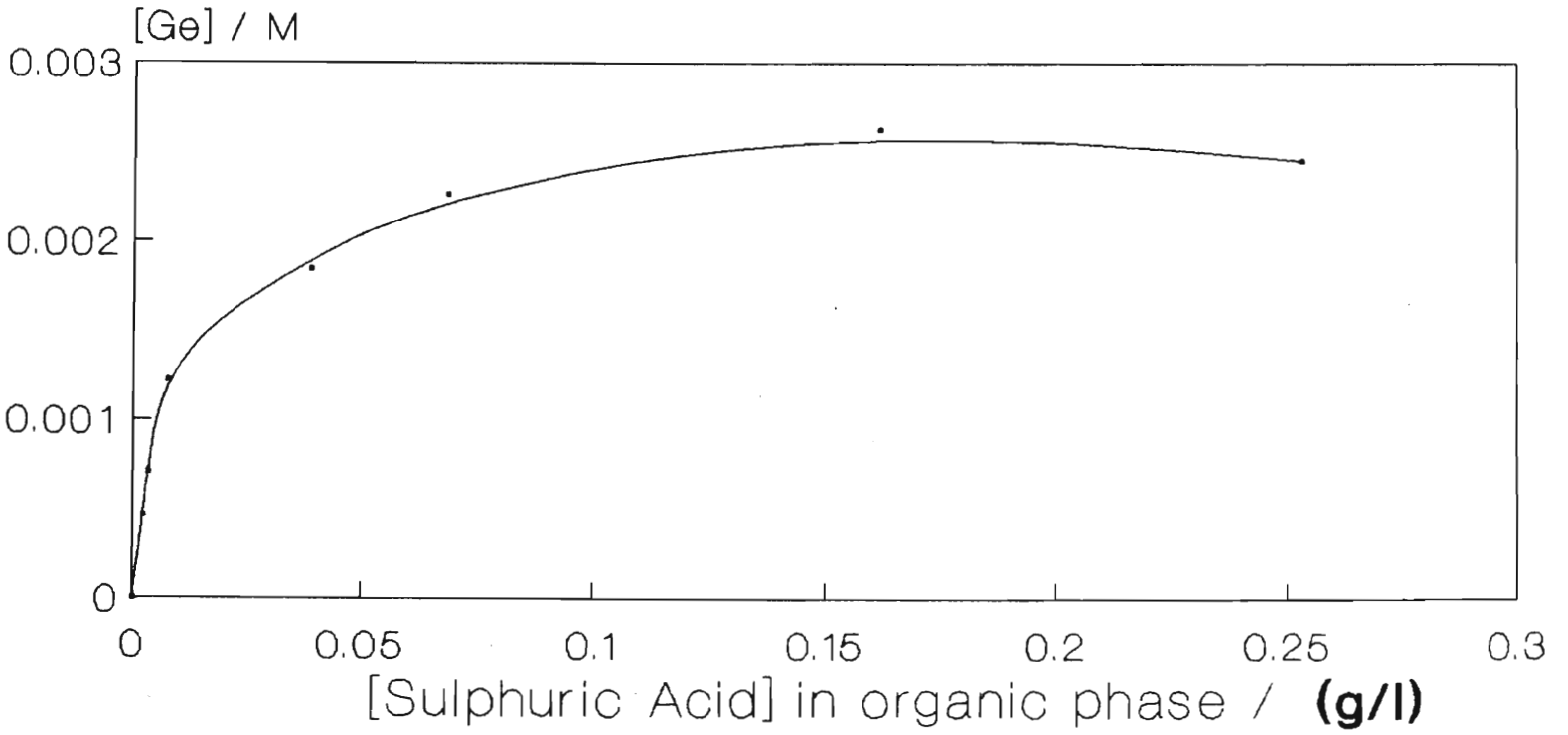


Figure 40

In previous considerations (in this thesis) the rate determining step for the extraction of germanium has been represented as:

$$Ge^{4+}_{aq} + 3\ HL_{org} + HSO_4^-{}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{GeL_3^+\ HSO_4^-{}_{org}\} + 3\ H^+_{aq} \quad (25)$$

This is in fact a simplification, since the addition of each ligand to the germanium atom being extracted is a one-step process. In addition it is likely that the $Ge(OH)_i^{4-i}$ (i = 1 to 4) species are also extracted into the organic phase although at slower rates than for Ge^{4+} (Section 3.2.2.2). The reaction is an interfacial reaction and the interfacial concentrations of any reacting species may or may not be proportional to their bulk concentration. This point means that kinetic analysis of a heterogeneous system reacting via an interfacial mechanism is complicated by the fact that certain assumptions have to be made regarding the available concentrations of the reacting species.

A further clarification of the following mechanism for germanium extraction will be considered in Section 3.3. An expansion of the reaction shown above serves to illustrate the general idea of this

fourth hypothesis.

$$Ge^{4+}_{aq} + 3\,HL_{org} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} GeL_3^{+}{}_{org} + 3\,H^{+}_{aq} \quad (26)$$

$$GeL_3^{+}{}_{org} + HSO_4^{-}{}_{org} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{GeL_3^{+}HSO_4^{-}{}_{org}\} \quad (27)$$

$HSO_4^{-}{}_{org}$ is the sulphuric acid that has been extracted into the organic phase by the KELEX 100.

$$Rate\ of\ extraction = \frac{d\,[GeL_3^{+}HSO_4^{-}{}_{org}]}{dt} = \frac{d\,[Product]}{dt} \quad (28)$$

$$= k_2\,[GeL_3^{+}{}_{org}]\,[HSO_4^{-}{}_{org}] - k_{-2}\,[Product] \quad (29)$$

$$\frac{d\,[GeL_3^{+}{}_{org}]}{dt} = k_1\,[Ge^{4+}_{aq}]\,[HL_{org}]^3 + k_{-2}\,[Product] - k_{-1}\,[GeL_3^{+}{}_{org}]\,[H_{aq}]^3 - k_2\,[GeL_3^{+}{}_{org}]\,[HSO_4^{-}{}_{org}] \quad (30)$$

$$= 0 \qquad Steady\ State\ Approximation$$

$$\therefore\ [GeL_3^{+}{}_{org}] = \frac{k_1\,[Ge^{4+}_{aq}]\,[HL_{org}]^3 + k_{-2}\,[Product]}{k_{-1}\,[H^{+}_{aq}]^3 + k_2\,[HSO_4^{-}{}_{org}]} \quad (31)$$

If this equation giving the concentration of $GeL_3^{+}{}_{org}$ is substituted into Equation (29) then,

$$\frac{d[Product]}{dt} =$$

$$k_2\left(\frac{k_1\ [Ge^{4+}_{aq}]\ [HL_{org}]^3 + k_{-2}\ [Product]}{k_{-1}[H^+_{aq}]^3 + k_2\ [HSO^-_4{}_{org}]}\right)[HSO^-_4{}_{org}] - k_{-2}[Product] \quad (32)$$

The second term in Equation (32) (i.e. k_{-2}[Product]) becomes small either far from equilibrium because [Product] is small, or when percent equilibrium extraction is close to 100, the reverse reaction rate is small.

Figure 41 shows a plot of the natural logarithm of sulphuric acid concentration in the organic phase versus the natural logarithm of KELEX 100 concentration in the organic phase for organic solutions that have been equilibrated with 1.50 M H_2SO_4 for 30 minutes. The slope of this plot is 2.5. From this plot an empirical formula can be derived relating the $[H_2SO_4]_{org}$ to $[HL]_{org}$ for the extraction experiments carried out with germanium dissolved in 1.50 M H_2SO_4.

$$[H_2SO_4]_{org} = k_3\ [HL]^{2.5}_{org} \quad (33)$$

where k_3 is an proportionality constant.

Substituting this expression into Equation (32).

$$\frac{d[Product]}{dt} = \left(\frac{k_2\, k_1\, [Ge^{4+}_{aq}]\, [HL_{org}]^3 + k_2\, k_{-2}\, [Product]}{k_{-1}[H^+]^3 + k_3\, k_2\, [HL_{org}]^{2.5}} \right) k_3\, [HL]^{2.5}_{org} \quad (34)$$

This equation predicts an interesting result, if $k_2k_{-2}[Product] << k_2k_1[Ge^{4+}{}_{aq}][HL_{org}]^3$ and $k_{-1}[H^+{}_{aq}]^3 >> k_3k_2[HL]_{org}{}^{2.5}$ and the assumptions made to derive Equation (34) are valid, then:

$$\frac{d[Product]}{dt} = \frac{k_3 k_2 k_1\, [Ge^{4+}_{aq}]\, [HL_{org}]^{5.5}}{k_{-1}\, [H^+_{aq}]^3} \quad (35)$$

$$i.e. \quad \frac{d[Product]}{dt} = k'[Ge^{4+}_{aq}]\, [HL_{org}]^{5.5} \quad (36)$$

$$where \quad k' = \frac{k_3 k_2 k_1}{k_{-1}\, [H^+_{aq}]^3} \quad (37)$$

The derivation of Equation (36) required a number of assumptions which are discussed below:

(1) The first assumption (which has already been mentioned) is that available interfacial reagent concentrations are proportional to bulk reagent concentrations. This assumption enables the heterogeneous system to be analyzed using the same kinetic analysis that would be used for a homogeneous system, this assumption must always be

I n [sulphuric acid] in organic phase as a function of I n [KELEX 100] in the organic phase

1.5 M sulphuric acid in the aqueous phase

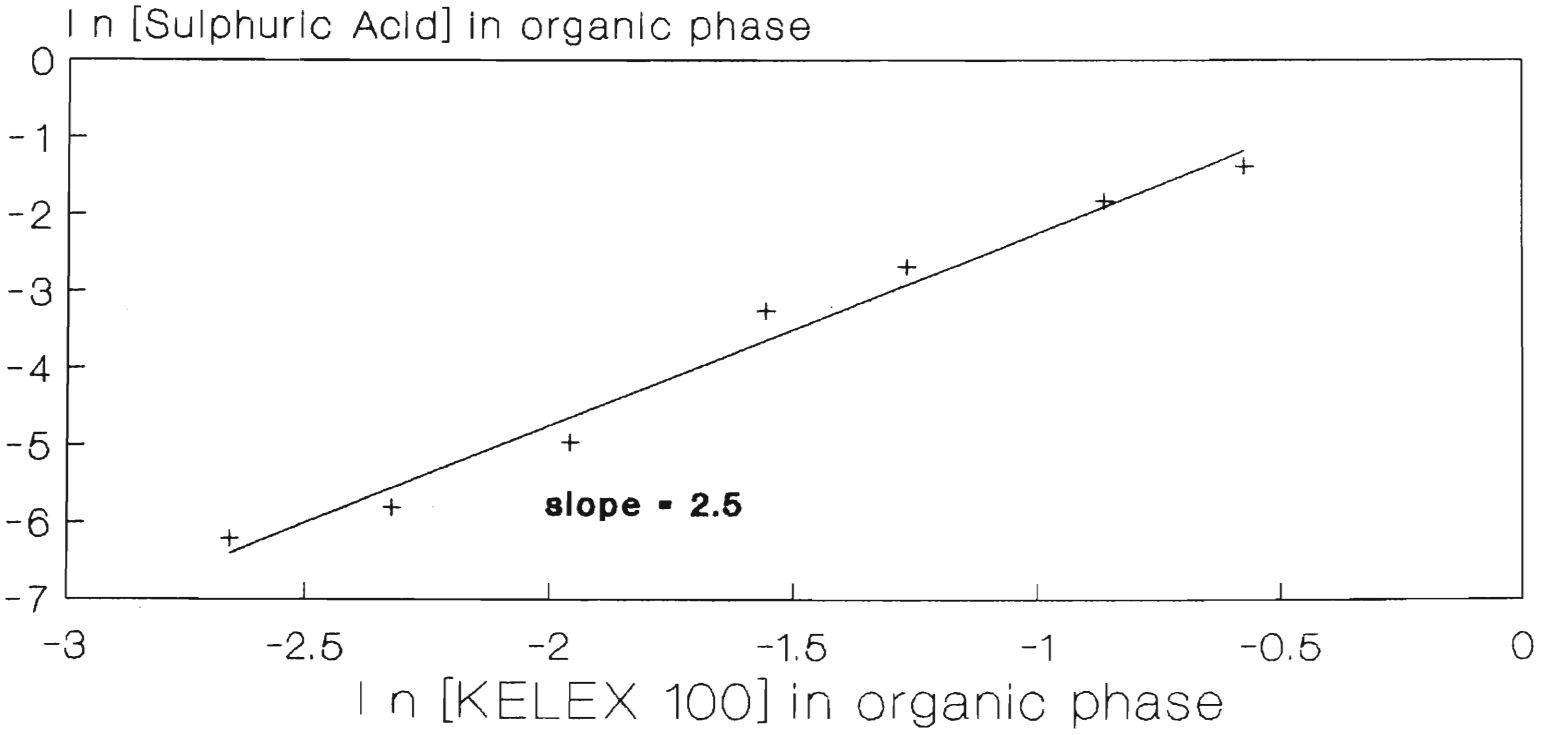


Figure 41

remembered as it may hold at lower ligand concentrations, but at higher ligand concentrations it is unlikely that this assumption is valid.

(2) The existence of GeL_3^+ in the organic phase is another assumption and perhaps the weak point of the argument. However, molecular modelling shows that the positively charged germanium atom in the centre of the three ligand molecules is well shielded from external influences, the positive charge can also be delocalised over the three aromatic ring systems of the three ligand molecules. Figure 42 shows the germanium-ligand complex. This argument proposes that GeL_3^+ exists for some period of time in some concentration in the organic phase, not as $GeL_3^+HSO_4^-$ but as GeL_3^+. However, the GeL_3^+ is expected to react quickly to produce $GeL_3^+HSO_4^-$.

(3) The third assumption is that $k_2k_{-2}[\text{Product}] << k_2k_1[Ge^{4+}_{aq}][HL_{org}]^3$. This assumption basically proposes that the reverse reaction of product to GeL_3^+ and HSO_4^- can be ignored. This is a reasonable assumption as the validity of Equation (36) is only investigated far from equilibrium or where equilibrium extraction is practically 100 percent.

(4) The fourth assumption is that $k_1[H^+_{aq}]^3 >>$

Three -dimensional image of the extracted germanium complex - GeL_3^+

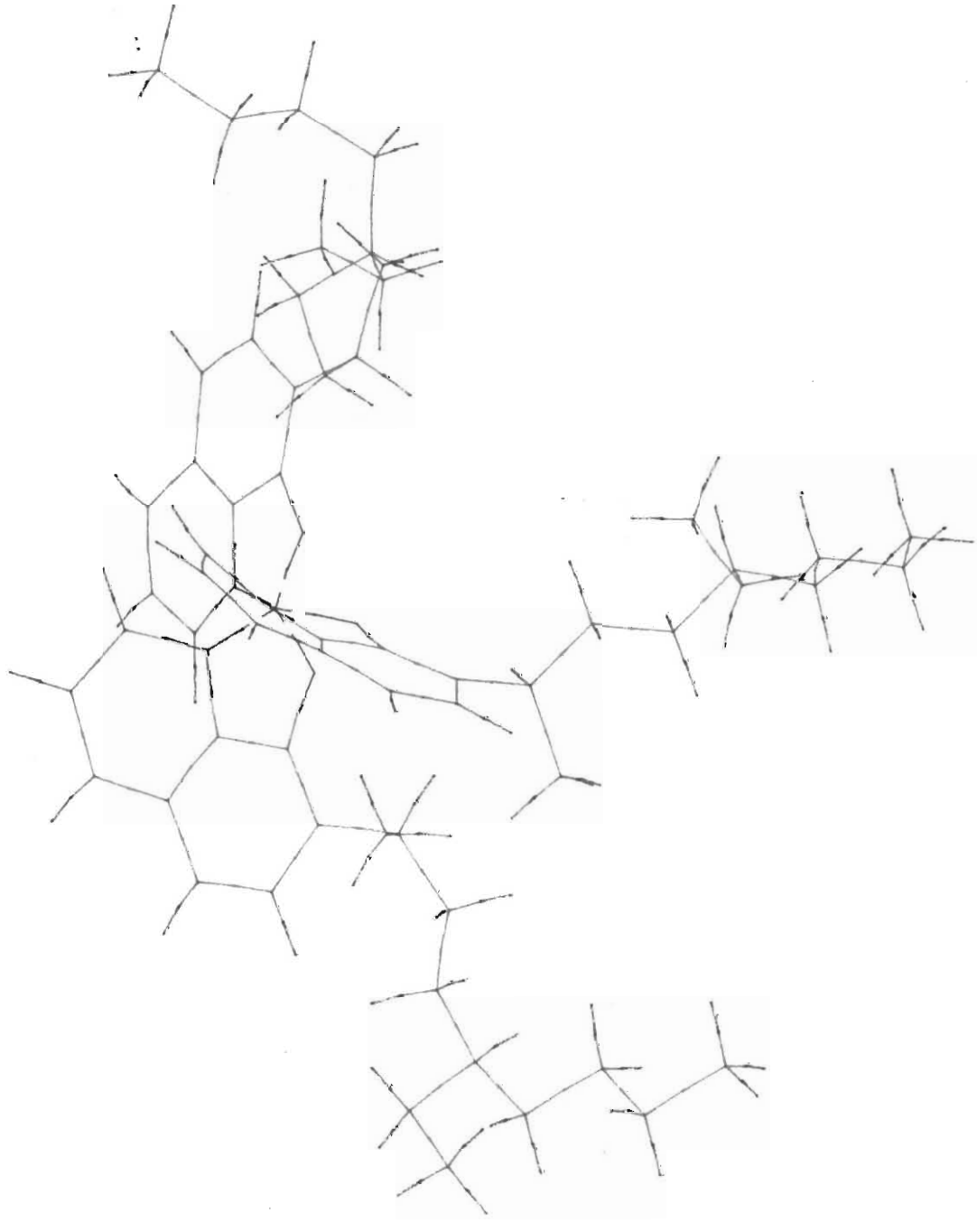


Figure 42

$k_3k_2[HL_{org}]^{2.5}$. This assumption is argued on the basis that $[H^+_{aq}]^3 >> [HL_{org}]^{2.5}$.

The consequences of Equation (36) will now be discussed.

The initial fast extraction period in a shaking run, represents the period where Reaction (26) is the rate determining step. The rate law is thus:

$$Rate = k_1 [Ge^{4+}_{aq}] [HL_{org}]^3 - k_{-1} [H^+_{aq}]^3 [GeL_3^+{}_{org}] \quad (38)$$

If $[GeL_3^+{}_{org}]$ (i.e. the rate of reverse reaction) is relatively small, the rate law predicts an order of 3 for the initial rate with respect to KELEX 100. An experimental order of 2.7 is observed in Figure 36. The levelling off of the plot of ln [initial rate] versus ln [KELEX 100] is due to the fact that the available interfacial concentration of KELEX 100 reaches a maximum where the interface is populated to a maximum extent and thus further increases in ligand concentration will not make more ligand available for extraction and a deviation from predicted reaction order occurs.

Once the concentration of $GeL_3^+{}_{org}$ builds up to a "critical" level, then the rate determining step

becomes Reaction (27) and Equation (36) is valid, thus the order of 5.5 can be obtained. This compares with the order of 6.6 obtained in Figure 34 between 25.00 g/l and 35.00 g/l. The fact that the observed order is greater than 5.5 must be attributed to experimental error in the determination of reaction rate constants at low ligand concentration due to the slow nature of the reaction. The decrease in slope of the curve (to values below 5.5) in Figure 34 (i.e. reaction order with respect to KELEX 100) can be attributed to: increased viscosity possibly reducing the effective surface area; lower aqueous pH caused by increased acid extraction by KELEX 100 and the attainment of a maximum interfacial population of ligand.

It can be noted from Figure 34 that the value of $\{-\ln k_f\}$ approached by the curve for AKUFVE data is greater than the value approached by the curve for shaking data. This is in spite of the fact that in the AKUFVE, a small fraction of the reacting phases (part of the contents of the centrifuge) is not involved in the extraction reaction. A suggested explanation of this phenomenon is that the interfacial area to phase volume ratio in the AKUFVE exceeds the interfacial area to phase volume ratio of the shaking experiments by a large enough amount to offset the loss of interfacial area in the AKUFVE

due to the centrifuge. Vigorous stirring would thus appear to generate more interfacial area for a set volume of phases than vigorous shaking.

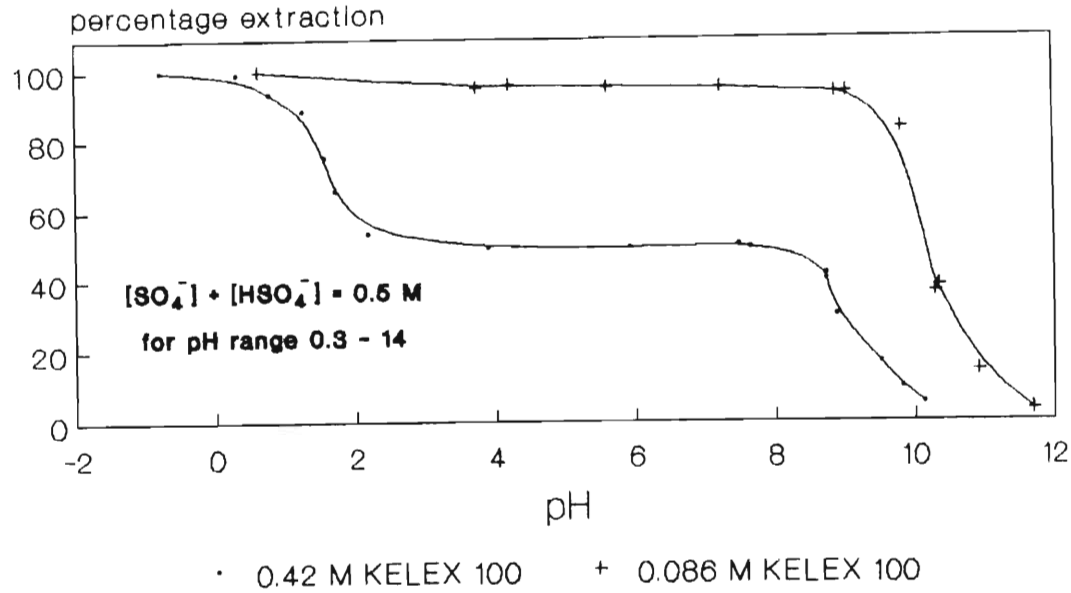
3.2.2.2 The Effect of pH on the Rate of Extraction

The pH dependence of germanium extraction by a 7-alkylated 8-hydroxyquinoline derivative has been examined by Cote and Bauer[15] and Marchon, Cote and Bauer[14] in two similar publications. Cote and Bauer report that below pH 2 germanium is extracted from sulphuric acid media as GeL_3^+ (where HL = "pre-1976" KELEX 100). Between pH 3 and pH 8, germanium is extracted as $GeL_2(OH)_2$. The equilibrium extraction by "pre-1976" KELEX 100 is reported for a variety of concentrations of ligand. Since "pre-1976" KELEX 100 and the KELEX 100 used in this study are both 8-hydroxyquinoline derivatives, differing only in alkyl side chain structure, there is little reason to suppose that the system under study in this project will yield results any different from those presented by Marchon et al.[14] and Cote and Bauer[15].

Figure 43 shows the percent equilibrium extraction versus pH for two different "pre-1976" KELEX 100 concentrations. The results indicate that at low pH (<0) good equilibrium extraction occurs. There is an intermediate range (pH 3 to 9) in which the

Percentage equilibrium extraction of as a function of pH "pre-1976 KELEX 100"

Determined by B. Marchon et al. (Reference 14)



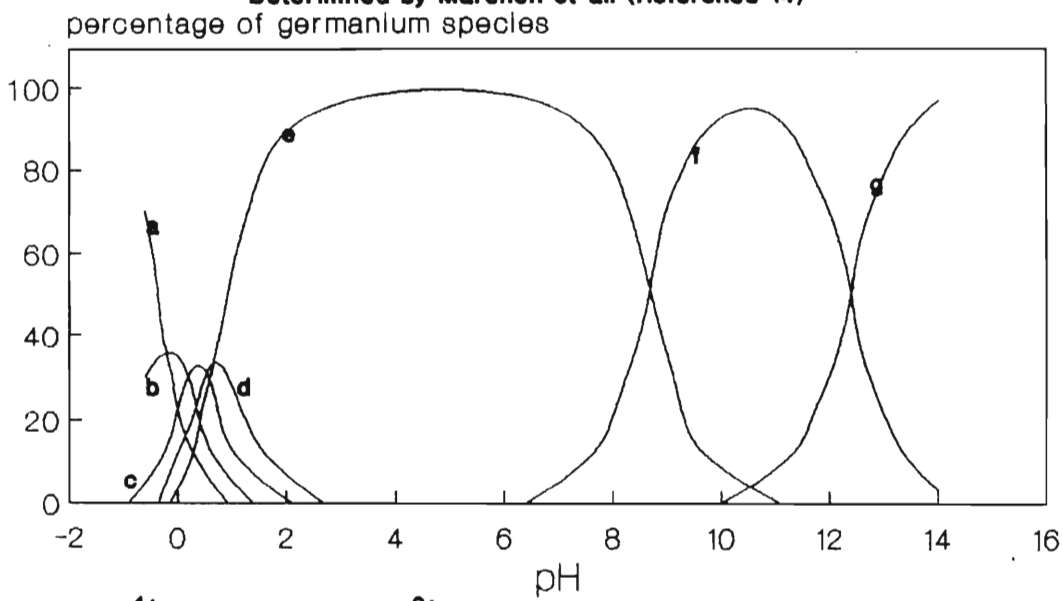
· 0.42 M KELEX 100 + 0.086 M KELEX 100

phase ratio 1 : 1 **organic phase: KELEX 100 in kerosene**
aqueous phase: 0.0004 M Ge in sulphuric acid

Figure 43

Percentage of the various monomeric germanium species as a function of pH

Determined by Marchon et al. (Reference 14)



(a) Ge^{4+} (c) $Ge(OH)_2^{2+}$ (e) $Ge(OH)_4$ or H_4GeO_4

(b) $Ge(OH)^{3+}$ (d) $Ge(OH)_3^+$ (f) $H_3GeO_4^-$ (g) $H_2GeO_4^{2-}$

percentage equilibrium extraction is independent of pH. From pH 9 to 12 , percentage equilibrium extraction drops rapidly, and above pH 12, Marchon et al.[14] observe that no germanium is extracted into the organic phase.

Directly below Figure 43 is a plot showing the various monomeric germanium species that are present as pH changes. This plot has also been taken from Marchon et al.'s publication[14]. Marchon et al.[14] derived this plot from values for the equilibrium constants of the various monomeric germanium species reported in Nazarenko[29]. Both plots have the same scale for the x-axis (i.e. pH) enabling a comparison between the two plots can be made. It is apparent that the region of best equilibrium extraction in Figure 43 corresponds to the region in Figure 44 where germanium is present as Ge^{4+}, $Ge(OH)^{3+}$ and $Ge(OH)_2^{2+}$. The intermediate region (pH 3 to 9) corresponds to the region where germanium is present as $Ge(OH)_4$. The region where percentage equilibrium extraction starts to decrease corresponds to the decline in the $Ge(OH)_4$ species concentration and the appearance of $H_3GeO_4^-$ and $H_2GeO_4^{2-}$.

In Section 3.2.1.1 the general reaction for the extraction of germanium from an aqueous sulphuric

acid solution (pH < 0) into an organic solution containing KELEX 100 (HL) was given as:

$$Ge(OH)_{i\,aq}^{(4-i)+} + 3\,HL_{org} + HSO_{4\,aq}^{-} + (i-3)\,H_{aq}^{+} \rightleftarrows GeL_3^{+}HSO_{4\,org}^{-} + i\,H_2O \qquad (39)$$

The extraction in the pH region < 0 can be represented as:

$$Ge_{aq}^{4+} + 3\,HL_{org} + HSO_{4\,aq}^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} GeL_3^{+}HSO_{4\,org}^{-} + 3\,H_{aq}^{+} \qquad (40)$$

$$Ge(OH)_{aq}^{3+} + 3\,HL_{org} + HSO_{4\,aq}^{-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} GeL_3^{+}HSO_{4\,org}^{-} + 2\,H_{aq}^{+} + H_2O \qquad (41)$$

$$Ge(OH)_{2\,aq}^{2+} + 3\,HL_{org} + HSO_{4\,aq}^{-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} GeL_3^{+}HSO_{4\,org}^{-} + H_{aq}^{+} + 2\,H_2O \qquad (42)$$

By Le Chatelier's principle, an increase in $[H^+]$ (i.e. low pH) would not favour extraction of Ge^{4+}, $Ge(OH)^{3+}$ and $Ge(OH)_2^{2+}$ if all other species in the Equations (40-42) were kept at constant concentration. By the same principle, an increase in $[HSO_4^-{}_{aq}]$ would favour extraction of germanium. Thus the improved extraction at low pH can be attributed to either the increase in $[HSO_4^-{}_{aq}]$ or the fact that as i becomes smaller for $Ge(OH)_i^{(4-i)}$ (i = 0, 1, 2) the forward rate constant for extraction (i.e. k_i)

of the aqueous germanium species {i.e. $Ge(OH)_i^{(4-i)}$} becomes larger, the magnitude of this increased rate is sufficient to outweigh the increased rate of reverse extraction produced by the increase in $[H^+]$.

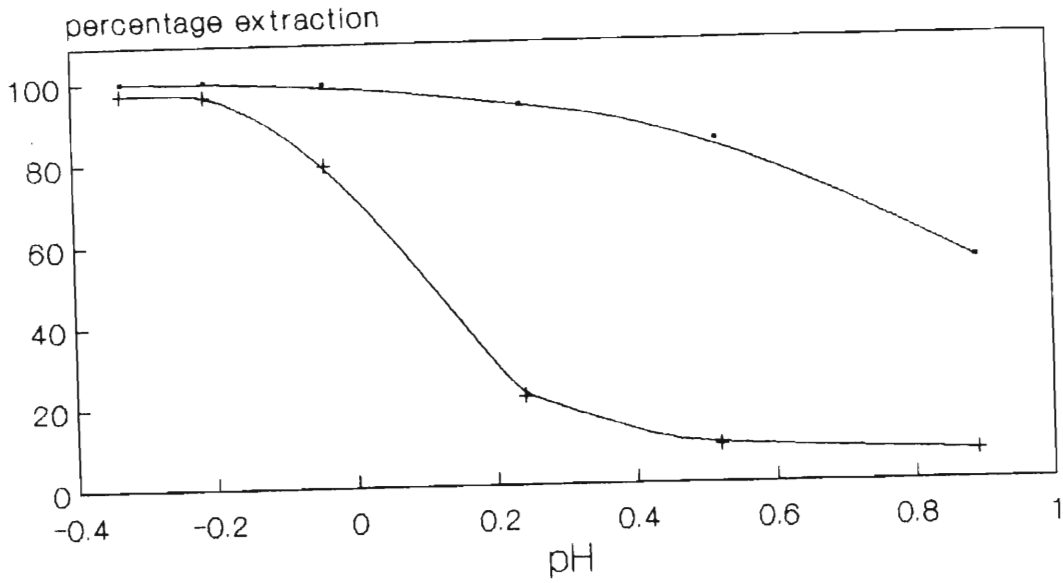
In the pH range 3 to 8, the extraction of germanium is represented as:

$$Ge(OH)_4 + 2HL \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} GeL_2(OH)_2 + 2H_2O \quad (43)$$

This reaction explains the independence of pH on percentage germanium extraction in Figure 43 as in the pH region 3 to 9 germanium is present in the aqueous phase as predominantly $Ge(OH)_4$.

The pH region where percentage extraction drops rapidly corresponds to the drop in the concentration of $Ge(OH)_4$ and the region where KELEX 100 has its pK_a. The pK_a of "pre-1976" KELEX 100 has been determined as 10.40 ± 0.05 by Bag and Freiser[16]. The pK_a of the KELEX 100 used in this study would be similar to the pK_a of "pre-1976" KELEX 100. The dramatic reduction in extraction efficiency could be attributed to the fact that it is unlikely that the two negatively charged germanium species ($H_3GeO_4^-$ and $H_2GeO_4^{2-}$) would react with the negatively charged

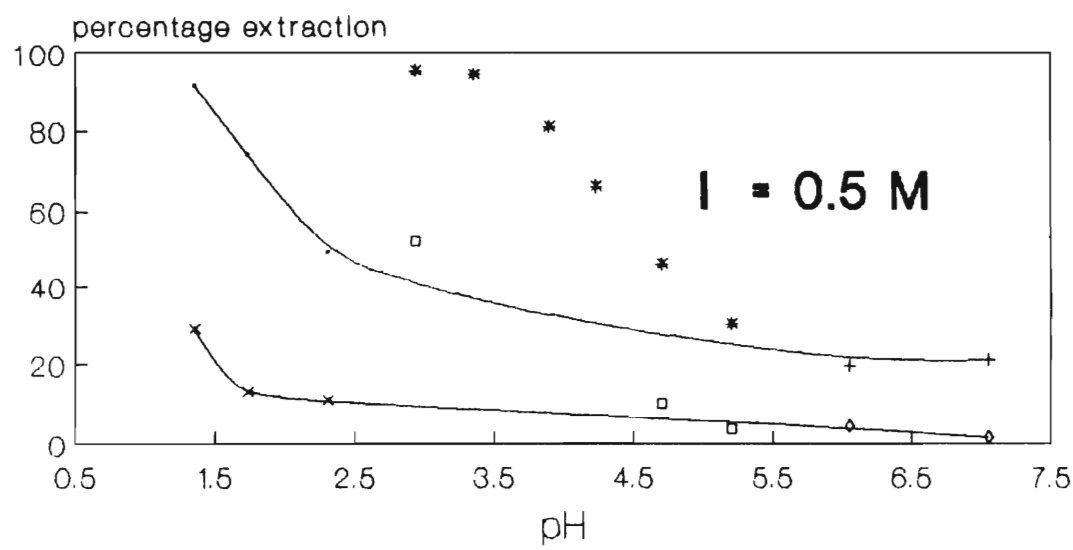
Percentage extraction versus pH
KELEX 100



[KELEX 100] · 100 g/l + 35 g/l

Figure 45

Percentage equilibrium extraction as a function of pH - KELEX 100



(100 g/l) · HCl/KCl + NaOH/KCl * KHP/HCl/NaOH

(35 g/l) □ KHP/HCl/NaOH × HCl/KCl ◇ NaOH/KDP

Figure 46

ligand anions.

Figure 45 shows the percentage equilibrium extraction of germanium from 0.200 g/l germanium in H_2SO_4 solutions into equal volumes of toluene solutions containing 35.00 g/l and 100.00 g/l KELEX 100 (experiment described in Section 2.5.3.2.6). The pH's of the H_2SO_4 solutions have been calculated assuming that the first proton of H_2SO_4 dissociates completely and the second proton has a K_a of 1.2×10^{-2} [37].

Figure 46 shows a plot of equilibrium extraction versus pH obtained using equal volumes of 0.200 g/l germanium in buffered solutions (described in Section 2.2.2.1.1 (3)) and 35.00 g/l & 100.00 g/l KELEX 100 in toluene solutions. Two curves have been drawn through the equilibrium data points obtained using the inorganic systems HCl/KCl and NaOH/KDP (KDP = potassium dihydrogen phosphate). The use of the NaOH/KHP and HCl/KHP buffers (KHP = potassium hydrogen phthalate) in the 2.5 to 5.0 pH range gave equilibrium extraction of germanium far in excess of the expected values. The use of an organic compound as a buffer that presumably can complex germanium and is soluble in the organic phase could possibly cause a synergistic effect. An alternative buffer system using trisodium citrate and citric acid

(described in Section 2.2.2.1.1 (3)) was used to buffer the germanium solutions in this pH range (2.5 to 5.0). Over a period of two days, no germanium was extracted from these solutions with 100.00 g/l KELEX 100 in toluene. This may be due to the germanium being complexed in the aqueous phase by the citrate and thus being unavailable for reaction with the ligand.

The results obtained with the organic buffers are thus indeterminate because the effect of the organic molecules cannot be predicted or accounted for. The inorganic buffers provide more reliable results as the inorganic ions are likely to have a similar effect on equilibrium extraction at constant ionic strength (I). However even the equilibrium extraction with inorganic buffers is comparatively high when compared to experiments conducted at a similar or lower pH in H_2SO_4, e.g. at pH = 0.9 (Figure 45) percentage equilibrium extraction is 60 % with 100.00 g/l KELEX 100, at pH = 1.3 (Figure 46) percentage equilibrium extraction is 90 % with 100.00 g/l KELEX 100. These differences highlight the fact that similar conditions must be used to enable experiments to be compared. Ligand concentration and pH are not the only parameters that affect percentage equilibrium extraction.

Figure 46 confirms the trend reported by Marchon et al.[14] for KELEX 100. The results with organic buffers show that the extractant performance can be vastly altered by the addition of relatively small amounts of chelating agents and highlight the potential for the use of synergists in extraction.

A usual practice in solvent extraction chemistry is to plot log D versus pH. According to Equation (18) derived in Section 3.2.1.1:

$$\log D = \log K + n\log[HL] - n\log[H^+] \quad (18)$$

where $D = [Ge]_{org} / [Ge]_{aq}$ at equilibrium

$$K = \frac{\{[GeL_n^{(4-n)}{}_{org}][H^+_{aq}]^n\}}{\{[Ge^{4+}_{aq}][HL_{org}]^n}$$

n = number of ligand molecules reacting with each germanium atom extracted

HL = KELEX 100

If $[HL_{org}]$ was constant and all the germanium in the aqueous solution was present as Ge^{4+}, a log D versus pH plot would yield a straight line of slope n. However in this system, as pH changes, the fractions of the various germanium species in solution change and each species would yield slope of a log D versus pH plot that was different. For example,

$$Ge^{4+}_{aq} + 3\,HL_{org} \rightleftharpoons GeL_3^{+}{}_{org} + 3\,H^{+}_{aq} \quad (44)$$

$$Ge(OH)^{3+}_{aq} + 3\,HL_{org} \rightleftharpoons GeL_3^{+}{}_{org} + 2\,H^{+}_{aq} + H_2O \quad (45)$$

Thus using the data in Figure 45 and 46 to provide log D versus pH plots would not yield a straight line graph of integral gradient, but a curve with slope dependent on the germanium species present in the aqueous solution at that pH. For this reason, log D versus pH curves are not presented here.

Figure 47 shows the rate of germanium extraction versus time for various concentrations of aqueous H_2SO_4. The rate of extraction of germanium is vastly improved by increased H_2SO_4 concentration. This result is not unexpected since the general equation for germanium extraction is:

$$\mathbb{R} + Ge_{aq} + 3\,HL_{org} + HSO_4^{-}{}_{aq} \rightleftharpoons GeL_3^{+}HSO_4^{-}{}_{org} + \mathbb{R}' \quad (46)$$

where Ge_{aq} = any aqueous germanium species

HL = KELEX 100

$\mathbb{R}$ and $\mathbb{R}'$ = species required to balance reaction such as H^+ or H_2O

In the previous discussion on explaining shaking kinetic data for constant sulphuric acid concentration in the aqueous phase (Section

Percentage Ge extracted as a function of time for various aqueous sulphuric acid concentrations

100 g/l KELEX 100

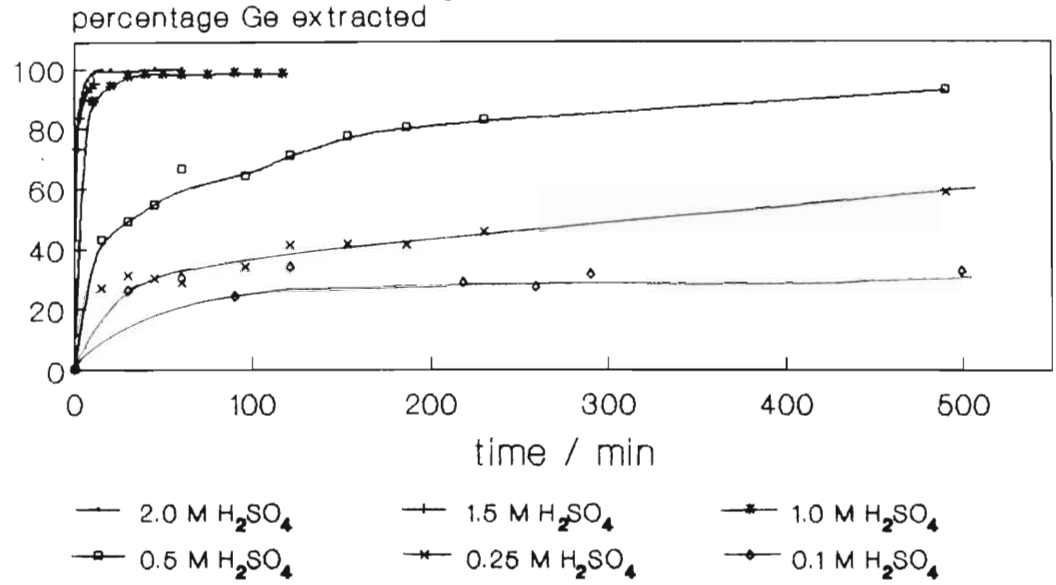
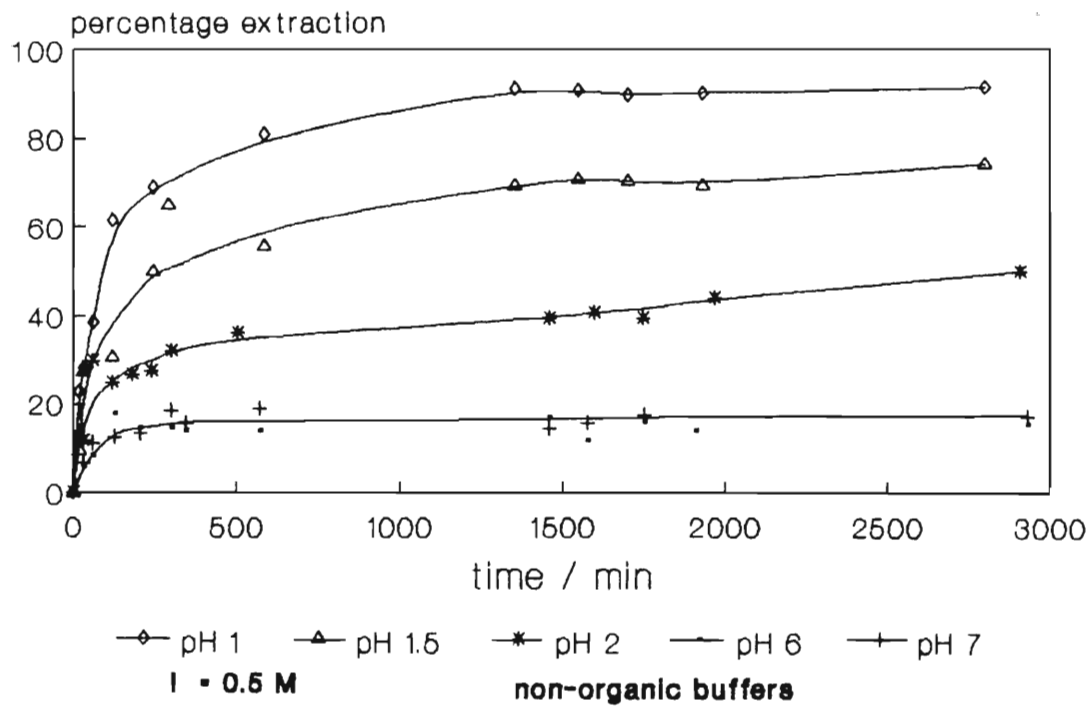


Figure 47

Percentage extraction versus time for various pH's



100 g/l KELEX 100 in organic phase

Figure 48

3.2.2.1), it was shown that sulphuric acid is extracted into the organic phase by KELEX 100. As the aqueous phase H_2SO_4 concentration increases, more H_2SO_4 is extracted into the organic phase at constant KELEX 100 concentration. Marchon et al.[14] have shown that the "pre-1976" KELEX 100-containing organic phase will extract H_2SO_4 until a stoichiometric amount of H_2SO_4 is extracted, this occurs after the organic phase has been contacted with greater than 4.0 M H_2SO_4. Thus the increased amount of H_2SO_4 in the organic phase will also cause increased equilibrium extraction.

Another major factor in accounting for the faster extraction rate has been mentioned earlier in this section. It is likely that as the germanium species in solution have a lower number of hydroxyl groups, they will react at a faster rate with the interfacial ligand and thus be extracted more rapidly, i.e. Ge^{4+} is extracted at a faster rate than $Ge(OH)^{3+}$ etc. As higher sulphuric acid concentrations are reached, $Ge(OH)_i^{(4-i)}$ will form $Ge(OH)_{i-1}^{(5-i)}$ until at extremely low pH (not shown in Figure 44) all the aqueous phase Ge will be present as Ge^{4+}.

A note should be made that at extremely high aqueous phase H_2SO_4 concentrations (above 2 M), Marchon et

al.[14] have observed that the equilibrium percentage of germanium extracted decreases. This may be caused because oxidation of the ligand molecules may occur at high acid concentrations.

Figure 48 shows the percentage germanium extracted versus time for the various pH runs carried out using the inorganic pH systems at ionic strength 0.50 M. These curves show a gradual reduction in extraction rate until at pH 6 and 7 very similar extraction kinetics are observed. This trend is expected considering the earlier discussion of percentage equilibrium extraction obtained.

3.2.2.3 The Effect of a Modifier on the Rate of Extraction

Cote and Bauer[15], and Marchon, Cote and Bauer[14] use an organic diluent of 10 % octanol in kerosene throughout their work. This prompted workers in this laboratory[33,34] to examine the effect of alcohol modifiers on the extraction kinetics of germanium.

Figure 49 shows the percentage germanium extracted versus time from 0.200 g/l germanium in 0.50M H_2SO_4 solutions (experiment described in Section 2.5.3.2.3) into solutions containing alcohol modifiers in toluene (10 % v/v) and KELEX 100.

The order of activity of the modifiers is: benzyl alcohol > n-butanol, n-pentanol > n-octanol, n-propanol. This order of activity may reveal something about the mode of action of the modifier.

Table 15 shows the aqueous solubilities of the alcohols used.

In the extracting reaction mixtures, the modifier with the largest aqueous solubility would be expected to be the most soluble in the aqueous phase. A possible explanation for the mode of action of the modifiers is that by dissolving in the

Comparison of the effect on extraction efficiency by different modifiers

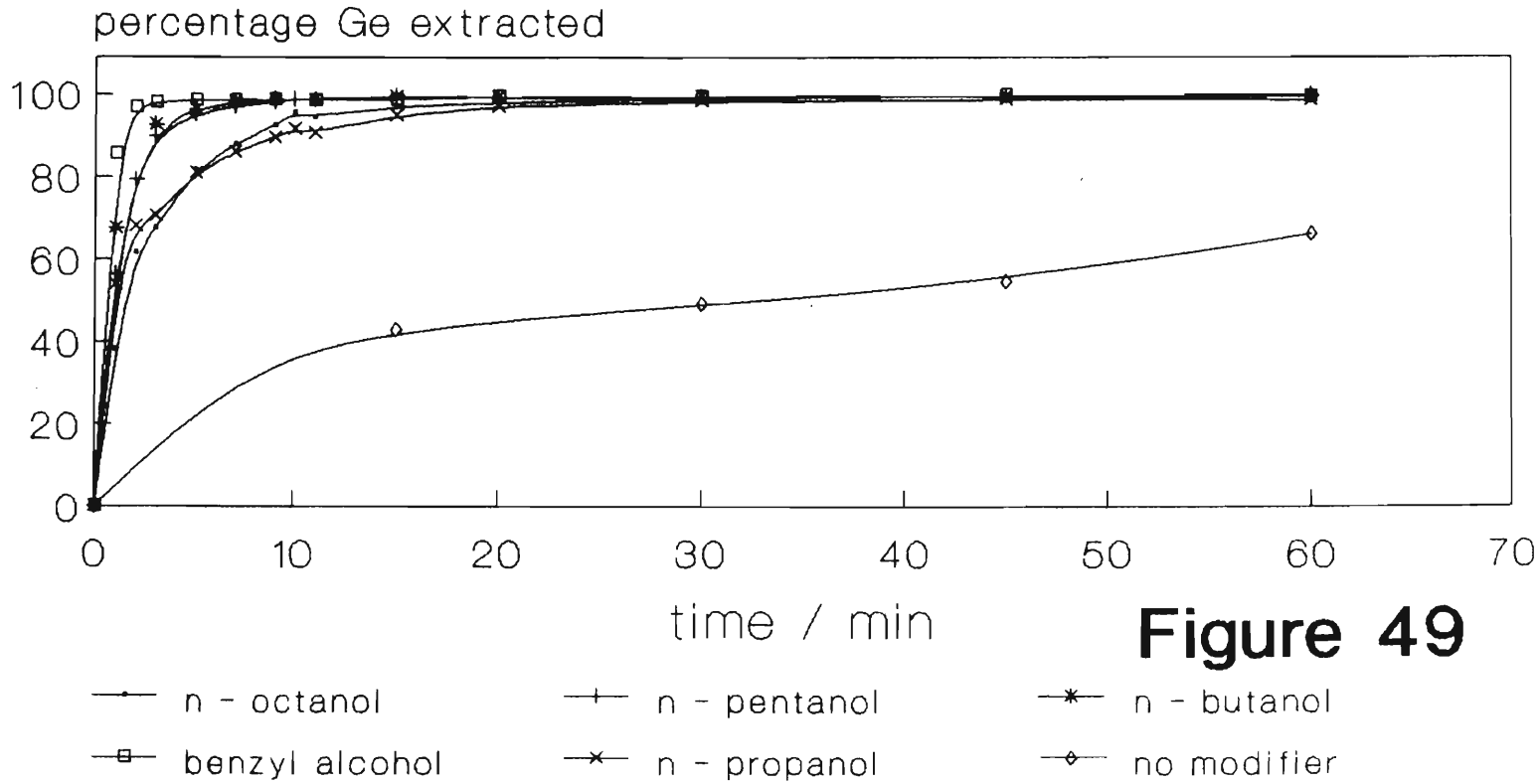


Figure 49

aqueous phase: 0.2 g/l Ge in 0.5 M H_2SO_4
organic phase: 100 g/l KELEX 100 in 10 % alcohol modifier in toluene

Table 15 - Aqueous solubility of alcohol modifiers

alcohol	Solubility - (g/100 g)
n - propanol	soluble in all proportions
n - butanol	7.90 @ 20 ^{O}C
benzyl alcohol	3.80 @ 20 ^{O}C
n - pentanol	2.36 @ 20 ^{O}C
n - octanol	0.0586 @ 25 ^{O}C

aqueous phase, the solubility of KELEX 100 becomes greater in the aqueous phase and thus the aqueous reaction of germanium and ligand would contribute to germanium extraction and thus improve the extraction rate. This factor may contribute to an increased extraction rate but it is unlikely that this is the cause as propanol is extremely soluble in water (and presumably the 1.50 M H_2SO_4 aqueous phase) and the propanol modifier is one of the worst synergists out of the five alcohols. In fact, the degree to which extraction rate is improved has no simple correlation to aqueous phase solubility, so the explanation of the activity series for the modifiers is likely to be multifactorial.

The results presented in Figure 49 show that a modifier greatly improves the rate of extraction.

Equilibrium extraction is also improved by the addition of a modifier. The percentage equilibrium extraction (after 24 hours) reached by the plot in Figure 49 where no modifier has been used is 93.3 %, the plots where modifiers have been used all obtain equilibrium extraction levels of above 99 %. The role of the modifier is thus not only catalytic.

The precise mechanism of modifier action is not known and provides a topic for speculation. Possibly, the mode of action is related to changes in the nature of the interface and interfacial region in the reacting system. The presence of a component that has solubility in both organic and aqueous phases would undoubtedly accelerate interfacial reactions by providing an interfacial medium that is more flexible to penetration by the long chain KELEX 100 molecules that are required to react with, and orientate themselves around, each germanium atom that is extracted.

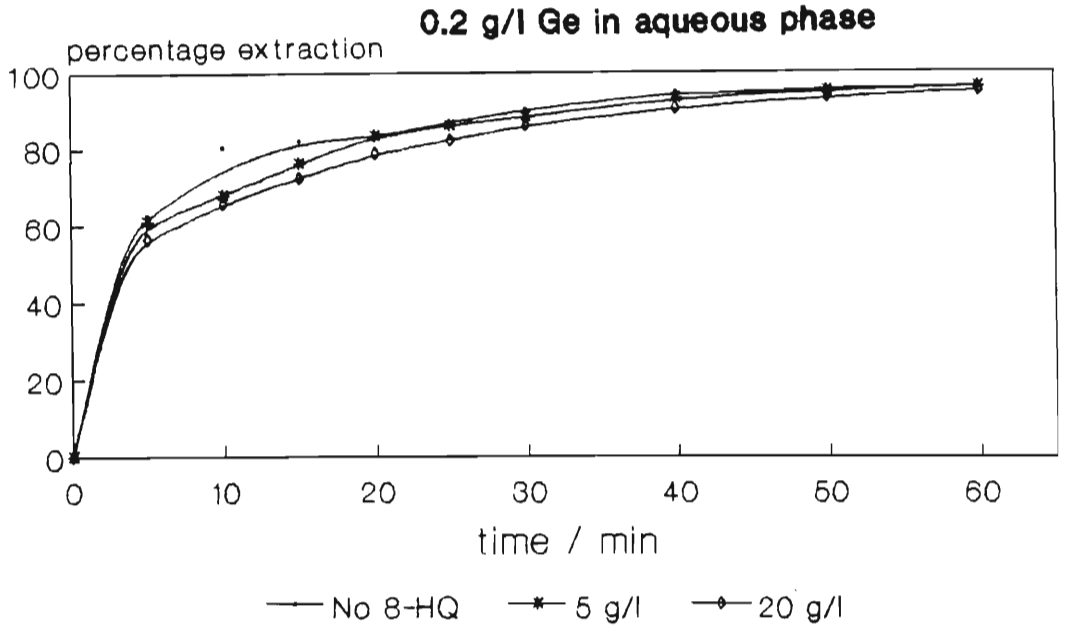
The improvement of equilibrium extraction may be attributed to the improved solubility of the extracted complex in the organic phase. An organic species containing an alcohol would have a higher dielectric strength as well as a better ability to solvate the extracted charged germanium complex.

3.2.2.4 The Effect of 8-Hydroxyquinoline on the Rate of Extraction

Figure 50 shows a plot of percentage extraction versus time for 0.200 g/l germanium in 1.50 M H_2SO_4 containing zero g/l; 5.0 g/l and 20.0 g/l 8-hydroxyquinoline solutions and 50.00 g/l KELEX 100 in toluene solutions (described in Section 2.5.3.2.4). The three curves show very similar extraction kinetics and indicate that although 8-hydroxyquinoline does retard the extraction kinetics slightly, the presence of < 1 % of 8-hydroxyquinoline in commercial KELEX 100 is not likely to affect the extractant performance of KELEX 100 at high KELEX 100 concentration. Figure 51 shows a plot of percentage extraction after five minutes versus the concentration of 8-hydroxyquinoline in the aqueous phase. This plot also shows that a slight decrease in extraction rate occurs as the concentration of 8-hydroxyquinoline increases in the aqueous phase.

8-Hydroxyquinoline is known to extract metal ions from aqueous solutions into organic solutions[42,45-47] but at high aqueous acid concentrations, the solubility of 8-hydroxyquinoline is high in the aqueous phase. This is verified by the fact that even 20.0 g/l of 8-hydroxyquinoline

The effect of 8-hydroxyquinoline on the rate of Ge extraction - shaking experiments



aqueous phase: varying [8-hydroxyquinoline] in 1.5 M H_2SO_4
organic phase: 50 g/l KELEX 100 in toluene

Figure 50

Percentage extraction after five minutes as a function of aqueous 8-hydroxyquinoline concentration

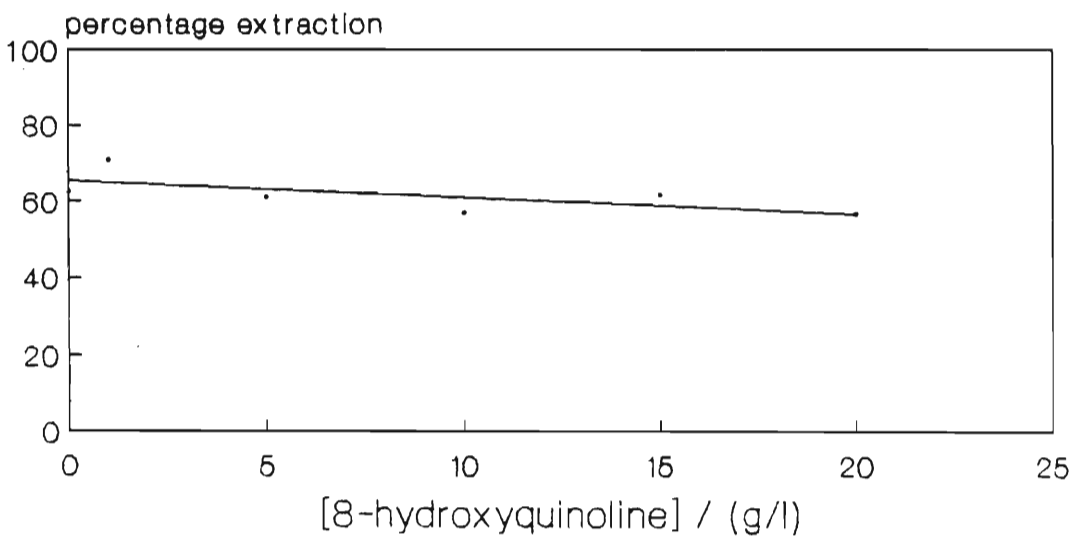


Figure 51

easily dissolved in the 1.50 M H_2SO_4 solution used to obtain these results. In extraction experiments where the aqueous phase is strongly acidic and some (< 1 % of the mass of KELEX 100 used) 8-hydroxyquinoline is present, the 8-hydroxyquinoline is likely to be extracted into the aqueous phase where it has little influence on extraction kinetics. The 8-hydroxyquinoline is not likely to complex germanium in the aqueous phase since it has a pK_b of 4.99[74]. All the 8-hydroxyquinoline in the acid phase will be protonated and thus unavailable to chelate germanium.

At higher pH's where 8-hydroxyquinoline is deprotonated, extraction of germanium by 8-hydroxyquinoline derivatives is poor as a result of the stable germanium hydroxy species forming in solution, so extraction experiments with KELEX 100 containing small amounts of 8-hydroxyquinoline are not likely to be compromised.

3.2.2.5 The Effect of Ionic Strength on Rate of Extraction

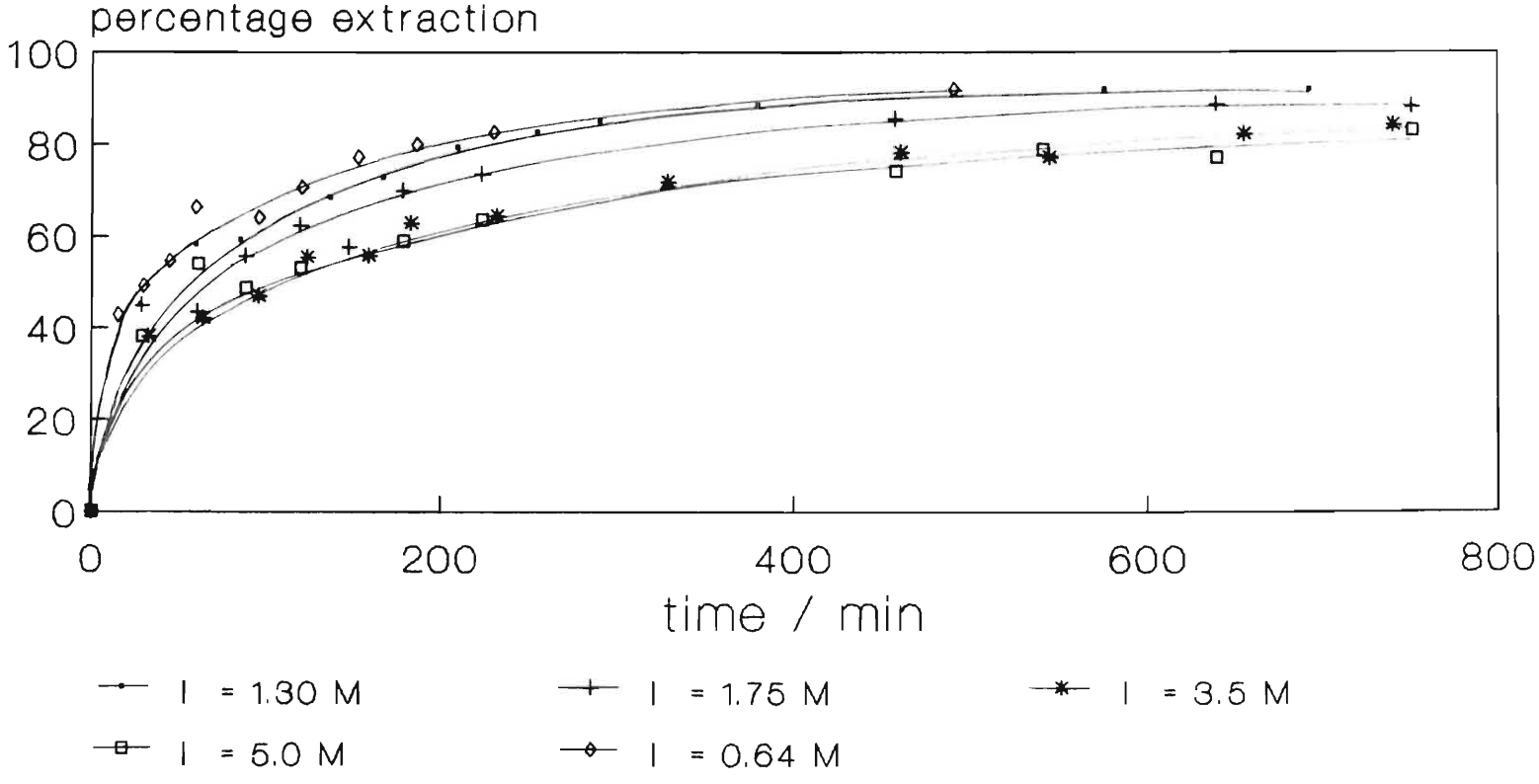
Figure 52 show plots of percentage extraction versus pH for shaking experiments with an organic phase of 100.00 g/l KELEX 100 and an aqueous phase of 0.200 g/l germanium in 0.50 M H_2SO_4 containing varying amounts of Na_2SO_4 (experiment described in Section 2.5.3.2.5). Table 16 shows the calculated pH for each solution (taking into account the increased $[SO_4^{2-}]$ in each aqueous solution) used in the extraction experiments shown in Figure 52.

Table 16 - I, $[Na_2SO_4]$ and pH for solutions used to examine the effect of I on extraction kinetics

I - (M)	$[Na_2SO_4]$ - (M)	calculated pH i.e. {- log $[H^+]$}
0.64	0	0.242
1.30	0.25	0.283
1.75	0.50	0.291
3.50	1.00	0.296
5.00	1.50	0.297
6.50	2.00	0.298

Although pH is not constant for all the extraction plots shown in Figure 52, it is apparent that the

The effect of ionic strength on the rate of extraction of germanium (percentage extraction versus time)



aqueous phase: 0.2 g/l Ge, varying I, 0.5 M H_2SO_4
organic phase: 100 g/l KELEX 100 in toluene

Figure 52

increase in pH as I increases shown in Table 16 is not entirely responsible for the reduction in extraction rate. The greatest difference in pH in Table 16 occurs when I changes from 1.30 M (i.e. $[Na_2SO_4]$ = 0.25 M) to 0.64 M (i.e. $[Na_2SO_4]$ = zero), if the change in pH was the cause for reduced extraction then the difference in extraction rate (shown in Figure 52) between the I = 0.64 M and the I = 1.30 M solutions would be greater than the difference between the I = 1.30 M and I = 6.50 M solutions. This is not the case. Clearly the inconsistency of pH is not the cause of the reduced extraction rate in Figure 52, but some effect related to the increased I.

Laidler[76] gives a discussion of the theoretical treatment of the influence ionic strength on the rate of reaction between ions. The reaction considered is of the type:

$$A + B \rightarrow X \rightarrow Products \quad (47)$$

X is an intermediate formed by the addition of A and B and is regarded as an intermediate complex. The rate of reaction is proportional to the concentration of X.

$$\frac{d[Product]}{dt} = k'[X] \quad (48)$$

Using an expression for the equilibrium constant for reaction (47) and the Debye-Huckel expression relating activity coefficients to ionic strength, the following equation can be derived for aqueous solutions at 25 ^{0}C.

$$\log_{10} k = \log_{10} k_0 + 1.02\, z_a z_b \sqrt{I_m} \quad (49)$$

where k = reaction rate constant defined by

d[Product] / dt = k [A][B]

$k_0 = k'K$

K = equilibrium constant for A + B $\rightleftharpoons$ X

$$i.e.\ K = \frac{a_X}{a_A\, a_B} = \left(\frac{[X]}{[A]\ [B]}\right)\left(\frac{\gamma_X}{\gamma_A\ \gamma_B}\right) \quad (50)$$

a_i = activity of i th species

γ_i = activity coefficient of i th species

defined by $a_i = \gamma_i[i]$

z_i = charge of i th species

From Equation (49) a plot of log k versus $\sqrt{(I)}$ will give a straight line of slope $z_A z_B$ 1.02.

Section 3.2.1.1 described how pseudo first order rate constants can be obtained from the slope of F(a) versus time plots. Also mentioned was the fact

that extraction kinetics using the AKUFVE displayed a fast then a slower extraction period. Rate constants obtained from F(a) versus time plots refer to the second extraction period. Section 3.2.2.1 reported that this kinetic behaviour also occurs for shaking experiments. Figure 53 shows plots of F(a) versus time for the shaking runs shown in Figure 52. Clearly extraction rate decreases with increasing I. Figure 54 shows a plot of log k_f versus $\sqrt{I}$ (k_f is the slope of the straight lines in Figure 53). In Section 3.2.2.1.1 the rate determining step in the linear region of the F(a) versus time plots was explained as:

$$GeL_{3\,org}^{+} + HSO_{4\,org}^{-} \rightleftharpoons \{GeL_3^{+}HSO_{4\,org}^{-}\} \quad (51)$$

Thus the slope of the plot in Figure 54 should be $(z_A \times z_B) \times 1.02 = -1.02$. The actual slope is -0.46. This result is not surprising as the Debye-Huckel expression relating activity coefficient to ionic strength will only be valid where I < 0.01 M. More accurate expressions relating activity coefficient to ionic strength are available, e.g. the Davies Equation - even this equation will only be valid for I < 0.5 M . If it is assumed that the γ_{Ge} is < 1 and decreases with increasing ionic strength for all the ionic strengths studied, then

F (a) versus time for kinetic experiments at various ionic strengths

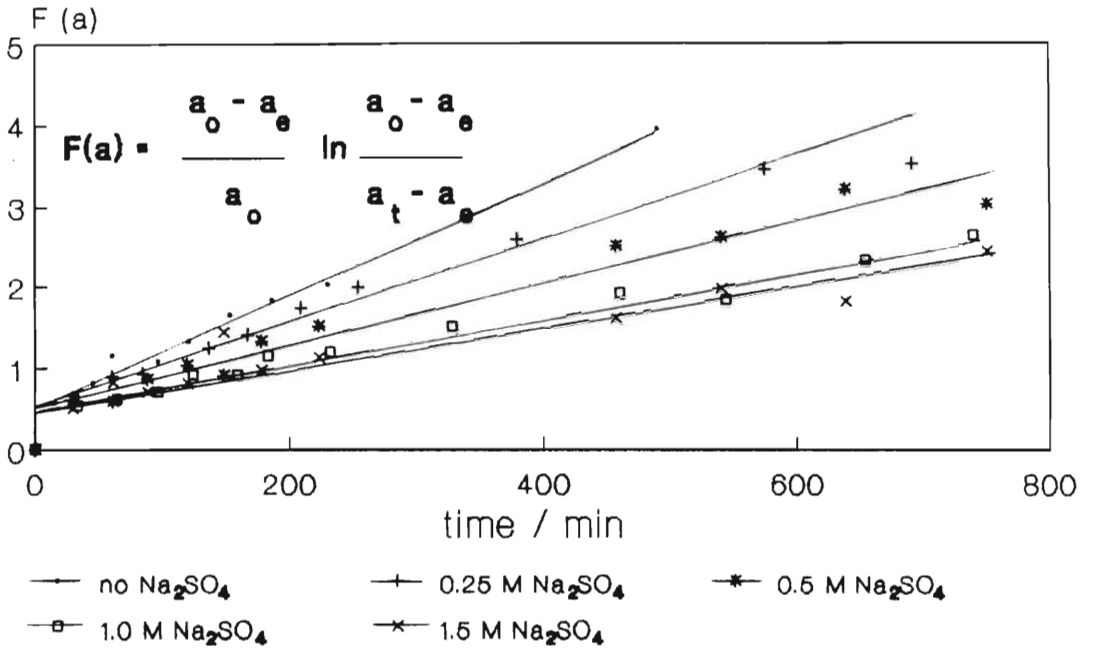


Figure 53

log k_f versus $\sqrt{I}$

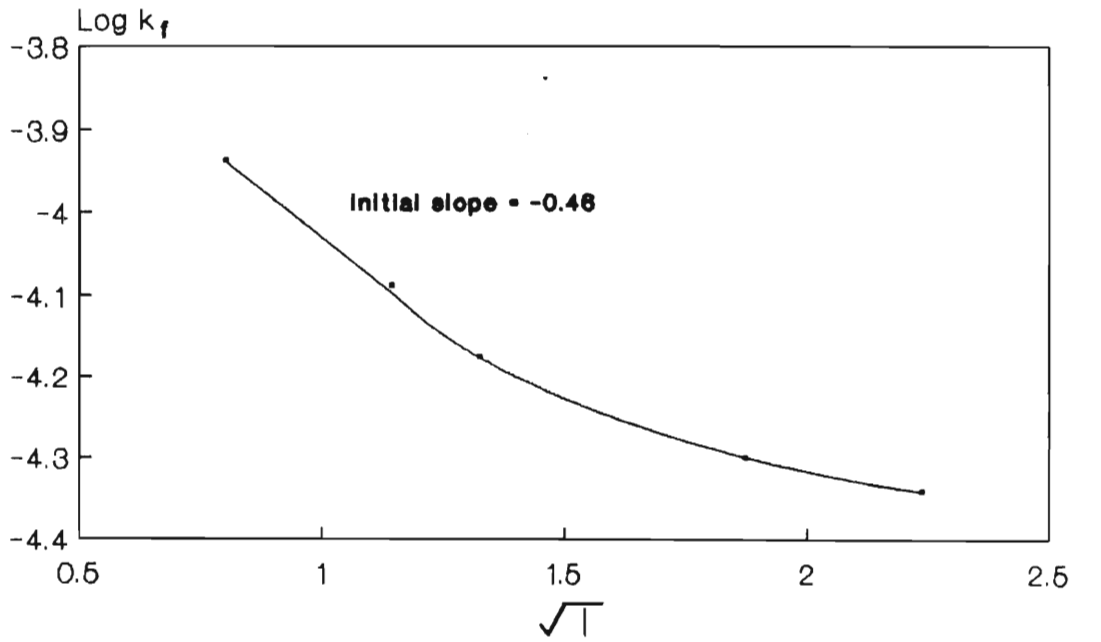


Figure 54

strength for all the ionic strengths studied, then the qualitative result can be obtained from Figure 54 that the rate constants used to obtain the figure refer to a reaction between a negative and positive ion, because the product of z_A and z_B is negative. This is in accordance with the proposal that the rate determining step in the second region is as proposed and not a reaction between Ge^{4+} and HL or H_2L^+.

3.2.2.6 Comparison of AKUFVE and shaking techniques

A shaking regime can be used to obtain many of the experimental results that may be obtained using the AKUFVE. However there may be circumstances where the AKUFVE will produce results at a faster rate than a simple shaking regime. These circumstances are met when the conditions described in Section 3.2.1.4 are satisfied. However it should be noted that a simple shaking regime is relatively inexpensive and the effort and expense required to obtain an AKUFVE for solvent extraction studies provides, in the author's opinion, relatively minor advantages over a conventional shaking system.

3.2.3 Lewis Cell Experiments

These experiments were conducted to complement the AKUFVE and shaking experiments obtained studying the effect of changing ligand concentration on extraction rate. Experiments were conducted as described in Section 2.5.2. Work in this laboratory[33] has shown that at an impeller speed of 80 r.p.m. the reaction kinetics are not diffusion controlled i.e. transport of reactants or products towards and away from the interface is not rate determining.

Figure 55 shows the percentage extraction versus time curves obtained for various ligand concentrations. It is apparent from the figure that above concentrations of 75.00 g/l KELEX 100 in the organic phase, the extraction rate is not increased by a higher concentration of ligand.

Figure 56 shows the typical plot for obtaining the first order rate constant for the extraction reaction

$$Ge_{aq} \overset{k_f}{\rightarrow} Ge_{org} \quad (52)$$

The function F(a) becomes invalid close to

Percentage extraction of Ge as a function of time - Lewis Cell experiment

The effect of ligand concentration on extraction rate

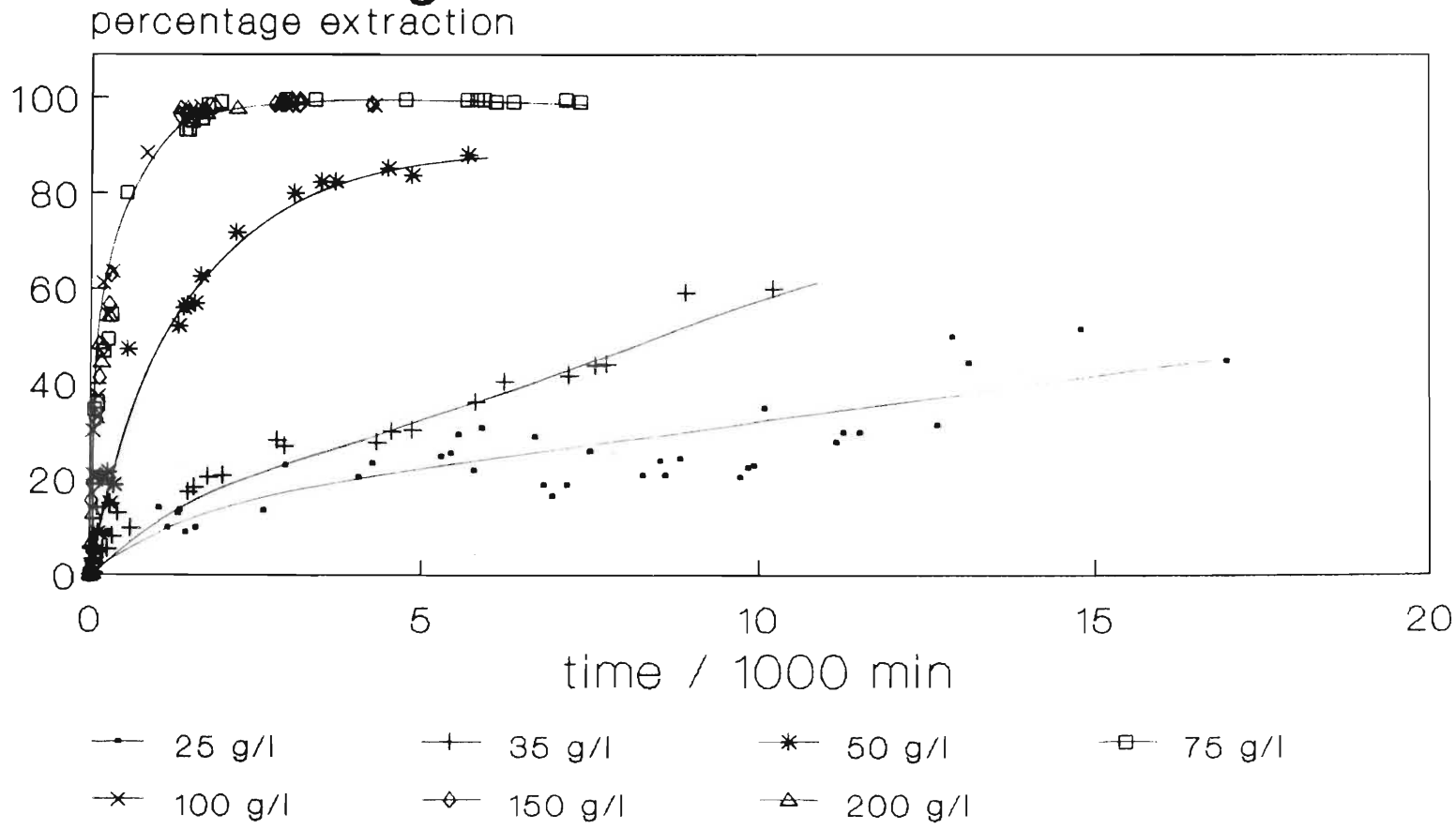


Figure 55

F(a) versus time
Lewis Cell Kinetic Experiment
75 g/l KELEX 100

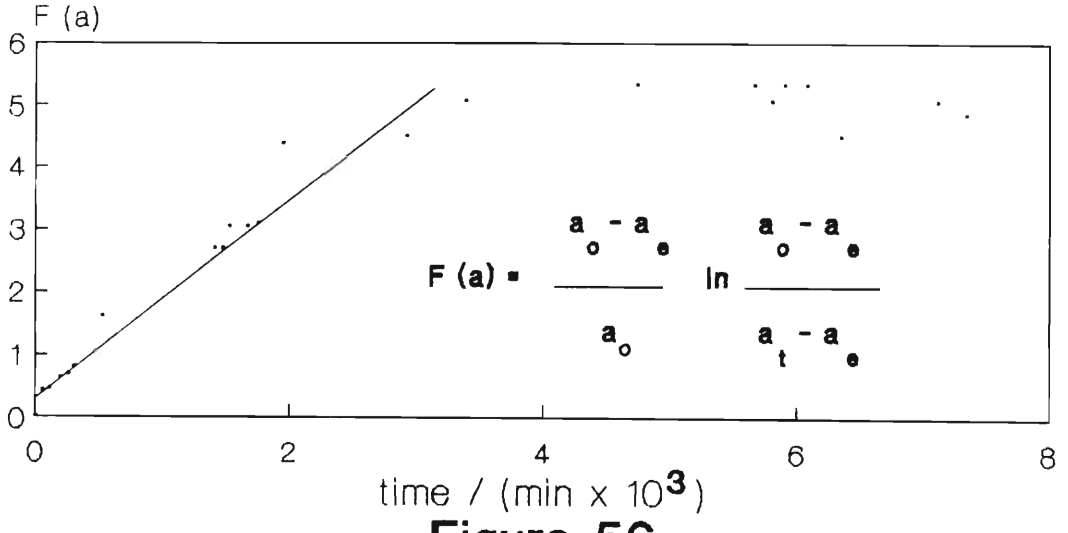


Figure 56

ln k_f versus ln [KELEX 100]
Lewis Cell experiments

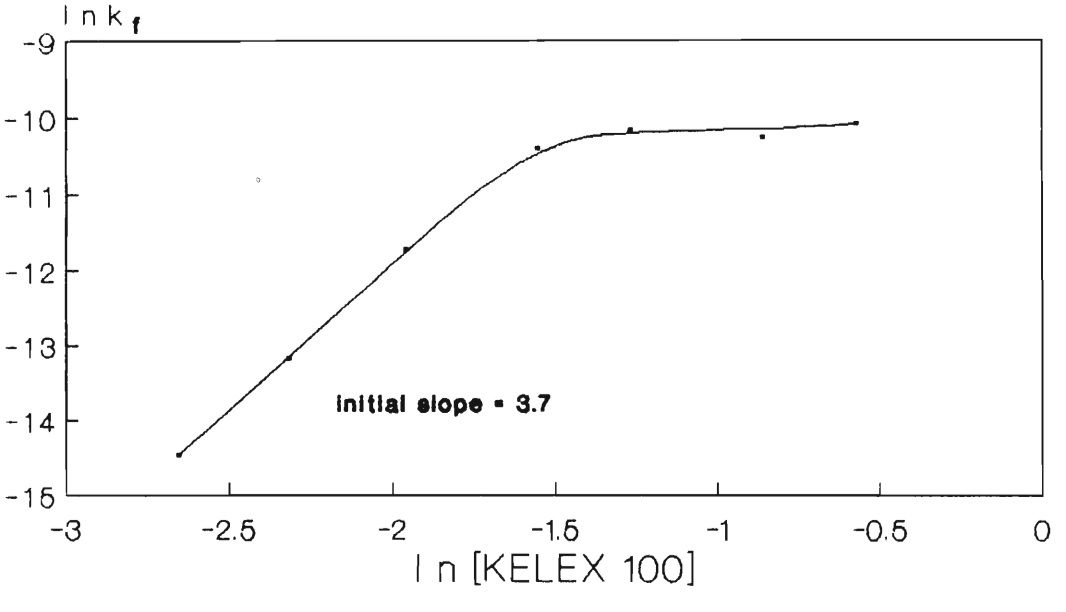


Figure 57

linearity after 3000 minutes in Figure 56. Figure 57 shows a plot of ln k_f versus ln [KELEX 100]. Section 3.2.1.1 explained how the slope of this plot yields the order of the rate of the extraction reaction with respect to ligand concentration. Between 25.00 and 75.00 g/l KELEX 100 in the organic phase, the order of the extraction reaction with respect to ligand concentration is 3.7.

$$i.e.\ Rate = \frac{d[Product]}{dt} = k'[Ge_{aq}]\,[HL_{org}]^{3.7} \quad (53)$$

This reaction order can be taken to represent an order of 3 to 4. If in the region 25.00 g/l to 75.00 g/l KELEX 100 concentration in the organic phase the concentration of the available ligand at the interface is proportional to the concentration of KELEX 100 in the organic phase, the following reaction is believed to be the rate determining step for the Lewis Cell experiments:

$$Ge(OH)_i^{(4-i)+} + 3\,HL_{org} + (i-3)\,H^+_{aq} \rightarrow GeL_3^+{}_{org} + i\,H_2O \quad (54)$$

Section 3.2.2.1.1 proposes this step as the rate determining step in the fast initial extraction period observed in AKUFVE and shaking experiments. The reaction of $HSO_4^-{}_{org}$ and $GeL_3^+{}_{org}$ then becomes the

rate determining step when [$GeL_3^+{}_{org}$] builds up to a certain critical concentration.

In Lewis Cell experiments, because the surface-area-to-phase-volume ratio is so low, the reaction rate between $GeL_3^+{}_{org}$ and $HSO_4^-{}_{org}$ does not become rate determining. Since the rate determining step in the initial period for shaking and AKUFVE experiments involves an interfacial reaction, the magnitude of the rate constant for this reaction is proportional to the interfacial area of the reacting phases. The reduction of interfacial area to the size experienced in the Lewis Cell reduces the rate constant for the interfacial reaction. (The mass transfer coefficient across the interfacial will not be altered though.) The reduction of the rate of mass transfer across the interface thus reduces the rate at which $GeL_3^+{}_{org}$ is formed, because the value of the rate constant for the reaction of $GeL_3^+{}_{org}$ with $HSO_4^-{}_{org}$ is unaltered (it is a homogeneous reaction), the concentration of $GeL_3^+{}_{org}$ never attains the critical level described for shaking and AKUFVE experiments, and the reaction of germanium with ligand is always the rate determining step.

In a non-stirred system where aqueous and organic phase are allowed to reach equilibrium, a maximum

population of the interface is achieved with as little as 10 g/l ligand in the organic phase. This is revealed by interfacial tension measurements described in Section 3.1.3. In the stirred Lewis Cell, the situation is somewhat different as indicated by the fact that the extraction rate increases until a concentration of 75.00 g/l KELEX 100 is reached in the organic phase. If maximum interfacial ligand concentration were attained at an organic extractant concentration of 10 g/l in the Lewis Cell, then the rate of extraction in the Lewis Cell would reach a maximum level at this extractant concentration.

The Lewis Cell experiments highlight the fact once again that the experimental technique employed to study a solvent extraction process influences the nature of the information that is obtained about the system studied. Even the mechanism of extraction can be different as in the case of the Lewis Cell and shaking experiments.

3.3 A PROPOSED MECHANISM FOR GERMANIUM EXTRACTION BY KELEX 100

In this thesis, previous discussions of the mechanism of germanium extraction by KELEX 100 have mostly been cursory. In this section a more complete mechanism for extraction will be considered and some aspects of the extraction previously overlooked will be discussed.

Section 3.3.1 will discuss further the data presented in Section 3.1.1. The self-association of ligand is discussed with the aim of showing that the effective monomer concentration of ligand in an organic solutions is not reduced by dimer formation or higher ligand association. The significance of interfacial tension is also discussed, and the validity of Gibb's adsorption isotherm is also discussed for the kinetic experiments reported in this thesis.

3.3.1 The Kinetic Treatment of a Heterogeneous Reaction System

Mention was made earlier that the assumption that the concentrations of reactant in the germanium-KELEX 100 system at the reaction site (i.e. the interface) are proportional to the bulk concentrations of reactant. This assumption allows the kinetic treatment of the reaction kinetics similar to the kinetic treatment of a homogenous reaction system. Section 3.3.1.1 shows that bulk ligand concentration does not have to be corrected for dimer or other ligand self-association. Section 3.3.1.2 will attempt to provide experimental evidence for the assumption in kinetic treatments that the interfacial ligand concentration is proportional to bulk ligand concentration.

3.3.1.1 **The Effect of Extractant Dimerization on Available Ligand Concentration**

In Section 3.1.1 it was shown that at the concentrations of KELEX 100 used in this investigation, dimerization of extractant was not occurring. This indicates that association in the bulk of extractant will not cause the bulk concentration of ligand (present as monomer) to be less than the amount of extractant originally

dissolved in the organic diluent. Thus the amount of ligand potentially available for reaction at the reaction site is always directly proportional to the formal concentration of ligand dissolved in the organic phase. Hence, any analysis is not complicated by ligand dimerization.

The next section examines some experimental evidence for the assumption that the interfacial concentration of ligand is proportional to the bulk organic ligand concentration.

3.3.1.2 Analysis of Interfacial Ligand Concentration via Interfacial Tension Measurements

A publication by Van Der Zeeuw[67] in which the use of the Gibb's adsorption isotherm is made to relate interfacial tension data for the copper-β-hydroxyoxime system to the surface excess of β-hydroxyoxime adsorbed at the interface at various β-hydroxyoxime concentrations suggested that the experiments described in Section 3.1.3 may give results that shed light on the dependence of the interfacial concentration on the bulk concentration of ligand. Van Der Zeeuw[67] reasoned that in the region where the surface excess of the interfacially adsorbed species was constant with increasing concentration of the adsorbed species the

interfacial concentration of the adsorbed species was directly proportional to the bulk concentration of ligand. Van Der Zeeuw[67] uses this proposal to explain why the order of the extraction reaction with respect to ligand for the copper-β-hydroxyoxime system varies from zero to two (the number of ligand molecules complexing with each extracted copper atom is two). The overall extraction reaction is shown below in Equation (55).

$$Cu^{2+}_{aq} + 2\,HL_{org} \rightleftharpoons CuL_{2\ org} + 2\,H^{+}_{aq} \quad (55)$$

where HL = β-hydroxyoxime

Equation (56) shows the step-wise reaction:

$$Cu^{2+}_{aq} + HL_{i} \overset{K_1}{\rightleftharpoons} CuL^{+}_{i} + H^{+}_{aq} \quad (fast)$$

$$CuL^{+}_{i} + HL_{org} \overset{K_2}{\rightleftharpoons} CuL_{2\ org} + H^{+}_{aq} \quad (slow) \quad (56)$$

where K_1 and K_2 are equilibrium constants

i indicates species at (or close to) the interface

Van Der Zeeuw[67] derives the following rate law for the above reactions:

$$Rate = \frac{d[Cu^{2+}_{aq}]}{dt} = kS\frac{[Cu^{2+}_{aq}]}{[H^{+}_{aq}]}[HL]_{M,i}[HL]_{M} \quad (57)$$

where k = forward rate constant for the slow step in Equation (56)

S = interfacial area

$[HL]_{M,i}$ = concentration of ligand monomer at the interface

$[HL]_{M}$ = concentration of ligand monomer in the bulk

If $[HL]_{M,i} \propto [HL]_{M}$ then the order of the extraction reaction with respect to ligand will be two. According to Van Der Zeeuw[67], this occurs where the interfacial excess of the absorbed ligand is constant.

The implications of Van Der Zeeuw's[67] proposals concerning the germanium-KELEX 100 system are that for KELEX 100, the data presented in Figure 20 show that the interfacial concentration of ligand is only proportional to the bulk concentration of ligand in the region of the curve shown where the curve is linear. The interfacial tension experiments show that above a concentration of 10 g/l of KELEX 100 in the organic phase, the interfacial tension is too small to measure with the experimental technique described in Section 3.1.3. Thus, in the kinetic

experiments with germanium, Van Der Zeeuw's[67] analysis would predict that the order of the extraction reaction with respect to KELEX 100 would only be three for KELEX 100 concentrations corresponding to the linear region of the interfacial tension versus ln [KELEX 100] (Figure 21).

Kinetic experiments described in Section 3.2 show that reaction orders of three (for the initial rate of the shaking experiments and for the Lewis Cell experiments) occur well above concentrations of 10 g/l KELEX 100 in the organic phase.

Hence this suggests Van Der Zeeuw's[67] approach is inappropriate for experiments where the interface exists under conditions that are different to the conditions under which the interfacial measurements were made (i.e. both phases static, at equilibrium), thus interfacial excesses determined under the conditions described in Section 3.1.3 are inappropriate for any of the kinetic experiments described in this thesis.

The interfacial tension experiments thus do not provide any justification for the assumption that the interfacial concentration of ligand is always proportional to its bulk concentration.

3.3.2 The Detailed Mechanism for Germanium Extraction

This section will be used to present the mechanism referred to throughout the previous sections of the Results and Discussion. Since one of the goals of a kinetic study such as this is to present a kinetic simulation of the extraction reaction that could be used to predict extraction rates for the Ge-KELEX 100 system, attempts at simulation will also be discussed.

3.3.2.1 A Kinetic Model

The site of the rate determining step for the germanium-KELEX 100 extraction system has been discussed in the Introduction, the mechanism of germanium extraction is believed to be interfacial.

The work of Cote and Bauer[15] and Marchon, Cote and Bauer[14] has established that germanium is extracted by "pre-1976" KELEX 100 as a $GeL_3HSO_4^-$ (where HL = "pre-1976" KELEX 100) ion pair into the organic phase from a sulphuric acid aqueous phase at pH < 2. Work presented here (Section 3.2.1.1) shows that the extracted germanium species in this project is similar in structure to the complex reported previously[14,15] at low pH (aqueous phase of 1.50 M H_2SO_4) i.e. $GeL_3HSO_4^-$, (where HL = KELEX 100).

Any proposed mechanism would thus have the essential features of showing that $GeL_3HSO_4^-$ was the extracted germanium species in the organic phase and that the extraction was interfacial. The presentation of a mechanism thus involves a consideration of the possible steps that would form the extracted complex at the indicated reaction site.

Outlined below is the likely extraction mechanism for the extraction reaction at low pH i.e. ignoring the contribution to germanium extraction made by $GeL_2(OH)_2$ which Marchon et al.[14] report is the germanium species extracted at pH > 3.

A extraction mechanism for Ge^{4+} will be considered first, then the discussion will be broadened to include the other germanium species present in the aqueous phase at low pH.

The first consideration is the diffusion of the germanium species in the aqueous phase to the interface. This can be written in Equation (58) below:

$$Ge^{4+}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ge^{4+}_{int} \quad (58)$$

where aq = species present in bulk aqueous phase

int = species present at the interface

also indicated are the forward and reverse rate constants.

The next consideration is the diffusion of the extractant (HL) to the interface.

$$HL_{org} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HL_{int} \quad (59)$$

The stepwise reactions of Ge^{4+}_{int} are presented below:

$$Ge^{4+}_{int} + HL_{int} \overset{K_3}{\rightleftharpoons} GeL^{3+}_{int} + H^{+}_{aq} \quad (60)$$

$$GeL^{3+}_{int} + HL_{int} \overset{K_4}{\rightleftharpoons} GeL_2^{2+}{}_{int} + H^{+}_{aq} \quad (61)$$

$$GeL_2^{2+}{}_{int} + HL_{int} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} GeL_3^{+}{}_{org} + H^{+}_{aq} \quad (62)$$

Reaction (62) is assumed to be significantly slower than reactions (60) and (61). In support of this, molecular modelling (using Alchemy - a molecular modelling computer program) shows that at the site of reaction (i.e. the interface), the third ligand will not easily orientate itself to react with GeL_2^{2+} because the two hydrocarbon chains on the ligands

already co-ordinated to the germanium atom will tend to orientate the extraction intermediate with the potential reaction site for the third ligand pointing towards the aqueous phase at the interface and not the organic phase. This suggests that attachment of the third ligand would involve some potential solubilization of KELEX 100 in the aqueous phase. This is essentially unfavourable. Reactions (60) and (61) are represented as equilibrium processes.

The extraction of sulphuric acid is shown below as an equilibrium reaction. In Section 3.2.2.1 the extraction reaction of sulphuric acid into the aqueous phase was considered to be rapid compared to the germanium extraction reaction.

$$HSO_4^-{}_{aq} \overset{K_6}{\rightleftharpoons} HSO_4^-{}_{org} \quad (63)$$

The reaction of $GeL_3^+{}_{org}$ with $HSO_4^-{}_{org}$ is assumed to occur in the bulk organic phase.

$$GeL_3^+{}_{org} + HSO_4^-{}_{org} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \{GeL_3^+ HSO_4^+{}_{org}\} \quad (64)$$

Using the equations (58) to (64), the derivation of

the rate law expression follows the same treatment as for the reaction scheme outlined in Section 3.2.2.1.1 , Equations (28) to (32). The final rate law becomes:

$$\frac{d[Product]}{dt} = k_7\left(\frac{k_5 K_4 K_3\ [Ge^{4+}_{int}]\ [HL_{int}]^3 + k_{-7}\,[Product]\,[H^+_{aq}]^2}{k_{-5}\,[H^+_{aq}]^3 - k_7\,[HSO_4^-{}_{org}]\,[H^+_{aq}]^2 - k_{-8}\,[Product]}\right)[HSO_4^-{}_{org}] \qquad (65)$$

If it is assumed that the interfacial concentrations of the reactants are proportional to their bulk concentrations, then Equation (65) becomes:

$$\frac{d[Product]}{dt} = k_7\left(\frac{k_5 K_4 K_3 K'\ [Ge^{4+}_{aq}]\ [HL_{org}]^3 + k_{-7}\,[Product]\,[H^+_{aq}]^2}{k_{-5}\,[H^+_{aq}]^3 - k_7\,[HSO_4^-{}_{org}]\,[H^+_{aq}]^2 - k_{-8}\,[Product]}\right)[HSO_4^-{}_{org}] \qquad (66)$$

where K′ is the product of the proportionality constants relating the interfacial germanium and ligand concentrations to their bulk concentrations

Equation (66) is analogous to Equation (32) derived in Section 3.2.2.1.1, thus the kinetic treatment involved in the derivation of Equation (32) in Section 3.2.2.1.1 is supported.

Equation (66) has been derived considering only the Ge^{4+} in the aqueous phase. The overall general extraction reaction for all the germanium species has already been presented in Equation (6) (Section 3.2.1.1). Equations analogous to Equation (66) for the species $Ge(OH)^{3+}$, $Ge(OH)_2^{2+}$, $Ge(OH)_3^{+}$ and $Ge(OH)_4$ are obtained when a similar kinetic treatment to the treatment outlined above of the extraction reaction scheme for these four germanium species is done. However, the presence of hydroxyl groups bonded to the aqueous germanium causes the terms involving $[H^{+}_{aq}]$ in Equation (66) to have different reaction orders. For example, in the case of $Ge(OH)^{3+}_{aq}$, the $[H^{+}_{aq}]$ terms in Equation (66) will each have their indices reduced by one, this is because the hydroxyl group on the $Ge(OH)^{3+}_{aq}$ will at some stage of the extraction reaction scheme react with one H^{+} ion to cause the changes in the indices of the $[H^{+}_{aq}]$.

3.3.3 Computer Simulation of the Kinetic Model for Germanium Extraction

During the course of the work presented in this thesis, the possibility of providing a computer simulation of some or all of the kinetic data presented in this thesis was examined. Such a simulation would involve the proposal of a mechanism, the estimation of the various rate constants involved in the mechanism, then the testing of the mechanism with a suitable computer program that could predict product yields as a function of time given the mechanism and the various rate constants of the reaction steps in the mechanism.

The proposal of a mechanism is a relatively uncomplicated task. However the attempted simulation fails when estimates of the various rate constants in the proposed mechanism are required. For a reaction scheme in which there are a large number of steps, as in the germanium-KELEX 100 system, to reliably estimate a large number reaction rate constants is not possible without explicit measurement of some of the rate constants of the processes involved.

CHAPTER FOUR

SUMMARY OF CONCLUSIONS

1. Germanium is extracted from sulphuric acid solutions as $GeL_3^+HSO_4^-$ by KELEX 100 (a commercially available chelating extractant with 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline as major component) dissolved in an appropriate organic diluent (where HL = KELEX 100).

2. Infra-red and uv examination of the extractant has revealed that KELEX 100 does not self-associate (i.e. dimerize) in organic solutions.

3. The AKUFVE (an apparatus for solvent extraction designed in Sweden) has been critically examined and it has found to be limited in its application to solvent extraction studies. The apparatus is best suited to the determination of the percentage equilibrium extraction as a function of a specific parameter (e.g aqueous pH, organic extractant concentration etc.) for solvent extraction systems that attain equilibrium rapidly (i.e. less than five minutes). To take maximum advantage of the potential of the AKUFVE, a technique of analysis for the metal ion studied suitable to on-line determination of the metal ion should be used, if available.

4. The rate of extraction and the percentage equilibrium extraction of germanium from aqueous solutions by KELEX 100 containing organic solutions improves as the concentration of sulphuric acid is increased in the aqueous phase and/or the concentration of KELEX 100 is increased in the organic phase.

5. The reaction of aqueous germanium with KELEX 100 is believed to occur at the aqueous/organic interface because of the extremely low solubility of KELEX 100 in the aqueous phase.

6. The extraction kinetics of germanium from aqueous acidic solutions to organic solutions containing KELEX 100 are characterised by a fast initial extraction period, followed by a slower extraction period. The fast initial extraction period occurs in the first few minutes of an extraction experiment. These two kinetic regimes are believed to be caused by a change in the rate determining step in the extraction reaction. The rate determining step for the fast initial extraction period is believed to be the reaction of a KELEX 100 molecule with an interfacial intermediate (GeL_2^{2+} - where HL = KELEX 100) formed by the reaction of the aqueous germanium with two other KELEX 100 molecules. Once the concentration of the GeL_3^{+} species builds up to a

critical level where reverse reaction of GeL_3^+ to aqueous germanium becomes appreciable, the rate determining step is the reaction of GeL_3^+ with sulphuric acid that has been extracted into the organic phase by KELEX 100. Experimental evidence is assembled in this work to support this proposed mechanism.

7. The addition of an organic alcohol modifier to the Ge/KELEX 100 solvent extraction system is shown to greatly improve the rate of germanium extraction from aqueous to organic solutions containing KELEX 100.

8. An increase in ionic strength is shown to reduce the rate of extraction of germanium from aqueous solutions to organic solutions containing KELEX 100.

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APPENDIX

In December 1989 and January 1990, I aided in a project at the Weizmann Institute of Science (Rehovot, Israel), unrelated to my M.Sc.project, which involved the isolation of two pyrimidine-like compounds from the Actinomycin-D producer Streptomyces parvulus. The head of the research group that I worked in was Professor Aviva Lapidot and my supervisor was Dr Livia Inbar.

INTRODUCTION

Two novel compounds, 2-methyl,4-carboxy,5-hydroxy-3,4,5,6-tetrahydropryrimidine (THP A) and 2-methyl,4-carboxy-3,4,5,6-tetrahydropyrimidine (THP B), have been identified in the pool of Streptomyces parvulus. The aim of my project was to isolate both of these compounds from cells grown in the Department of Bacteriology at the Weizmann Institute of Science.

METHOD

Growth of Cells

S. Parvulus cells were grown for 2 days on NZ amine medium at 30 ^{0}C. After centrifugation and washing with 1 M NaCl, the cells were used as innoculum in the Department of Bacteriology to grow more bacteria cells. The two compounds of interest were produced by the growing bacteria cells. The growth medium used by the Department of Bacteriology consisted of 40 g fructose,

1 g K_2HPO_4, 25 mg $ZnSO_4.7H_2O$, 25 mg $CaCl_2.2H_2O$, 25 mg of $MgSO_4.7H_2O$, 25 mg $FeSO_4.7H_2O$ and 2.1 g L-glutamic acid per litre of deionised water at pH 7.1. The cells were grown in 2 litres of medium at 30 ^0C for 48 hours in a gyrating shaking incubator.

Once harvested, the pyrimidines (i.e. THP A and THP B) were extracted (along with various other compounds) by boiling the cells with approximately 500 ml of water. The cell wall was separated from the extracted liquor by centrifugation and the process was repeated to the cell wall. The cell residue was then discarded.

Separation of THP A and THP B from other Cell Extracts

The cell extract was mixed with 4 volumes of 1 M acetic acid and passed down a Dowex 50 (H^+) column. Amino acids, THP A and THP B were retained on the column and the carbohydrates and polyols washed off with water. The pyrimidines and amino acids were eluted with 3 M NH_4OH. The eluent was then evaporated and brought to pH 5, then passed down a Dowex 1 (acetate form) column. Acidic amino acids (e.g. glutamic acid) were retained on the column and THP A, THP B, alanine and peptides were eluted with water. The pyrimidines were separated from the remaining peptides on a Sephadex G-25 column. When washed with water, the peptides (and some remaining proteins) were eluted before the pyrimidines.

Separation of THP A and THP B

The sample from the Sephadex pyrimidine fraction was mixed with 4 volumes of acetic acid (1 M) then passed down a Dowex 50 (NH_4^+) column. THP A and some THP B are eluted with water. THP B and some THP A were eluted with 3 M NH_4OH. The procedure was repeated to get THP A with some acetic acid and THP B with some alanine. THP A is purified from acetic acid by using a Dowex 50 (H^+) column (as for separation of the pyrimidines from the carbohydrates), and THP B is separated from small amounts of alanine by pouring onto a Dowex 1 (OH^-) column. THP B is eluted before the alanine with 1 % formic acid.

The purity of the pyrimidines was checked after each extraction stage either on a 80 MHz n.m.r. spectrophotometer or a 250 MHz n.m.r. spectrophotometer by obtaining the proton n.m.r. spectrum at room temperature in D_2O.

CONCLUSION

Pure THP A and pure THP B were obtained. Purity was confirmed from the proton n.m.r. spectrum. After 3 weeks of work, approximately 90 mg of THP A was obtained and after 5 weeks of work, approximately 200 mg of THP B was obtained. Further yields of pyrimidines for subsequent work could not be evaluated because further amounts of the pyrimidines isolated had not been adequately purified.

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