TOWARDS THE SEPARATION OF LINEAR α-OLEFINS FROM INDUSTRIAL PROCESS STREAMS USING TRANSITION METAL MODIFIED STATIONARY PHASES.

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by

DAVID PHAHO B.Sc (Hons) (UCT)

University of Cape Town

Department of Chemistry
University of Cape Town
Rondebosch
7700
Republic of South Africa

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3.4 Silver ion exchanged zeolites as column packing material. 35
3.5 General discussion. 43

QUANTITATIVE SEPARATION OF OLEFINS USING METAL MODIFIED STATIONARY PHASES.

CHAPTER 4. INTRODUCTION. 47

4.1 Theory of Adsorption chromatography. 50
4.2 Silica gel as adsorbent in hydrocarbon separation. 52
4.2.1. Literature survey 52
4.3 Quantitative olefin separation using modified silica gel. 54
4.3.1 Use of unmodified silica gel as column packing material. 54
4.3.2 Use of $AgNO_3$ modified silica gel as column packing material. 60
4.4 Olefin recovery : Displacement Chromatography vs Temperature desorption. 65
4.4.1 The use of displacement chromatography in olefin recovery. 65
4.4.2 The use of temperature desorption in olefin recovery. 69
4.4.3. Effect of temperature desorption on olefin isomerization. 83
4.5 General discussion. 86

CHAPTER 5 GENERAL DISCUSSION AND CONCLUSIONS. 89

CHAPTER 6 EXPERIMENTAL. 92

6.1 Chemicals, Reagents and Glassware. 92
6.2 Apparatus. 93
6.3 Preparation of ion exchange resin. 94
6.4 Preparation of ordinary and ion exchanged zeolites. 96
6.5 Preparation of modified silica gel. 97
6.6 Preparation and analysis of synthetic hydrocarbon mixtures. 98

REFERENCES 99

APPENDICES 104

CONTENTS

ACKNOWLEDGEMENTS (iv)

SUMMARY (v)

LIST OF ILLUSTRATIONS (vii)

CHAPTER 1. INTRODUCTION 1

1.1 Literature survey 3
1.2 Objectives of research. 5
1.2.1 Separation principle. 5

SCREENING OF POTENTIAL SUPPORT MATERIALS USING GAS SOLID CHROMATOGRAPHY (G.S.C).

CHAPTER 2. THE USE OF ION EXCHANGE RESIN AS COLUMN PACKING MATERIAL. 8

2.1 Hydrocarbons analysis using Gas Chromatography. 8
2.1.1 Introduction. 8
2.1.2 Literature survey. 9
2.2 Screening of Ion exchange resin using G.S.C. 10
2.2.1. Screening of Amberlite IR-120 ion exchange resin. 11
2.2.2. Screening of Amberlyst A-15 ion exchange resin. 15
2.3 Results and discussion. 15

CHAPTER 3. THE USE OF ZEOLITES AS COLUMN PACKING MATERIAL. 26

3.1 Introduction 26
3.2 Literature survey 28
3.3 Screening of different types of zeolites using Gas Solid Chromatography. 30

APPENDIX 1 104
APPENDIX 2 106

APPENDIX 3 108
APPENDIX 4 114

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To my fiancee Esther, for a wonderful three years

I, the undersigned, hereby declare that this is my own unaided, original work and has not been presented previously, in full or in part, at any other University, for the purpose of obtaining a degree.

Signature Signed by candidate

Date Signature removed

SUMMARY

The use of silver modified stationary phases for the separation of olefins from hydrocarbon mixtures was investigated.

Gas solid chromatography (GSC) was found to be a quick and efficient technique for screening ion exchange resins and zeolites as potential support materials in olefin separation. Using GSC, the efficiency of Ag^+ exchanged resin in retaining olefins relative to alkanes in a given mixture was found to be dependent on the porosity of the resin used. The silver form of the porous, macroreticular type Amberlyst A-15 resin strongly retained olefins in the GC column as compared to the microporous Amberlite IR(120) resin. Olefins were so strongly retained on the Ag^+ exchanged Amberlyst A-15 resin that they could only be eluted efficiently from the GC column at elevated temperatures. The Ag^+ exchanged resin was however found to undergo degradation at elevated temperatures (> 140°C) and hence the resin packed columns could not be re-used.

On screening a series of zeolites of differing pore sizes, it was found that unmodified zeolites with large pore sizes (≥ 5Å) strongly adsorbed both alkanes and olefins while zeolites with pore sizes < 5Å did not. On ion exchanging one of the small pore sized zeolites (pore size 4Å) to the silver form, olefins were found to be strongly retained relative to alkanes as was the case with ion exchange resin. Evidence of catalytic oligomerization of the adsorbed olefin on the Ag^+ exchanged zeolite at high column temperatures was observed.

In the second phase of the project, a separation rig was constructed to study quantitative olefin separation from synthetic hydrocarbon mixtures using a transition metal modified stationary phase. The rig was primarily made up of an oven into which a column which was packed with the transition metal modified material was fitted and two cold traps, one used to collect non-olefinic hydrocarbons from the column while the other trap was for collecting previously retained olefins.

Silica gel was the next stationary phase to be considered for olefin separation. Using $AgNO_3$ modified silica gel as packing material in the separation rig column, linear olefins were selectively retained from hydrocarbon mixtures and subsequently recovered in a relatively pure form. Attempts to displace the retained long chain olefins from the $AgNO_3$ modified silica gel column using simple olefins were

unsuccessful. Temperature desorption on the other hand was found to be an efficient method of recovering the olefins from the $AgNO_3$ modified silica gel column.

The olefins recovered using temperature desorption were found to contain traces of alkanes and hence were not 100 % pure. These traces of alkanes were presumably physically adsorbed onto the modified silica gel surface or trapped in the column dead volume during sample introduction and could only be desorbed at high temperatures.

The extent of formation of the Ag^+ - olefin complex was found to be dependent on the olefin chain length and other steric factors. Samples containing longer chain olefins had to be reinjected in some instances to optimize olefin retention on the $AgNO_3$ modified silica gel. The selective retention of a branched olefin by the $AgNO_3$ modified silica gel column was found to be much lower as compared to the corresponding straight chain olefin.

Finally, negligible olefin isomerization and/or polymerization was evident when the temperature desorbed olefins were analyzed by gas chromatography.

LIST OF ILLUSTRATIONS.

Fig 1.1 Dewar's model of Ag^+ - olefin complex.

Fig 2.1 Internal structure of typical ion exchange resin.

Fig. 2.2 Schematic diagram showing column packing for screening support materials.

Fig 2.3 The chromatograms of a hexane/1-hexene mixture obtained from a Ag^+ exchanged Amberlyst A-15 resin column.

Fig 2.4 (a) The Chromatograms of a pentane, 1-pentene and 1-hexene mixture obtained from a Ag^+ exchanged Amberlyst A-15 resin column.

(b) The chromatogram of a mixture containing pentane, 1-hexene and cyclohexane.

Fig 2.5 The chromatogram of a C_5 - C_8 alkane mixture spiked with 1-hexene obtained from a Ag^+ exchanged Amberlyst A-15 resin column.

Fig 2.6 The chromatogram obtained of a mixture of pentane, cyclohexane, octane, 1-hexene and 1-octene obtained from a Ag^+ exchanged Amberlyst A-15 resin column.

Fig 3.1 Internal structure of (a) an A type zeolite and (b) X or Y type zeolite.

Fig 3.2 Chromatograms of (a) pentane and (b) hexane obtained from an unmodified NaY type zeolite packed column.

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modified silica gel.

Fig 4.5 Series of chromatograms obtained from GLC for the quantitative separation of 1-octene from a a more complex hydrocarbon mixture using a $AgNO_3$ modified silica gel.

Fig 4.6 Series of chromatograms obtained from GLC for the quantitative separation of 1-decene from a a more complex hydrocarbon mixture using a $AgNO_3$ modified silica gel.

Fig 6.1 Column packing for screening support material using GSC.

Knowledge is an ornament in prosperity, a refuge in adversity and a provision in old age.

Aristotle

CHAPTER 1

INTRODUCTION

Over the past sixty years there has been an urgent need in the rapidly growing petrochemical industry for efficient and economically viable purification processes. Of particular interest is the separation of major olefin building blocks from hydrocarbon process streams. The wealth of patent literature published in this regard clearly shows the intensive research which is being undertaken in this field.

The early research focussed mainly on the separation of simple olefins like ethylene, propylene and butene isomers while limited success was achieved in the efficient separation of long chain olefins from their corresponding alkanes. This is primarily because as the molecular weights of the olefins and their respective alkanes in a given hydrocarbon mixture increase, their relative volatilities decrease making it difficult to separate them using established methods.

Among the long chain olefins, the linear α-olefins (1-alkenes) in the C_8 - C_{12} range are becoming more important in industry as they are used as raw material in the synthesis of plastisizers and biodegradable detergents. The economic importance of these raw materials cannot be overemphasized. About 34% (500 million tons) of the world α-olefin production was used in the detergent industry in 1992, generating an estimated 16,5 billion dollars in revenue in the United States alone [1]. It is because of this lucrative detergent market and the global drive towards biodegradable industrial products that the research for cost effective methods of separating these olefins from other co-products in hydrocarbon process streams has intensified over the past few years.

Linear a-olefins are synthesized industrially via a number of processes:

1. Ethylene/propylene polymerization.
2. Catalytic dehydrogenation of alkanes.
3. Catalytic dehydration of 1-alcohol.
4. As co-products of coal gasification in the Fischer Tropsch process.

The Fischer Tropsch process is well developed in South Africa and it is one of the country's biggest suppliers of chemical raw materials and an important source of revenue for the economy. The process is basically a heterogeneous reaction of H_2 and CO (from coal gasification) catalyzed by various metals such as Fe, Co, Ni or Ru mounted on a suitable support. The reactions which characterize the process are thought to occur via the following equations:

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O$$

$$nCO + nH_2 = nHCHO$$

$$nCO + 2n\,H_2 = C_nH_{2n+1}OH$$

These equations give rise to a unique and complex process stream which contains a wide variety of marketable products in addition to the long chain linear α–olefins. These include petrol, diesel, alkanes (branched and long chain), aromatics, waxes (high molecular weight alkanes) and small amounts of oxygenates (e.g alcohols, carbonyls). Finding an efficient and economically feasible way to separate and purify these compounds has proved to be a daunting task for the local petrochemical industry. This has led to a huge capital investment in expensive equipment and technology for purification of Fischer Tropsch and related process streams.

1.1 Literature Survey

The following literature survey highlights some of the methods used in the industrial separation of olefins from other *co*-products. Conventional distillation appears to be the method of choice worldwide in the recovery of olefins from simple and multicomponent systems. Conventional distillation simply refers to the physical separation of a mixture into two or more fractions that have different boiling points. This form of separation is however energy intensive and hence very expensive and at present olefin purification by conventional distillation is the single largest consumer of energy in the chemical industry, using close to 50 trillion Btu per year [2]. Another problem with conventional distillation is that it does not provide an economic and practical way of separating compounds with closely related boiling points in complex streams.

A form of distillation which is becoming more popular is extractive distillation. In this type of distillation, a solvent is used to improve the relative volatility of the components of interest, hence the solvent is selected to have a particular affinity for the desired components. In the first step, the extracting solvent attaches itself to one component while the other components are distilled off. In the subsequent step, the captured component is stripped from the extracting solvent, usually by addition of heat.

Chambers [3] used furfural as a solvent in the extractive distillation of olefins from other hydrocarbons. Bogdanov and *co*-workers [4] used acetophenone as an extracting solvent to increase the percentage recovery of olefins from a hydrocarbon mixture. Even better olefin recovery was achieved by the same group using aqueous acetonitrile [5] to separate olefins and dienes in a C_5 hydrocarbon fraction. Extractive distillation has turned out to be a more successful form of distillation but like conventional distillation it is also very expensive in terms of energy costs and the fact that it is a batchwise process. The subsequent separation of olefins from the extracting solvent also poses a further problem of olefin purity. A combination of conventional and extractive distillation has proved to be more popular and efficient in some of the separation processes [6].

Another industrial olefin separation method used is the selective adduction of olefins using compounds such as urea. Leibitz and co-workers [7] used urea and mercury (II) salts to separate olefins from other hydrocarbons in a Fischer Tropsch process stream. The use of urea was found to be impractical as it also formed adducts with alkanes. Urea is now generally used to separate long chain hydrocarbons (alkanes and olefins) from their branched isomers as branching along the hydrocarbon chain inhibits the formation of the urea adduct. In this form of separation the long chain hydrocarbons are first separated from urea, and then the hydrocarbons are subsequently separated into olefin and alkane fractions by conventional distillation. Mercury salts on the other hand only formed adducts with olefins. The use of mercury compounds on a large scale was however not feasible because mercury compounds are protoplasmic poisons and hence pose a serious environmental and health hazard if extraordinary safety measures are not taken.

A novel method of removing oxygenates from an olefin containing process stream was reported by Rylander [8] who successfully extracted alcohols and aldehydes by introducing an equivalent volume of 2-pyrrolidone to form adducts selectively with these compounds. The general and more successful method of removing oxygenates from the Fischer Tropsch stream is the use of the process referred to as methanol wash [9]. Methanol is used to dissolve the oxygenates in the stream. After phase separation, the methanol is recovered by heating the extract. The remaining olefins are separated from other hydrocarbons by distillation.

From the discussion given above, it is clear that most of the methods employed in industrial olefin separation from multicomponent systems are used in conjunction with other purification processes to ensure proper and better olefin recovery. Rising operational and labour costs incurred in the separation and purification of precious chemicals from Fischer Tropsch process streams gave rise to a need to search for an alternative method of separating linear olefins from these complex streams. Hence the overall aim of this project is to devise a simple, yet economically viable way to separate linear α-olefins in the C_8 - C_{12} range from alkanes and oxygenates in Fischer Tropsch process streams at minimum possible cost.

1.2. OBJECTIVES OF RESEARCH.

The main objectives of this project were:

(a) To find a suitable support material on which transition metal ions e.g Ag^+ or Cu^+ could either be (1) exchanged for other ions in the proposed support material or (2) be deposited as a salt onto the support material surface so that the metal ion can selectively retain linear α-olefins in the C_8 - C_{12} range from hydrocarbon mixtures. Some of the suggested support materials were:

(i) Ion exchange resin.

(ii) Deactivated alumina.

(iii) Zeolites.

(iv) Silica gel.

(b). The design and construction of an apparatus with a suitable column from which α-olefins, after being selectively adsorbed on the chosen modified support material, could subsequently be recovered in high purity in an unaltered form.

1.2.1. Olefin separation principle.

The key concept of this project as mentioned above was to separate long chain linear α-olefins from a Fischer Tropsch process stream by the selective adsorption of these compounds onto a transition metal modified support material. This could hopefully be achieved by firstly passing an olefin containing hydrocarbon mixture through a column packed with a suitable metal modified support. After the olefin had been retained relative to the other mixture components, it was hoped that the olefins can be subsequently recovered in a pure and unaltered form.

Olefinic compounds are known to form complexes with selected transition metal ions e.g Ag^+ or Cu^+ via dative covalent bonds between these metal ions and the olefin double bonds. A comprehensive review on this subject was done by Quinn [10]. According to a model put forward by Dewar [11], metals near the end of the transition series form stable complexes with olefins, since these metals have filled *d*-orbitals available to overlap with the antibonding orbital of the olefin double bond.

In the Dewar model, as illustrated in Fig 1.1, the σ component of this dative covalent bond is formed by the overlap of the occupied bonding σ molecular orbital of the olefin double bond with the vacant 5*s* orbital of the silver(I) ion and the π component of this interaction is formed by the overlap of the occupied 4*d* orbital of the silver(I) ion with the vacant antibonding orbital of the olefin double bond. In the case of the Cu(I) species, it is the vacant 4*s* and the occupied 3*d* orbitals of the metal ion that are involved.

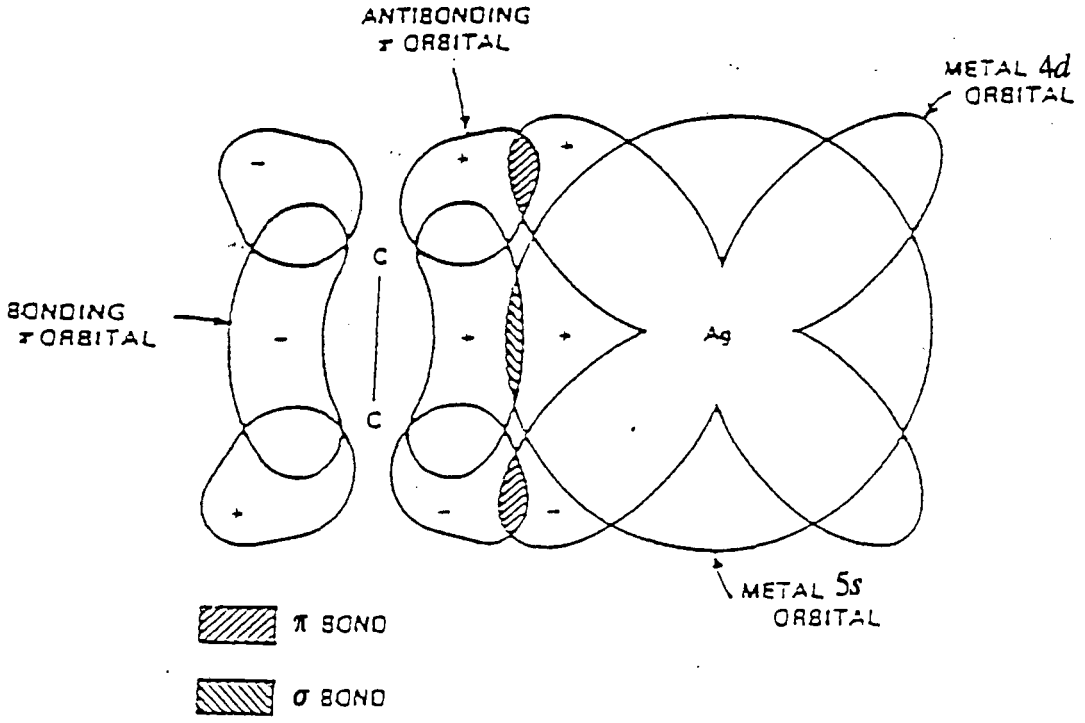


Fig 1.1. Dewar's model for Ag^+- olefin complex.

The interactions of Cu^+ and Ag^+ with olefins were first studied more than sixty years ago by Tropsch [12] and Winstein [13] respectively. Subsequently a number of workers have used this phenomenon to try to separate olefins from other compounds.

Thomas [14] separated olefins from saturated hydrocarbons by passing the hydrocarbon stream over ion exchange resins containing Ag^+ and Cu^+ ions. More recently Hirsch and *co*-workers [15] showed that aromatics and olefins are retained on a silver(I) form of ion exchange resin. Stern [16] used copper(I) modified silica gel to separate 1-heptene from heptane.

The use of this charge transfer phenomenon to separate olefins from other hydrocarbons has however been restricted to simple olefin containing mixtures and as will be shown in subsequent chapters, most of the research undertaken was specifically for the separation of short chain olefins.

The possible practical use and commercial success of the proposed separation method will depend on a number of factors:

(a) Complexing and dissociation of the olefins and metal ions should take place at a fast rate and at acceptable temperatures and pressures.

(b) The olefins should be regenerated unaltered, i.e without polymerization or isomerization.

(c) The transition metal used should be recyclable without degradation or loss.

(d) The process should have economic and other practical advantages over competing physical separation methods.

SCREENING OF POTENTIAL SUPPORT MATERIALS USING GAS SOLID CHROMATOGRAPHY.

CHAPTER 2

THE USE OF SILVER ION-EXCHANGED RESIN AS COLUMN PACKING MATERIAL IN GAS SOLID CHROMATOGRAPHY.

2.1. HYDROCARBON ANALYSIS USING GAS CHROMATOGRAPHY.

2.1.1. **Introduction.**

The rapid development of chromatography as a powerful analytical technique owes its origins to the pioneering work of the Russian botanist M Tswett, who in 1906, showed that when a mixture of coloured solutes is allowed to pass through a vertical glass column filled with suitable adsorbing material, the individual components of the material adsorbed on the column appear as a series of coloured bands which he referred to as a "chromatogram".

Chromatography as it is known today usually achieves a separation by means of two phases namely, the mobile phase which carries the components through the column and the stationary phase with which the components selectively interact as a consequence of differing physical properties such as increasing polarity or boiling points. Chromatography can be subdivided into two basic types, according to the nature of the mobile phases. These are liquid and gas chromatography . In the former the mobile phase is a liquid while in the latter the mobile phase is an inert gas.

Of the two types, gas chromatography has found extensive application especially in order to study the selective adsorption and partition methods for analysis of gases and volatile liquids.

Gas chromatography can, in turn, be subdivided into two classes, namely **gas solid** and **gas liquid chromatography**. In the former case the stationary phase is a solid adsorbent, while in the latter the stationary phase is a high boiling liquid coated

onto an inert support material. The two types of gas chromatography have been used widely in the chemical industry for the analysis of hydrocarbons and other substances.

2.1.2. **Literature survey.**

A number of workers have used chromatography to separate hydrocarbons containing alkanes and their corresponding olefins. Patton and *co*-workers [17] {and the references therein} separated olefins and alkanes using a GC column packed with unmodified silica gel while Scott [18] used alumina in the analytical separation of simple olefins from their corresponding alkanes.

The low relative volatility of high molecular weight olefins and related alkanes makes it quite difficult to separate these compounds in gas chromatography. This problem gave rise to the use of metal ion modified support material (usually Ag^+ or Cu^+ions) which tended to selectively retain olefinic compounds (including aromatics) relative to non-olefinic compounds. A considerable number of papers based on this GC technique have been published .

The first reported chromatographic application of silver ion-olefin complexation involved gas liquid chromatography (GLC). Bradford [19] reported the high olefin selectivity of a silver nitrate-ethylene glycol stationary phase for the separation of butenes from butanes. Armitage [20] used a GLC column with silver nitrate in benzyl cyanide as stationary phase to separate olefins from alkanes.

Smith and Olsen [21] also used silver nitrate in ethylene glycol to separate unsaturated hydrocarbons for GC analysis while Shabtai and *co*-workers [22] used the same stationary phase to separate cyclic olefins. Shabtai [22] and Devries [23] showed that the strength of silver ion-olefin interaction was greatly influenced by the stereochemistry of the olefin involved, with *cis*-isomers having higher retention times than the *trans*-isomers. Mubs and Weiss [24] used a GLC column to determine the equilibrium constants of a series of silver ion-olefin complexes and found that steric factors influenced the stability of the Ag^+ - olefin complex. In spite of the success achieved with gas liquid chromatography for hydrocarbon analysis, it has a serious limitation. The silver containing stationary phase is

thermally unstable and this fact rules out its possible use in the separation of higher boiling hydrocarbons. Keulemans [25] noted that the temperature of a silver nitrate GLC column should be kept below 40°C because above this temperature olefin-metal ion adducts did not form.

One of the earliest reports of gas solid chromatography using silver nitrate was published by Scott [26] who separated olefins and aromatics from other hydrocarbons using silver impregnated alumina as column packing material. Scott and Phillips [27] analyzed paraffinic hydrocarbons for traces of olefins using a silver nitrate modified alumina column.

Hirsch and *co*-workers [15] investigated the use of ion exchange resin for selective olefin retention using the Ag^+ exchanged resin as column packing material to enhance olefin separation from other hydrocarbons. Quinn [10] also evaluated Ag^+ exchanged resin for olefin-paraffin separation in GSC. Magidman and *co*-workers [28] used a Ag^+ form of sulfobenzyl Porasil C in the GC analytical separation of olefins from alkanes.

2.2. SCREENING OF Ag^+ ION EXCHANGED RESINS USING GSC.

In the first phase of the project, potential support materials were modified with metal ions and screened using gas solid chromatography to determine their potential for the retention of olefin via olefin-metal ion complexation. The first material to be screened was ion exchange resins and the detailed preparation is described in the experimental section.

Ion exchange resins are insoluble, cross-linked polymers having ionic or ionizable groups attached to the resin structure. Whether the resin will be cationic or anionic is dependent on the particular functional group attached to the resin structure. An example of a cation exchange resin internal structure is shown in Fig 2.1:

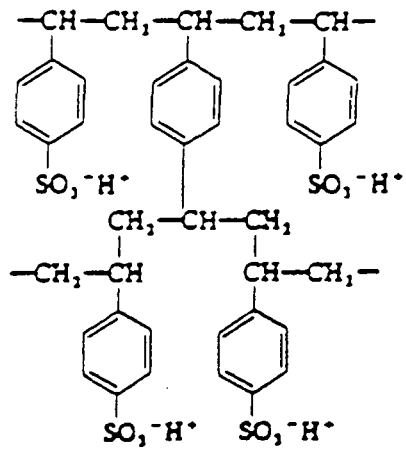


Fig 2.1. The internal resin structure of a typical cation-exchange resin.

The SO^{3-} groups in this resin are covalently attached to the resin structure while the H^+ cation can be easily exchanged for a more favourable cation if a solution containing that ion is passed over the resin, hence the name ion-exchange resin. The total amount of ions that can be exchanged per gram of resin is expressed as the total ion exchanged capacity of that resin usually measured as milliequivalents per gram of the resin (~ mmoles/gram). The determination of the total capacity is dealt with in Chapter 6 (experimental).

2.2.1. **Amberlite IR-120(H) type resin as support material.**

In order to investigate the extent to which Ag^+ exchanged resin could retain an olefin relative to its corresponding alkane, a series of Amberlite IR-120 ion exchange resin samples with 5, 10, 50 and 100% of the total exchange capacity exchanged for Ag^+ ions were prepared. The Ag^+ exchanged resin was then packed in the GC glass column as illustrated in Figure 2.2. In all the cases the packed column was conditioned in the GC oven overnight at 80°C under nitrogen.

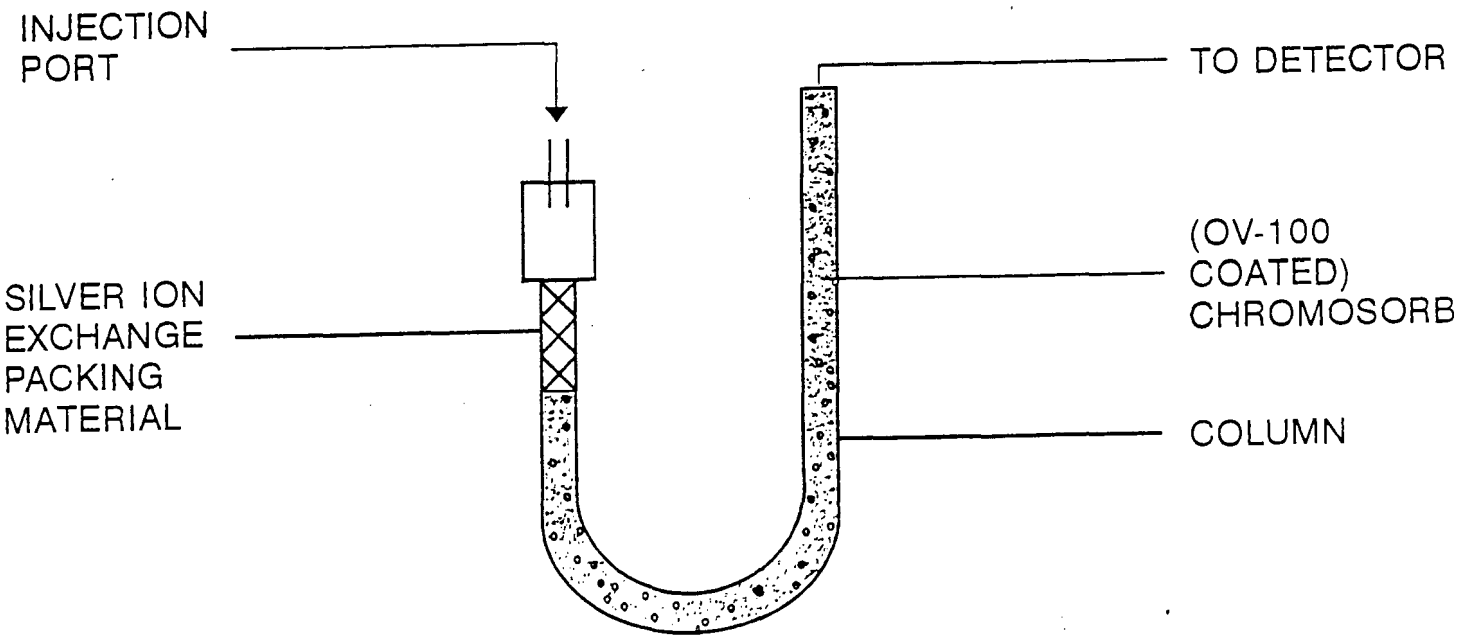


Fig 2.2. Column packing for screening support material in gas solid chromatography.

A 1-octene/octane mixture was prepared and injected into the resin packed column (the GC conditions used are listed in Appendix 1(a)). Table 2.1 shows the relative retention times of the 1-octene and octane as a function of silver ion content of the resin when the GC column was packed sequentially with the series of resin samples mentioned above.

Table 2.1. Retention times of octane and 1-octene as a function of % Ag^+ exchanged Amberlite IR-120 type resin capacity. Column temperature = 100°C.

	Retention times (s)	
% Ag^+ exchanged	octane	1-octene
0	148	129
5	87	87
10	108	90
50	162	129
100	102	105

From the retention times obtained in Table 2.1, it is clear that no specific retention of the olefin (1-octene) relative to octane occurred as was expected. The corresponding chromatograms showed poor peak resolution between the two compounds. Even with the resin in a 100% silver loaded form, poor peak resolution between octane and 1-octene was observed as shown in Table 2.1.

Further attempts to improve the Ag^+ - olefin interaction by increasing the length of the column occupied by the Ag^+ exchanged resin proved fruitless. Table 2.2 shows the effect of increasing the total amount of Ag^+ exchanged resin in the column on the octane and 1-octene retention times.

Table 2.2. The effect of amount Ag^+ exchanged Amberlite IR-120 type resin on olefin retention. Column temperature = 60°C.

	retention time (s)	
*Column length(cm)	octane	1-octene
10	162.0	129.0
25	58.5	58.5
50	9.0	9.0

* Refer to the total length of the GC column filled with 100% Ag^+ exchanged resin.

From Table 2.2, it is clear that the retention times of 1-octene and octane actually decreased as the amount of Ag^+exchanged resin in the column increased. The higher retention times obtained when only 10 cm of the column was packed with Ag^+ exchanged resin were due to the sample interaction with analytical part of the column (see experimental). As illustrated in Figure 2.2, the analytical part of the column was filled with OV-101 coated chromosorb which was tightly packed because of the small particle size. As the total length of the column filled with resin beads, which have much bigger diameter than modified chromosorb particles, was increased the retention times of 1-octene and octane decreased because the resin beads are not as tightly packed as the modified chromosorb and hence the components in the injected hydrocarbon sample were eluted much quicker from the column. This gave rise to the general decrease in the retention times shown in Table 2.2.

The short retention times of 1-octene indicated that no significant Ag^+- olefin interaction occurred on the Amberlite IR-120 (Ag^+) resin packed column. Increasing the amount of Ag^+ exchanged Amberlite resin in the column did not

make much difference in the retention time of 1-octene but led to a general decrease in the overall retention times of octane and 1-octene. The reason for this unexpected trend was postulated to be due to the relatively small effective surface area and low porosity of the gel type Amberlite IR-120 resin. These results suggested the use of the highly porous macroreticular resin, Amberlyst A-15.

2.2.2. **Amberlyst A-15 resin as support material.**

Amberlyst A-15 type resin belongs to the group of resins referred to as macroreticular ion exchange resins. These are highly porous and are known to have large surface areas. Most macroreticular type resins are thermally stable at least under the conditions used in gas solid chromatography. The cation exchange resin can be readily converted to many metal ion forms without the anionic polymer matrix being greatly changed by the process.

The Amberlyst A-15 was converted to the silver form with the following loadings, 5.02%, 13.3%, 50% and 100% Ag^+ of the total exchange capacities as described in the experimental section. In each case the packed column was conditioned overnight at 80°C under nitrogen. Unless otherwise stated the gas chromatographic conditions used are as reported in Appendix 1(a).

2.2.3. **Results and discussion.**

2.2.3.1. **The influence of % silver capacity on olefin retention.**

A series of experiments were performed to investigate the effect of increasing the amount of silver exchanged onto the resin on the retention times of olefins relative to their corresponding alkanes.

Microliter samples of a hexane and 1-hexene mixture were injected into a series of columns packed with Amberlyst A-15 resin with different % Ag^+ loaded capacities. The results obtained are shown in Table 2.3.

Table 2.3. The retention of 1-hexene as a function of % Ag^+ loaded capacity. Temperature = 100°C.

	retention times (s)	
% Ag^+ exchanged	hexane	1-hexene
5.02	18	33.0
23.3	6.3	43.5
50.0	9.0	84.0
100	9.0	140.0

From Table 2.3 it can be noted that as the Ag^+ loadings was increased, the retention of 1-hexene also increased significantly. For resin completely Ag^+ loaded (100% of the total ion exchange capacity), 1-hexene was so strongly retained that it eluted as a broad peak as shown in Figure 2.3.

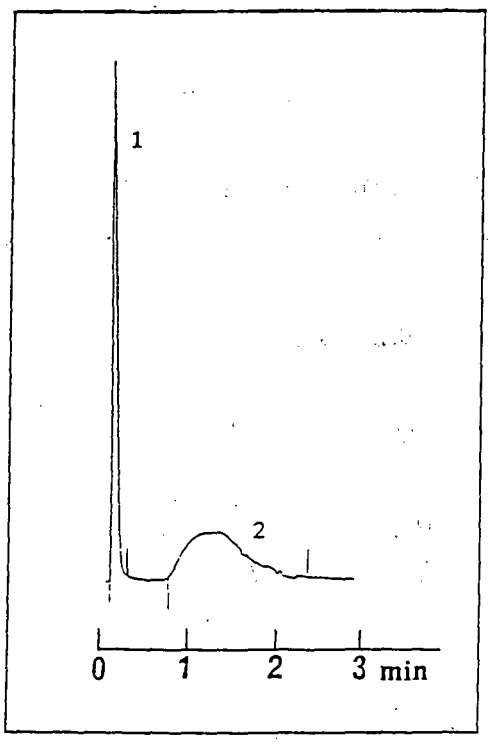


Fig 2.3. The chromatogram of a (1) hexane and (2) 1-hexene mixture using a 100% Ag^+ exchanged Amberlyst A-15 resin column. Column temperature = 100°C.

Table 2.5. The influence of temperature on olefin retention times. Amberlyst A-15 resin exchanged to 100% of the total capacity.

	Retention time (s)			
Hydrocarbon	100°C	120°C	150°C	170°C
hexane	16.5	6.0	6.0	3.0
1-hexene	*465	*375	84	36

* very broad peaks.

The effect of temperature on olefin retention was even more pronounced at higher column temperatures as shown in Table 2.5. 1-Hexene is initially very strongly retained so that the actual peak was spread over 465 s. However the retention time decreased significantly with increasing temperature. Of special importance is the fact that the broad peaks assigned to the olefin in the mixture began to acquire a more symmetric shape as the column temperature was increased.

The trend obtained above clearly shows that the formation of the Ag^+- olefin complex is temperature dependent, and that retained olefins could be desorbed at higher temperatures leading to more rapid elution from the column. Quinn [29], using the silver form of the macroreticular Amberlite IRC-50 resin found that the ethane-ethylene peak resolution decreased with increasing temperature, a reflection of decreasing stability of the Ag^+- olefin complex as the column temperature is increased.

2.2.3.3. Effect of resin surface area on olefin retention.

The work done until now has shown that the highly porous, Ag^+ loaded macroreticular Amberlyst A-15 resin has proved to be very efficient in retaining olefins as compared to the Amberlite IR-120 type resin. When the two resin types were ion-exchanged with silver ions, Amberlite IR-120 did not significantly retain olefins as was expected. The difference in this behaviour towards olefins can be attributed to the difference in their surface areas. Amberlyst A-15 resin has a highly porous structure and hence a larger surface area, making it easier for olefinic molecules in the gas phase to diffuse to Ag^+ sites in the resin interior. In the case of IR-120 resin, it is clear that the olefins could not effectively diffuse into the resin for significant Ag^+- olefin interaction to occur, so that olefins are not selectively retained as expected. This is illustrated by the unexpectedly low retention times obtained for olefins when the silver form of this Amberlite IR-120 was used as column packing material.

Table 2.6 shows the difference in 1-octene retention times when the two resin types were used.

Table 2.6. A comparison of the olefin retention for two types of resin.

	retention times (s) on	
Hydrocarbon	*IR-120 (50% Ag^+)	**A-15 (13% Ag^+)
heptane	15	12
1-octene	30	84

---

* column temperature = 80°C. ** column temperature = 110°C.

Despite the lower silver loadings of A-15 type resin compared to that of IR-120 resin, 1-octene retention on the Ag^+ exchanged A-15 resin was significantly higher than that of the Ag^+ exchanged Amberlite IR-120 type resin.

2.2.3.4. Separation of olefins from complex hydrocarbon mixtures.

In this section the selective retention of the olefin from more complex hydrocarbon mixtures was investigated. The previous results indicated that due to the selective retention of Ag^+ exchanged resin column, the olefin peaks in the chromatograms were exceptionally broad. It was also noted that at higher column temperatures, the stability of the Ag^+- olefin complex decreased. It was therefore decided to examine temperature programming to achieve less peak broadening while maintaining the selective retention of the column for olefins.

In temperature programming mode of operation, the sample is injected at a lower column temperature and after a set time, the temperature of the oven is increased at a specified rate to a higher temperature, where it can be set to remain for a specific period of time. In using this method for the Ag^+- exchanged resin column, it was hoped that while non-olefinic components in an injected hydrocarbon mixture are eluted from the column at the lower temperature, the more strongly retained olefin(s) could then be eluted at a higher temperature and this would hopefully result in sharper and more symmetrical peaks.

In the first set of experiments, two sample mixtures were prepared. One mixture (to be referred to as sample A) contained pentane, 1-pentene and 1-hexene. The other mixture (sample B), contained pentane, 1-hexene and cyclohexane. Both samples were injected into a column packed with 100% Ag^+ exchanged Amberlyst A-15 resin. Figure 2.4(a) shows the chromatogram for sample (A) while Figure 2.4(b) shows that obtained when sample (B) was injected. From Figure 2.4(a) it can seen that 1-pentene and 1-hexene were eluted from the column as a single broad peak. In Figure 2.3(b) 1-hexene was also eluted as a broad peak and its retention time was twice that of cyclohexane even though the former has a boiling point half that of cyclohexane.

Temperature program used for complex mixtures:

Initial column temperature, T1 = 60°C	time at T1 = 0.2 min
Temperature ramp = 20°C/min	
Final column temperature, T2 = 130°C	time at T2 = 0.5 min

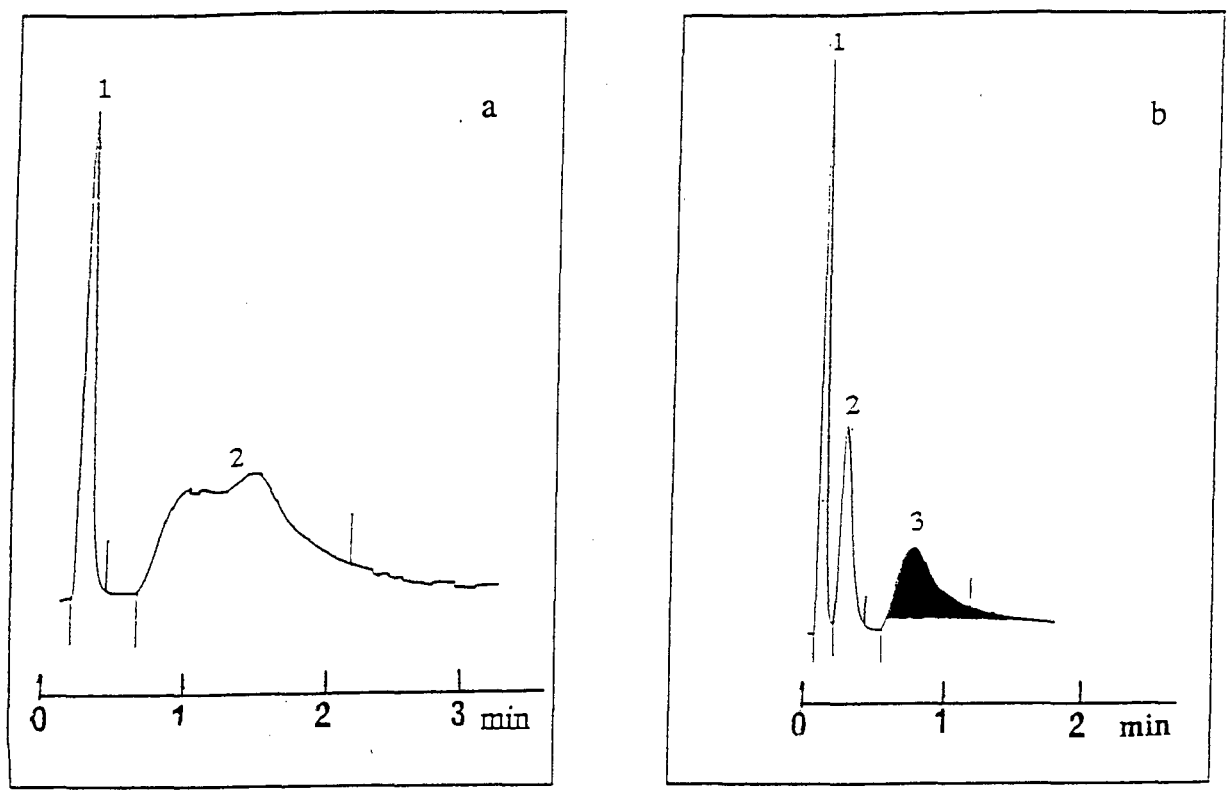


Fig 2.4. Chromatograms obtained for (a) sample (A) containing (1) pentane, (2) 1-pentene and 1-hexene and (b) sample (B) containing (1) pentane, (2) cyclohexane and (3) 1-hexene. Column packed with 100% Ag^+ loaded capacity Amberlyst A-15 resin.

Another complex hydrocarbon mixture in which a C_5 - C_8 alkane reference mixture was spiked with 1-hexene was injected into the column under the same GC conditions as above. Figure 2.5 shows the chromatogram obtained and it is clear that 1-hexene was eluted as a broad peak with a longer retention time when compared with the higher boiling heptane and octane.

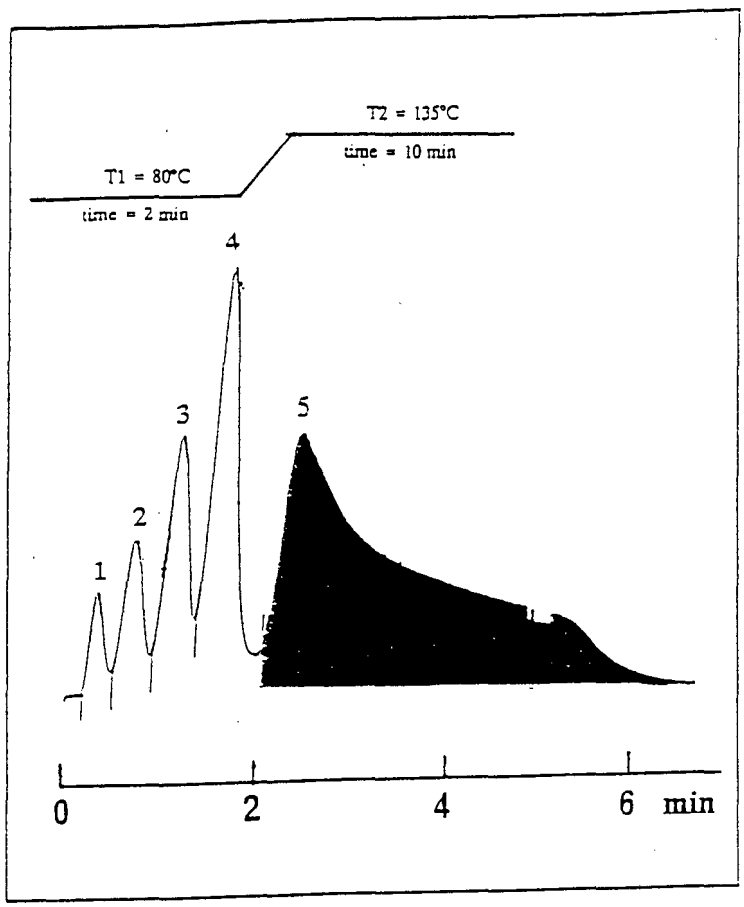


Fig 2.5. Chromatograms obtained for sample containing (1) pentane, hexane, heptane, octane and (5) 1-hexene (shaded). Column packed with 100% Ag^+ loaded capacity Amberlyst A-15 resin.

Another example to further illustrate the selective retention of olefins on Ag^+ exchanged resin is shown by the chromatogram in Figure 2.6. The chromatogram was obtained when a sample containing pentane, cyclohexane, heptane, 1-hexene and 1-octene was injected into the column.

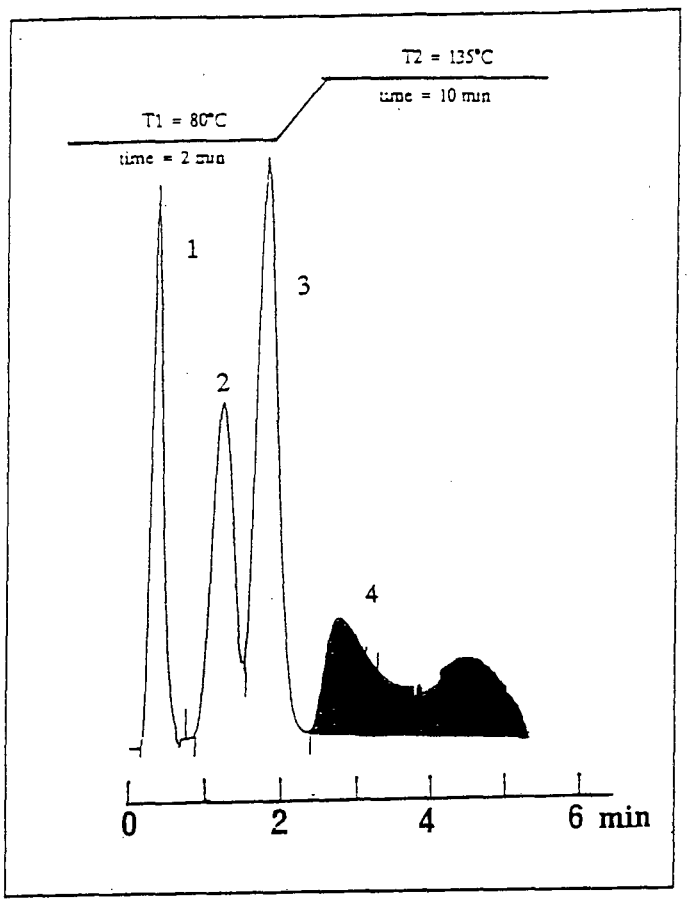


Fig 2.6. Chromatogram obtained for a mixture of (1) pentane, (2) cyclohexane, (3) octane and (4) 1-octene + 1-hexene (shaded). Column packed with 100% Ag^+ loaded capacity Amberlyst A-15 resin.

Another example to further illustrate the selective retention of olefins on Ag^+ exchanged resin is shown by the chromatogram in Figure 2.6. The chromatogram was obtained when a sample containing pentane, cyclohexane, heptane, 1-hexene and 1-octene was injected into the column.

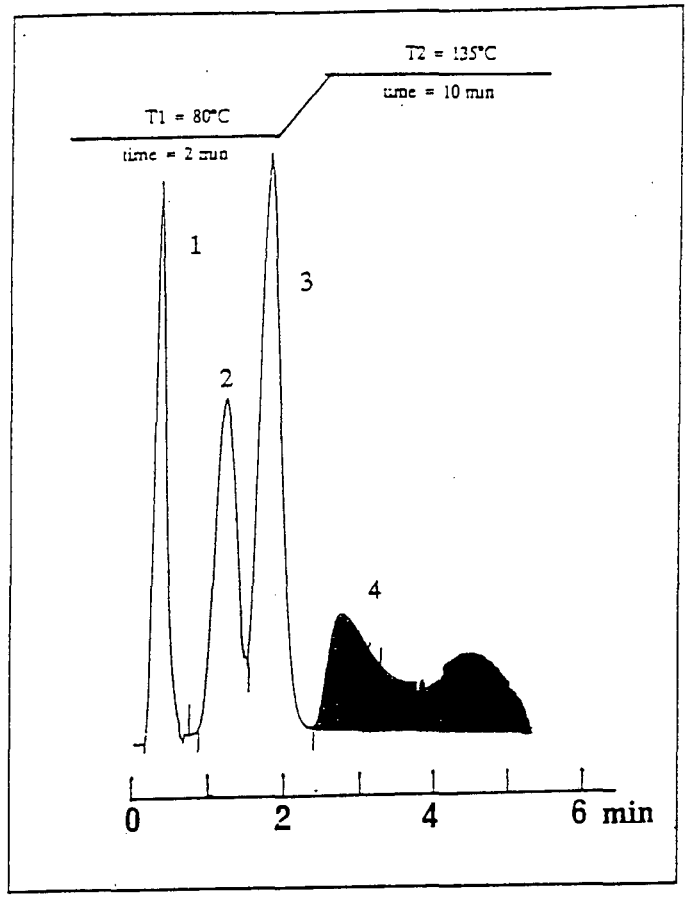


Fig 2.6. Chromatogram obtained for a mixture of (1) pentane, (2) cyclohexane, (3) octane and (4) 1-octene + 1-hexene (shaded). Column packed with 100% Ag^+ loaded capacity Amberlyst A-15 resin.

From Figure 2.6 it is clear that the three alkanes pentane, cyclohexane and octane were eluted in order of their increasing boiling points while the, 1-hexene and 1-octene are eluted together as a poorly resolved broad peak. The latter separation probably occurred when the two olefins were both strongly retained on the column initially at the lower column temperature. At higher temperature they were eluted from the Ag^+ exchanged resin part of the column and on entering the analytical part of the column (as was illustrated in Figure 2.2), they separated out in order of their boiling points with 1-hexene eluting first, followed by 1-octene (see Experimental).

2.2.3.5. **General discussion.**

The use of the Ag^+ exchanged Amberlyst A-15 resin as a packing material has clearly shown that olefins are selectively retained via the Ag^+- olefin complexation. For example, 1-hexene, with a boiling point half that of octane has a retention time almost twice that of octane due to this strong Ag^+- olefin interaction.

With regard to the two resin types, it is clear that the Ag^+ exchanged macroreticular Amberlyst A-15 resin was the more efficient in selectively retaining olefins when compared to the Amberlite IR(120) resin. Ohzeki and Kambara [30] observed that in order for a type of resin to have GSC application it must have a permanent pore structure. The porous nature of Amberlyst A-15 resin probably allowed for maximum interaction between the olefin molecules and the silver ions in the resin interior while the gel type Amberlite IR-120 which has a microreticular structure, probably prevented olefin molecules rapid access to the silver ion sites in the resin interior so that no significant olefin retention was observed. Hirsch *et al* [31] compared the efficiency of Amberlyst A-15 type resin (specific surface area = 50 m^2/g) with AG-50W-X8 resin which has a much lower surface area (0.1 m^2/g) than A-15 type resin. They observed that the retention times obtained for found cyclohexene on Ag^+ exchanged A-15 resin was 110 times higher than those observed when Ag^+ exchanged AG-50W-X8 resin was used as column packing material.

In spite of the strong olefin retention observed for Ag^+ exchanged Amberlyst A-15 resin in this work, the resin beads started decomposing and slowly turned jet black when column temperatures greater than 140°C were used. This low thermal stability would prevent regeneration of adsorbed species (especially high boiling hydrocarbons) if temperature desorption was used to effect olefin desorption. Duffield and Rodgers [32] observed that the strong interaction of the double bonds with silver ion exchanged resin required elevated temperatures (140-220°C) while Madigan and co-workers [28] showed that the retention times for homologues higher than 1-octene on the silver form of sulfurbenzyl porasil was too long for practical utility because high column temperatures required to desorb the retained olefins would also lead to decomposition of the resin beads.

Hence the low thermal stability of the Ag^+ exchanged resins and their reported low capacity for olefins [33] suggests that ion-exchanged resin as support material may not be practical or economically viable.

CHAPTER 3

THE USE OF ZEOLITES AS PACKING MATERIAL IN GAS SOLID CHROMATOGRAPHY

3.1 INTRODUCTION

The work reported in the previous chapter has shown that although Ag^+ exchanged resin did retain olefins relative to alkanes, the Ag^+ exchanged resin had a low thermal stability, and it showed signs of decomposition at temperatures greater than 140°C. This deficiency prompted the investigation of zeolites as potential support material for practical olefin separation.

Zeolites or molecular sieves are metal aluminosilicates which have a crystal structure such that there is a large internal surface for adsorption. Access to this surface is by way of pore openings of fixed and uniform dimensions. Structurally the zeolites are a framework based on an infinitely extending three dimensional network of AlO4 and SiO4 tetrahedra. Their general chemical formula is:

$$x/n[M(AlO_2)x(SiO_2)y]\ n.H_2O$$

Because of the trivalency of the aluminium, each alumina tetrahedron introduces one negative charge to the lattice which is counterbalanced by the positive charge of an associated cation represented in the equation by the capital letter M. In general the metal ions found in most zeolites are either from group I or II e.g H^+, Na^+ or Ca^{2+}. These metal ions can be easily exchanged for other monovalent metal ions for example Ag^+, K^+, Cs^+, or Li^+.

The zeolite tetrahedra are joined through the oxygen atoms to form the so-called sodalite units containing 24 (Si, Al) atoms interconnected by 36 oxygen atoms. Zeolites in general are divided into two main groups namely type A and the second group which is in turn divided into type X and Y. The group a particular zeolite will be assigned to will primarily depend on the actual packing of its sodalite units.

The sodalite units can be packed in a simple cubic array to form Type A zeolites with four bridging oxygen atoms between neighbouring units. If these sodalite units are arranged in a tetrahedral (or diamond) array then they form Type X or Y zeolites with six bridge oxygen atoms. As illustrated in Figure 3.1, the main adsorption cavity of the type A zeolite is a space surrounded by eight sodalite units, where entry into the cavity is by means of a channel surrounded by four sodalite units, the channel having a diameter of about 4Å. The adsorption cavity of the X zeolite is a space surrounded by ten sodalite units, while the channels are surrounded by six sodalite units resulting in a channel with a diameter of about 9Å [34].

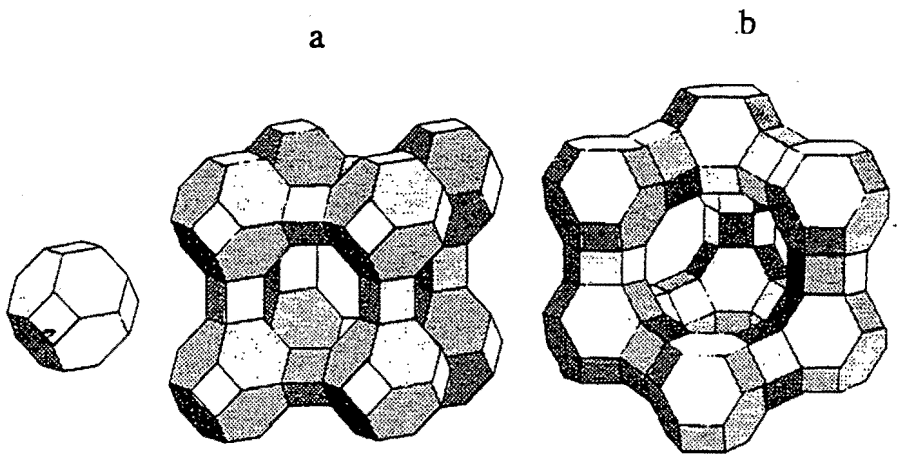


Figure 3.1. Structure of (a) A type zeolite and (b) X and Y type zeolite.

Whether the cubic or diamond array is obtained depends primarily on the SiO_4 : AlO_4 ratio of the zeolite. A wide variety of zeolites are known, some of which occur naturally, while others can be synthesized. Under ambient conditions the intracrystalline cavities and channels of these crystals are filled with water molecules. It is for this reason that zeolites do not develop their gas sorbing and molecular sieve behaviour unless the water is removed without collapsing the surrounding framework.

Zeolites are remarkably stable even when freed of their intracrystalline water and can stand temperatures of up to 500°C almost indefinitely. Due to their stability and uniform pore opening zeolites have found widespread application in the petroleum industry for hydrocarbon separation and catalysis.

These attractive features of zeolites, namely, (1) rigid framework, (2) thermal stability, (3) sieving properties and (4) ion exchange properties make them a potential support material for olefin separation.

3.2. LITERATURE SURVEY.

As early as 1938, R M Barrer had already classified zeolitic molecular sieves in terms of their ability to occlude or exclude certain molecules on the basis of their shapes and sizes. Barrer also noted that despite their porous character, zeolites were remarkably stable to heating and they could withstand temperatures of up to 500°C. In his 1959 review paper on selective sorbents [34], Barrer formulated a table showing the classification of molecular sieves according to their ability to separate hydrocarbons. (See Appendix 2(b) for classification table).

It was shown that Linde type zeolite of pore size 4Å will exclude all hydrocarbons with a critical diameter of more than 4Å. Schwartz and Brasseaux [35] used a column of molecular sieve 5Å to sorb *n*-alkanes from distillates while branched alkanes passed through without being adsorbed. Whitman [36] also used 5Å zeolite type to selectively sorb *n*-alkanes while branched alkanes were not adsorbed. Sunstrom and Krantz [37] used a 5Å type zeolite to adsorb *n*-alkanes from a stream containing branched paraffins. They also discovered that for a binary mixture of *n*-alkanes, the component with the lower molecular weight was preferentially adsorbed by the zeolite. These results were independently confirmed by Satterfield and Cheng [38] but in this case NaY type zeolite was used as adsorbent material.

Industrially, a number of processes are already in operation using zeolites in hydrocarbon separation. The Isosiv process (Union Carbide) uses zeolite type 5Å to separate *n*-alkanes from branched alkanes [39]. In the Universal Oil Products's Olex process [40], modified X or Y type zeolites are used to separate propylene

from C_3 mixtures. The technology was initially developed to separate higher boiling olefins from corresponding alkanes.

A more recent success was achieved for hydrocarbon separation by Seko and co-workers [41] at the Asahi Chemical Industry, who reported the separation of *p*-xylene and ethyl benzene from mixed xylenes using displacement chromatography. The separation was achieved on a column filled with X and Y-type zeolites. In this cost-effective process the selectivity and adsorption capacity of the zeolites were found to be strongly dependent on the physical characteristic of zeolite and those of the adsorbed material. The retained *p*-xylene and ethyl benzene were subsequently desorbed by a solvent (referred to as a displacer) which is more strongly adsorbed than the two hydrocarbons. The two desorbed components are eluted in order of their increasing adsorbability from the zeolite packed column.

Sherry [42] studied the ion exchange properties of Linde type NaX as well as type-A zeolites, and he observed that the Na^+ ions in both the two zeolites were readily exchanged by other cations in the following order $Ag^+ >> Tl^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The zeolite preference for Ag^+ ion was thought to be due to the high polarizability of Ag^+ ions relative to the other ions.

Although the separation of olefins from complex hydrocarbon mixtures using zeolites has not been reported, a few articles have been published in which an alkane and the corresponding olefins were separated from simple mixtures. Herden *et al* [43], showed that in a 1-tetradecene/dodecane mixture, 1-tetradecene was preferentially adsorbed on modified X and Y type zeolites. Using a liquid chromatography column Hruzik, Krypcik and Leclercq [44], showed that 1-heptene is preferentially adsorbed onto NaY and NaX type zeolites from a heptane/1-heptene system. The study also showed that Ag^+ exchanged zeolite will retain 1-heptene much more strongly than unmodified zeolites. Quinn [34] investigated the relative ability of AgX and NaX zeolites to extract 1-pentene from heptane. He observed that AgX was more efficient in adsorbing 1-pentene due to the Ag^+- olefin double bond interaction and the olefin could not be easily desorbed from the Ag^+ exchanged zeolite.

3.3. SCREENING OF ZEOLITES USING GSC.

In this part of the investigation for a suitable support material, a number of zeolitic types of different pore sizes were carefully prepared for gas solid chromatography as described in Chapter 6. The zeolites were all crushed and sieved to the same granularity and packed individually into the GC column as was the case in ion-exchange resin. Each zeolite tested was packed into the GC column and then conditioned overnight in the oven under nitrogen.

3.3.1. **The use of zeolite with a 3Å pore size as support material.**

A series of hydrocarbons where injected in a column which were partially packed with 3Å pore sized zeolite (Na ion form). The rest of the glass column was packed with OV-101 coated chromosorb (see Fig 2.2) and this part of the column served as the analytical section of the column. The retention times obtained are shown in Table 3.1.

Table 3.1. The retention times obtained for 3Å zeolite packed column. Column temperature = 100°C. (Merck 3Å pore sized zeolite)

Hydrocarbon	Retention time (s)
pentane	60.0
1-pentene	81.0
hexane	81.0
1-hexene	97.2
octane	138.6
1-octene	156.6

The experiments were repeated to confirm the trend. From Table 3.1, it is clear that the retention times increased in order of increasing boiling points of members of a homologous series and the retention times of olefins were higher than those of their corresponding alkanes. The latter trend indicates that untreated zeolites tended to adsorb olefins slightly more strongly than the corresponding alkanes. Olefins are probably more strongly adsorbed on the zeolite surface because they are more easily polarizable than alkanes. The cations exposed at the adsorption surface may act as sites of strongly localized charge, which may induce dipoles in the polarizable molecules leading to a stronger retention of olefins as compared to alkanes.

3.3.2. **The use of zeolite with a 4Å pore size as column packing material.**

The next zeolite type to be screened had a 4Å pore size and was also prepared as described in the experimental section. The retention times obtained for a series of olefins and their corresponding alkanes are presented in Table 3.2 and it can be seen that they show a similar trend as the retention times obtained when 3Å zeolite was used as column packing material.

Table 3.2. The retention times obtained for the 4Å zeolite packed column. Column temperature = 100°C. (Merck 4Å pore sized zeolite)

Hydrocarbon	retention time (s)
pentane	2.7
1-pentene	5.4
hexane	4.2
1-hexene	7.8
heptane	7.2
1-heptene	13.9
octane	13.2
1-octene	22.2

As in the case of 3Å sized zeolite, the olefin retention times were much higher than those of their corresponding alkanes. The trend is further proof of the presumed specific interaction of olefins on the zeolite surface. The overall retention times for the respective hydrocarbons obtained for zeolite type 4Å were much lower than those obtained when type 3Å zeolite was used. This trend could probably be due to some difference in the physical properties of the two zeolite types e.g the zeolite binding material. The two commercial zeolites could possibly have different zeolite binding material and this might have affected the relative hydrocarbon interaction on the zeolite surface. The clay binding material used in binding zeolite particles together is known to influence both the mechanical properties and sorption ability of zeolites [45].

3.3.3. **The use of zeolite with a 5Å pore size as column packing material.**

A commercially available Merck zeolite with a pore size of 5Å was treated and packed into a column as in the previous two cases.

On injecting pentane as a preliminary experiment into the column at 100°C, it was strongly retained at this temperature. Injecting other hydrocarbons also proved fruitless as no peaks were obtained on the chromatogram. The use of temperature programming (100°C to 250°C) also proved unsuccessful as none of the hydrocarbons could be eluted from the column. Even at higher temperatures, these compounds were strongly retained by the zeolite but it was possible that these compounds could have slowly bled from the column after a prolonged elution time. A possible explanation for this effect is that the hydrocarbon molecules, on gaining access to the internal zeolite structure through the pore openings were so strongly adsorbed by the 5Å zeolite surface that they could not be eluted under ordinary GC conditions.

3.3.4. The use of NaY zeolite as column packing material.

The NaY type zeolite with a pore size of ~9Å was prepared and packed into the GC column as described.

On injecting pentane into the column at 180°C, the peak obtained, as illustrated in Figure 3.2(a), was exceptionally broad and pentane had a retention time of about 8 minutes. On injecting hexane and other hydrocarbons even broader peaks were obtained as illustrated by the hexane chromatogram in Figure 3.2(b). For long chain alkanes like octane, a broad peak was obtained only after 20 minutes. No attempt was made at this stage to try injecting the corresponding olefins.

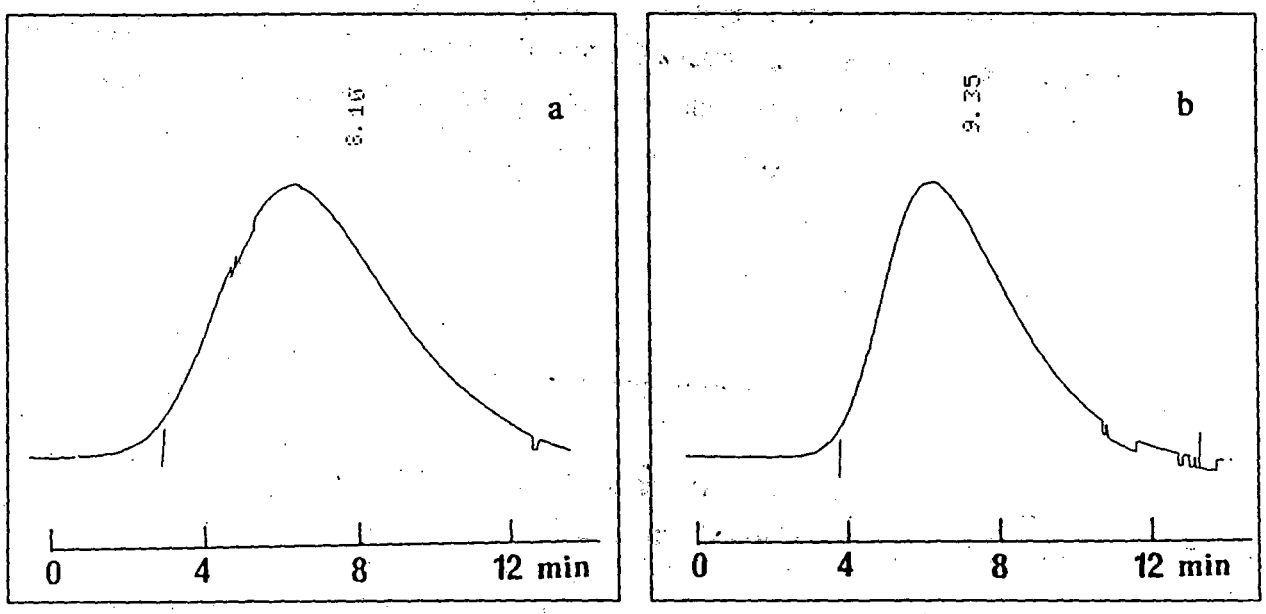


Figure 3.2. The chromatograms of (a) pentane and (b) hexane were injected into a NaY type zeolite packed column. Column temperature = 180°C.

3.4. SILVER ION EXCHANGED ZEOLITE AS COLUMN PACKING MATERIAL.

Of all the zeolite types screened, the 4Å pore size zeolite gave the lowest retention times for hydrocarbons up to decane (C_{10}) under reasonable GC conditions. It was for this reason that the 4Å zeolite was chosen for silver ion exchanging experiments. With conventional ion exchange techniques, the sodium ion of the crystalline zeolite could be replaced by many other metal ions [42] such as Ag^+. When the zeolite carries a cation such as Ag^+, which is known to coordinate with an olefin as was the case with Ag^+ exchanged resin, very strong olefin adsorption would be expected.

A known mass of Ag^+ exchanged 4Å type zeolite (assumed to be 100% Ag^+ exchanged form) was packed into the column as previously described. Table 3.4 shows a comparison between the retention times obtained using unmodified 4Å type zeolite and those obtained using Ag^+ exchanged 4Å zeolite for a series of alkanes and their corresponding olefins.

Table 3.4. The retention times using column packed with unmodified and Ag^+ exchanged 4Å zeolite. (Merck 4Å pore sized zeolite)

	Retention times (s)	
Hydrocarbon	Unmodified zeolite	Ag^+ exchanged zeolite
pentane	3.0	7.2
1-pentene	5.4	270.0
hexane	3.6	10.2
1-hexene	6.0	372.0
octane	15.0	25.2
1-octene	21.6	450.0
decane	43.8	36.6
1-decene	52.2	588.0

The peaks obtained for the olefins were exceptionally broad as compared to their corresponding alkanes, which is an indication of the strong olefin retention by the Ag^+ exchanged 4Å zeolite. These results are consistent with previous observations when Ag^+ exchanged resin was used as column packing material.

Figure 3.3(a) shows a typical chromatogram obtained when an octane and 1-octene mixture was injected into the Ag^+ exchanged zeolite column at 120°C. The broad peak (peak 2) is that of 1-octene.

When a binary mixture containing pentane and 1-pentene was injected into a column packed with Ag^+ exchanged 4Å zeolite using a three step temperature program as shown in Figure 3.4, an unexpected third peak was eluted. As illustrated in Figure 3.4(a), the peak was eluted at very high temperatures.

It was speculated that catalytic oligomerization of the olefin (in this case 1-pentene) on the zeolitic surface at high temperature led to the formation of dimers or higher order oligomers which may account for the third peak. This is in view of the known acidic and catalytic nature of zeolites [58]. In order to test this hypothesis, a sample of pure 1-decene was injected into the column using the same GC conditions. As shown in Figure 3.4(b), the 1-decene peak came off with a similar retention time as that of the third peak in Figure 3.4(a).

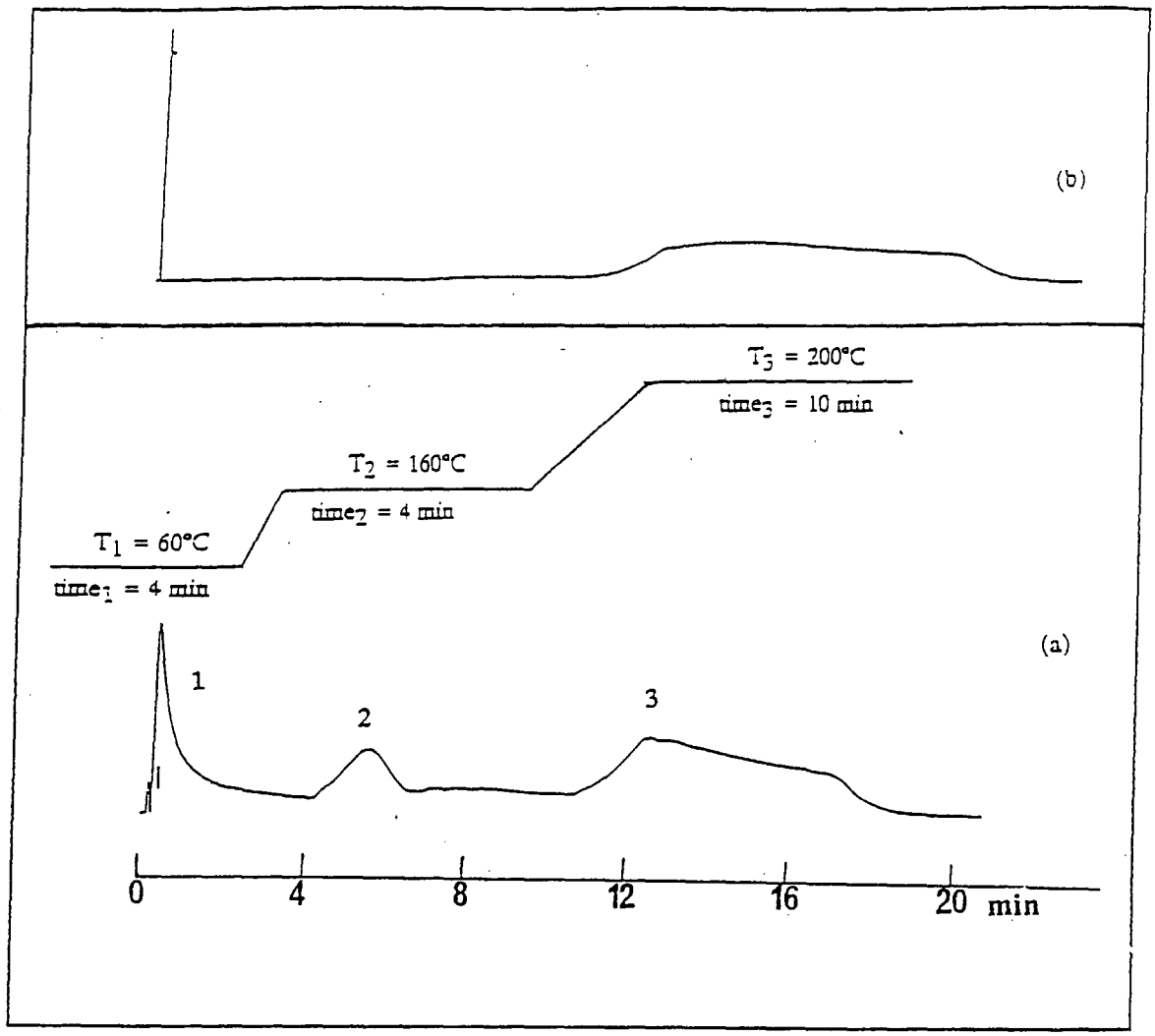


Figure 3.4. The Chromatograms of (a) mixture of (1) pentane, (2) 1-pentene and (3) unknown and (b) a sample of pure 1-decene using temperature program shown between the two chromatograms.

In order to further investigate the possibility of olefin oligomerization on the zeolite surface, two other experiments were performed. Two mixtures containing pentane and 1-pentene were prepared and one was then spiked with decane while the other sample was spiked with 1-decene. The chromatograms obtained for the two mixtures are shown in Figures 3.5 and 3.6 respectively.

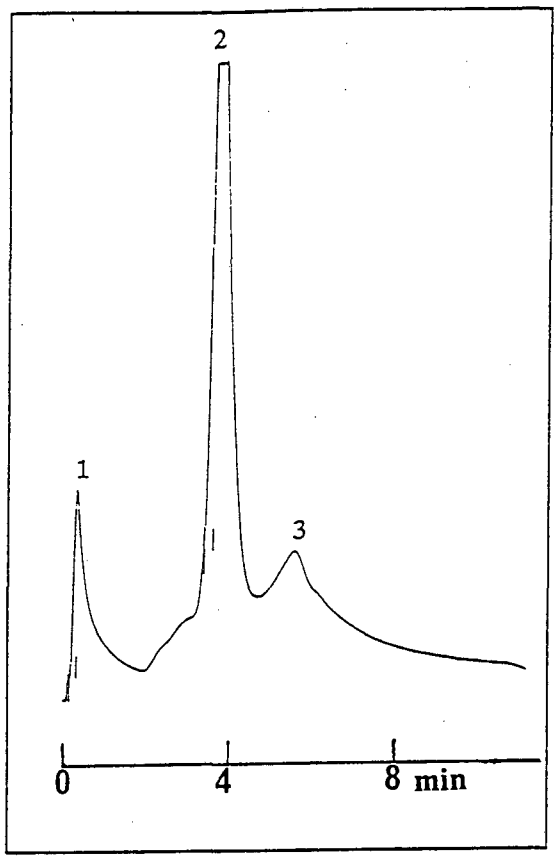


Figure 3.5. The chromatogram of the hydrocarbon mixture containing (1) pentane, (2) decane and (3) 1-pentene.

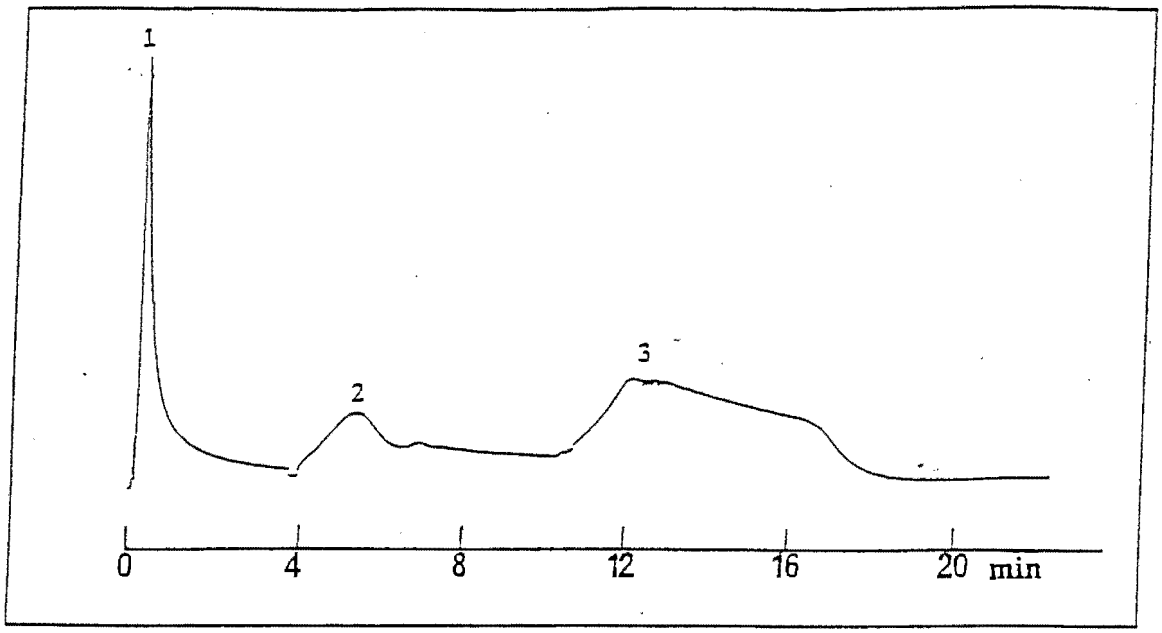


Figure 3.6. The chromatogram of the hydrocarbon mixture containing (1) pentane, and (2) 1-pentene and 1-decene.

The temperature program used was the same as the one in Figure 3.4.

The chromatogram shown in Figure 3.5 was obtained when the mixture containing pentane, 1-pentene and decane was injected into the column. This chromatogram depicts a distinct decane peak (confirmed by separately injecting pure decane into the column and comparing the retention times) in addition to those assigned to pentane and 1-pentene. On the other hand for the chromatogram obtained for the mixture containing pentane, 1-pentene and 1-decene, only an increase in the total peak area of the third peak was observed, as shown in Figure 3.6. This is consistent with the results obtained in Figure 3.4 where the 1-decene peak was eluted from the column a similar retention time to that of the third peak. Due to a temporary shortage of longer chain olefins, it was not possible to extend the study to include 1-hexene and 1-heptene and hence confirm this result.

The above results however do suggest that it is quite possible that olefins may undergo oligomerization on the zeolite surface at higher temperatures to form dimers. In the case of 1-pentene, the results indicate the possible formation of 1-decene whose retention time might have accounted for the third peak observed in Figure 3.4(a).

In zeolites, olefin isomerization and/or polymerization is usually catalyzed by acid sites (protons) on the zeolite surface. The Brønsted acidity which accounts for the catalytic nature of commercial zeolites is probably due to protons on some surface sites which balance the negative charge brought about by alumina tetrahedra as illustrated in Figure 3.7. Most commercial zeolites are usually in Na form but are known to have some of their alumina sites protonated. The results obtained above also seem to suggest that not all AlO_4- sites were exchanged for Ag^+ ions and some of the alumina sites were protonated and this may have led to dimerization of 1-pentene .

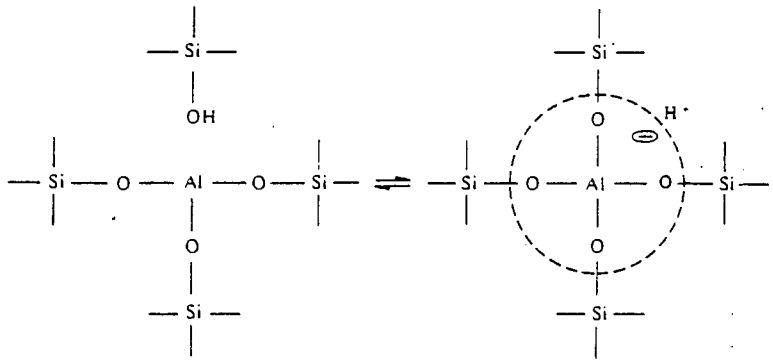


Figure 3.7. Representation of an acidic site in zeolites.

These acidic sites are thought to catalyze olefin reactions via a carbonium ion species. From the results obtained and the fact that zeolites have catalytic tendency, it can be deduced that the unidentified peak is probably a longer chain olefin which resulted from the oligomerization of a short chain olefin. The peak broadening and long retention time supports the suggestion that a long chain olefin could account for the third peak. Although the results are not conclusive at this stage, the use of a GC-Mass Spectrometer could help to properly identify the compound which gave rise to the third peak.

3.5. GENERAL DISCUSSION.

The work done using zeolites as GC column packing material has shown that the hydrocarbon retention times obtained for small pore sized zeolites (3Å and 4Å) as packing material are much lower when compared with the retention times obtained when zeolites with large pore sizes were used. These low retention times are probably because straight chain hydrocarbons molecules, with a critical diameter of 4.9Å [34], are hindered from gaining access to the internal zeolite structure of these narrow pore zeolites, so that these hydrocarbons molecules only interact with the external surface of the zeolite, resulting in relatively poor retention of the hydrocarbons.

When the 5Å pore sized zeolite was used as column packing material, the hydrocarbons were so strongly retained that it was not possible to elute them , even at high column temperatures. This trend suggests that although straight chain hydrocarbons can diffuse into the internal zeolite structure via the pore openings, it is relatively difficult for the hydrocarbon molecules to diffuse out of the zeolite pores fast enough under ordinary GC conditions.

For zeolites with a larger pore size (> 5Å), the hydrocarbons were also strongly retained in the zeolite packed column. Unlike in the case of the 5Å zeolite, the hydrocarbons could be eluted from the column at high temperatures. A possible explanation for this opposing trend is that the hydrocarbon molecules can diffuse in and out of the larger pore openings relatively more quickly, while for the 5Å sized pores, the rate of diffusion in and out of the pore openings is much slower. In spite of this "ease " of diffusion, the hydrocarbon molecules were strongly adsorbed in the zeolite internal structure as was illustrated by their experimentally long retention times and resulting broad peaks.

The primary objective of these experiments was to find a suitable zeolite support material, which on being converted to the Ag^+ ion form would selectively retain olefins while other non-olefinic hydrocarbons passed through the zeolite packed column unretained in the minimum possible time. It was against this background that a small pore sized zeolite was chosen for the Ag^+ ion exchange experiments. On ion exchanging 4Å Na-zeolite for Ag^+ ions, the olefin molecules could conceivably only interact with Ag^+ ions on the external surface of the zeolite. The broad peaks obtained clearly show that even on this limited scale, the Ag^+ exchanged 4Å zeolite material had the desired ability to selectively retain olefins via the Ag^+- olefin interaction while alkanes passed through without appreciable retardation.

When zeolites in general are exchanged into the Ag^+ form as in the case of the 4Å zeolite, very strong adsorption of the olefin molecules could be expected. The work done with the silver form of 4Å zeolite and previously with ion exchange resin has illustrated this charge transfer phenomenon. The olefins in some cases were so strongly retained that temperature programming was used to effect olefin desorption. Sherry [42], found that ethylene, on being adsorbed on type X zeolite, showed a marked irreversibility on AgX but complete reversibility on NaX form of the zeolite, another illustration of the strength of the Ag^+- olefin complex. The major drawback as far as the 4Å zeolite or other smaller pore-size zeolites are concerned is that the olefins are denied access to the internal zeolite surface where most of the Ag^+ sites are situated. This factor would obviously affect the total olefin capacity of the zeolite if a small pore sized zeolite was to be used for the large scale separation of olefins.

The potential use of the Ag^+ exchanged form of the larger pore sized zeolites for selective olefin retention is however not feasible as the results obtained showed that hydrocarbons (olefins and alkanes) were strongly adsorbed by unmodified zeolites. Hence even though olefin molecules might have access to the large internal surface area of the Ag^+ exchanged zeolites where most of the cation sites are thought to be located [42], the strong physical adsorption of both alkanes and olefins would make the separation of long chain olefins from corresponding alkanes impractical.

The use of Ag^+ exchanged zeolites in olefin separation also highlighted the potential of zeolites to catalyze olefin polymerization and/or isomerization. The separation of 1-pentene from pentane using temperature programming showed evidence (although not conclusive), of 1-pentene polymerization at high temperatures. The potential of zeolites to induce catalysis is thought to be due to the strong Brønsted acidity of these aluminosilicates [57]. This adverse effect could become even more important if zeolites were to be used in large scale separation of olefins and if high temperatures were used to desorb the retained olefins.

The work done with zeolites indicated that despite the attractive physical properties of these aluminosilicates, there were other factors which had adverse effect on olefin separation and these led to the further study of zeolites as support material to be abandoned. These adverse factors were:

(a) potential catalytic activity

(b) excessive resistance to the diffusion in and out of the internal structure of the zeolites (Ag^+ modified or not).

(c) strong physical adsorption of both alkanes and olefins.

This undesirable alkane adsorption would become more important if these modified zeolites were to be considered for olefin separation from more complex hydrocarbon mixtures. Further literature studies [44, 45] show that olefin separation using zeolites is restricted to simple systems, usually two component mixtures. Industrial hydrocarbon streams in general and the Fischer Tropsch process stream in particular do contain some branched hydrocarbons and among them branched olefins. These olefins, which can also be retained on a metal modified support material like their linear isomers, can contaminate the linear olefins in the subsequent desorption step. The branched olefins are not desirable as they could give rise to non-biodegradable detergents.

Although the use of zeolites in the large scale separation of olefins from hydrocarbon streams is not practical, zeolites could possibly be used to separate linear olefins from branched olefins by size exclusion chromatography due to sieving properties of zeolites.

QUANTITATIVE SEPARATION OF LINEAR α-OLEFINS USING METAL-MODIFIED STATIONATIONY PHASES

It is in this regard that zeolites, with the ability to discriminate hydrocarbons according to size as a result of their sieving properties, could be used in this subsequent step of olefin separation.

Although the use of zeolites in the large scale separation of olefins from hydrocarbon streams is not practical, zeolites could possibly be used to separate linear olefins from branched olefins by size exclusion chromatography.

CHAPTER 4

THE USE OF SILICA GEL AS SUPPORT MATERIAL IN OLEFIN SEPARATION.

INTRODUCTION

The work done up to this stage has clearly shown that silver modified support material can retain olefins much more strongly than non-olefinic hydrocarbons in a given mixture. The use of gas solid chromatography (GSC) also provided a quick and efficient method of screening candidate support material for possible use in practical olefin separation.

Ag^+ exchanged resin was found to be effective in the selective retention of olefins but the study of resin as a potential support material was not continued as the ion exchange resin was found to have low thermal stability. Zeolites on the other hand, although thermally stable, strongly retain both alkanes and olefins. Zeolites also exhibited the potential to catalyze olefin oligomerization. It was then decided that the potential use of silica gel as support material in the selective retention of olefins from hydrocarbon mixtures should be investigated.

Despite the success achieved using GSC for screening potential support material, GSC had one major limitation. The olefin containing sample is not recovered at the end of the experiment when the destructive flame ionization detector is used in order to obtain a response in the form of a chromatogram. Furthermore GSC is a microanalytical technique and the scaling up of any potential separation scheme using conventional narrow bore GSC columns would not be practical.

It was therefore decided that a suitable apparatus for olefin separation and recovery using metal modified support material should be designed and constructed. It was hoped that this apparatus will not only allow the selective retention of olefins on the chosen metal modified support material, but also allow for the retained olefins to be desorbed and recovered in a pure and hopefully in an unaltered state on a large scale. The apparatus, henceforth to be referred to as the "Separation Rig" was constructed. The schematic diagram of the separation rig is shown in Figure 4.1.

The apparatus is primarily made up of the following major parts: an oven in which a specially designed column can be inserted, a column temperature regulator, a nitrogen source, 2 cold traps for collecting effluents from the column and a glass bridge which connects the column to the cold traps and it also provides a pathway through which hydrocarbon effluent from the column could flow into the cold traps.

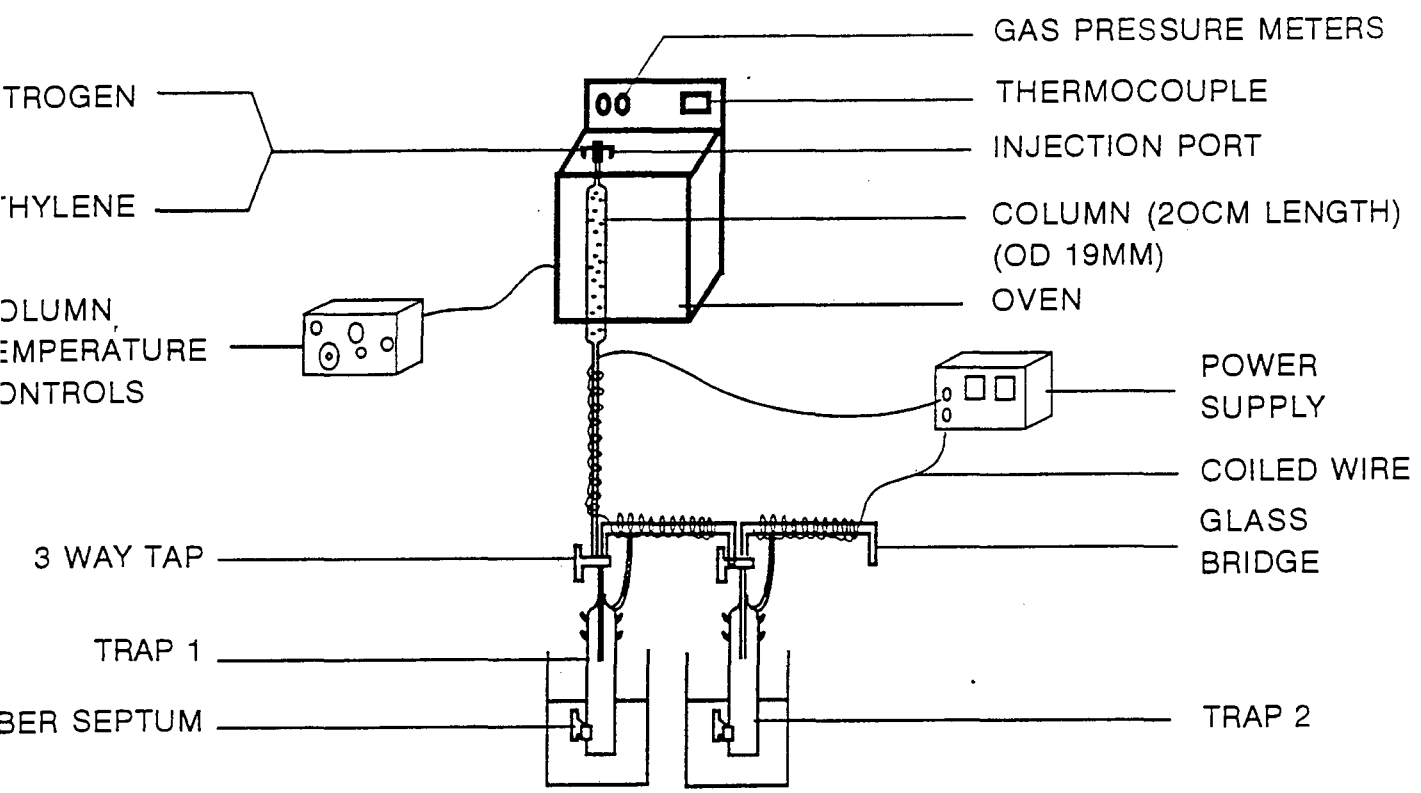


Figure 4.1. Schematic diagram of the "Separation Rig".

The rig can be operated as follows: A sample of a hydrocarbon mixture is injected via the **injector port**, into the vertical column which is filled with metal modified material. The solid adsorbent is held in place at the bottom of the glass column by **scintered glass frit.**

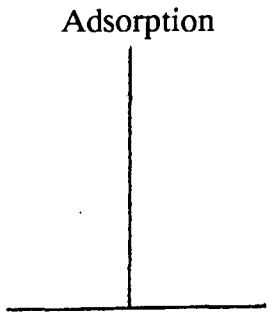
The hydrocarbon sample is injected slowly to ensure maximum interaction between sample and support material. The sample is allowed to percolate down the column under a low nitrogen pressure and usually at room temperature. The nitrogen is used to force the hydrocarbon mixture down the column. The temperature of the oven and hence that of the column is regulated by the **temperature controls** which also have temperature programming features. The **gas flow meters** are used to monitor the nitrogen flow rate and pressure. The column is connected to the exterior via an opening drilled through the bottom of the oven. The column is connected to the glass bridge via a ball and socket joint which is held in place by a stainless steel clamp. This **glass bridge** is maintained at 150°C during rig operation by a coiled **conducting wire** which is connected to a **power source.** The wire is in turn wrapped with **asbestos tape.** The bridge, which provides a path for gases or liquids from the column, is in turn connected to two **cold traps** (1 and 2) which are maintained at sub zero temperatures using ice or dry ice mixed with acetone.

The injected sample is vapourized on entering the glass bridge and the nitrogen-hydrocarbon vapour stream is directed into cold trap 1 by the **three way tap** where the hydrocarbon sample is condensed and collected. When any hydrocarbon material which has been selectively retained on the column is desorbed, usually by increasing the column temperature, the three way tap is switched to another position so that the hydrocarbon-nitrogen stream is directed to trap 2 so as to recover the desorbed material, in our case olefins in a relatively pure form. The percentage hydrocarbon composition in the effluents collected in the two traps is monitored at regular intervals by withdrawing microliter samples of the effluent via the rubber septum which covers the opening near the bottom of the receivers in both trap 1 and 2 and analyzing the samples by conventional gas liquid chromatography.

Using this apparatus, it was hoped that not only could candidate support materials be screened, but also quantitative separation of olefins on a practical scale could be achieved.

4.1. THEORY OF ADSORPTION.

Adsorbents, for example zeolites, alumina, silica gel *etc.* as the name suggests, adsorb hydrocarbon substances, gases, ions and other materials onto their surfaces. The **Adsorption** phenomenon can be described as the process whereby surface forces are used to concentrate materials (adsorbates) on the surface of solid material. Adsorption can be divided into two broad categories as illustrated by the following scheme:



Physical adsorption	Chemical adsorption
(a) Van der waals', forces	(a) Chemical forces
(b) Low adsorption enthalpy	(b) High enthalpy
(c) Low Activation energy	(c) Higher Activation energy

From the scheme shown above, it is clear that physical adsorption (physisorption) occurs as a result of physical forces of attraction between the adsorbate and the adsorbent surface without any well defined chemical reaction. These forces include electrostatic attraction in the case of molecules with permanent dipole moments, induced dipole attraction with readily polarizable molecules and dispersion forces caused by slight fluctuations in electron density [46]. Chemical adsorption (chemisorption) on the other hand may be described as a chemical reaction because the adsorbate molecules react with the adsorbent surface via a somewhat drastic rearrangement of electrons within the adsorbate molecule.

Hence as a result of the weak van der Waals', forces associated with physisorption, the adsorbed material may be easily desorbed from the adsorbent surface, particularly if the temperature is raised slightly. In the case of chemisorption on the other hand, molecules are held tenaciously by the adsorbent surface and usually require much higher temperatures to effect desorption. Another important difference between the two forms of adsorption is that in chemisorption only one layer of molecules is usually adsorbed onto the adsorbent surface whereas more than one layer of the adsorbed material is possible in physisorption.

Physisorption processes have low activation energy while for chemisorption to occur, a non-zero activation energy is required. This led Taylor [47] to name chemisorption an activated adsorption process. Physisorption will thus occur at a much faster rate and in general, via non-specific interactions while the rate of chemisorption (e.g. as in catalysis) will rely on a number of factors which includes the orientation of the molecule being adsorbed at that particular time as illustrated by the following equation:

$$K_c = \sigma Z exp\ (-E_c/RT)$$

K_c = rate constant of chemisorption
σ = Sticking probability of molecule
Z = no of collisions of the adsorbent molecules per cm^3 of surface in unit time.
E_c = Activation energy of chemisorption.

This brief description of the adsorption phenomenon clearly indicates that although both the two types of adsorption are likely to occur simultaneously, physisorption will probably occur at a much faster rate primarily because it occurs via non-specific interactions and zero activation energy is required.

The relevance of the adsorption phenomenon to this project becomes clear if we consider the proposed olefin retention mechanism. Because it is believed to occur via a charge transfer mechanism between the adsorbate (olefin) and the adsorbent (metal modified support), it can be described as a form of chemisorption. From this observation we could envisage that the aim of achieving good olefin retention and recovery will not only depend on optimizing selective olefin retention by the metal modified surface, but will also depend on minimizing or eliminating competitive physisorption of all the hydrocarbons in a given mixture.

4.2. SILICA GEL AS ADSORBENT IN HYDROCARBON SEPARATION.

As was mentioned earlier on, the next support material to be considered for selective olefin retention was silica gel. Silica gel in general has a large surface area which is covered with hydroxyl groups which are tenaciously attached to the surface of silica gel. Silica gel has been used extensively as column packing material in chromatography and also in industry in quantitative and qualitative analysis of permanent gases, biochemicals and hydrocarbons.

4.2.1. **Literature survey.**

The use of unmodified and modified silica gel in hydrocarbon analysis and/or separation has been widely reported. As early as 1935, Mair and White [48] were using silica gel to separate mixtures of hydrocarbons into two fractions, namely alkanes and aromatics with water as the eluent (desorbing solvent). Mair [49] reported the separation of a mixture of alkanes, cycloalkanes, olefins and aromatics into four fractions using a silica gel column with methanol as eluent.

Hirschler and Amon [50] separated hydrocarbons in a homologous series and observed that the extent of adsorption of an adsorbate onto silica gel is a function of molecular weight of the adsorbate. Dinneen and *co*-workers [51] noted that on introducing a sample of shale oil onto a silica gel column, the various classes of compounds arranged themselves in order of their increasing tendency to be adsorbed onto the silica gel surface. Guyani and Gannuly [52] noted that aromatics, alkanes and olefins are usually adsorbed onto the silica gel surface as monolayers.

Smit [53] separated a complex hydrocarbon mixture into pure components on a silica gel column. In this method, the mixture was first introduced onto the silica gel column and the components were then separated and collected in pure form using a series of volatile solvents e.g pentane and methanol which were referred to as *developers*.

In the petrochemical industry, the characterization of the chemical compositions of the feedstocks and petroleum products is done using a silica gel column via what is termed fluorescent indicator adsorption [9]. The column, with deactivated silica gel and a series of dyes, separates the sample into coloured bands of alkanes, olefins and aromatics.

The use of metal modified silica gel in the industrial separation of olefins has being reported in the patent literature. Most of the olefin separation processes highlighted in the following review show that the early attempts to use this charge transfer phenomenon were restricted to simple, low boiling point olefins from hydrocarbon process streams. Schulze [54] separated simple diolefins from hydrocarbon fluids by passing the sample over Cu_2Cl_2 modified clays and silica gel. Hillyer and Dees [55] used CuCl halide on silica gel to selectively separate diolefins from a C_4 hydrocarbon stream. De Feo [56] used a slurry of cuprous (I) halide on silica gel to recover 1,3 butadiene from hydrocarbon streams in high yield while Stern [11] managed to separate 1-pentene from pentane using CuCl coated silica gel.

4.3. QUANTITATIVE OLEFIN SEPARATION USING METAL MODIFIED SILICA GEL.

As already mentioned, in this phase of the project the silver modified support material was not packed into a narrow column for screening by GSC instead the new support material was packed into a wide and straight column specially designed for the Separation Rig in order to investigate this material for potential selective olefin retention and subsequent desorption.

4.3.1. **Unmodified silica gel as column packing material.**

The first set of experiments performed was to investigate the extent to which ordinary silica gel would physically adsorb hydrocarbons and to observe any class preference in this type of adsorption. Secondly, even more important, the possible catalytic effect of the acidic silica gel surface on the olefinic component of the hydrocarbon mixture, especially at elevated column temperatures was also investigated.

The silica gel used was spherical in shape and came in bead form and was specified by the suppliers to have a large pore diameter. For these experiments, a sample of the silica gel beads (14 grams) was packed into the vertical rig column and conditioned overnight under nitrogen at 100°C. A 5 ml sample of an 18% 1-hexene in heptane mixture was injected into the rig column at room temperature. After 30 minutes, a microliter sample of the hydrocarbon effluent collected in trap 1 was withdrawn via the septum as was previously described and injected into the GLC in order to determine the relative composition of the components in the effluent collected.

The rig column temperature was then increased to 100°C and after another 30 minutes a second microliter sample was withdrawn from trap 1 and analyzed. The results obtained are shown in Table 4.1.

Table 4.1. Adsorption of hydrocarbons on unmodified silica gel.

	% by weight		
Hydrocarbon	*initial	**final	***desorption (100°C)
1-hexene	17.9	14.5	15.5
heptane	82.1	85.5	84.5

*Initial refers to the % by weight of the components in the original hydrocarbon mixture.

**Final refers to the % by weight of the components in the effluent collected in trap 1.

***Desorption refers to % by weight of the components in the trap on increasing the column temperature to effect elution of adsorbed components. (In this case all the temperature desorbed hydrocarbon material was also collected in trap 1)

Total volume of hydrocarbons recovered = 4.28 g
Percentage of original sample recovered = 85.6 % (relative to the original mixture)

From the results obtained it can be seen that the olefin component of the sample, 1-hexene is preferentially retained as compared to the heptane as indicated by the decrease in the actual % composition of 1-hexene in the effluent collected (see Table 4.1 column 3). Two possible explanations could be given for this observation. Firstly, 1-hexene could be preferentially adsorbed as a result of its lower molecular weight as compared to heptane. The dependency of physisorption on the molecular weight of hydrocarbons was previously reported by Hirschler and Ammon [50].

The second reason for the preferred adsorption of 1-hexene on silica gel could be as a result of some specific interaction of the olefin molecules on the silica gel surface which may have led to the decrease in the % composition of 1-hexene in the effluent recovered in trap 1. The decrease in the overall sample recovered (85.6 %) could either be as a result of incomplete desorption of hydrocarbons at 100°C and/or sampling or handling loss when the sample was injected into the column.

In order to establish which of the postulates led to the result obtained in Table 4.1, another similar experiment was performed but in this case a three component mixture containing pentane (molar mass = 72 g/mol), 1-hexene (84 g/mol), and heptane (100 g/mol) was prepared. The results obtained when 5 ml of the mixture was injected using the same procedure are shown in Table 4.2.

Table 4.2. Adsorption of three hydrocarbons on silica gel.

	% by weight		
Hydrocarbon	initial	final	desorption (150°C)
pentane	31.9	42.7	33.5
1-hexene	11.4	9.9	8.5
heptane	56.6	47.4	57.9

Total volume of sample recovered = 4.36 ml

Percentage of original sample recovered = 87.2%

From the results shown in Table 4.2 it is clear that the % 1-hexene composition in the effluent collected in trap 1 decrease as was the case in the previous experiment. The fact that 1-hexene is preferentially adsorbed onto the silica gel as compared to pentane which has a lower molecular weight suggests that specific interactions between olefin molecules (at the double bond) and the silica gel surface have a

greater influence on the adsorption of 1-hexene onto the silica gel than molecular weight.

Comparing the relative adsorptions of the two alkanes, pentane and heptane, it can be seen from Table 4.2 that the % composition of the higher molecular weight heptane actually decreases in the effluent collected (see Table 4.2 column 3) while % composition of pentane as observed before increased. This result suggests that although lower molecular weight components in a given hydrocarbon mixture could be preferentially adsorbed onto the silica gel surface, high molecular components in the hydrocarbon mixture percolate much slower down the packed column as compared to lower molecular weight components so that at a given time the relative composition of the former appears to decrease in the effluent collected. This is illustrated by the fact that on increasing the temperature of the column to effect complete desorption of any physisorbed hydrocarbon material, the % composition of heptane (see Table 4.2 column 3) actually increased as compared to its % composition in the original sample.

From the results obtained in Tables 4.1 and 4.2, it appears as if 1-hexene and hence olefins in general will be preferentially adsorbed on the bare silica gel surface as compared to alkanes. This selective adsorption probably occurs via "specific" interactions between the olefin pi bond and the surface hydroxyl groups of the silica gel.

Silica gel has a surface which exhibits mild Brønsted acidity [58] and the use of high temperatures is known to initiate catalysis of some of the adsorbed material e.g olefin isomerization on these acidic surfaces. It was against this background that a series of experiments were performed to determine whether temperature desorption of hydrocarbons from the ordinary silica gel surface has any adverse effect on adsorbed hydrocarbon components.

In each of the experiments exactly 14 grams of silica gel were packed into the rig column and 5 ml samples of a 1-hexene in heptane mixture were injected dropwise at room temperature into the silica gel packed column. After the mixture was added, the adsorbed hydrocarbon was desorbed from the silica gel column as a function of temperature. Table 4.3 shows the % hydrocarbon recovered with increasing column temperature.

Table 4.3. The% sample olefin recovery as a function of desorption temperature.

Desorption temperature (°C)	*% Sample recovery
60	78.2
80	83.0
100	88.7
140	90.0
180	92.3

* refers to the % of the hydrocarbon recovered after desorption relative to the total adsorbed hydrocarbon.

Total adsorbed hydrocarbon = initial volume hydrocarbon sample - volume unadsorbed hydrocarbon.

On analyzing the respective samples for any evidence of olefin isomerization and/or polymerization, a marked increase in 1-hexene isomerization was observed as the desorption temperature was increased. Figure 4.2 show % 1-hexene isomerization as a function of desorption temperature [The chromatograms showing 1-hexene isomer distribution are shown in the Appendix 3(a)].

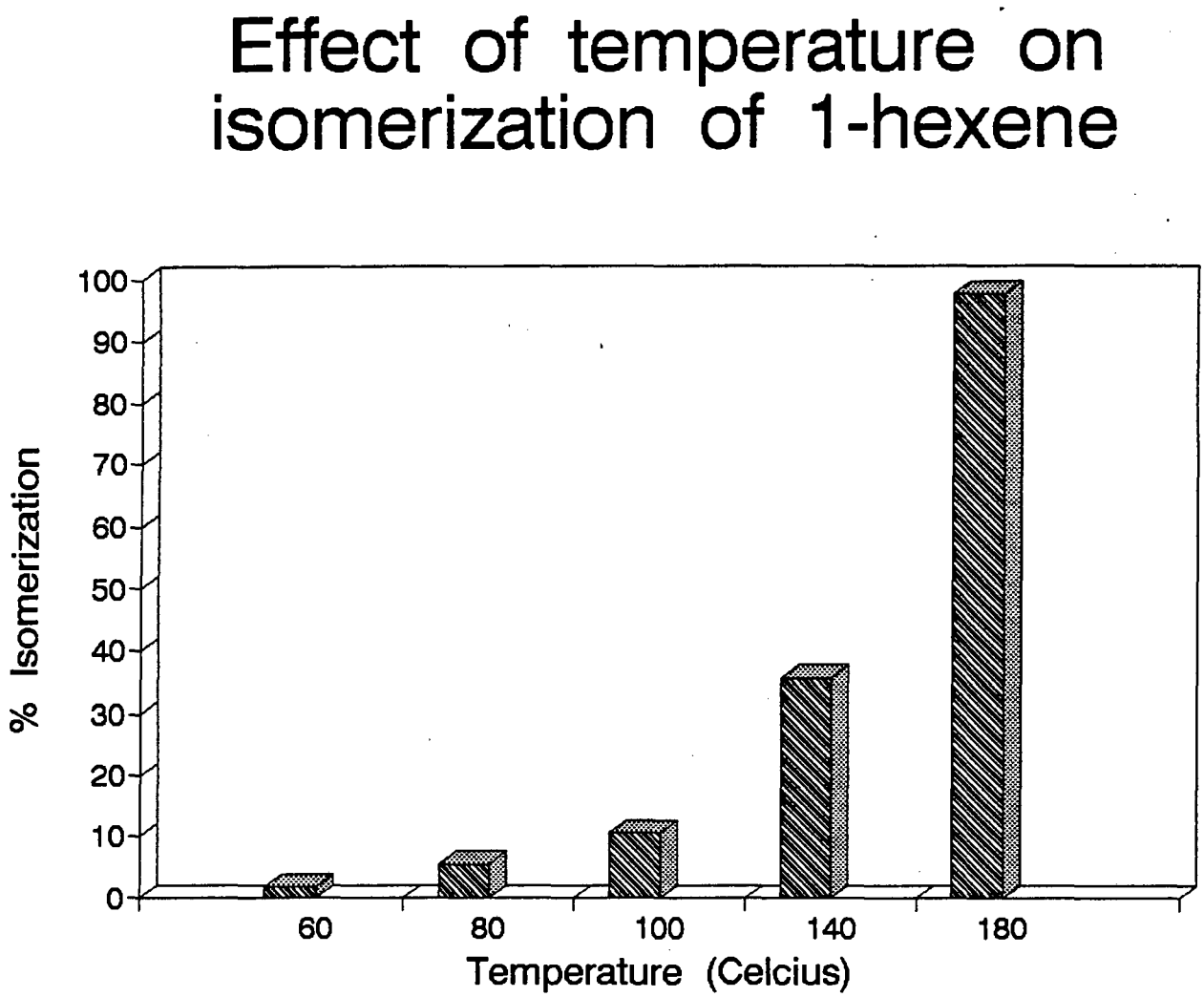


Figure 4.2. The % 1-hexene isomerization as a function of hydrocarbon desorption temperature.

* % 1-hexene isomerization refers to the ratio of the amount of 1-hexene which isomerized to the total original amount of 1-hexene in the sample injected. This value was calculated using the chromatograms obtained at the different desorption temperatures by dividing the sum total of the peak areas of the isomers formed by the sum of total peak areas of the new isomers plus the peak area of unaltered 1-hexene.

The above results show two important trends which are noteworthy. Firstly, at high temperatures physisorption takes place to a lesser extent as shown in Table 4.3 where the amount of hydrocarbon sample recovered increased as the desorption temperature is increased. At 180°C, most of the hydrocarbon sample was recovered (>90 %). The difference could be attributed to experimental error. Hence physisorption on silica gel can be reduced at high temperatures.

Secondly and more importantly, the bare silica gel surface seems to have a tendency to catalyze olefin isomerization especially at high temperatures. [Further discussion on olefin isomerization on pure silica gel is done later to compare these results with those obtained for metal modified silica gel]

The work done using pure silica gel has shown that hydrocarbons could be adsorbed by the silica gel and temperature could be used to recover most if not all the adsorbed hydrocarbons. Silica gel had also proved to be thermally stable and it did not undergo degradation at high temperatures. The undesirable olefin isomerization on the silica gel surface at high temperatures was probably catalyzed by acid sites on the pure silica gel surface. It was hence worthwhile to continue the study of silica gel as a potential support material for olefin separation and hence determine if metal modification of silica gel will not only lead to selective olefin retention, but also minimize or eliminate olefin isomerization on the silica gel surface especially at high temperatures.

4.3.2. Use of $AgNO_3$ modified silica gel as column packing material.

In this section of the project the potential use of $AgNO_3$ modified silica gel as support material in the selective retention of olefins using the "Separation rig" was investigated. The salt, $AgNO_3$ was used earlier to convert zeolites and the ion exchange resins into silver form. As it was not possible to effect silver ion exchange directly in the case of silica gel, $AgNO_3$ was directly deposited onto the silica gel surface. The amount of $AgNO_3$ deposited onto a given mass of silica gel was expressed as percent by weight of the modified silica gel.

Of critical importance for both laboratory and industrial olefin separation is the determination of the minimum amount of the transition metal salt that would achieve an optimum olefin retention under ideal experimental conditions. Once these factors have been established the next step would be to determine an efficient method of recovering these retained olefins in a pure and unaltered state from the column.

4.3.2.1. **Choice of metal salt.**

Silver nitrate ($AgNO_3$), silver tetrafluoroborate ($AgBF_4$) and silver perchlorate ($AgClO_4$) are the most widely used silver salts in olefin separation though their application has been restricted mostly to low boiling point olefins [10]. $AgNO_3$ was chosen in this project as it was readily available and cheaper than the other silver salts.

The efficiency of a transition metal cation to form a stable complex with an olefin is expected to be dependent on the anion associated with the metal cation. In particular for silver salts such as AgI and AgCl do not complex with olefins probably because the Ag^+ion's ability to form a dative covalent bond with olefins is adversely affected by the electronegativity of I^- and Cl^- anions.

Highlights from the literature [29, 59, 63] show that $AgNO_3$ and $AgBF_4$ have been widely used in the separation of simple olefins from simple hydrocarbon mixtures while $AgClO_4$ has not been used as extensively as the other two salts for olefin separation because perchlorate complexes tend to become explosive upon heating. $AgBF_4$ tends to form the most stable Ag^+- olefin complex of the three silver salts, while $AgClO_4$ form the least stable complexes. Again this trend can be explained in terms of the weaker interaction between the silver ion and the anion in the $AgBF_4$ than in the other two salts.

4.3.2.2. Olefin adsorption as a function of % AgNO3.

A series of AgNO3 modified silica gel beads with varying weight percentages of the silver salt were carefully prepared and packed into the rig column in order to determine the ideal amount of the silver salt required to achieve optimum olefin adsorption from a given hydrocarbon mixture. In each experiment, 5 ml samples of simple olefin and alkane mixtures were introduced into the rig column packed with exactly 14 grams of the AgNO3 modified silica gel. The hydrocarbon sample was introduced dropwise and allowed to percolate through the column at room temperature and under a low nitrogen flow rate. After introducing the sample, the temperature was increased to 80°C to remove any excess physisorbed hydrocarbons. The composition of the original sample and the effluent collected after the introduction (1 hour) were determined by GLC. Some of the results obtained are given in Table 4.4.

Table 4.4. Olefin adsorption as a function of % AgNO3.

		% by weight		
*Olefin	**%AgNO3	initial	final	***ml/14g
1-pentene	10	28.0	12.9	0.683
1-hexene	10	22.2	7.9	0.566
	15	18.4	2.2	0.575
1-heptene	5	16.9	8.0	0.404
	10	22.0	11.2	0.479
	20	21.0	0	0.984
1-octene	20	25.8	2.8	0.851
1-decene	20	21.1	3.4	0.821

* olefin was mixed corresponding alkane to obtain the % composition (column 2).

** refers to the percentage by weight of $AgNO_3$ which was deposited on silica gel.

*** refers to the volume (ml) of olefin selectively adsorbed from a hydrocarbon mixture per 14 gram of $AgNO_3$ modified silica gel assuming that all the olefin is adsorbed via the Ag^+ - olefin interaction.

The volume of olefin selectively adsorbed by the modified support is calculated using the following equation put forward by Hirschler and Amon [50]:

$$\frac{V = v(Co - C)}{100}$$

where V = volume of hydrocarbon preferably adsorbed.

v = volume of the collected sample.

C_o = original % concentration of component in volume.

C = % concentration remaining in the effluent volume collected.

From the results shown in Table 4.4, it is clear that increasing the amount of $AgNO_3$ deposited onto the silica gel surface tends to increase the selective retention of the olefin from a given mixture. This is because increasing the amount of $AgNO_3$ also increase the Ag^+: olefin mole ratio and hence more Ag^+ sites are available to improve selective olefin retention. The results are consistent to those obtained by Stern [16] who used CuCl modified silica gel to separate 1-pentene from pentane. Stern also noted that on doubling the amount of CuCl salt deposited on a given mass of silica gel, not only does the total amount of retained olefin increase but the level of alkane physisorption also decreased substantially.

An increase in the amount of transition metal salt on silica gel will probably block the silica gel pores and hence decrease the physical adsorption of hydrocarbons in the internal silica gel surface while the surface metal ion-olefin interaction will increase as the amount of salt deposited on the surface is increased. Hence optimum olefin retention could be achieved if the amount of salt deposited is increased substantially. From the results shown in Table 4.4, it could be deduced that in order to achieve optimum olefin retention on metal modified support material, a higher percentage of the transition metal salt must be deposited onto a given mass of support material.

The result shown in Table 4.4 also illustrated a correlation between the extent of olefin retention with olefin chain length. Using columns packed with 20 % $AgNO_3$ silica gel, it was observed that all the 1-heptene in the mixture was selectively retained (assuming that all the olefin retained was due to Ag^+- olefin bond) while for the two longer chain olefins, 1-octene and 1-decene not all the olefin was selectively retained onto the $AgNO_3$ modified silica gel. This is further illustrated by the volume of 1-heptene which was selectively retained onto the column relative to the other two olefins (see Table 4.4 column 5). This trend could possibly be due to a steric dependence of the Ag^+- olefin complex. Short chain olefins will probably interact with the silver ions to form the complex at a much faster rate than longer chain olefins. For the 1-octene and 1-decene containing samples, the effluent collected in trap 1 was re-injected into the rig column in order to improve olefin retention while for 1-heptene, optimum retention was achieved after only one injection as shown in Table 4.4 columns 2 and 3.

4.4 OLEFIN RECOVERY: DISPLACEMENT vs DESORPTION.

The next step to be considered after achieving selective olefin retention from hydrocarbon mixtures, was to find an efficient mechanism by which the retained olefins could be recovered from the separation rig column. Two mechanisms were considered to effect olefin recovery from the column namely, displacement chromatography and temperature desorption.

4.4.1. **Displacement Chromatography in olefin recovery.**

In order to recover selectively retained olefins the principle of displacement chromatography (DC) was considered. In DC, the sample mixture containing a desired component is first introduced into the column and allowed to percolate down the column. The desired component is usually strongly retained by the chosen column packing material as compared to the other components in the sample mixture. The adsorbed component is subsequently displaced from the column by a more strongly adsorbed compound (usually a solvent) which is called a displacer. The chief merits of displacement chromatography are:

(a) its ability to concentrate substrates and

(b) the relatively low temperatures used to achieve displacement.

In order to achieve olefin displacement, the use of a low boiling olefin was considered. The low boiling olefin would hopefully interact strongly with the silver ions than the sterically hindered long chain olefins leading to displacement of long chain olefins. Ethylene gas, the simplest olefin was considered for olefin displacement experiments.

To test whether ethylene gas could displace previously retained long chain olefins from the metal modified support material, the following experiment was performed. 14 grams of 15% $AgNO_3$ modified silica gel were prepared as described in the Experimental. The modified silica gel was then packed carefully into the rig column. The rig column was inserted into the separation rig and conditioned for a few hours at 80°C under nitrogen.

The column was then cooled to room temperature. A 5 ml mixture containing 1-heptene and hexane was injected dropwise into the column at room temperature. The temperature was then increased to 70°C to remove any excess physisorbed hydrocarbons. The oven temperature was then lowered to 35°C. The three way tap was then switched so that any displaced olefin could be directed and collected into trap 2 (see rig operation). The column was then flushed with a 50:50 mixture of ethylene and nitrogen gas (100 ml/min) for 90 minutes. The results obtained are shown in Table 4.5.

Table 4.5. The displacement of retained olefins using ethylene gas as displacer.

	% by weight		
Hydrocarbon	Initial	final	*content in trap 2
1-heptene	16.7	5.8	8.6 (0.052 ml)
heptane	83.2	94.1	91.3 (0.550 ml)

* The percentage by weight of the components from the effluent collected in trap 2 volume collected ~0.6 ml. The values in brackets are volumes (ml) calculated.

From Table 4.5, it can be deduced that no significant olefin displacement occurred. The small amount of material recovered in the cold trap 2 (for olefin recovery) and the relative % olefin composition of the mixture indicates that the material displaced was probably only excess physisorbed hydrocarbons on the column and not displaced olefins. Further attempts to effect olefin displacement by ethylene gas were done. In other instances the gas mixture flow rate was first decreased (20 ml/min), then increased (150 ml/min) and finally the column was flushed with pure ethylene gas for varying lengths of time but this varying of parameters proved fruitless as no quantitative olefin displacement using ethylene gas was achieved.

In subsequent series of experiments another low boiling olefin, 1-pentene was considered as a possible long chain olefin displacer. Flushing the modified silica gel column which had previously adsorbed olefins from a hydrocarbon mixture with an excess amount of 1-pentene proved fruitless as the effluent collected in trap 2 only contain very small trace amounts of alkanes and olefins from the injected mixtures.

Another low boiling liquid displacer to be tried was methanol. A small amount of olefin displacement was achieved with this polar solvent but the use of methanol

caused some unforeseen problems because the solvent started to remove the $AgNO_3$ coating on the silica gel and hence reducing the efficiency of the column. Methanol and other related solvents dissolve silver nitrate and other silver salts. Hence the study of methanol as a potential olefin displacer was not pursued.

The displacement experiments undertaken in this section of the project were based on the fact that the equilibrium constants of olefin-silver interactions are known to decrease with the increase in olefin alkyl chain length because of steric factors. Hence it might be possible in theory to displace long chain olefins with simple lower boiling point olefins. The properties of an olefin that might influence the metal-olefin complex can be divided into two groups namely, steric and electronic [24, 60] but as to which one will dominate is not clear. The steric bulk of the alkyl chain will prevent optimum approach of the olefins to the metal ion and will either affect the stability or rate of interaction to form the Ag^+- olefin complex. Muhs and Weiss [24] concluded from their studies of equilibrium constants of silver-olefin complexes that steric factors do predominate while Quinn and Glew [61] found that alkylated olefins form stronger bonds with silver(I) than ethylene and Gilliland *et al* [62] came to the same conclusion using Cu(I).

Infrared studies by Quinn *et al* [63] also showed a stronger interaction of the more basic olefins with Ag^+ ions. Qualitative estimates by Traynam and Olechowski [64] and Kramer [65] indicated that the σ component (which is strengthened by electron donating alkyl substituents) should predominate and hence the Ag^+- olefin complex should become more stable as the alkyl chain increases. Scott and Phillips [27] had previously used 1-octene to displace trace amounts of 1-heptene from $AgNO_3$ coated alumina column.

The lack of success in displacing the longer chain olefins by simple olefins tend to confirm this suggestion and to imply that long chain olefins are somehow strongly retained. Although the rate of retention will probably decrease with an increase in olefin alkyl chain length because of steric considerations, the stability of the Ag^+-olefin complex is enhanced by the alkyl group. It is might be possible to use longer chain olefins to effect olefin displacement but it would not be practical to do so on a large scale.

The unsuccessful attempts to use displacement chromatography to achieve significant olefin recovery prompted the investigation into the potential use of temperature desorption as an alternative olefin recovery method.

4.4.2. **Olefin recovery using temperature desorption.**

The objective behind the following set of experiments was to determine the efficiency of temperature for the desorption of olefins from the $AgNO_3$ modified silica gel column. The efficiency of any olefin desorbing mechanism was based on the following criteria:

(a) optimum recovery of previously adsorbed olefins.

(b) recovery of olefins in an unaltered form i.e minimum polymerization and/or isomerization.

As a trial experiment, a simple olefin containing hydrocarbon mixture was prepared. The rig column was carefully packed with 14 g of 20% $AgNO_3$ modified silica gel. After conditioning the column at 100°C under nitrogen, a 10 ml sample of the mixture containing pentane, 1-octene and decane was injected dropwise into the column at room temperature. The effluent collected in trap 1 was found to still containing a significant amount of the olefin hence the effluent was re-injected in order to improve the olefin selective adsorption onto the modified silica gel. When no significant difference in the olefin % composition of two consecutive effluent samples (after re-injection) was observed, it was assumed that the maximum amount of olefin was retained.

The column temperature was then raised to 75°C to remove any excess physisorbed hydrocarbons. The three way tap was then switched to another position so that the effluent could be collected in trap 2 as previously described. In order to effect olefin desorption, the column temperature was then raised to 150°C under a nitrogen pressure of 10 lb/inch^2. The results obtained are reported in Table 4.6.

Table 4.6. Recovery of 1-octene from a 20% $AgNO_3$ modified silica gel column by temperature desorption.

	% by weight		
Hydrocarbon	Initial	Final	*Desorption (150°C)
pentane	21.0	12.2	10.9
1-octene	19.8	3.4	80.8
decane	59.1	84.4	8.3

Taking % by weight ≈ % by volume,

* total volume collected (by desorption) = 2.19 ml
hence volume 1-octene recovered = 1.77 ml

** The calculated values for % volume of olefin retained and recovered by desorption for this and subsequent experiments are summarized in Table 4.12 in order to compare the relative retentions and recovery of different long chain olefins.

Figure 4.3 illustrate the chromatograms obtained when the mixture containing original mixture containing 1-octene and the effluents collected in trap 1 and 2 from the rig were analyzed using conventional gas liquid chromatography.

From the results in Table 4.6 and the chromatograms illustrated in Figure 4.3, it can be deduced that 1-octene was selectively retained on the $AgNO_3$ modified silica gel column. Subsequent desorption of the retained olefin from the column showed an enrichment of 1-octene over time in trap 2 as more of 1-octene was desorbed from the column at high temperatures. The olefin recovered was however not 100% pure as traces of the two alkanes were observed on the chromatogram. The alkanes were probably physisorbed onto the silica gel and could only be desorbed at a higher temperature.

The use of temperature desorption for olefin recovery was extended to more complex mixtures.

The first complex mixture to be prepared contained cyclohexane, heptane, 20 % by weight 1-octene and octane. A 7 ml of the sample was injected into a 20 % $AgNO_3$ modified silica gel column (14 g). After 30 minutes the column temperature was increased to 70°C to desorbed any physisorbed hydrocarbons from the column. The effluent collected in trap 1 was re-injected to optimize the selective retention of the olefin in the original sample. The retained 1-octene was then desorbed from the column at 150°C and collected into trap 2 over a period of 2 hours. Microliter samples were withdrawn at regular intervals to monitor the olefin enrichment in the desorbed effluent in trap 2. Table 4.7 shows the results obtained.

Table 4.7. Quantitative olefin separation from complex mixtures.

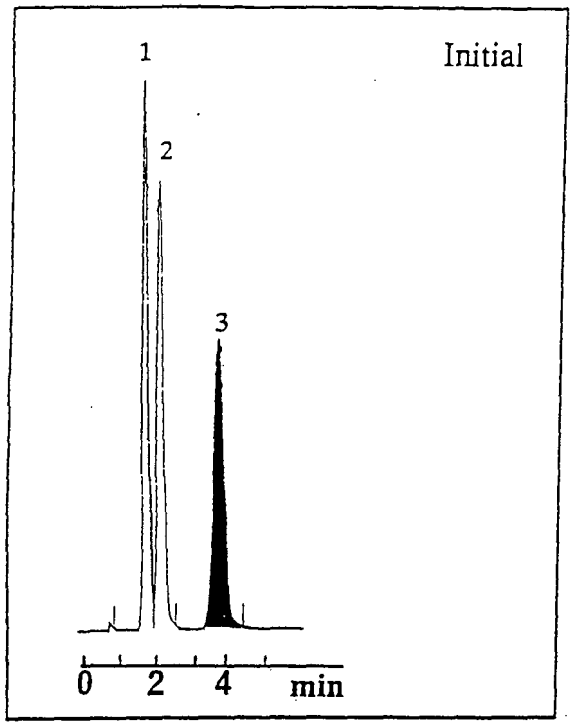
	% by weight		
Hydrocarbon	Initial	Final	Desorption (150°C)
cyclohexane	33.1	44.2	1.5
heptane	32.2	44.0	4.8
1-octene/ane	34.7	*11.8	93.7

* Assumed to be mainly remaining octane concentration with small traces of unretained 1-octene.

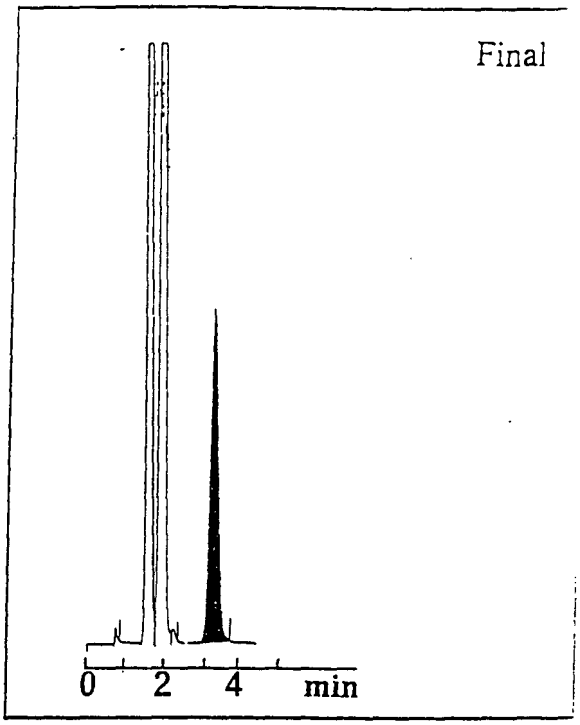
Total volume of sample desorbed (150°C) = 1.68 ml

hence volume of 1-octene recovered = 1.53 ml

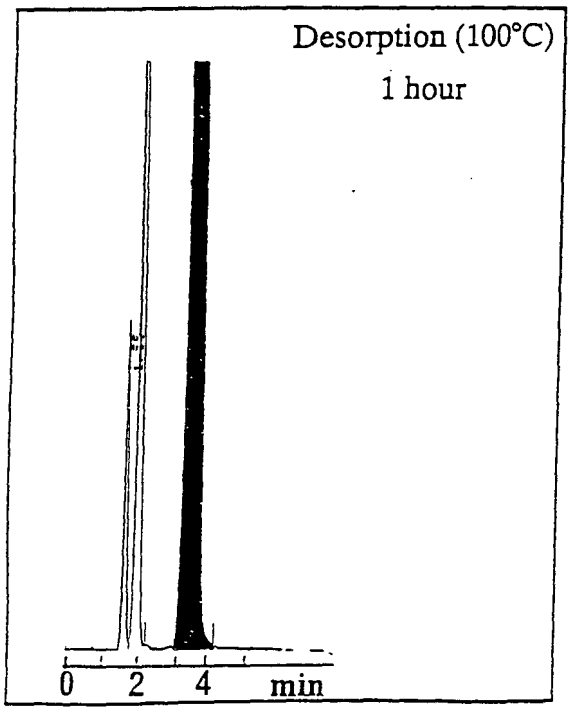
From the results summarized in Table 4.7 it is clear that a significant amount of 1-octene was retained and subsequently desorbed from the modified silica gel. The fact that the 1-octene/octane peak was not resolved to show the relative amounts of the two components in the final desorbed sample, it was not possible to calculate the accurate amount (in ml) of olefin recovered. Hence the value calculated above for 1-octene recovered (1.53 ml) is not entirely correct as there are possibly traces of octane in the effluent recovered in trap 2. From the chromatograms shown in Figure 4.4, it is clear that the third peak increased significantly on desorption. This is attributed to the enrichment by 1-octene when it is desorbed into trap 2 at elevated temperatures. The collected sample also contained traces of cyclohexane and heptane which were presumably physisorbed onto the silica gel.



Original sample



effluent (rig)



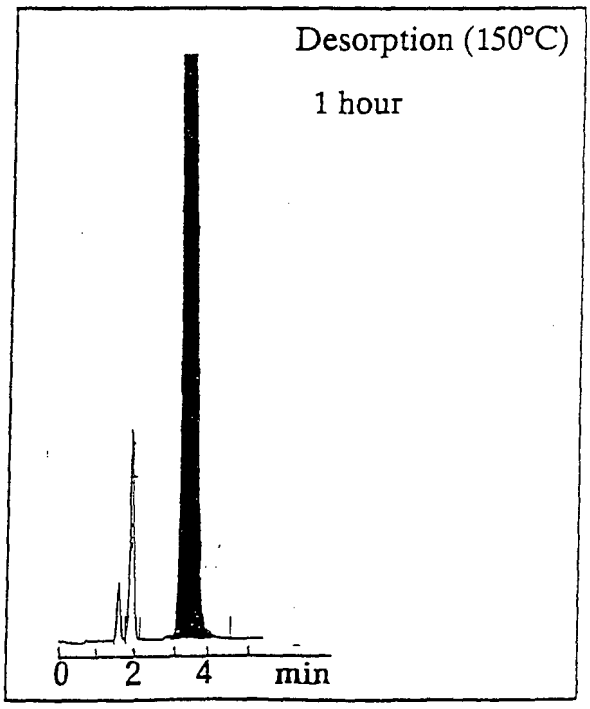


Figure 4.4. Chromatograms obtained for the selective retention and recovery of 1-octene containing mixture. Peak (1) cyclohexane, (2) heptane and (3) octane and 1-octene (shaded).

The next olefin containing mixture to be considered was a 15 ml mixture of pentane, cyclohexane, heptane, octane and 1-decene. The sample was injected dropwise into a column packed with 14 grams of 20% $AgNO_3$ modified silica gel at room temperature. After 30 min the effluent was re-injected into the column. After the fourth repeated injection, the temperature was then increase to 75°C to remove physisorbed hydrocarbons. The column temperature was then increased to 150°C and the retained olefin was collected in trap 2. Table 4.8 shows the results obtained when the original sample and effluent were analyzed using GLC.

Table 4.8. Separation and recovery of 1-decene in a complex mixture from $AgNO_3$ silica gel using temperature desorption.

	% by weight		
Hydrocarbon	Original	Final	Desorption (150°C)
pentane	11.2	26.3	2.1
cyclohexane	5.7	10.9	1.1
heptane	14.7	15.9	*
octane	33.3	36.1	7.2
1-decene	34.6	10.8	89.6

* only a single peak for both cyclohexane and heptane.

Total volume obtained on desorption(150°C) = 3.28 ml.
hence volume of 1-decene recovered (in trap 2) = 2.94 ml.

Figure 4.5 illustrates a series of chromatograms obtained when the original samples and effluents were analyzed by GLC.

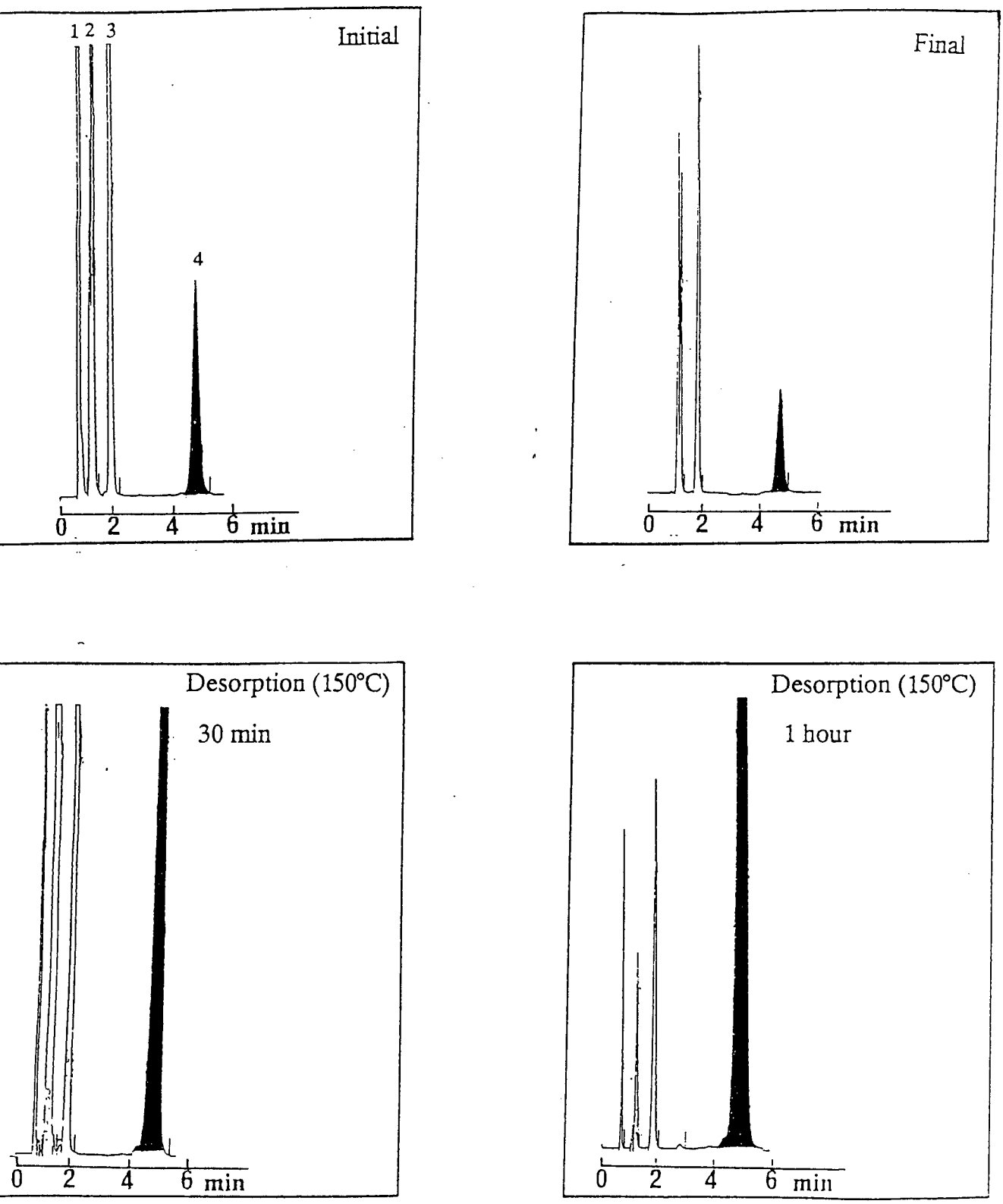


Figure 4.5. The chromatograms obtained for the selective adsorption and recovery of 1-decene in a given mixture. Peak (1) pentane, (2) cyclohexane, (3) heptane, (4) octane and (5) 1-decene (shaded).

As was observed with 1-octene, 1-decene was also selectively retained onto the $AgNO_3$ modified silica gel column. Again the olefin recovered was not 100% pure and traces of alkanes were detected after desorption from the column. The result is however important as it shows that even longer chain olefins like 1-decene could be selectively retained by the $AgNO_3$ modified silica gel. In order to test whether the column could be re-used without any significant decrease in efficiency, a freshly prepared 15 ml sample mixture also containing 1-decene was injected into the column using the same procedure as above. Table 4.9 compares the 1-decene selective retention for the first experiment (run 1) and the second experiment (run 2). (See Appendix 3(a) for chromatograms obtained ffrom run 2)

Table 4.9. Comparison between 1-decene retention and desorption for run (1) and run (2).

Sample	Run 1	Run 2
Initial (% weight)	34.90	30.20
Final (% by weight)	10.80	11.90
original volume 1-decene (ml)	5.19	4.52
volume 1-decene retained (ml)	3.30	3.18
*volume 1-decene desorbed (ml)	2.95	2.58
**% 1-decene recovery	89.6 %	88.0 %

* From the total desorbed sample (trap 2) at 150°C

$$\frac{\text{volume retained}}{}$$

** % of the retained 1-decene recovered by temperature desorption.

From Table 4.9, it is clear that there is no significant difference between the amount of 1-decene retained in run 1 and the amount 1-decene retained in run 2. This result not only illustrates that the metal modified silica gel column, if properly prepared and maintained, could possibly be re-used for selective olefin retention and subsequent recovery. Secondly, the result also illustrates the efficiency of temperature in desorbing most of the previously retained olefins so that the metal modified support material could be re-used for other olefin separation experiments. As mentioned previously, the commercial viability of the proposed method for olefin separation will depend primarily on the recovery of olefin in an unaltered form and on the recyclability of the metal modified support material without any degradation. In the previous experiments using temperature desorption to effect olefin recovery, the white $AgNO_3$ modified silica gel underwent degradation at elevated temperatures and turned dark brown and hence the modified silica gel column could not be re-used in subsequent experiments. This was postulated to occur as a result of a reaction between the $AgNO_3$ with physisorbed water in the silica gel at elevated temperatures to form silver hydroxide (AgOH). The silica gel used for the present experiment and subsequent ones was hence dried at very high temperatures (see Experimental) and modified in the absence of air and moisture. After desorbing the olefins retained in run 1, the modified silica gel did not change colour as in the previous cases. From the above observation, it is clear that the life time of a column will depend on proper preparation and handling of the modified silica gel. The exclusion or elimination of water in preparation, made it possible for the modified silica gel column to be re-used for another olefin separation experiment.

In the selective retention of the longer chain olefins namely 1-octene and 1-decene, the effluent collected in trap 1 had to be re-injected so that retention of olefins on in the effluent collected in trap 1 could be selectively adsorbed onto the metal modified silica gel and hence optimize the amount of olefin retained in the original sample. This procedure, although successful, could lead to sample loss and experimental error. In order to avoid re-injecting the effluent to maximize olefin retention, a column with a much bigger capacity for the modified silica gel was used. The newly designed column was used in the following experiment.

The aim of the next experiment was to compare the selective retention of a branched olefin and a related long chain olefin. The new column (20 cm . 40-mm o.d) was packed with exactly 45 g of 20% $AgNO_3$ modified silica gel. After the column was conditioned at 100°C under nitrogen, 25 ml of a hydrocarbon mixture containing pentane, decane, 1-undecene and 2-methyl-1-undecene was injected dropwise into the column. The temperature was again increased to 80°C to remove any physisorbed hydrocarbons. The column temperature was then increased to 150°C to effect olefin desorption into trap 2. Table 4.10 shows the results obtained when the sample and effluent were analyzed by GLC.(see Appendix 3(c) for chromatograms)

Table 4.10. Olefin adsorption and desorption using complex mixtures

	% by weight		
Hydrocarbon	Initial	Final	Desorption (150°C)
pentane	25.5	38.3	3.4
decane	43.2	51.0	31.1
1-undecene	20.6	7.5	57.2
2-methyl-1-undecene	10.7	3.0	8.2

total volume recovered after desorption (150°C)	= 6.7 ml.
hence total volume 1-undecene desorbed	= 3.9 ml
total volume 2-methyl 1- undecene desorbed	= 0.54 ml

Table 4.11. Comparison of the effective olefin retention and recovery from 20% $AgNO_3$ silica gel of four different olefins.

Olefin	Boiling Point	[a]original volume (ml)	Retained volume (ml)	[b] % olefin retained	[c]Recovered volume (ml)	[d] % vol recovered
1-octene (Table 4.6)	122 - 123°C	1.98	1.86	93.9	1.77	95.0
1-decene (Table 4.8)	166 - 173°C	5.19	3.29	63.4	2.94	89.3
1-undecene (Table 4.10)	192 - 193°C	5.15	4.02	78.0	3.90	75.7
2-methyl-1-undecene Table (4.10)	209 - 215°C	2.70	1.70	62.9	0.54	31.7

[a] volume olefin in the specified sample

[b] percentage of the olefin volume which is retained

[c] volume of olefin recovered by temperature desorption (150°C)

[d] % volume of olefin recovered as a percentage of the volume olefin which was retained on the column.

From the results shown in Table 4.10, it is clear that longer chain olefins were selectively retained from complex mixtures onto the $AgNO_3$ modified silica gel but not as efficiently as it was hoped as excess support material was used to retain the olefins in this case. The quantitative results calculated from Table 4.10 are summarized in Table 4.11 where the effect of olefin structure on retention and desorption is discussed (see Appendix 3(e) for calculations based on Table 4.10 results).

In Table 4.11 the quantitative retention and recovery of four different olefins are compared. Table 4.11 is also used to compare the effect of branching along the olefin chain on the selective retention of that olefin. From Table 4.11, it is clear that for all the olefins relatively high percentages of the olefins from the original samples were retained on the modified silica gel. For 1-octene and 1-decene, 14 grams of 20% $AgNO_3$ silica gel were used for the selective retention of these olefins and as can be seen from Table 4.11 (column 5) relatively high percentages of the two olefins from the respective original samples were retained on the column. The higher percentage retention of 1-octene as compared to 1-decene is due to the fact that a larger volume of 1-decene was injected relative to 1-octene on a similar column (14 g of modified silica gel). Hence for the results shown in Table 4.11 (column 4) it is clear that in the injection of 1-octene, the capacity of the $AgNO_3$ modified silica gel for selective olefin retention was under-used hence most of the 1-octene originally injected was retained as compared to 1-decene.

Column 7 in Table 4.11 compares the % olefin recovery of the four olefins. From the results obtained, it is clear that % olefin recovered from the column by temperature desorption is dependent on the boiling point of the olefin being desorbed. 1-Octene, was successfully recovered (> 80%) from the modified silica gel as compared to other olefins, with the recovery of 2-methyl-1-undecene the lowest (31.7%). An explanation for this could be that as the boiling point of the olefin increases, it is not efficiently vapourized and hence it is not completely desorbed from the column at 150°C. 1-Octene is in vapour phase at 150°C (desorption temperature) while 2-methyl-1-undecene (b.p. 209 -215°C) is probably still in liquid phase and hence it is not removed efficiently from the rig column.

From these observations it could be argued that the recovery of olefins from the column is not only dependent on the strength of the Ag^+- olefin bond, but also depends on how efficiently it is desorbed from the column. Because different amounts of the four olefins were injected, no comparison could be made for the effect of olefin chain length on the stability of the Ag^+- olefin complex.

Table 4.11 is also used to compare the selective retention of a long chain olefin and that of a corresponding branched olefin. When a sample containing both 1-undecene and the branched olefin, 2-methyl-1-undecene (Table 4.10) was injected in the column packed with 45 g of $AgNO_3$ modified silica gel, 1-undecene was retained more efficiently than the branched olefin as shown by the relative amounts of 1-undecene and 2-methyl-1-undecene adsorbed (Table 4.11, column 6). The reason for this preferential retention of the straight chain olefin is probably due to steric factors. The methyl group on the C_2 position in 2-methyl-1-undecene is close to the double bond and somehow affects the proximity of the Ag^+- olefin interaction and leads to a the lower % olefin retention of the branched olefin as compared to 1-undecene.

Hirsch *et al* [75] on comparing the retention times of straight chain olefins with those of branched olefins observed that although 1-hexene had a high retention time on a Ag^+ exchanged resin, the branched 2-methyl-1-pentene had a lower retention time due to the alkyl chain near to the double bond. Muhs and Weiss [24] also noted that the equilibrium constant for the formation of silver nitrate - olefin complex is very low for olefins with alkyl substituents b to the olefin double bond. Hence the stability of the complex is greatly influenced by the steric factors in the case of branched olefins. Limited supply of pure branched olefins prevented the extension of this study to other branched olefin- straight olefin pairs.

The steric argument could quiet possibly be extended to the effect of chain length on the formation of the Ag^+- olefin bond. The rate with which this interaction can occur will probably be dependent on the orientation of the olefin double bond relative to Ag^+ ion at a given instance. Hence it could be argued that for simple olefins like ethylene, the rate of formation of the Ag^+- olefin bond will probably be faster as compared to longer chain olefins because of the steric hindrance brought

about by the bulky alkyl chain in the longer chain olefins. Hence although the stability of the Ag^+ - olefin complex bond might be enhanced by the increasing alkyl chain length of the olefin, the chain length could on the other hand affect the actual formation of the bond.

4.4.3. Effect of desorption temperature on olefin isomerization.

The use of unmodified silica gel as column packing material had previously shown (section 4.3.1) catalytic activity at elevated temperatures where an olefin in a given hydrocarbon mixture was isomerized to other positional isomers. It was thus important to establish whether the $AgNO_3$ modified silica gel would have similar effects on the olefins.

A series of hydrocarbon samples recovered when retained olefins were desorbed at high temperatures were analyzed for olefin isomer distribution using a gas chromatograph with a polar capillary column in order to obtain good peak resolution of any possible olefin isomers. Table 4.12 shows a comparison between the isomer distribution of the pure olefin and that of the desorbed olefin when it is the $AgNO_3$ modified silica gel column.

Table 4.12. Comparison between the isomeric distribution of the pure olefins and temperature desorbed olefins.

	*% isomers	
Olefin	pure	effluent
1-heptene	0	0
1-octene	0.51	0.96
1-decene	0.87	0.92

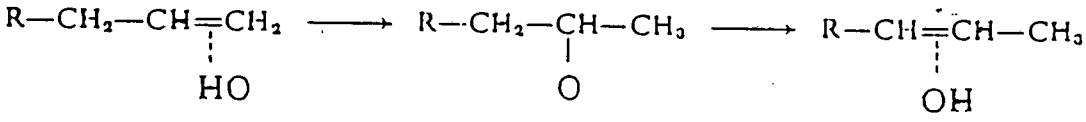
* refers to the total sum of the peak areas (from chromatograms) of all the olefin isomers formed divided by the peak area of the original linear a-olefin. Hence any significant increase of this ratio as compared to that of the pure olefin will signify isomerization of that particular olefin at high temperatures.

The results obtained in Table 4.12 indicate that no significant olefin isomerization occurred on the $AgNO_3$ modified silica gel when the olefins were desorbed from the column at high temperatures.

In the high temperature desorption of hydrocarbon mixtures from unmodified silica gel (see section 4.3.1), 1-hexene was isomerized to 3-hexene and other positional

isomers. This effect was even more pronounced at elevated temperatures. The isomerization of olefins on the silica gel surface could possibly be attributed to the acidic nature of the silica gel surface. Although the hydroxyl groups on the silica gel are tenaciously held, chemical [70] and adsorption [71, 72] investigations have shown that the hydrogens attached to these surface hydroxyl groups are highly acidic. According to Kieselev and co-workers [73], the hydroxyl hydrogens can either be hydrogen bonded to adjacent oxygens or be unbonded. Hence at high temperatures, these hydrogens can be added to the adsorbed olefin molecule leading to isomerization of the olefin.

The following isomerization mechanism via the formation of the olefin carbocation was envisaged. The first step could presumably involve the addition of a proton from the bare silica gel surface to the coordinated olefin. This step is probably followed by the re-formation of the O-H bond on the silica surface accompanied by a stepwise migration of the double bond:



The final step could then be the an abstraction of a proton from the coordinated olefin, followed by addition of the proton to another carbon different from its original location.

Careful coating of $AgNO_3$ onto the silica gel surface appeared to retard olefin isomerization. The metal salt probably "deactivated" the acidic sites on the silica gel and hence no significant isomerization occurred on the $AgNO_3$ modified silica gel even when high temperatures were used to desorb olefins. This was in sharp contrast to the results obtained when unmodified silica gel was used. As shown in Table 4.9, little or no isomerization was observed when olefins desorbed from $AgNO_3$ modified silica gel were analyzed for isomers using GLC.

The high amount of $AgNO_3$ salt deposited in most of the experiments seem to play a significant role in the reduction of acid induced isomerization. The even coating of the silica gel surface with AgNO3 will, as mentioned before block the pore openings on the silica gel. This could quiet possibly inhibit both alkanes and olefins from gaining access through the silica gel pores into the internal surface. This could decrease the physisorption of hydrocarbons while at the same time improve the olefin retention due to the increase in Ag^+: olefin mole ratio.

4.5 GENERAL DISCUSSION.

Silica gel has proved to be an ideal support material for practical olefin separation. Unlike ion exchange resin, carefully prepared modified silica gel was found to have a much higher thermal stability and hence could be regenerated by removal of the adsorbed olefins at high temperatures. Although pure silica gel was found to catalyze olefin isomerization, the $AgNO_3$ coated silica gel did not show any catalytic tendency to catalyze olefin isomerization. In the case of silica gel it was also possible to recover adsorbed hydrocarbon material at reasonable temperatures as compared to zeolites where very high temperatures were used to desorb material.

The efficiency of the $AgNO_3$ modified silica gel in the selective retention of olefins from hydrocarbon mixtures was shown to be somehow dependent on olefin structure. Longer chain olefins in given samples were sometimes re-injected into the column in order to improve the retention while shorter chain olefins were retained in most cases by one with only one sample injection. A comparison of branched olefin with a corresponding straight chain olefin showed that the long chain olefin was preferentially adsorbed. This and the effect of chain length was attributed to chain steric factors.

The use of temperature to desorb retained olefins from the AgNO3 modified silica gel have proved to be a success as compared to displacement chromatography with up to 85 % recovery in some instances for example with 1-octene (Table 4.8). The loss could be due to a combination of factors principal among them are (a) sample and handling loss and (2) limiting our desorption temperature to 120 - 150°C might have led to incomplete desorption. Schulze [54] desorbed olefins from a CuCl modified support at 175°C while Stern [16] used 180°C to effect 1-pentene desorption from a metal modified silica gel. The lack of success in recovering long chain olefins by displacement chromatography using simple olefins tends to confirm the suggestion that long chain olefins are probably more strongly retained onto the $AgNO_3$ modified silica gel because the electron donating alkyl chain probably enhances the stability of the Ag^+- olefin complex

One of the measures taken in this project to minimize alkane physisorption and hence improve olefin purity at the desorption step was to dilute the olefin containing sample mixture with pentane. Smit [53] had previously used pentane (which he called a developer) to force long chain alkanes down a column packed with ordinary silica gel used for hydrocarbon class separation. Pentane is

preferentially physisorbed by silica gel because in a given hydrocarbon sample the hydrocarbon with the lowest molecular weight is usually the most strongly physisorbed [51]. Hence preferred physisorption of a low boiling alkane (e.g pentane) in the place of say, decane during the separation of 1-decene from a C10 fraction could be an advantage as pentane (b p = 29°C) could be easily evaporated off or even recycled after the desorption step. This could this could improve olefin purity at the desorption stage. In the experimental work the adoption of this approach plus the removal of any physisorbed material at a slightly higher temperature (60 - 80°C) helped to decrease the alkane physisorption. In spite of these measures, some physisorbed material including pentane was found in the desorbed sample containing olefins. For sample containing long chain components see Table 4.11, physisorption was more pronounced with up to 29% of the desorbed olefin sample being alkanes

Another important observation regarding the use of temperature for olefin recovery is that the removal of physisorbed or trapped hydrocarbon material from the column using temperatures between 60 and 80°C is not adequate to remove high boiling alkanes like decane as is illustrated by its % content in the desorption step in Table 4.10. It would seem like to achieve an efficient removal of these higher boiling olefins, we need to go to higher temperatures but at the risk of removing chemisorbed olefins from the silver modified column.

The results obtained using metal modified silica gel have illustrated a number of important point:

(a) Long chain olefins can be selectively retained onto AgNO3 modified silica gel.

(b) The metal modified silica gel could be re-used for further olefin separation provided it is properly prepared and maintained.

(c) Metal modified silica gel did not show any tendency to catalyze olefin isomerization and/or polymerization.

These results are very important as the economic viability of using metal modified support material to separate olefins on an industrial scale will depend heavily on the recyclability of the modified support and the recovery of the desired olefin in an unaltered state.

CHAPTER 5

GENERAL DISCUSSION AND CONCLUSIONS

The use of gas chromatography for the selective retention of olefins on modified stationery phase via dative covalent bonds between the olefin double bonds and Ag^+ ions was successful. GSC has also proved to be a versatile and practical technique for the rapid screening of potential support materials practical olefin separation.

The potential use of ion exchange resin as a support material for selective olefin retention was extensively investigated using GSC. From the results obtained it was clear that Ag^+ exchanged resin did retain olefins selectively and at very high Ag+ ion capacity (50-100%), the specific olefin retention was so strong that temperature programming was necessary to elute olefins from the GC column. The broad olefin peaks and their high retention times clearly illustrated the strength of the Ag^+-olefin bond.

From the work done with two types of ion exchange resin namely, Amberlite IR-120(H) and Amberlyst A-15, it was also evident that olefin retention is not only dependent on silver content in the resin but also on the porosity of that particular resin. The gel type Amberlite IR-120 resin did not retain olefins relative to alkanes even when it was in silver form while the Ag^+ exchanged Amberlyst A-15 resin proved to be efficient in retaining olefins relative to alkanes in a given hydrocarbon mixture. A possible reason for this observation is that the macroporous Amberlyst A-15 resin has a higher sorption capacity and will allow olefins molecules access to its internal structure. This lead to the strong olefin retention by the resin. In Ag+ exchanged Amberlite IR-120, olefin molecules were probably denied access to the internal resin surface and hence no specific adsorption was observed even though the ion exchange capacity of the two resin types were found to be the more or less the same.

Although Ag^+ exchanged Amberlyst A-15 resin was efficient in the selective retention of olefins from synthetic hydrocarbon mixtures, its low thermal stability and reported low adsorption capacity for olefins does not make ion exchange resin a practically viable stationary phase for large scale olefin separation.

On screening a series of zeolites of different pores sizes using GSC, it was discovered that unmodified zeolites with pore sizes 5Å or greater strongly adsorbed alkanes and olefins. The retention times obtained when hydrocarbons were injected into a column packed with these zeolites, and the column temperatures used to elute them were very high. The chromatogram peaks were exceptionally broad which resulted in poor peak resolution in more complex mixtures. On the other hand the use of small pore sized zeolites as column packing material gave rise to small retention times and sharp peaks. This sharp contrast illustrates that for large pore sized zeolites, the hydrocarbon molecules can make their way through the pores into the internal channels of the zeolites where they are strongly adsorbed. In contrast for small pore sized zeolites (3Å or 4Å) the molecules probably interact only with the external surface of the zeolite particles without gaining access into the internal pore structure.

On ion exchanging the 4Å pore sized zeolite into the silver form, olefins were strongly retained as compared to their corresponding alkanes. This interaction however, is probably only an outer surface interaction between the olefins and the silver sites while the narrow pore structure of the zeolites prevents significant olefin - Ag^+ interaction with the Ag^+ sites inside the zeolite. The work done with the Ag^+ exchanged 4Å zeolite seem to indicated the oligomerization of 1-pentene to 1-decene at high temperatures. This potential for catalytic oligomerization and the strong adsorption of both alkanes and olefins by zeolites (Ag^+ exchanged or not) made these materials not ideal support materials, so that further study of zeolites was abandoned.

Using a specially designed separation rig, $AgNO_3$ modified silica gel proved to be successful in selectively retaining olefins from hydrocarbon mixtures while temperature turned out to be an efficient method of desorbing these long chain olefins from the rig column. Although olefins were selectively retained by the modified silica gel, the physisorption of alkanes had an adverse effect on the purity of the olefin recovery by temperature desorption. $AgNO_3$ modified silica gel surface did not show any tendency to catalyze olefin isomerization at high temperatures as compared to unmodified silica gel and the desorbed olefins were recovered in a relatively unaltered form.

The overall objectives of this project have been met. Firstly, modification of silica gel with a transition metal salt ($AgNO_3$) has proved to be a success in selectively retaining olefins in a given hydrocarbon mixture. Secondly, the separation rig proved to be an efficient apparatus in the selective retention and subsequent recovery of olefins in relatively high percentages.

From the results obtained, the following conclusions could be made:

(1) The research done thus far clearly illustrated the potential that transition metal modified stationary phases have in the large scale separation of long chain olefins from real hydrocarbon streams and that they could provide an economically viable alternative to existing methods currently used in the separation of olefins on an industrial scale.

(2) Silica gel appears to be an ideal support material for separating olefins on a large scale but the use of much cheaper Cu(I) salts instead of Ag(I) salts on a large industrial scale could be economically more viable.

(3) Temperature desorption was probably the most efficient method investigated thus far for recovering olefins from the metal modified support material.

CHAPTER 6

EXPERIMENTAL

6.1. Chemicals, Reagents and Glassware.

All the chemicals used were analytically pure and were obtained from different suppliers. The solvents and acids used were A.R grade and where necessary were dried with 4Å type zeolite (Merck).

Pentane, hexane, *iso*-octane, heptane, octane, decane, C_5 - C_8 alkane reference mixture, methylene chloride, acetonitrile (Saarchem Ltd, Krugersdorp), 1-hexene, 1-heptene, 1-octene, (Merck, Schuchardt), 1-pentene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 2-methyl 1-undecene, 2-methyl-1-hexene, 2-methyl-1-heptene (Aldrich, Milwaukee, WI, U.S.A), cyclohexane (BDH Chem Company, Poole, England). Silver nitrate was supplied by Merck, Damstadt.

Silica gel beads used were obtained from Shellchem, Cape Town, South Africa.

Amberlite IR-120(H) ion exchange resin was obtained from Saarchem, Krugersdorp while Amberlyst A-15 macroreticular resin was obtained from Rohm and Haas, Philadelphia, U.S.A.

Zeolites used in this project were obtained from the following suppliers:
3Å, 4Å and 5Å type zeolites were obtained from Merck, Damstadt.
NaY type zeolite was prepared in the Department of Chemical Engineering, UCT.
Zeolite type 13X was kindly supplied by Separations, Cape Town.

Commercial grade hydrogen, nitrogen, ethylene and compressed air were supplied by Fedgas, Cape Town.

All the glassware used in instrumentation i.e. for the separation rig and glass columns were designed and made in the glass blowing facility in the Chemistry Department, UCT.

6.2 Apparatus.

6.2.1. The Chromatograph.

The screening of the candidate support materials and general chromatographic work were done using a Phillips Pye Unicam series 304 Gas Chromatograph with a flame ionisation detector (FID). A Waters 754/745 Data module integrator was attached to the Gas Chromatograph. The quantitative analysis of hydrocarbon samples was done using a stainless steel GC column packed with 10% OV-101 coated chromosorb (2 m.and i.d 3-mm) supplied by Phase Separations Ltd, U.K.

For screening support material, GC glass columns (60 cm i.d. 6-mm) were packed as as illustrated in the following in Figure 6.1.

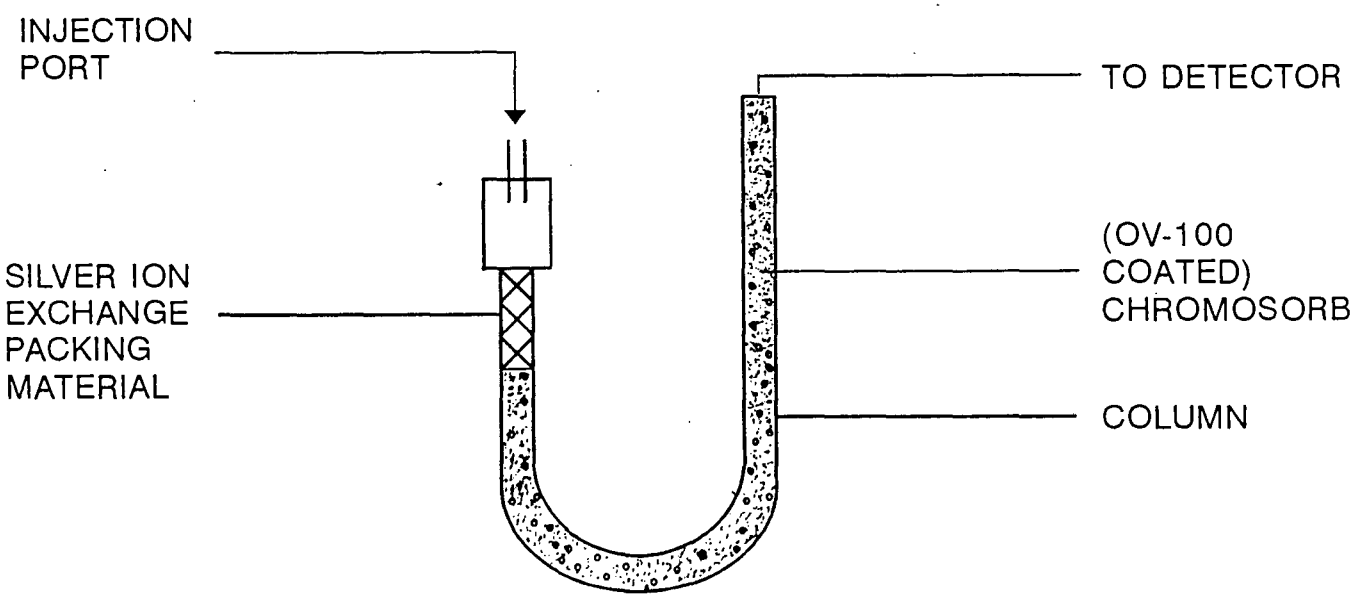


Fig 6.1. Packing of the column used for screening candidate support material.

About 10 cm of the the total length of the glass column from the injector side was packed with either the unmodified or modified candidate material. The rest of the column was then packed with chromosorb coated with 10% by weight OV-101 and

this part served as the analytical column for separation of the hydrocarbons which passed through the modified portion of the column in order of their increasing boiling points.

For the chromatographic work done to determine isomer distribution after olefin desorption in the separation rig, a Carlo Erba model 4200 Gas Chromatograph with an FID detector was used. The column used in this case was a polar capillary column type Supelcowax 10 50-280 (0.25-mm. 25m). A Sp4290 model Integrator was attached to the GC for peak integration.

6.2.2. **Separation rig.**

In constructing the rig, an old gas chromatograph was first stripped of the parts except the temperature controls, GC oven and the gas flow meters. The flow meters were connected to a nitrogen and ethylene source. The rig went through a series of designs and setups until a satisfactory component arrangement was achieved. The final set up is illustrated in Chapter 4.

6.3. **Preparation of ion exchange resin.**

The two resin types, Amberlite IR-120(H) and Amberlyst A-15 macroreticular resin were both exchanged with silver ions using the same procedure. The extent to which cations (or anions) can be exchanged for other ions is called the ion exchange capacity of that resin and is expressed as milliequivalent/gram (~ millimoles of ions/gram of resin). Cation exchange resins are usually in hydrogen ion form or are changed completely to this form before the desired ion exchange is performed.

The total ion capacity of the two resin types was calculated as follows. A gram of resin was first converted completely to hydrogen ion form by washing the resin with excess HCl. After rinsing with glass distilled water, the resin was converted to a Na+ form by washing it with 250 ml of 0.25 M sodium sulphate. The eluent was then titrated with standardized NaOH (~0.1 M) [66].

Hence the total ion exchange capacity = Mv/m (1)

where M = molarity of NaOH solution.
v = volume of NaOH titre in ml.
m = mass of resin in grams.

The calculated ion exchange capacities of the two resin used were:

Amberlite IR-120(H) resin = **4.56 meq/g**

Amberlyst A-15 macroreticular resin = **4.24 meq/g**

6.3.1. **Silver ion exchanged resin.**

The amount of silver ions exchanged on a given mass of resin was expressed as a percentage of the calculated total capacity of that particular resin. For example, in order to have only 50% of the total ion exchange capacity of a gram of Amberlyst A-15 resin in the silver form, the following procedure was used.

Calculated total ion exchange capacity of Amberlyst A-15 = 4.24 meq/g,

Hence 50% of the total ion exchange capacity = 2.12 meq/g

≈2.12 millimoles Ag^+ ions/g

In order to have at least 50% of the total ion exchange capacity of a gram of resin in silver ion form, 2.21 millimoles of a silver salt was required (silver nitrate ($AgNO_3$ was used).

2.12 Millimoles (0.360 g) $AgNO_3$ was dissolved in minimum amount of glass distilled water and the gram of resin was slurried gently in the solution for 30 minutes to effect the ion exchange. This operation was done in the absence of light.

In order to confirm the percentage capacity of the resin in silver form, the effluent collected was titrated with standardized NaOH and using equation 1, the % capacity was calculated. In general the theoretical and calculated values were found to be in agreement. The Ag^+ exchanged resin was then packed as illustrated in Figure 6.1.

6.4 Preparation of Zeolites.

All the zeolites used in the GSC part of this project except for the 13X type zeolite were prepared for screening in exactly the same way. The 3Å, 4Å and 5Å zeolites were obtained in bead form while the NaY type was in rod shaped form. The zeolites were first crushed and sieved to obtain a granularity of between 0.180 and 0.425 mm. Prior to packing in the glass column, each zeolite sample was re-activated in an oven at 400°C for 4 hours. After cooling in a desiccator, the zeolite was immediately packed into the column as illustrated in Figure 6.1. To fill up 10 cm of the glass column approximately 0.570 grams of crushed zeolite was required. The packed column was then conditioned overnight at 100°C under nitrogen.

6.4.1. Preparation of Silver Ion exchanged 4Å zeolite.

A sample of the 4Å type zeolite (in Na^+ ion form) was prepared as described above. The crushed zeolite was then soaked successively in five 20 ml portions of a 2% AgNO3 solution. The resin was then soaked in a 5% AgNO3 solution for 30 minutes to ensure total silver ion exchange. The entire operation was performed in the absence of light. The zeolite was then washed and rinsed with glass distilled water and dried in an oven for 4 hours at 400°C.

The zeolite was then cooled in a desiccator which was shielded from light, the reactivated zeolite was the quickly packed into the glass column (10 cm) and the packed column was conditions overnight at 100°C under nitrogen in the GC. Unlike with ion exchange resin, no attempt was made to determine the amount of silver ions exchanged and it was assumed that the zeolite was 100% silver exchanged.

6.6. Preparation of $AgNO_3$ modified silica gel.

The amount of silver salt which was deposited onto a known mass of silica gel was expressed as a % by weight of the total mass of modified silica gel. In order to deposit the required amount of $AgNO_3$ on a given mass of silica gel beads, glass distilled water was used initially but due to the difficulty in removing water from the silica gel, other low boiling solvents were considered. Methanol (bp = 64°C) was used but only small amounts of $AgNO_3$ could be dissolved (~0.5%w/w $AgNO_3$ in methanol). Acetronitrile was eventually chosen as solvent as it was previously used to successfully dissolve $AgNO_3$ [67].

The required amount of $AgNO_3$ to be deposited onto the silica gel was dissolved in minimum dry acetonitrile (dried by passing it through a column packed with 4Å zeolites). The operation was performed in the absence of light. The solution was then transferred to a dry box and mixed with a weighed amount of silica gel in a round bottom flask which was then stoppered. The mixture was allowed to stand for a few minutes. The round bottom flask was then removed from the dry box and the solvent was slowly removed using a rotary evaporator. All these operations were also performed in the dark. The free flowing white $AgNO_3$ modified silica gel beads were then dried in an oven for 30 minutes at 90°C. In order to avoid caking of $AgNO_3$ on the silica gel especially when large amounts of $AgNO_3$ were used, deposition was done batchwise i.e. instead of dissolving the entire mass of $AgNO_3$ in a volume of dry acetonitrile, the mass was divided into small samples and these were deposited sequentially onto the silica gel.

The silica gel was weighed in order to confirm the % by weight of the $AgNO_3$ deposited. A weighed mass of the modified silica gel was carefully packed into a specially designed column . The packed column was then fitted into the separation rig and a nitrogen flow was maintained throughout the time the separation rig was in use.

Initially when high temperature desorption was used in olefin recovery, the modified silica gel turned dark brown. This ruled out the re-use of the column for other experiments. A possible explanation could be that at high temperatures, silver nitrate reacts with physisorbed water trapped in the silica gel beads to form silver

hydroxide (AgOH) which is also known to have a brownish colour [74]. , The following reaction probably occurred at high temperatures:

$$AgNO_3 + H_2O = AgOH + HNO_3$$

Hence drying the silica gel in the oven at 100°C before modifying with the silver salt does not reduce the water content of the silica gel substantially. To overcome this problem, the silica gel beads were dried by heating them at very high temperatures (>500°C) for at least four hours before use. Scott and Kureca [68] reported that at 600°C, the water content of silica gel was reduced to only 1,62% of the original water capacity.

6.6. Preparation and analysis of Hydrocarbon mixtures.

The amounts of the individual components in the hydrocarbon mixtures were expressed as % by weight. The mixtures were prepared by mixing weighed amounts of the components in that particular mixture. The original samples were also injected into the GLC to confirm the weight percentage Although there was no significant difference between the two values, the value obtained from the GLC was taken as the original % composition. The effluent from the separation rig was also analyzed by GLC.

The GLC used in this project had a flame ionization detector. The hydrocarbon detector response factors are different not only for the members of a individual member of a particular homologous series but also between different classes of hydrocarbon compounds. Hence in order to find the true % by weight of each component up to C_{10} hydrocarbons, the area of each component peak in the chromatogram was divided by the relative sensitivity value as found in tables [70]. On normalizing the result, the actual weight percent of each component is obtained.. The % by weight values reported in this project were all obtained using this procedure.

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APPENDICES

APPENDIX 1

Appendix 1(a)

Gas Chromatograph conditions

Column temperature: Variable
(temperature programming option used where applicable)

Carrier gas: nitrogen.

Detector: FID.

Carrier gas flow rates: 125ml/min

for screening material (glass column) = 80 ml/min

for analysis of sample = 120 ml/min

Injector temperature: 180°C

Detector temperature: 250°C

Sample volume: 0.2 - 1μl

Appendix 1(b)

Separation rig conditions.

Column temperature (sample injection):	25-35°C.
Desorption temperature:	100-150°C
Temperature of cold traps:	-30°C - 0°C
Temperature of rig glass bridge:	150°C

Nitrogen gas flow rate:

(a) for sample injection:	50-80 ml/min
(b) for olefin desorption:	100-180 ml/min (15 lb/inch^2)

APPENDIX 2

Appendix 2 (a)

Table for classifying natural and synthetic zeolite to the kind of molecules they can adsorb. From R.M. Barrer, Journal of British Chemical Engineering, May 1959, p 271.

Classification of some Molecular Sieves

Molecular Size Increasing ⟶

Type 5

He, Ne, A, CO, H_2, O_2, N_2, NH_3, H_2O

Size limit for Ca- and Ba-mordenites and levynite about here (~3.8Å)

Kr, Xe, CH_4, C_2H_6, CH_3OH, CH_3CN, CH_3NH_2, CH_3Cl, CH_3Br, CO_2, C_2H_2, CS_2

Type 4

Size limit for Na-mordenite and Linde sieve 4A about here (~4.0Å)

C_3H_8, n-C_4H_{10}, n-C_7H_{16}, n-$C_{14}H_{30}$ etc., C_2H_5Cl, C_2H_5Br, C_2H_5OH, $C_2H_5NH_2$, CH_2Cl_2, CH_2Br_2, CHF_2Cl, CHF_3, $(CH_3)_2NH$, CH_3I, B_2H_6

Type 3

Size limit for Ca-rich chabazite, Linde sieve 5A, Ba-zeolite and gmelinite about here (~4.9Å)

CF_4, C_2F_6, CF_2Cl_2*, CF_3Cl, $CHFCl_2$

SF_6, iso-C_4H_{10}, iso-C_5H_{12}, iso-C_8H_{18} etc., $CHCl_3$, $CHBr_3$, CHI_3, $(CH_3)_2CHOH$, $(CH_3)_2CHCl$, n-C_3F_8, n-C_4F_{10}, n-C_7F_{16}, B_5H_9

$(CH_3)_3N$, $(C_2H_5)_3N$, $C(CH_3)_4$, $C(CH_3)_3Cl$, $C(CH_3)_3Br$, $C(CH_3)_3OH$, CCl_4, CBr_4, $C_2F_2Cl_4$

C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, Cyclohexene, Cyclohexane, Thiophen, Furan, Pyridine, Dioxane, $B_{10}H_{14}$

Type 2

Size limit for Linde sieve 10X about here

Naphthalene, Quinoline, 6-decyl-1, 2, 3, 4-tetrahydro-naphthalene, 2-butyl-1-hexyl indan, $C_6F_{11}CF_3$

1, 3, 5 triethyl benzene

1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16-decahydro-chrysene

Type 1

Size limit for Linde sieve 13X about here (~10Å)

$(n\text{-}C_4F_9)_3N$

* Freon-type molecules provide interesting border-line cases and can differentiate between certain of the zeolites grouped as Type 3. Simple ketones and esters are also border-line cases.

APPENDIX 3.

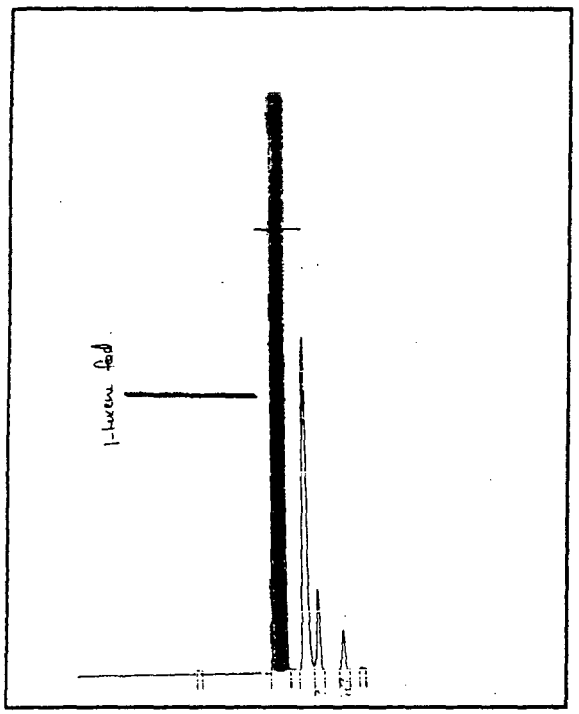
Appendix 3(a)

Effect of temperature on olefin form. (Chapter 4

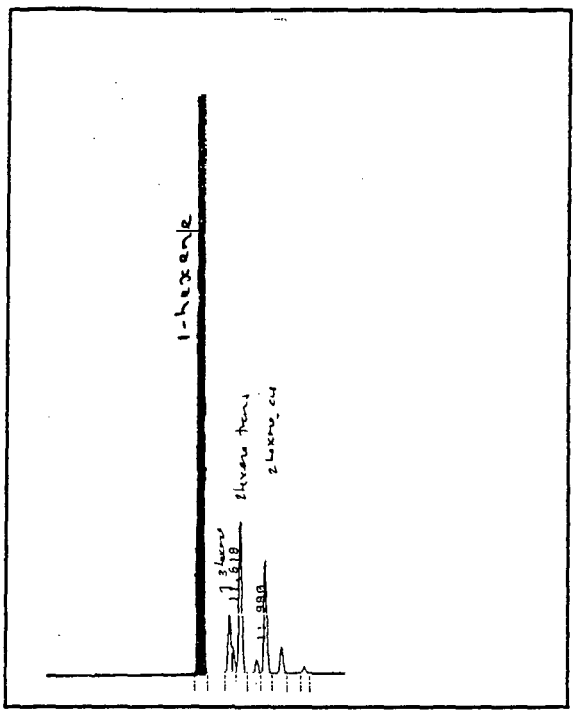
Desorption of 1-hexene from unmodified silica gel.

1-Hexene isomer distribution as a function of desorption temperature.

pure 1-hexene



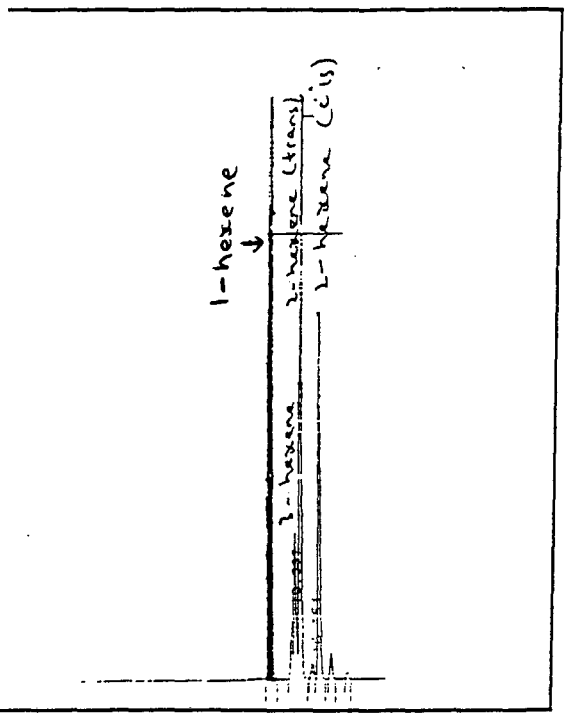
desorption at 60°C



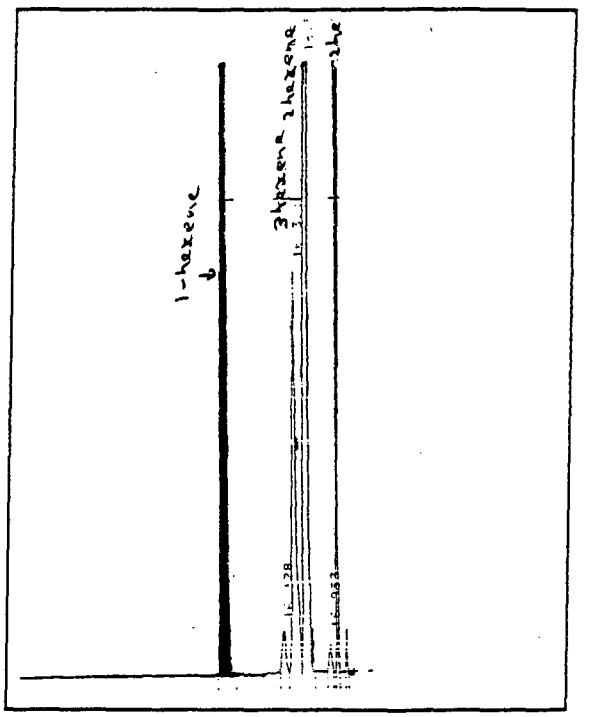
Appendix 3(a) (continued)

(a) 1-Hexene isomerization as a function of desorption temperature.

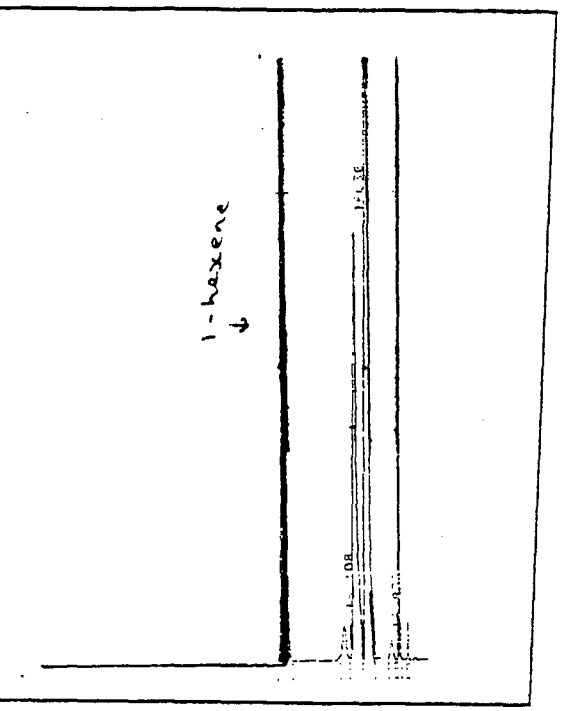
desorption at 80°C



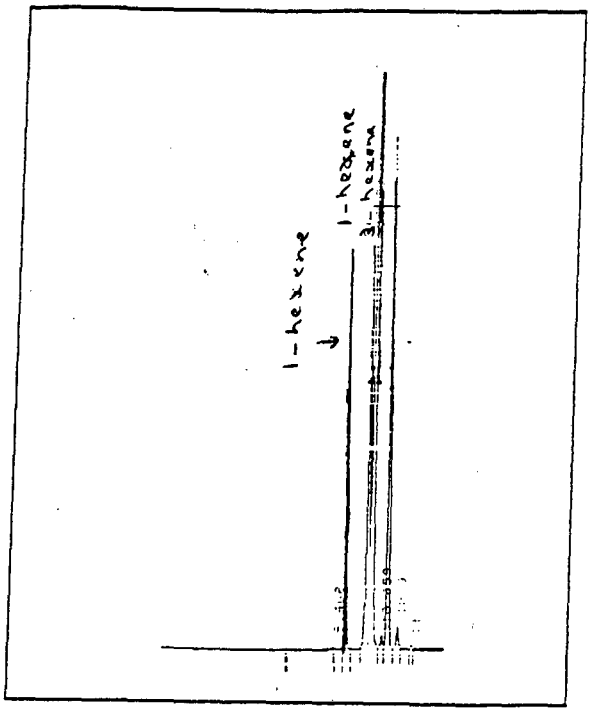
desorption at 100°C



desorption at 140°C



desorption at 180°C

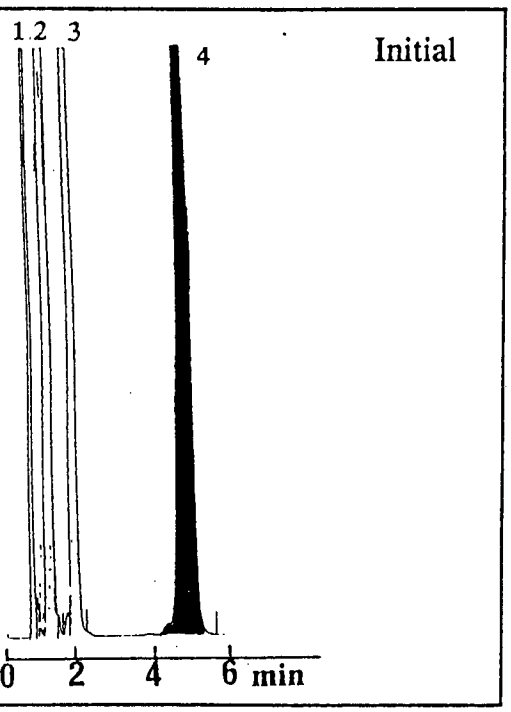


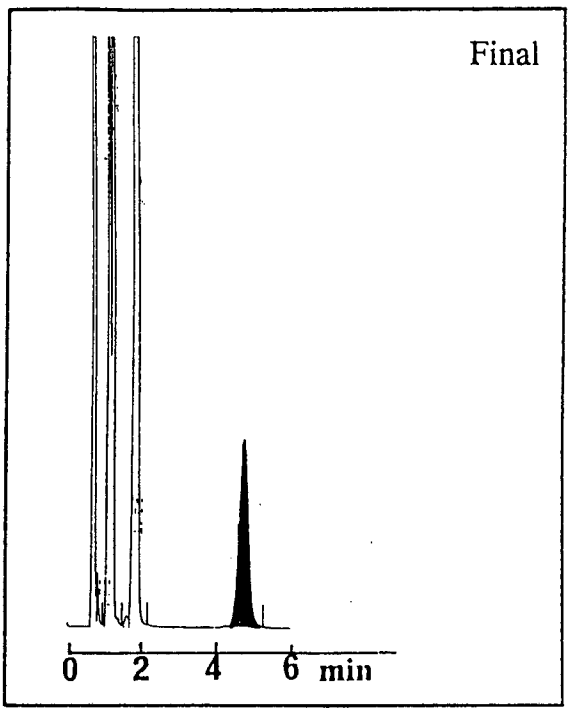
APPENDIX 3 (continued)

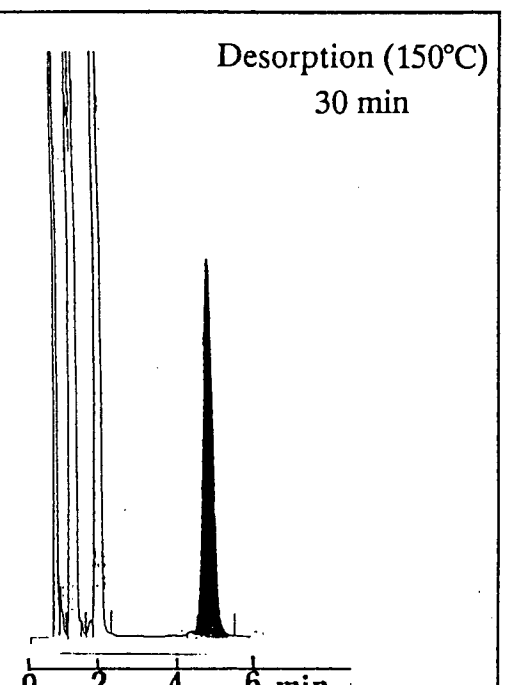
Appendix 3 (b)

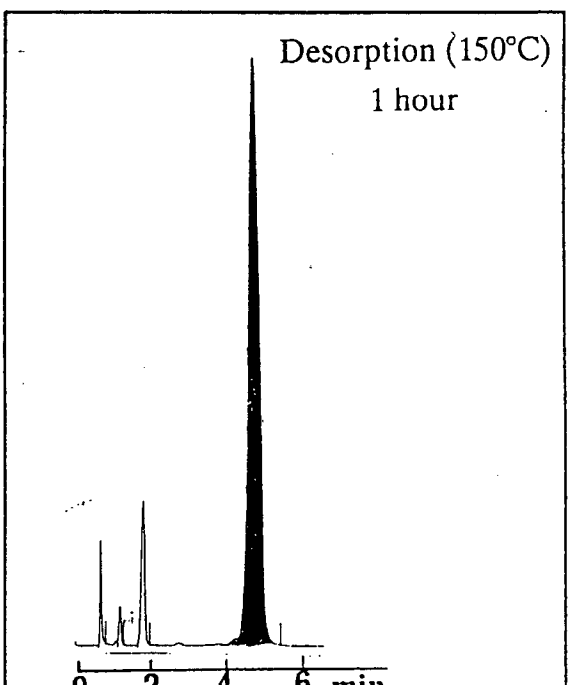
Chromatogram of complex mixtures

Mixture containing (1) pentane, (2) cyclohexane, (3) heptane, (4)octane an (5) 1-decene (22%). Second Run



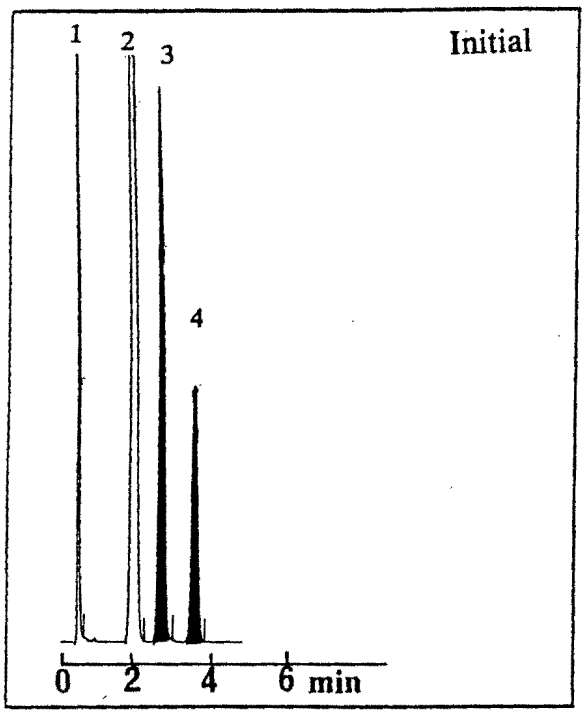


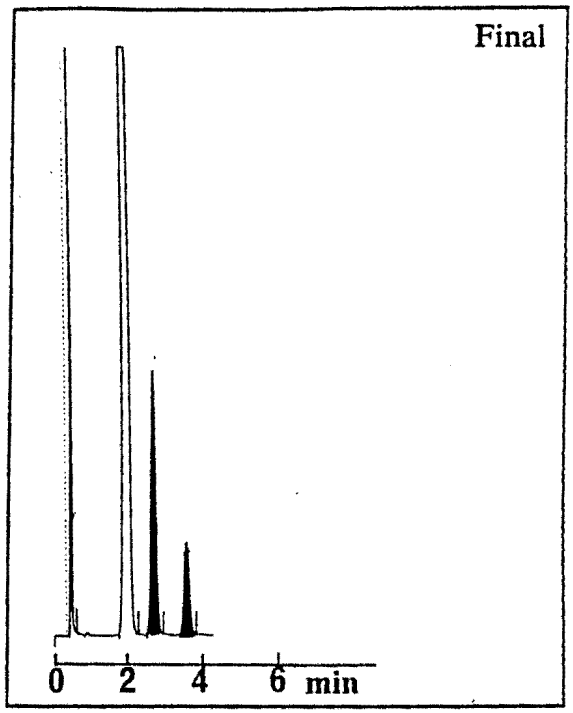


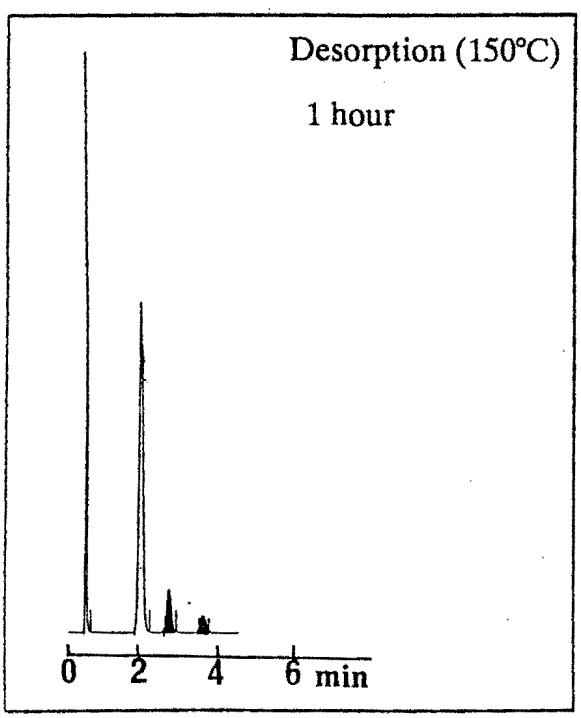


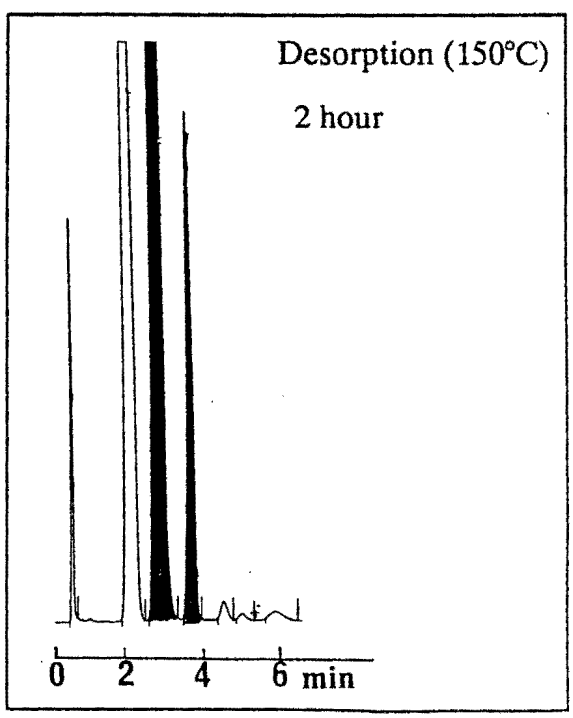
Appendix 3(c)

Chromatograms for sample containing (1) pentane, (2)decane, **(3)1-undecene (20%)** and **(4) 2-methyl-1-undecene(10.7%)**









APPENDIX 3 (continued)

Appendix 3(e) Calculation for olefin recovery in Chapter 4.

As indicated, to calculate the amount of olefin adsorbed onto the modified silica gel, the following equation was used:

$$V = \frac{v(Co - C)}{100}$$

where V = volume of component adsorbed.

v = volume of effluent collected after run.

Co = Initial concentration of component in weight %

C = % by weight of component left after run.

The total volume of material not adsorbed:
= % composition*volume effluent collected.

Volume of olefin eventually desorbed:
= % composition olefin * total volume desorbed.

Hence % pure olefin recovery = $\frac{\text{volume desorbed(150°C)}}{\text{volume adsorbed}} * 100$

For complex mixture containing pentane, decane, 1-undecene and 2-methyl-1-undecene, the following calculations were made:

Total volume of original sample = 25 ml.

Total volume recovery after 4th injection = 15.38 ml.

Total volume of sample retained = 9.62 ml.

Total volume recovered after desorption (150°C) = 6.7 ml.

Total volume of 1-undecene in original sample = 5.15 ml.

Total volume of 1-undecene not retained = 1.15 ml.

Total volume of 1-undecene retained = 4.02 ml.

$$\% \text{ pure 1-undecene recovered} = \frac{3.87 \text{ ml}}{4.02 \text{ ml}} * 100$$

$$= 96.7\ \%$$

For 2-methyl-1-undecene,

Total volume of 2-methyl-1-undecene in original = 2.67 ml.

Total volume of 2-methyl-1-undecene not retained = 0.97 ml.

Total volume of 2-methyl-1-undecene retained = 1.7 ml.

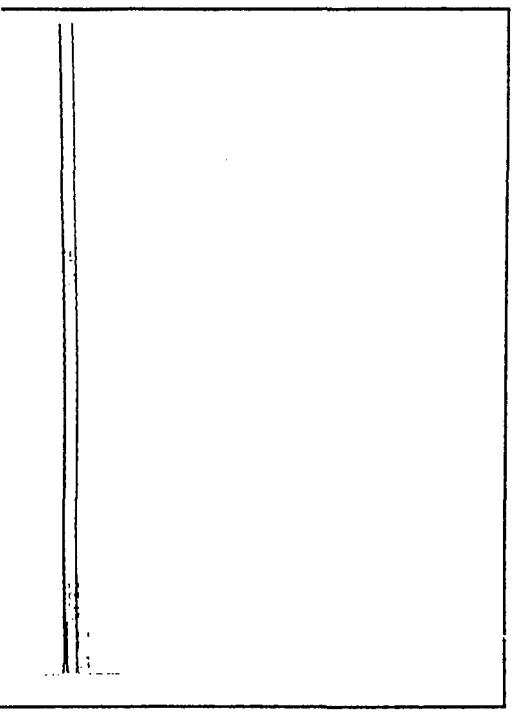
Total volume of 2-methyl-1-undecene desorbed = 1.21 ml

% pure 2-methyl -1-undecene recovered = 71.1%

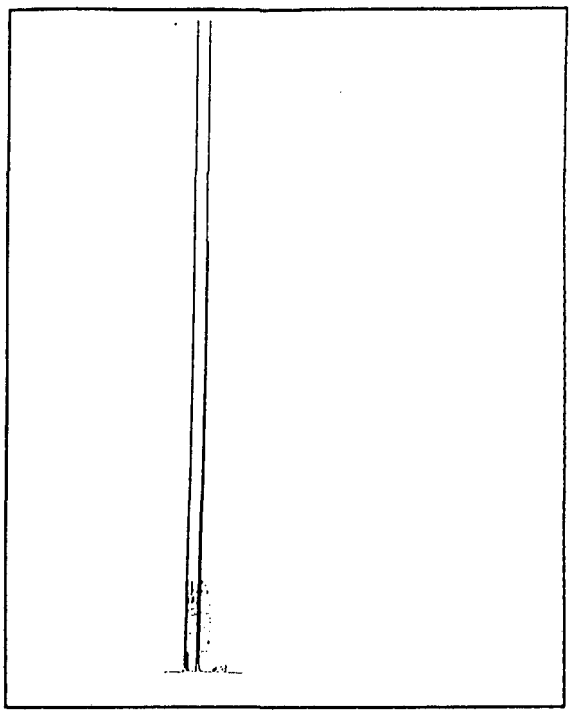
APPENDIX 4

The effect of temperature desorption on olefin form (Chapter 4).

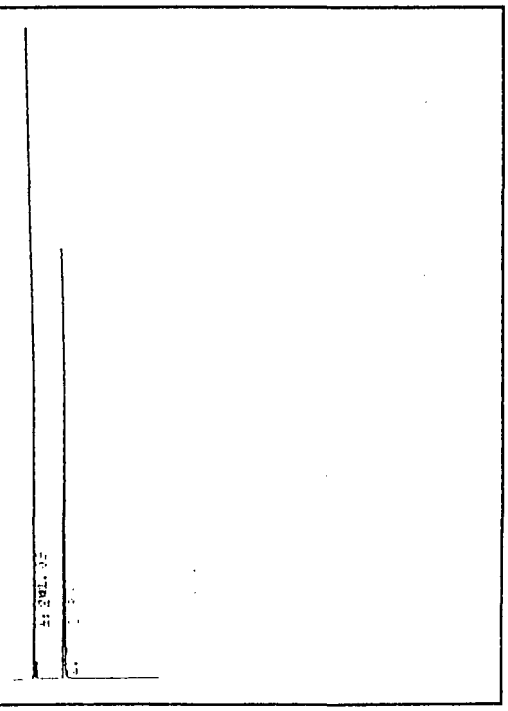
Olefin isomer distribution studies on desorbing olefins from the separation rig. Comparison berween pure and desorbed olefin. Solvent used: pentane.



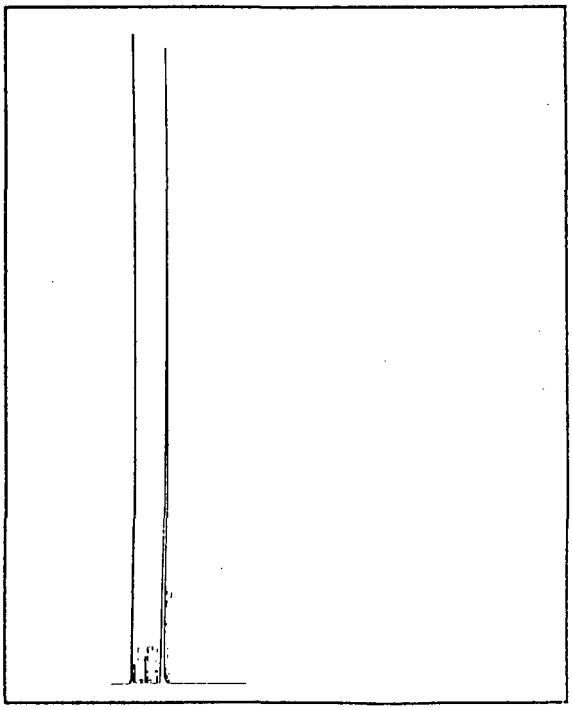
pure 1-heptene

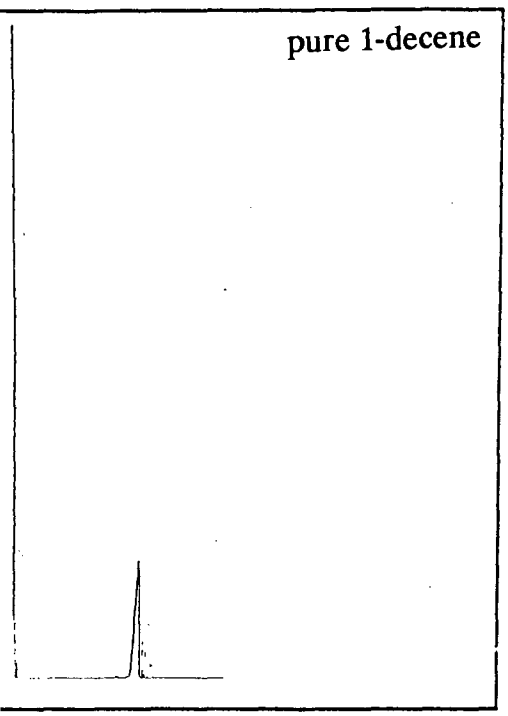
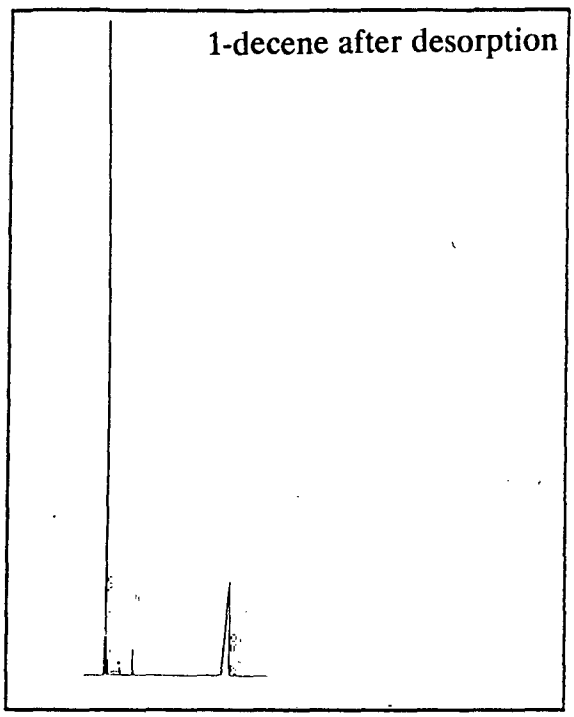


1-heptene after desorption



pure 1-octene



1-octene after desorption

APPENDIX 4 (continued)