THE USE OF ORGANIC CATIONS IN ZEOLITE SYNTHESIS

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ABSTRACT

This thesis describes an investigation into the use of organic cations in zeolite synthesis. The work carried out can be divided into three sections; low temperature zeolite synthesis from mixed base systems, high temperature zeolite crystallisation in the presence of organic cations and the effect of organic cations on the anion distribution of aqueous silicate solutions.

An investigation of the zeolitic materials formed from systems containing an alkali metal cation and an organic cation, has been carried out. Systems of different compositions were investigated and the effect of the quaternary ammonium species on the reactivity of the system, and the nature of the product(s) obtained has been discussed.

A study was carried out on the synthesis of zeolites at high temperatures. The systems studied contained quaternary ammonium cations and much less aluminium than the previous low temperature synthesis. The formation of several novel zeolitic species was observed and the effect on their formation of varying various physical and chemical parameters was investigated. The reactions were monitored by the change in pH during the crystallisation; it is believed that this is the first time that this technique has been used to follow the crystallisation of zeolites.

The anion distribution in aqueous silicate solutions was examined by ^{29}Si F.T. n.m.r. spectroscopy. Aqueous solutions of alkali metal and quaternary ammonium silicate solutions were examined by this technique. It was shown that the anion distribution in these solutions was controlled by the nature of the cation as well as by pH, temperature and the concentration of the base. These studies gave an insight into the action of cations during the crystallisation of zeolites.

DECLARATION

I declare that this thesis, which is of my own composition is an accurate record of work which I carried out in the Department of Chemistry, University of Edinburgh and at I.C.I. Ltd., Agricultural Division, Billingham, between October 1977 and September 1980. During this period I was supervised by Drs. B.M. Lowe and T.V. Whittam.

During the above period I also attended the following lectures/courses:-

Fortran 'B' computing course - E.R.C.C.
Cage and cluster compounds - T.A. Stephenson
Silica and silicates - B.M. Lowe
Detergency and the design of surface active agents - W.D. Cooper
Organic chemistry of dyes - I.C.I. Organics
X-ray crystallography - R.O. Gould
Zeolites - B.M. Lowe

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The study of zeolites first began in 1756 with the discovery of the mineral stilbite by the Swedish minerologist Cronstedt[1]. The name zeolite was derived from the Greek; Zeein - to boil, and Lithos - a stone, thus reflecting one of the properties of zeolites, their ability to undergo reversible dehydration.

A zeolite is a crystalline alumino-silicate in which each tetrahedrally co-ordinated aluminium or silicon atom is linked by oxygen to four others, such that the (Si+Al)/O ratio is 1/2, giving a framework which encloses cavities occupied by cations and water molecules, both of which have considerable freedom of movement permitting cation exchange and reversible dehydration. This is a variation of the definitions proposed by Smith[2] and Meier[3] and includes the modification suggested by Barrer.

In the 200 years between the discovery of stilbite and the first commercial use of zeolites as sorbents in late 1954, the study of zeolites changed from a mainly geological interest to one in which the chemistry of their synthesis and properties is dominant. It has been estimated[4] that the market for zeolites had grown to 250,000 tons by 1978 and generated an estimated[5] 15,000 scientific contributions and over 10,000 patents. Such figures illustrate the commercial importance of these materials and their widespread scientific interest.

1.2 OCCURRENCE

Although the first natural zeolites were found in igneous rocks they also occur, as extensive deposits, in sedimentary rocks. The igneous deposits are usually found in the fissures and cavities of fine grained rocks such as basalt. These zeolites often occur as well-developed crystals which can be several centimetres in diameter[6,7]. All the naturally occurring zeolites have been found in igneous rocks, although they occur in widely differing quantities with such minerals as faujasite occurring only rarely while mordenite has been reported[8] to comprise 20% of the basaltic rock in some areas of Nova Scotia. However, the fraction of zeolite in the parent rock does not normally exceed 5% (by volume).

The formation of zeolites in the vesicles and fractures of igneous rocks is believed to have occurred in the final cooling of the molten basalt, and it has been suggested[9] that crystallisation only proceeds after a critical thickness of lava has accumulated allowing the build-up of sufficient heat. The seepage of water into the fissures in the basalt leads to the formation of hot alkaline alumino-silicate solutions from which the zeolites crystallise. As the crystallisation proceeds the composition of the solution changes resulting in the co-crystallisation of different zeolites together with quartz and calcium carbonate. The type of zeolitic species produced also depends on the temperature and pressure of the system.

The compositions of the zeolitic materials formed have been shown[10,11] to be similar to that of the parent rock so that igneous rocks rich in silica produce zeolites rich in silica such as mordenite and wairakite, while those deficient in silica produce chabazite and phillipsite.

The occurrence of sedimentary zeolites was first reported in the scientific results of the Challenger expedition[12] in which sedimentary deposits of phillipsite were noted on the bottom of the Central Pacific Ocean. These deposits have led to the belief that this zeolite is one of the most abundant minerals on earth since the sediments have been reported[13] to cover large areas. Furthermore extensive deposits of phillipsite have also been found in the U.S.A. and Africa. Although first discovered in 1891 the sedimentary zeolites were not investigated until after 1950. This was mainly because unlike the igneous deposits the sedimentary zeolites occur as very small crystals which could only be identified by powder x-ray diffraction. The sedimentary zeolites have been divided into two groups[10], based on the environment in which they were found, .

1) Saline, alkaline non-marine deposits.

2) Fresh water and marine deposits.

These are also called 'closed' and 'open' systems respectively. In the closed system the deposits often occur as relatively pure beds several metres thick. Erionite and chabazite are often found in this system. The deposits found in the open systems (marine deposits) however, can be very substantial, with beds several hundred metres thick. The zeolites commonly found in these deposits are phillipsite and clinoptilolite.

The mechanism of formation of sedimentary deposits is not fully understood but it probably involves the action of water on volcanic ash. A recent report[14] deals with crystallisation of zeolites from solutions containing salts, alkali and rhyolitic ash which may reflect the factors which produce sedimentary deposits of zeolites.

1.3 NOMENCLATURE

The methods used to name zeolites clearly illustrate many of the problems associated with their study. The natural zeolites have been named in accordance with the traditional methods of minerology and have been classified according to their structures into seven groups as described by Meier[3]. The synthetic zeolites are usually designated by letters of the Roman or Greek alphabets (e.g. zeolites A, X and Ω) by their discoverers or more recently by groups of letters and numbers (e.g. zeolites ZSM-5, ZSM-23 and FU-1). Problems arise because the same zeolite may have been called by several different letters by workers in different laboratories, for example zeolite P was also called zeolite B. Further ambiguities often arise because the crystallites of many synthetic zeolites are so small that it is not possible with present techniques to elucidate their structure. Also, there is a tendency for inventors to attempt to "... secure proprietary rights on the composition or on the synthesis of compounds which were, at the time of patent filing, insufficiently characterised."[15] Confusion also arises when a synthetic material is later found to occur naturally (e.g. zeolite Ω and the mineral mazzite[16]).

It is to be hoped that the rules set out in a recent article by Professor R.M. Barrer[17], on the nomenclature of synthetic and natural zeolites will be adhered to.

1.4 STRUCTURE AND CLASSIFICATION

Zeolites are tectosilicates. The presence of aluminium in the zeolite lattice contributes a negative charge to the framework which is balanced by the presence of cations, normally of groups I and II of the periodic table. The three dimensional network of AlO_4 and SiO_4 tetrahedra gives rise to a structure which contains cavities of constant dimensions which are joined together by regularly arranged channels or pore systems. These cavities, first described by Smith[2], contain water molecules and the cations present to compensate for the negative charges on the framework associated with each aluminium atom. The openness of the zeolitic framework allows these cations and water molecules to have considerable freedom of movement giving rise to their ion-exchange and sorptive properties.

Although zeolites are alumino-silicates other analogous species in which silicon and aluminium atoms are replaced by germanium and gallium should also be considered. These replacements have been reported for zeolites A, X and P by Barrer et al[19] and by Selbin and Mason[20]. The substitution of the framework atoms (Si and Al) by Phosphorous and Boron have also been reported. It is known that in the rare, naturally occurring materials kehoeite and viseite, phosphorous is present as PO_4 tetrahedra. Flannigen and Grose[21] have reported the preparation and characterisation of phosphorous-containing zeolites. The preparation first involved the co-polymerisation of phosphorous with the other oxides followed by crystallisation from the gel. The major problem with all these reports is that it is possible for the replacing element, e.g. phosphorous, to be present within the framework as an occluded species such as phosphate. Conventional chemical analysis of such materials cannot show whether the phosphorous has been incorporated into the framework. The preparation of molecular sieve borosilicates has also been recently reported[22].

In zeolites the primary structure or building units are the SiO_4 and AlO_4 tetrahedron. In a classification of zeolite structures proposed by Meier[3], the structures were classified according to the units which go to make up the framework. These units Meier called, "Secondary Building Units" (S.B.U.). The eight S.B.U.(s) proposed by Meier can be seen in Fig. 1.1. Seven groups, each named after one of their members, were suggested and the allocation of zeolites to each group was based on the S.B.U.(s) used to generate their structures. Breck[23] also proposed a classification of zeolite structure types, this was similar to that proposed by Meier and was based on the same S.B.U. but the groups were numbered rather than named.

Zeolite structures can also be considered in terms of polyhedral units such as the β (or sodalite) and C (or cancrinite) cages. Fig. 1.2 shows the relationship between the β cage (a) and structures of sodalite (b), zeolite A (c) and Faujasite (d). It is worth noting that although the sodalite structure is closely related to those of faujasite and zeolite A, sodalite occurs in a different group to that of zeolite A and Faujasite in the classifications of Meier[3] and Breck[23].

Many of the applications of zeolites depend on their channel structure. In such applications as catalysis the diameter and shape of the 'pores' are important as well as whether the channels are 1, 2 or 3 dimensional (as determined by their connectivity). Breck, includes these parameters in a classification of zeolite structures[24].

The total number of known zeolitic frameworks is 38. Of these 26 are found in the 37 natural zeolites and the other 12

Fig. 1.1 Secondary building units

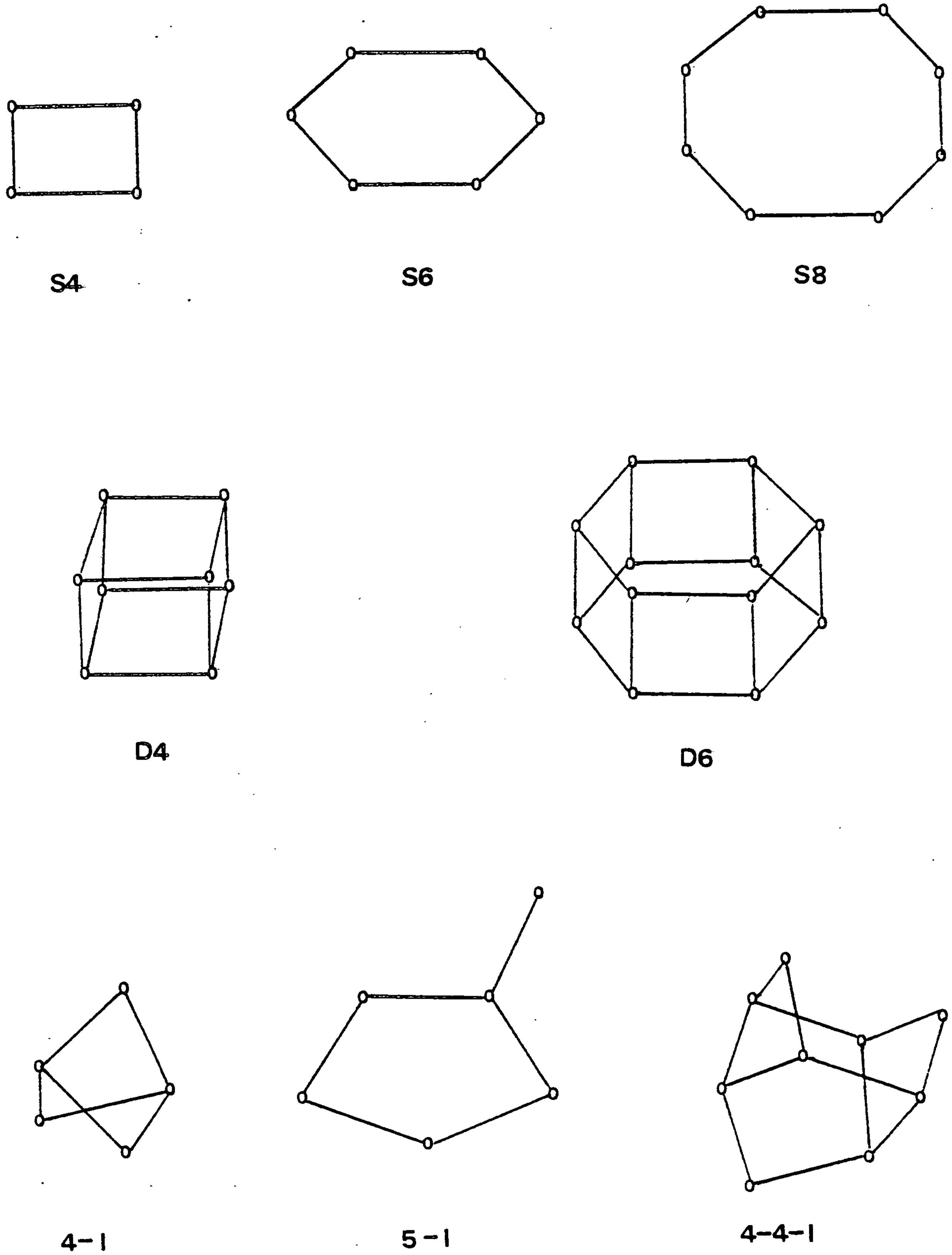
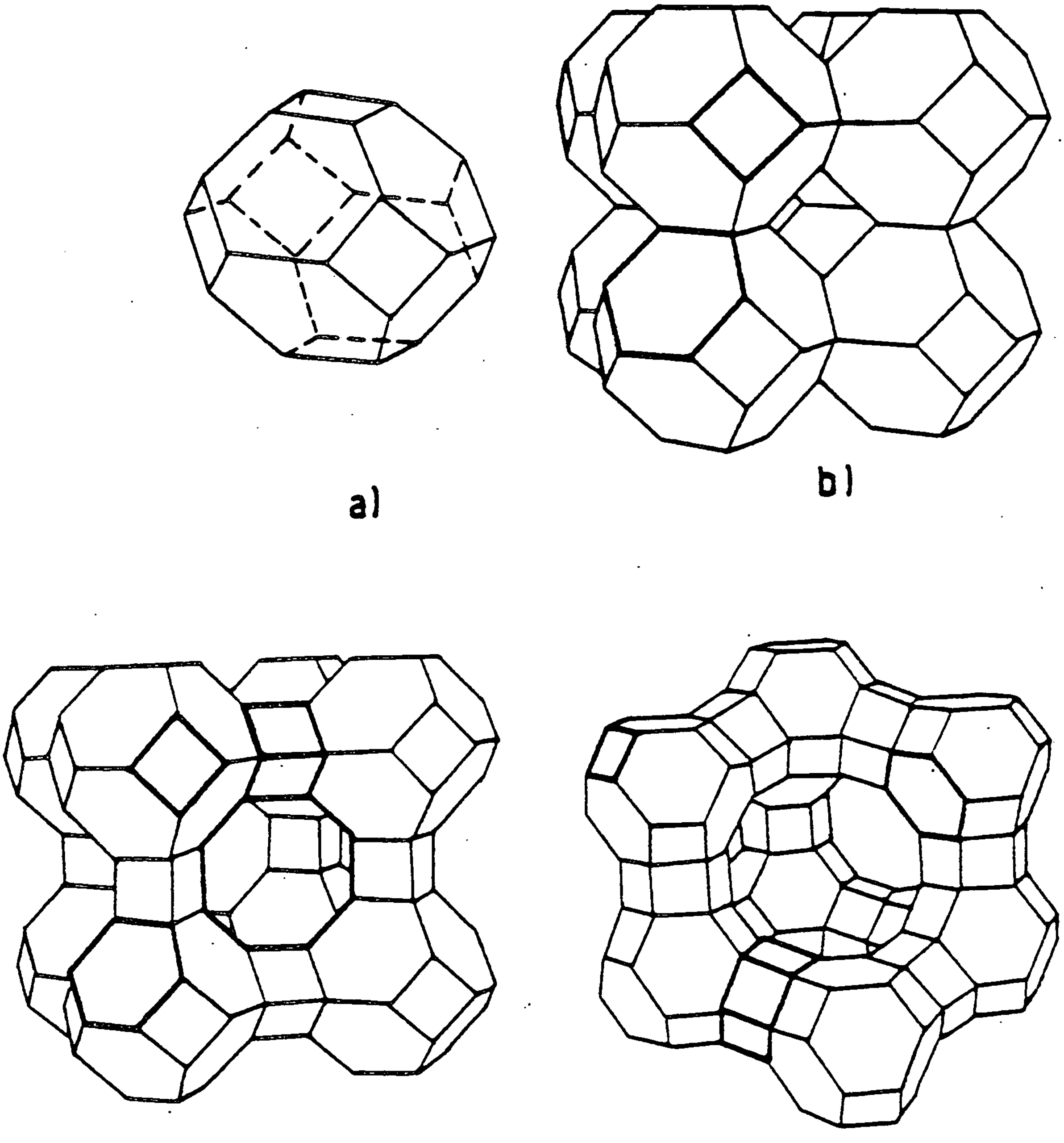


Fig. 1.2 Relationship between polyhedral building units and zeolite structures



a)

b)

c)

d)

frameworks have only been made synthetically. However, over 100 synthetic zeolites have been prepared and it is only the problems associated with structure elucidation that prevents the number of different synthetic frameworks being greater. There are almost an infinite number of possible frameworks and indeed Breck[24] describes some work on theoretical zeolite structures.

The original classification of zeolites by Bragg[25] was based on the zeolite's morphological properties. Thus they were classified as three-dimensional, lamellar or fibrous. In all zeolites the framework is three-dimensional however this classification refers to the crystal-habit or cleavage of the zeolite. More recently Flannigen[5] classified zeolites according to their SiO_2/Al_2O_3 ratios. A similar classification will be used in this thesis, however, the terms will be changed slightly. The classification can be seen in Table 1.1. As with all classifications there are ambiguities in this classification. In the low silica zeolites (i.e. with $SiO_2/Al_2O_3 < 10$) the properties change as the SiO_2/Al_2O_3 ratio is increased from 2 to 10 in that the zeolites change from being 'stable' to alkali and 'reactive' to acid (i.e. zeolite A) to being 'stable' to acid and 'reactive' to alkali (i.e. mordenite). The expressions stable and reactive are not strictly appropriate. The stability of zeolites to

TABLE 1.1 Classification of Zeolites

SiO_2/Al_2O_3 (x) [a]	Classification	Examples
$x < 10$	Low silica	Mordenite, A, X, P
$10 < x < 300$	Medium	ZSM-5, EU-1, FU-1
$x > 300$	High silica	Silicalite, Silicalite-2

[a] Note: figures are only approximate

alkali is relative since even zeolite A will be broken down by alkali, although, not as readily as for example mordenite. Similarly although the structure of mordenite may not be destroyed by acid it can significantly reduce the aluminium content by 'leaching' it from the structure. Indeed this leaching of aluminium by acid is the basis of several modification techniques.

The classification shown in Table 1.1 is based mainly on the synthesis of zeolites rather than their properties. Thus although species can be synthesised over two 'ranges' e.g. ZSM-5 can occur in the medium class and in the high silica class (as silicalite), this is unusual, and as yet no species has been synthesised over the complete range. The species silicalite and silicalite-2 have also been included as zeolites since they do contain aluminium (albeit in small quantities) and are therefore zeolitic. Changes in the zeolitic properties i.e. low ion-exchange capacity are fully explained on the basis of the SiO_2/Al_2O_3 ratio.

1.5 PROPERTIES AND APPLICATIONS OF ZEOLITES

1.5.1 Sorption

McBain[26] in his monograph on physical sorption first used the term 'molecular sieve' in connection with the sorptive properties of zeolites. This expression was used because it had been shown[27] that the quantity of material sorbed by chabazite depended on the molecular dimensions of the sorbate. Before this microporous carbons and silica gels had exhibited a very crude form of molecular sieving. However, reports by Barrer[28,29,30] showed that the molecular sieving by zeolites was much more selective. The molecular sieving properties of zeolites are based on the uniform size of the pores which allow access to the zeolitic framework. Thus molecules are accepted or rejected on the basis of their critical size. The selectivity of their sorptive properties is so quantitative that it has been used[28,31] as a basis for their classification.

The species which are sorbed by zeolites depend on two factors, the size of the pores or openings and when a mixture of sorbates are used their relative strengths of sorption. The size of the pores in zeolites obviously depends on the number of tetrahedral atoms (Si or Al) which make up the ring. Table 1.2 shows the correlation between the number of tetrahedral atoms and the pore size. It should be noted that these are the theoretical dimensions. For a given zeolite, with a fixed number of tetrahedral atoms, the pore size can be altered by temperature and by ion-exchange. Temperature affects the thermal vibration of oxygen atoms which surround the apertures and their vibrational amplitude can vary by 0.1 to 0.2 Å over the range 80 to 300°C.[32] Ion-exchange of the

<u>TABLE 1.2</u> <u>Theoretical dimensions of pore openings in zeolites</u>

Number of tetrahedra in ring	dimensions/Å
4	1.2
5	2.0
6	2.8
8	4.3
10	6.3
12	8.0

cations within the zeolite structure can also affect the pore size. The classical example of this is zeolite A the pore size of which can be varied from 3 to 4 to 5 Å[a] depending on whether the cation is K, Na or Ca respectively. In an article on zeolite sorbents, Barrer[33], describes the effect of salt inclusion on the zeolite's molecular sieving properties, particularly in zeolites whose pore systems are either 1 dimensional or 2 dimensional.

When two (or more) molecules can both enter a zeolite, the differences in their relative sorption selectivities will determine which will be sorbed. Thus, CO_2, water and CO are removed from hydrogen by zeolites during steam reforming. In general the low-silica zeolites, e.g. A, X and chabazite prefer more polar molecules while the medium and high-silica zeolites exhibit considerable hydrophobic/organophilic behaviour and 'silicalite' can be used to remove trace amounts of organic compounds from water[34].

The first commercial use of zeolites was based on their sorptive properties; they were introduced in late 1954 for industrial separations and purifications[5]. They are used particularly in the petrochemical industry for the separation of straight chain from cyclic and branched chain species[35] and in the separation of xylene isomers[36,37].

1.5.2 Ion Exchange

The ion exchange properties of zeolites was first demonstrated by Eicham in 1858 when he used chabazite and natrolite to exchange Na and Ca ions from solution. For

[a] These are only approximate figures.

sometime after that the term zeolite was used to describe all ion exchange species (e.g. smectites) and this led to some confusion in the early literature.

The ability of zeolites to undergo ion exchange is due to the cations situated within the framework being sufficiently mobile to be exchanged by ions from solution. The zeolite's exchange capacity is therefore highest for zeolite A which can have an exchange capacity of approximately 7 meq g^{-1} [15], which is similar to that of organic exchange resins.

Exchange from solution can be presented by the following equilibrium,

$$z_A \underset{(z)}{B^{z_B+}} + z_B \underset{(s)}{A^{z_A+}} \rightleftharpoons z_A \underset{(s)}{B^{z_B+}} + z_B \underset{(z)}{A^{z_A+}}$$

where z_A and z_B are the charges on cations A and B and subscripts s and z refer to the solution and zeolite phases respectively. The equivalent fractions of the exchanging cations in the solution and zeolite are defined by:

$$A_z = \frac{\text{number of equivalents of exchanging cation A}}{\text{total equivalents of cations in the zeolite}}$$

$$A_s = \frac{z_A m_s^A}{z_A m_s^A + z_B m_s^B}$$

where m_s^A and m_s^B are the molalities of ions A and B respectively. A plot of A_z against A_s at a given total concentration and temperature produces an ion exchange isotherm. Positive and negative deviations occur if the entering or leaving cation is preferred, other variations can also occur e.g. a sigmoidal isotherm indicates that the selectivity varies with the degree of exchange. Incomplete exchange, or no exchange, is often associated with an ion-sieving effect, that is, ions are rejected on the basis of their size. An example of this is zeolite A which exhibits a double ion-sieving effect since entrance to the α-cage is via 8-ring windows while the entrace to the β-cage is through a 6-ring window. The degree of exchange is also affected by temperature, concentration of exchange species, solvent employed and nature of the anion. Several reviews[6,38,39] have described the effects of these factors.

The commercial applications of the ion-exchange properties of zeolites have not been as well developed as those of their sorptive and catalytic properties. This is mainly because they do not have as large an exchange capacity as other ion-exchange species. However, the unique properties associated with zeolites i.e. their stability to ionising radiation, temperature and extremes of pH combined with their ion-sieving properties has meant that they are used in several special areas. The first application was in the separation and purification of radioisotopes (^{90}Sr and ^{137}Cs) using zeolites mordenite, clinoptilolite and chabazite[40,41]. However, zeolites are also being used in waste water purification[42] particularly for the removal of NH_4^+. More recently zeolites have been used in detergents[43,44] in which they replace the tripolyphosphate builder and thus prevent the eutrophication associated with phosphates.

The above examples indicate why there is commercial interest in the cation exchange properties of zeolites. However apart from the commercial interest in zeolites as ion-exchange materials their ion-exchange behaviour has been extensively studied because of the effect it can have on a zeolite's thermal stability, adsorption behaviour and acidity and selectivity in catalytic reactions. It should be noted that all of the detailed studies of ion-exchange which have been published describe work on low-silica zeolites such as A, X, Y, mordenite, etc. Although ion exchange work on the medium and high silica zeolites has been described e.g. in the preparation of the H-form and exchange with Cs, Ba, Mn[45,46] and others, these experiments have been carried out to produce a result rather than to give detailed information on the degree of exchange and location of the cations.

1.5.3 Catalysis

While the first commercial use of zeolites was based on their sorptive properties the real break-through for zeolites as industrial compounds resulted from their ability to catalyse the cracking of hydrocarbons. Before the introduction of zeolites in 1962[47] almost all hydrocarbon cracking catalysts were amorphous aluminosilicates. An illustration of how effective zeolites are as cracking catalysts compared to the amorphous materials, which they have largely replaced, can be seen in Table 1.3[48]. The use of zeolites has revolutionised catalytic cracking, since, because of their increased activity

TABLE 1.3 Relative activities of zeolites and amorphous aluminosilicate cracking catalysts

	T/°K	Relative Activity
Silica-alumina	540	1.0
Ca-Faujasite	530	10
NH_4-Faujasite	350	250
RE-Faujasite	250	10 000

much higher yields of gasoline can be obtained for a given quantity of naphtha. More recently the use of zeolites has been patented in catalytic hydrocracking[49,50] as well as in catalytic cracking[51,52].

The basis of the acidity, in zeolites and indeed for all their catalytic applications is due to the fact that the cations within the structure can be readily exchanged. The H-form of zeolites can be formed by direct exchange with acid, exchange with NH_4 ions followed by thermal decomposition or by exchange with rare earth cations followed by calcination.

The nature of the acidity in zeolites (particularly the variations in acidity) is obviously of fundamental importance to an understanding of their catalytic activity. Dempsey[53] first related the variation in acidity to aluminium atom location and to framework interactions. More recently Barthomeuf[54] compared the acidity in zeolites to acid solutions and proposed that activity coefficients should be defined because of the similarity of the cation and proton interactions in zeolites and in concentrated solutions.

However it is not just the acidity of zeolites but also their unique structural properties which are important in catalysis. Not only can reactant molecules be accepted or rejected on the basis of their size but the products obtained are influenced by the dimensions of the channels, cages and intersections. This has given rise to the term "shape selective" when applied to the effect of the structure on the product distribution. This "shape selectivity" can operate in two ways;

a) "Transition state selectivity" is when the dimensions of the active site govern the size of the transition state which is allowed. An example of this is in toluene disproportionation in ZSM-5 in which the two toluene molecules approach so as to produce benzene and p-xylene rather than the ortho or meta isomers.

b) This relies on the channel dimensions being smaller than dimensions of the active site in which the reaction occurs. Thus molecules are formed within the constraints of a) above, but only these molecules smaller than the channel dimensions desorb from the structure. An example of this is in methanol conversion in small pore zeolites (e.g. erionite) in which aromatics can be formed in the cages yet cannot desorb from the structure because the channel dimensions are smaller than the dimensions of the aromatic species.

The combination of shape selectivity and high activity has meant that zeolites are used in several areas in the petrochemical industry, e.g. toluene alkylation[55] and disproportionation[56], hydrodewaxing of oils[57] and xylene isomerisation.

One of the most recent and possibly most important applications of zeolites has been in the conversion of methanol to hydrocarbons. There have been a great number of publications in both the academic and the patent literature in which the use of ZSM-5 to convert methanol to gasoline[58-60] is described. It should be noted that as well as being capable of methanol conversion ZSM-5 can be used in all of the other applications listed above, and thus indicate the potential use of this material.

The most recent development in zeolite catalysis is the use of metal promoted zeolites. In this, noble metals and non-noble transition metals are exchanged or impregnated into the zeolite. These metal loaded zeolites can be used in a variety of catalytic reactions (e.g. hydrogenation, oxidation and CO/H_2 conversion). This subject has been recently reviewed by Uytterhoeven[61].

1.6 SYNTHESIS

1.6.1 General Remarks

Zeolites are hydrated alumino-silicates which are formed under hydrothermal conditions. Most synthetic zeolites are formed as metastable species and, if left too long in their synthesis mixtures can undergo various transformations to more thermodynamically stable phases. Some zeolites, however, appear to be equilibrium species; in the low silica (sodium) system (see section 1.4) zeolites P and sodalite are often the end result of several transformations. In the medium and high silica systems crystalline forms of silica, such as α-quartz or cristobalite, are often the result of the recrystallisation of the original zeolite. A possible exception may be the zeolite ZSM-5 which appears to be a stable phase. However, as with sodalite and zeolite P this apparent stability of ZSM-5 may be because over-runs of much longer duration than usual may be required for their transformation to more thermodynamically stable phases.

While zeolites are metastable with respect to their synthesis magna they can remain stable for long periods once isolated (c.f. diamond). Exposure of these isolated zeolites to reactive conditions such as acid/alkali at high temperatures can result in lattice destruction or re-crystallisation to other crystalline phases.

1.6.2 Early Synthesis

While the first zeolite was discovered in 1756, the first attempts at synthesis began about 1850. The early attempts at synthesis were carried out by geologists as part of a series of experiments with the objective of synthesising naturally occurring minerals. The conditions employed were based on, the then current, ideas about how mineral zeolites had been formed in nature. Since the occurrence of only igneous deposits had been appreciated at that time the conditions used reflected this, in that very high temperatures (several hundred degrees centigrade) were employed with corresponding high pressures. "Reaction mixtures" tended to have the same stoichiometry as the mineral under study except that water was not regarded as being an important variable and a large excess tended to be used. It is interesting to speculate on how the rate of advancement of zeolite synthesis would have been altered had the widespread occurrence of sedimentary deposits been appreciated at an earlier stage, since conditions closely related to those involved in the formation of sedimentary deposits (e.g. lower temperatures and presence of salts) are currently the most successful for the synthesis of both naturally occurring and novel zeolites.

It is known that the first mineral to be synthesised in the laboratory was quartz; this synthesis is attributed to Schafhautle (1845). However, the first zeolite to be synthesised was Levyne by St. Claire Deville in 1862. While the above syntheses have been recognised much of the early reports of zeolite synthesis cannot be substantiated due to a lack of analytical data. The absence of suitable analytical techniques (mainly powder x-ray diffraction) led to many erroneous reports. This is illustrated by an example given by Breck[62] who reports that the "potassium faujasite" described by Baur was in fact K_2SiF_6 formed from the HF used in the preparation.

The early synthesis of zeolites up to 1937 has been reviewed by Morey and Ingerson[63].

1.6.3 The First Systematic Studies

The first novel zeolite (i.e. with no natural counterpart) to be synthesised, was formed as the species P and Q by Barrer[64]. P and Q have a framework structure similar to the zeolite ZK-5, later synthesised by Kerr[65] using sodium and a quaternary ammonium compound. The synthesis of this zeolite which Barrer described as "Chabazite-like" was carried out using a quite novel technique. Natural (or synthetic) analcite was heated with water and an excess of salt such as barium chloride (to give P) or barium bromide (to give Q) at temperatures between 180 and 220°C for 2 to 6 days. The salt used in the synthesis was occluded in the structure but could be removed by hydrothermal washing with distilled water at 200°C. This 'recrystallisation technique' of synthesis is all the more remarkable since in this example it results in the formation of a species with a more open framework. The use of potassium chloride or bromide resulted in the formation of species designated N and O while other salts such as $CaCl_2$, $SrCl_2$ and KF were relatively ineffective as mineralising agents. Zeolites X and Y could also be used instead of analcite as well as amorphous aluminosilicate gels of similar compositions. However the use of amorphous gels is somewhat different since no recrystallisation occurs and is an example of the use of inorganic salts in conventional zeolite synthesis which will be discussed later. It is interesting to note that this 'recrystallisation technique' which led to the first novel zeolitic structure has received relatively little attention. This could be, partly, because additional work resulted in species (N and O) from which it was more difficult to remove the salt, that is, feldspathoids rather than zeolitic materials were formed.

Much of the first systematic studies of zeolite crystallisation were carried out by Barrer and co-workers. These are published as the early members of the two series, "Hydrothermal Chemistry of Silicates" Parts 1 to 22 and "Chemistry of Soil Minerals" Parts 1 to 14. Both series were published in J. Chem. Soc. These, together with earlier publications[66] by Barrer on zeolite synthesis exemplify the approach which was adopted. Unlike the above recrystallisation technique the method employed was similar to those used in the earlier attempts at zeolite synthesis, in that, very high temperatures were used (150 to 450°C) and gels although prepared, were dried before reaction with water or alkaline solution, and in a study of the synthesis of mordenite[66] the composition of the gel was similar to that of the desired product.

A major breakthrough in zeolite synthesis was initiated by Milton at Union Carbide in the late 1950's. This, the 'Gel Synthesis Method' involved the use of very reactive components, low temperatures, and equipment closely related to that used in organic synthesis. The gel formation and reaction to form zeolites is exemplified by the following scheme.

$$\begin{array}{c}
\mathrm{M\,OH\,(aq)} \quad + \quad \mathrm{M\,Al(OH)_4\,(aq)} \quad + \quad \mathrm{M_2\,SiO_3\,(aq)} \\
\Big\downarrow \mathrm{Ti} \\
[\,\mathrm{M_x\,(AlO_2)_y(SiO_2)_2\,.\,MOH\,.\,H_2O}\,] \\
\Big\downarrow \mathrm{(GEL)} \\
\Big\downarrow \mathrm{T_2} \\
\mathrm{M_a\,[\,(AlO_2)_a\,.\,(SiO_2)_b\,]\,.\,c\,H_2O + solution}
\end{array}$$

(CRYSTALLINE ZEOLITE)

Thus silicate and aluminate solutions are brought together at a temperature T_1 to form a gel, (normally room temperature (RT)). The gel can be aged or it can be reacted directly at temperatures between RT and 100°C (although higher temperatures, up to about 220°C have been used). Important variables in these reactions are reaction composition, temperature, source of reagents, order of mixing of individual components and history of the gel (i.e. whether it is aged or reacted directly).

The major advantage of the 'gel synthesis method' is that rapid crystallisation rates can be achieved (of the order of hours) at relatively low temperatures, and hence sophisticated pressure vessels are not required. Early successes were the formation of a novel zeolite, zeolite A[67], and a synthetic analogue of the mineral faujasite, zeolite X[68], both of which have had considerable commercial importance.

1.6.4 Zeolites of the Alkali Metals and Alkaline Earths

Table 1.4 gives an indication of the zeolites which have been synthesised from single cation systems of the alkali metals and alkaline earths. Both synthetic analogues of naturally occurring and novel zeolites are included. Tables 1.5 - 1.10 give more details about the conditions required for the synthesis of zeolites from systems containing Li, Na, K, Ca, Sr and Ba respectively. Much of the information for these tables was taken from Breck[91].

The most striking feature about Table 1.4 is the absence of any zeolites for caesium and magnesium. This is for quite different reasons. In the case of caesium, feldspathoids tend to be produced rather than zeolites, especially pollucite[92]. From systems containing magnesium, layered materials such as montmorillonite predominate and no zeolite has been formed. In the study by Barrer and McCallum[92] of rubidium and caesium aluminosilicates, two hydrated Rb-aluminosilicates were formed (Rb-D and Rb-E). Rb-D was believed to be similar to zeolite Z from the K-system while there was some question as to the zeolitic nature of Rb-E. However, apart from these, as with caesium, rubidium tended to produce analcite-like species[93].

Examination of the zeolites formed from the other alkali metals illustrates the importance of the gel synthesis. In particular the extensive studies of Na at high temperatures, Table 1.6A, produced relatively few zeolites while by the "gel synthesis", Table 1.6B, a large number of novel species were formed. One other feature of the Na system should be mentioned, that is the formation of ZSM-5. This preparation is quite different from all the others in Table 1.4 in that the product's

TABLE 1.4 Zeolites synthesised from single cation systems of alkali metals and alkaline earths

Li	Known	Novel			
	Bikitaite Li-Clinoptilolite Li-Analcime Li-Mordenite Li-Phillipsite	Li-A Li-H ZSM-2			
Na	Analcime Natrolite Mordenite Cancrinite Ferrierite Sodalite Faujasite	A Pc(Pt) R S Z-21 ZSM-5	Mg		
K	E (K-Analcime) G (K-Chabazite)	F H J L M Q W Z	Ca	Known	Novel
				Ca-D (Wairakite) Ca-E (Analcime) Ca-I (Thomsonite) Ca-J (Epistilbite) Ca-L (Harmotome) Ca-Q (Mordenite) Clinoptilolite Ferrierite Heulandite Scolecite	
Rb		Rb-D (= Z from K system) Rb-E (?)	Sr	Clinoptilolite Sr-D (Ferrierite) Sr-G (Chabazite) Sr-F (Gmelinite) Sr-I (Analcime) Sr-M (Mordenite) Sr-Q (Yagawaralite) Sr-R (Heulandite)	
Cs			Ba	Clinoptilolite	Ba-G Ba-J Ba-K Ba-M

TABLE 1.5 Lithium Zeolites

Zeolite	Composition of Reaction Mixture				T/°C	t/ h-hours d-days	Ref.
	SiO_2	Al_2O_3	LiO_2	H_2O			
Li-A	2	1	1	XS	250	36 h	69
Li-H	8	1	>1	XS	220	36 h	69
ZSM-2	9	1	6	5	60	30 d	70
Bikitaite	4	1	2	-	300	-	71
Li-Clinoptilolite[a]	8	1	2	8.5	254	-	72
Li-Analcime	4	1	1	34	152	67 h	73
Li-Mordenite[b]	40	1	3	314	150	65 h	73
Li-Phillipsite[b]	34.3	1	12	270	150	370 h	73

[a] XRD is very similar to clinoptilolite except for the line at 7.76 Å.

[b] Products from these reactions were not single phases.

TABLE 1.6A Sodium Zeolites - high temperatures

Zeolite	Composition of Reaction Mixtures				T/°C	t/d-days	Ref.
	SiO_2	Al_2O_3	Na_2O	H_2O			
Analcime	2-6	1	1	XS	200	-	74
Natrolite[a]	3	1	1	XS	120-180	103-19 d	75
Mordenite	15.6	1	2.6	56	175	16 d	73
Hydroxy Cancrinite	2	1	3	XS	390	-	76

[a] Reaction was "seeded".

TABLE 1.6B Sodium zeolites - gel synthesis

Zeolite	Composition of Reaction Mixtures				T/°C	t/ h-hours d-days	Ref.
	SiO_2	Al_2O_3	Na_2O	H_2O			
A	2	1	2	35	20-175	-	67
Pc(Pt)	3.8	1	2	94	60-150	-	77
R	4	1	3.2	260	100	-	78
S	6	1	2.4	80	80-120	-	77,79
Z-21	2	1	30	504	100	1 h	80
ZSM-5	80	1	6.5	3196	150	122 h	85
Faujasite							
X	3	1	3.6	144	20-120	-	68
Y	20	1	8	320	20-175	-	81
Sodalite	3	1	2.8	34	150	-	67
Ferrierite	10	1	1	-	150	-	82

TABLE 1.7 Potassium Zeolites

Zeolite	Composition of Reaction Mixture				T/°C	Ref.
	SiO_2	Al_2O_3	Na_2O	H_2O		
F	1	1	2	20	100	84
H	2	1	6	150	100	84
J	4	1	16	160	100	84
L	20	1	8	200	100-150	84
M	10	1	49	420	100	84
Q	4	1	16	190	50	84
W	5	1	3	75	100	84
Z	4	1	1.7	-	120-150	83
E (K-Analcime)	5	1	1	-	150	83
G (K-Chabazite)	5	1	2.5	-	150	83

TABLE 1.8 Calcium Zeolites

Zeolite	Composition of Reaction Mixtures				T/°C	t/d-days	Ref.
	SiO_2	Al_2O_3	CaO	H_2O[b]			
Ca-D (Wairakite)	4	1	1	XS	260	24 d	86
Ca-E (Analcime)	4	1	1	XS	340	4 d	86
Ca-I (Thomsonite)	1-2	1	1	XS	245	34 d	86
Ca-J (Epistilbite)	6-7	1	1	XS	250	31 d	86
Ca-L (Harmotome)	3-4	1	1	XS	250	31 d	86
Ca-Q (Mordenite)	7	1	1	XS	390	-	86
Clinoptilolite	5-7	1	1	XS	340-380	-	87
Ferrierite	7	1	1	XS	350-370	-	87
Heulandite	7	1	1	XS	200	14 d	8
Scolecite[a]	3	1	1	XS	230-285	-	8

[a] Reaction was seeded with scolecite (mineral)

[b] Method of preparation was to form a gel of reactant composition which was separated, dried then reacted with excess water at the reaction temperature. In the work of Barrer and Denny[86] 10 g water per 0.75 g gel were used. In the work of Koizumi and Roy the quantity of water added to the gel was not specified.

TABLE 1.9 Strontium Zeolites

Zeolite	Composition of Reaction Mixture				$T/^{o}C$	t/d-days	Ref.
	SiO_2	Al_2O_3	SrO	H_2O[a]			
Sr-D (Ferrierite)	9	1	1	XS	340	10 d	89
Sr-F (Gmelinite)	4.4	1	1	XS	205	6 d	89
Sr-G (Chabazite)	3	1	1	XS	150	35 d	89
Sr-I (Analcime)	3	1	1	XS	380	3 d	89
Sr-M (Mordenite)	7	1	1	XS	300	5 d	89
Sr-Q (Yugawaralite)	8	1	1	XS	340	47 d	89
Sr-R (Heulandite)	9	1	1	XS	250	23 d	89
Clinoptilolite	10	1	1	XS	300-360	-	89

[a] Method of synthesis was to prepare a gel of reactant composition which was separated, dried and then reacted with water (7 g water per 0.5 g dried gel).

TABLE 1.10 Barium Zeolites

Zeolite	Composition of Reaction Mixture				T/°C	t/d-days	Ref.
	SiO_2	Al_2O_3	BaO	H_2O			
Ba-G	3	1	1	xs[a]	150-200	21-28 d	90
Ba-J	8	1	1	xs[a]	300	9-13 d	90
Ba-K	8	1	1	xs[a]	300	16 d	90
Ba-M (Harmotome)	7.5	1	1	xs[a]	220-250	21 d	90
Clinoptilolite	6	1	1	xs	250-300	-	88

[a] Method of synthesis was to prepare a gel of reactant composition which was separated, dried then reacted with water (7 g water per g of dry gel).

SiO_2/Al_2O_3 ratio was not of the low silica group but was about 60/1. ZSM-5 was first, and is usually, synthesised using an alkali metal with a quaternary ammonium compound (see later) and its synthesis from an inorganic, single cation system is included here only for the sake of completeness.

A large number of synthetic analogues of mineral zeolites have been formed from systems containing alkaline earths particularly Ca and Sr. Because the systems were so unreactive very high temperatures were employed (see Tables 1.8 and 1.9). Consequently these reactions are closely related to those which formed many of the mineral-analogues in the Li and Na systems. This illustrates an important, though obvious point, that because zeolites are metastable species high temperatures tend to result in more thermodynamically stable phases, which are generally denser or more compact structures. Consequently if Ca and Sr systems could be made more reactive at lower temperatures they could well result in the formation of novel structures. In a recent review article[94] Robson expressed the view that, "Far from being uninteresting, this group (alkaline earths) may provide our second or third generation catalysts where selectivity rather than brute-force is the watchword".

1.6.5 Zeolite Crystallisation From Mixed Cation Systems

The combination of two or more cations in zeolite synthesis is not a recent development. It has been mentioned that the first zeolite to be synthesised was levyne. The method employed by St. Claire Deville was to heat at 170°C a mixture of potassium silicate and sodium aluminate. This synthesis was prompted by the fact that levyne occurs with either calcium as the charge compensating species or sodium and potassium together.

One of the first systematic studies of zeolite crystallisation from mixed base systems was carried out by Barrer et al[77] with Na, K-aluminosilicate gels. In this study a comparison was made with the species prepared from the individual homoionic Na and K gels and this led Barrer[95] to suggest that in general "The nucleation and crystal growth of zeolites from aqueous aluminosilicate magmas in presence of more than one base can yield products which are not simply mixtures of those formed when the single bases are present".

Many possible combinations of two or more inorganic bases are possible and Table 1.11 gives examples of some of the studies which have been carried out. It should be noted that some "mixed base" studies resulted in the formation of non-zeolitic species (e.g. the Rb-Cs study of Barrer and McCallum[92] resulted in the formation of a series of feldspars).

While the above has dealt with zeolite crystallisation from mixed base systems, frequently studies in which two or more cations have been used, involved the addition of the second (and subsequent) cation(s) as a salt. Examples of such syntheses have been included in Table 1.12. These examples illustrate syntheses in which the addition of the "salt" resulted in the formation of a different species. In the case of the syntheses of the sodalites and cancrinites some points are worth noting. The thermal stability of these materials was dependent on the nature of the occluded species as was the quality of the powder XRD pattern[99] (i.e. the

TABLE 1.11 Examples of some of the mixed base systems used for zeolite crystallisation

	Zeolite Formed		
Cations	Known	Novel	Ref.
Na, Li		ZSM-3	96
Na, K	Chabazite Phillipsite Analcite		77
Na, K		T	98
Na, Cs	Analcite		93
Na, Cs		RHO	97

TABLE 1.12 The use of salts as mineralising agents in zeolite crystallisation

Base	Salt	Zeolite	Ref.
Na	Na Cl Na Br Na I	Sodalite	99
Na	$Na_2 MoO_4$ $Na_2 CrO_4$	Cancrinite	99
Na	NaOH[3]	Hydroxysodalite Hydroxycancrinite	99
Na	T.M.[1]	KSO7[2]	100

1. Complexes of Rh, Pt, Ni and Co were used, e.g. $[Rh(NH_3)_5Cl]Cl_2$
$[Pt(NH_3)_4]Cl_2$

2. KSO7 is similar to zeolite PHI of Flanigen and Grose[101].

3. This has been included because the occluded species in these "zeolites" was NaOH.

sample's crystallinity). However, most importantly the synthesis was effectively directed by the nature of the anion. While it is true that the sodalites and cancrinites so produced are feldspathoids, since it is almost impossible to remove a significant amount of the occluded materials by exchange/washing, this may not be too much of a disadvantage when complexes such as those used in the formation of KSO7 are used. Such species may result in desirable catalytic properties (see section 1.5.3) and in such a case their occlusion may be advantageous. Zeolite KSO7 (equivalent to Union Carbide's zeolite PHI[101]) is the first novel zeolite to be formed using transition metal species. While the expense associated with the use of some of these species is likely to be prohibitive for general use, they could find use in special areas, in particular, in the preparation of bi-functional[102] catalysts.

The examples of salt addition, described above, illustrate their use as mineralising agents. However, in many cases the addition of salts does not alter the nature of the product but affects the reaction rate and/or yield.

1.6.6 Nitrogeneous Zeolites

The extension of the many possible combinations of inorganic cations to include organic cations was first carried out by Barrer and Denny[103]. This study (published in 1961) described zeolite crystallisation from a "single" cationic system. The bases used were mono, di-, tri- and tetra-methylammonium hydroxide and NH_4OH itself. Although some non-zeolitic species were formed, zeolites A, faujasite and sodalite were also synthesised. Concern over the partial hydrolysis of some of the methylammonium bases leading to a variety of cationic species led to the designation of sodalite as N-T or nitrogeneous -T. The form of this designation has been adopted by many other workers e.g. N-A etc. even when the nature of the cation was unambiguous. While a subsequent paper by Barrer and Denny[86] described zeolite crystallisation from the $CaO-TMA_2O$ mixed base system, the original report[103] dealt with a (nominally) alkylammonium only system. However the choice of reagents meant that this was almost certainly not the case. The silica source used in this initial study was "Syton" silica sol. Such sols have NaOH added as a stabilising agent. Breck[104] reports that subsequent work with NH_3 stabilised sols carried out in stainless steel autoclaves showed that N-A could not be crystallised in 11 weeks at 100°C and that "... traces of sodium help to nucleate crystallisation of zeolites N-A and N-Y". Thus it seems likely that the original work of Barrer and Denny actually dealt with crystallisation from a mixed cation system even though the sodium was present in small quantities.

Zeolitic species were formed mainly from the alkylammonium systems while the NH_4 (and Na) system led to the formation of mica, cristobalite, boehmite and corundum although some NH_4-analcite was formed.

The powder XRD patterns of the nitrogeneous forms of A(N-Q), X(N-R) and P(N-L) were compared with those of their Na counterparts and significant differences in their unit cell dimensions were noted. The reason for these variations was subsequently shown to be the higher SiO_2/Al_2O_3 ratio of the nitrogeneous zeolites. Although no analytical data were presented in the original report by Barrer and Denny[103] they surmised "... that these zeolites tend to be silica-rich relatives to their analogues containing only simple inorganic cations, although no proof can be offered".

The formation of silica rich forms of zeolite A was reported by Kerr[105] (as ZK-4) and patented by Flanigen et al[106]. In both cases TMA was used in the preparation. The silica-rich forms of A, X, Y, P, etc. although much more siliceous (relatively) than their alkali metal counterparts did not have SiO_2/Al_2O_3 ratios greater than about 10/1.

N.B. By using quaternary ammonium compounds several novel zeolites have been formed as well as the more siliceous forms of known zeolites. Examples of these novel zeolites together with the cations used in their synthesis can be seen in Table 1.13. It should be noted that zeolites ZSM-4 and Omega have similar structures and are related to the mineral mazzite discovered after their synthesis[94]. In all the zeolites described in Table 1.13 (with the exception of Losod) both inorganic and organic cations were found in the structure. The presence of methylammonium species was demonstrated by Barrer and Denny[103] by both chemical and thermal analysis. Thermal analysis of, for example, N-A indicated that the organic species could be removed by calcination. Strictly speaking the as synthesised forms of nitrogeneous zeolites are more closely related to feldspathoids than zeolites since the presence of the organic cations prevent/suppress sorption or ion-exchange. Calcination, however, can remove the organic cations and result in zeolites which can have significant sorptive (and ion-exchange) capacities.

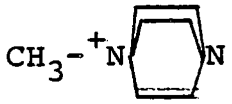
Losod contains only Na ions in its as synthesised state. The explanation for this, given by Meier and Sieber[114], was that

TABLE 1.13 Novel low silica zeolites formed using organic species

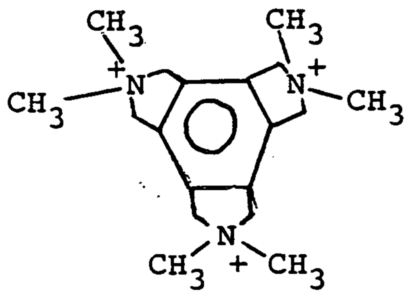
Zeolite	Inorganic Cation	Organic Species	Ref.
α	Na	TMA	116
ZK-5	Na	a	107
ZK-20	Na	b	108
ZSM-4	Na	TMA	109
ZSM-10	K	a	110
ZSM-18	Na	c	111
ZSM-34[f]	Na+K	Choline d	112
ZSM-43	Na+Cs	Choline d	128
Phi	Na	TMA	101
Omega	Na	TMA	113
Losod	Na	e	114
N	Na	TMA	115

a

b

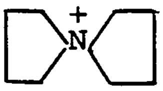


c



d $(CH_3)_5NCH_2CH_2OH$

e



Neopentyltrimethylammonium

f ZSM-34 is structurally related to zeolites erionite and offretite.

the organic base was too large to be occluded in the structure and served only as a source of hydroxyl ions in the synthesis.

From a simplistic view it is easy to understand why the use of organic cations resulted in more siliceous forms of known structures. Tetramethylammonium (TMA), for example, occupies much more space than Na and consequently its occlusion in a similar framework (e.g. zeolite A) means that less aluminium must be present. While methods for the synthesis of low-silica zeolites have frequently employed reaction mixtures with SiO_2/Al_2O_3 ratios greater than 12/1 e.g. mordenite, phillipsite, etc., their products have always contained sufficient aluminium to keep them in the low-silica (or aluminium-rich) class of zeolites. The first report of the combination of a higher SiO_2/Al_2O_3 ratio reaction mixture with a quaternary ammonium compound was by Kerr et al[117]. The product, zeolite β, was the first member of the silica rich zeolites. (Zeolite β can be produced with SiO_2/Al_2O_3 ratios up to about 100/1).

A large number of novel zeolites with SiO_2/Al_2O_3 ratios between 10/1 and 300/1 have been synthesised using symmetrical quaternary ammonium compounds (Table 1.14). Alkali metal cations were also used in these syntheses. In the early work[122] on the synthesis of these zeolites the quaternary ammonium compound was added as the hydroxide, whereas in later studies the cheaper halide salts[121,123] were used. While many of the zeolites in Tables 1.13 and 1.14 were synthesised using reagents and conditions similar to those used in the gel synthesis method of low-silica zeolites reaction times at temperatures about 100°C were very much longer. For example ZSM-11 can require 9 days[123] to crystallise at 105°C while ZSM-34[112] has reaction times of about 25 to 30 days at similar

TABLE 1.14 Medium-silica (SiO_2/Al_2O_3 10/1 - 300/1) zeolites synthesised using quaternary ammonium compounds

Zeolite	Quaternary[e]	Ref.
NU-1	TMA[a]	118
FU-1		119
β	TEA[b]	117
ZSM-8		120
ZSM-12		121
ZSM-5	TPA[c]	122
ZSM-11	TBA[d]	123

[a] TMA = tetramethylammonium

[b] TEA = tetraethylammonium

[c] TPA = tetrapropylammonium

[d] TBA = tetrabutylammonium

[e] Alkali metal cations were also used in these syntheses.

temperatures and other zeolites can take very much longer. Consequently a move was made back to higher temperatures and most zeolites with SiO_2/Al_2O_3 ratios greater than 15/1 are crystallised at temperatures between 140 and 200°C.

Of the zeolites in Table 1.14 there is little doubt that most interest is in ZSM-5 mainly because of its applications in the petroleum industry (see section 1.5.3). It is worth noting that ZSM-5 and ZSM-8 are actually the same zeolite. The framework structures of ZSM-5[124] and ZSM-11[125] indicate that they are members of the same family of zeolites which Kokotailo and Meier[126] suggested should be called the "Pentasil family" of zeolites. Both zeolites have intersecting 10-ring channels and are regarded as being the end-members of their series, a view reinforced by a recent patent from Mobil[127] in which Kokotailo describes "... a unique crystalline porous tectosilicate possessing a structure intermediate that of ZSM-5 and ZSM-11 ...".

The extension of the range of SiO_2/Al_2O_3 ratios over which zeolites can be formed was first shown to include structures which contain Al only as an impurity, that is, with SiO_2/Al_2O_3 ratios of about 1500/1, by Dwyer and Jenkins of Mobil. This material which was designated an "organosilicate" not a zeolite has the same framework structure as ZSM-5, although SiO_2/Al_2O_3 ratios were typically 1290/1. Its method of preparation is almost identical with that of ZSM-5 except that an Al source is not added and pure reagents are used. Grose and Flanigen later patented a form of "crystalline silica"[130] and then published[131] an account of the synthesis of a material termed "silicalite". Both are almost certainly the same material as Mobil's organosilicate, yet, it is Union Carbide's name of silicalite which seems to have been accepted.

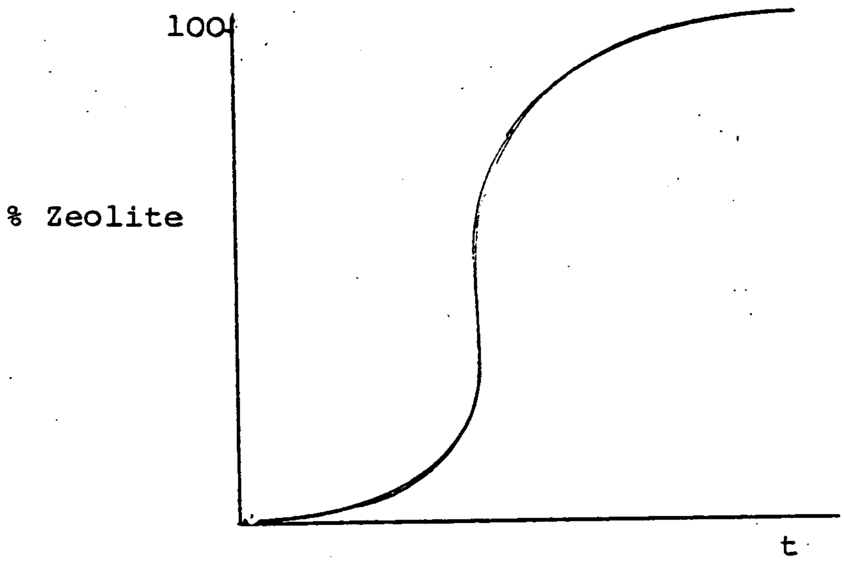
Further advances concerned with ZSM-5's synthesis have been described by Bibby et al[132] and by Dwyer and Chu[133]. Bibby et al described the synthesis of ZSM-5 from alkali metal free reaction mixtures, using TPA in conjunction with NH_4. Pure reagents were chosen to avoid Na contamination (cf. Barrer and Denny) and Na levels in the product were said to be less than 1 ppm. Dwyer and Chu described ZSM-5's synthesis using Pr_3N and PrBr added as separate components to the reaction mixture rather than as the quaternary salt.

While the purpose of the addition of the amine in the above example was to prepare the quaternary ammonium compound in situ, another Mobil patent[134] (Rubin, Rosinski and Plank) demonstrates the preparation of ZSM-5 with C_3-C_8 primary amines themselves. The formation of ZSM-5, -11 and -35 (a ferrierite type species) has been accomplished[138] using various C_2-C_{12} diamines, the product being dependent on the chain length. ZSM-35 has also been prepared using pyrrolidine as well as ethylenediamine[139]. The other ferrierite related structures ZSM-21 and -38 were synthesised[140] using both pyrrolidine and choline. Pyrrolidine was also used in the preparation of the zeolite ZSM-23[136]. Alkali metal cations, usually Na were used in conjunction with the N-containing species in the above syntheses.

One further class of organic species should be considered here although they do not contain N, that is, alcohols. Barrer and Denny[103] described the addition of an alcohol (methanol) to zeolite reaction mixtures because of concern over the partial hydrolysis of the alkylammonium bases used. The addition of alcohol did not effect the crystallisation. Whittam[137] however has demonstrated that the addition of alcohol (isopropanol) can result in the formation of zeta-3 a ZSM-5 type material.

1.6.7 Kinetics and Mechanism

A large number of studies have been carried out on the kinetics of zeolite crystallisation. A plot of zeolite growth against time produces the classic "s" shaped growth curve of Fig. 1.3.



This sigmoidal growth curve is the result of an induction period being required during which nuclei grow to a "critical size to become viable and crystal growth begins".[141] Thus zeolite crystallisation is divided into two parts, the induction (nucleation) and growth periods.

For zeolites prepared from gels the traditional methods used to follow the increase in the crystalline fraction of the solid were water vapour adsorption and x-ray diffraction[142-144]. Breck[145] has illustrated that simply a visual examination of samples taken throughout zeolite X formation can indicate the onset of crystallisation by the separation of the zeolite from the gel. However, this method was not quantified. A more recent paper[146] indicates that a method based on the difference in the cation exchange properties of the zeolite and amorphous solid can be used to quantitatively follow the crystallisation of zeolite A. However, it is not clear if such a method could be used for medium and high-silica zeolites, which have much smaller ion-exchange capacities.

The kinetics of zeolite crystallisation can be affected by the same factors which influence the nature of the product, i.e. temperature[147], composition (e.g. pH[141]) and source of reagents[148,149]. In addition the rate of crystallisation can be affected by stirring[150] and the nature of the reactor wall[151]. In studies on the effect of temperature on zeolite crystallisation, apparent activation energies for the formation of zeolites A, X and mordenite have been determined, by Breck[152] and Culfaz and Sand[147], while Breck tried to give some physical significance to these values by relating the activation energy for the synthesis of zeolites A and X to the energy required to depolymerise silica in a similar temperature range, Culfaz and Sand reported separate activation energies for the nucleation and growth periods. The effect of adding preformed zeolite crystals to aid in the nucleation step, i.e. seeding was also examined by Culfaz and Sand. The reduction/removal of the induction period observed is consistent with a similar (earlier) observation by Kerr[153]. In this study by Kerr on the rate of crystallisation of zeolite A it was found that at 100°C the reaction followed approximately first order kinetics and was proportional to the quantity of zeolite already present in the system, that is, the reaction was autocatalytic.

The study of the mechanism of zeolite crystallisation has attracted both academic and industrial interest. While the complexity of the system makes it an interesting area for academic research, from an industrial viewpoint the "prize" must be the preparation of better sorbents and catalysts. However the prospect of synthesising a structure, (as yet unknown) tailored to a specific task, is still some way off.

Essentially two mechanisms for crystallisation have been proposed, the 'solid-gel transformation' and 'solution phase' mechanisms. Both have considerable support. The solid-gel transformation of amorphous gel into crystalline zeolite has been suggested by several workers, including Khatami and Flanigen[154]. In their study[154] an amorphous gel which had a composition that would normally lead to the crystallisation of zeolite X was separated and dried to a powder containing about 20% (w/w) water. After several weeks at ambient temperature this material had substantially converted to zeolite X. However, the presence of much less than the usual quantity of water (so that the material was free-flowing) does not preclude the action of solution species. In a separate study McNicol, Pott, Loos and Mulder[155] added small quantities of Fe^{3+} ions to substitute for Al^{3+} in gels used to prepare sodalite and zeolite A. Spectroscopic examination of Fe^{3+} was then used to indicate the environment of the iron. The results obtained indicated that Fe^{3+} ions in the gel were in a tetrahedral environment and this was interpreted as support for the solid-phase mechanism.

The mechanism by which nucleation and crystal growth proceeds via solution species appears to be gaining more acceptance. The original report by Kerr[153] described an experiment which was almost the inverse of the one carried out by Khatami and Flanigen. In this study gel was separated into solid and liquid portions. The 'solution' phase was then recycled through a filter funnel containing solid. After some time the total weight of solid zeolite in the filter funnel had increased. This was reported as being proof of growth from solution species. Aiello, Barrer and Kerr[156] indicated that zeolites could be formed from very dilute "clear" solutions of metal silicate and aluminate solutions. Once again no reference was made to colloidal species which could have been present in either/both cases.

While the debate on the mechanism of crystallisation continues one fundamental point should be noted: the species described by Meier[3] as the Secondary Building Units of zeolite structures are themselves found in aqueous silicate solutions[157]. Since the formation of the gel is accomplished by adding aqueous silicate and aluminate solutions it would seem proper that an understanding of the mechanism should begin with an understanding of these fundamental solutions.

1.6.8 The role of quaternary ammonium compounds in zeolite synthesis

It has already been pointed out that the addition of different quaternary ammonium compounds to otherwise similar reaction mixtures can result in quite different zeolites. The possible action of the quaternary ammonium compound was first discussed by Aiello and Barrer[113] when during a description of the synthesis of the zeolites offretite (O) and Ω using Na and TMA they described the specificity of the TMA by: "The affinity observed between Me_4N^+ and 14-hedral gmelinite cages in Ω and O may play an important part in their synthesis, through a template action involving the association of Me_4N^+ and of aluminosilicate precursors of the gmelinite cage". The term template, as applied to the action of quaternary ammonium compounds in zeolite synthesis was first used in the above description by Aiello and Barrer. It is interesting that in this case the term template is used to describe the association of the quaternary with a specific alumino-silicate unit which goes to make up the cages of the structure. In Flanigen's plenary paper in Naples[5], however, the term template had altered to describe a "clathration mechanism" in which the structure grows around the quaternary cation. Since quite differently shaped N-containing organic species have been used in the synthesis of a single zeolite e.g. ZSM-35 and -38 using pyrrolidine and ethylenediamine, or ZSM-5 using TPA and hexamethylenediamine (see section 1.6.6) it is difficult to see how the 'clathration mechanism' can operate, although it is obviously attractive when describing the synthesis of ZSM-5 using TPA.

In a paper on "Templates in Zeolite Crystallisation" Rollmann[158] describes the conditions which must be met before a "template effect attributable to the quaternary cation" can be correctly assigned. The formation of Losod by Sieber and Meier[114] fits Rollmann's first condition that an addition of that quaternary a "different zeolite structure is obtained". However none of the bulky quaternary cations used in the synthesis of Losod were incorporated into the structure. Thus the clathration mechanism cannot hold in this case.

It is evident that there is still some considerable doubt as to the action of quaternary ammonium compounds in zeolite synthesis.

1.7 THE OBJECTIVE OF THIS WORK

The aim of this work was to examine the use of quaternary ammonium cations in zeolite synthesis. To further this objective two types of study were carried out; the first involved an examination of zeolite crystallisation in the presence of quaternary ammonium cations, while the second dealt with their effect on the anion distribution of aqueous silicate solutions.

The synthesis studies describe the crystallisation of zeolites from systems containing both sodium and the quaternary ammonium cation hexamethonium. There is no record of the use of hexamethonium in zeolite synthesis prior to this study. The compositions of the reactions carried out ($5/1 < SiO_2/Al_2O_3 < 1500/1$) covered almost the complete range of SiO_2/Al_2O_3 ratios possible.

Chapter 3 describes the crystallisation of low silica zeolites from reaction mixtures in which both sodium and hexamethonium were added as their hydroxides, and is therefore analogous to the studies of Barrer and Denny[86,103] and others[107-116], in which zeolite crystallisation from systems containing mixed bases were examined.

The formation of medium and high-silica zeolites from systems containing sodium and hexamethonium is described in Chapter 4. The kinetics of formation of the zeolites produced was examined in some detail and in addition the effect of replacing the hexamethonium with a number of structurally related compounds is described.

One further synthesis study was carried out, this did not involve any organic cations but instead examined the use of an organic solvent in zeolite crystallisation. This is described in Chapter 5.

The current view of the action of quaternary ammonium compounds in zeolite synthesis as described by Flanigen[5] and Rollmann[158] has already been discussed. In an attempt to gain a more fundamental understanding on the action of quaternary ammonium in zeolite crystallisation a study was carried out on the anion distribution of aqueous silicate solutions of inorganic and organic cations. This work is described in Chapter 6.

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CHAPTER 2

EXPERIMENTAL

2.1 INTRODUCTION

The experimental techniques used in this work are of two main types; those associated with the synthesis of zeolites and those techniques used to identify and characterise the products obtained. Only those analytical techniques common to all sections on synthesis will be discussed in this Chapter while a description of the apparatus and techniques used in the synthesis of zeolites will be discussed in the relevant sections of Chapters 3, 4 and 5. For a similar reason a description of the techniques and apparatus used to obtain ^{29}Si nuclear magnetic resonance spectra of silicate solutions will be included in Chapter 6.

The analytical techniques used are of fundamental importance to this type of work, indeed, it was mentioned in Chapter 1 that much of the early work on mineral synthesis cannot be substantiated due to a lack of analytical data.

While the techniques described in this section are used to identify and characterise the products obtained by crystallisation from alumino-silicate gels, this identification and characterisation does not involve structure determination. The crystals of the zeolitic materials obtained were too small for examination by single-crystal X-ray techniques and in any case such studies are outwith the scope of this work. The techniques described here are aimed at a more qualitative approach in which the X-ray powder diffraction pattern is used as a "finger-print" of the compound while other techniques either give information on the framework composition, crystal size and shape and thermal stability of the materials or allow the reaction pathway to be followed.

2.2 X-RAY POWDER DIFFRACTION

X-ray diffraction is based on Bragg's Law which takes the form of equation (2.1), which relates the wavelength of the radiation (λ) to the angle of incidence

$$n\lambda = 2\ d\ \mathrm{Sin}\ \theta \qquad (2.1)$$

(θ) and the distance (d) between the Bragg planes. Thus when X-rays impinge upon a crystalline material they give rise to a series of reflections, the diffraction pattern.

Since most synthetic zeolites have crystals smaller than that required for single-crystal X-ray studies (minimum, about 75 μ), X-ray powder diffraction patterns are obtained. While each zeolite has a particular pattern, it can be altered slightly by the framework composition (see Chapter 3), the degree of hydration and by ion-exchange.

X-ray powder diffraction patterns were obtained using a Guinier-Hagg camera (Philips, XDC-700) and a Philips powder diffractometer. The diffractometer was installed as this work was being completed, consequently most X-ray diffraction analysis was carried out using the Guinier-Hagg camera.

2.2.1 THE GUINIER-HAGG CAMERA

The Guinier-Hagg camera is a focussing camera in which a quartz crystal is used as a monochromator. This camera was mounted on a Philips PW1010 generator for the early work and a Philips PW1720, 'tabletop' generator for the more recent studies. Cu $K\alpha_1$ radiation, $\lambda = 1.5405$ Å was used. The camera was capable of observing reflections from $2\theta = 5^o$ to $2\theta = 90^o$, however very low angle reflections (2θ approximately 5^o) were often obscured by a general blackening of the film in this region.

Two types of X-ray sensitive film were used, Kodirex double-sided and Kodirex single-sided film. When the double-sided film was used only one side was developed otherwise two lines (one on each side of the film) were observed instead of one. The method employed to develop only one side was as follows: when taken from the camera the side of the film which had been furthermost from the radiation was attached with "bluetack" to a strip of perspex. Care was taken to ensure that the bluetack covered the whole of the film's surface. The film was then treated in the usual way. Once exposure was completed and before being developed a scale was printed on all films. The scale was used to measure line positions relative to the focal line. The scale was printed before the film was developed so that it was subject to the same shrinkage as the diffraction pattern. Thus values of 2θ and the d-spacings could be compared from one film to another. Intensities were measured visually on a scale from 1 to 5. 1 - very strong (vs); 2 - strong (s); 3 - medium (m); 4 - weak (w); 5 - very weak (vw). The position of each line was measured relative to the focal line (using the scale) and multiplication of this value by 0.572 converted it to θ. In practice a computer programme, STOD, written by Dr. B.M. Lowe was used to calculate values of 2θ and d from the line positions. A copy of the programme STOD can be seen in appendix 1. The error in the d-spacings was determined by estimating the reading error. The error in d is related to that in θ by equation 2.2, and is thus largest for the smallest values of θ.

$$\delta d = (- \lambda \cos \theta / 2 \operatorname{Sin}^2 \theta) \delta \theta \qquad (2.2).$$

The length of exposure was varied according to the quantity and crystallinity of the sample and the type of generator used, but was normally in the region of 15 to 45 minutes. Much longer exposures tended not to improve the line intensities because the background became darker as well, thus it became more difficult to improve the "signal to noise" ratio.

The major advantages of the Guinier-Hagg camera for this type of work are that films can be obtained in a short period of time, it requires only small amounts of material (approximately 5 mg), it is very sensitive to weak reflections and has excellent resolution. The advantages together with the major disadvantage are illustrated in Plate 2.1. In Plate 2.1, 5 films of samples containing varying amounts of zeolite EU-1 - see chapter 4 - can be seen. EU-1 was mixed with amorphous material from the initial stages of the same reaction, hence films were obtained for samples containing 100%, 75%, 50%, 12½% and 6¼% EU-1. All films were exposed for the same lengths of time. It can be seen that even a sample containing only about 6¼% EU-1 contains lines of sufficient intensity for that material to be identified. However the top three films in Plate 2.1 show the major disadvantage, which is that when a crystalline material is present in major quantities it is impossible to determine if the sample contains 50% or 100% of that material from the intensities, unless a series of exposures are taken.

The accuracy of the data produced by the camera was checked periodically using a "standard" sample of silicon, the line positions for which were calculated using its cell constants. In all cases the line positions measured matched the actual values within experimental error.

2.2.2 THE PHILIPS POWDER DIFFRACTOMETER

The Philips semi-automatic powder diffractometer used for these investigations was installed towards the end of the project. It comprised a PW1965/60 goniometer mounted on a PW1730 highly stabilised X-ray generator.

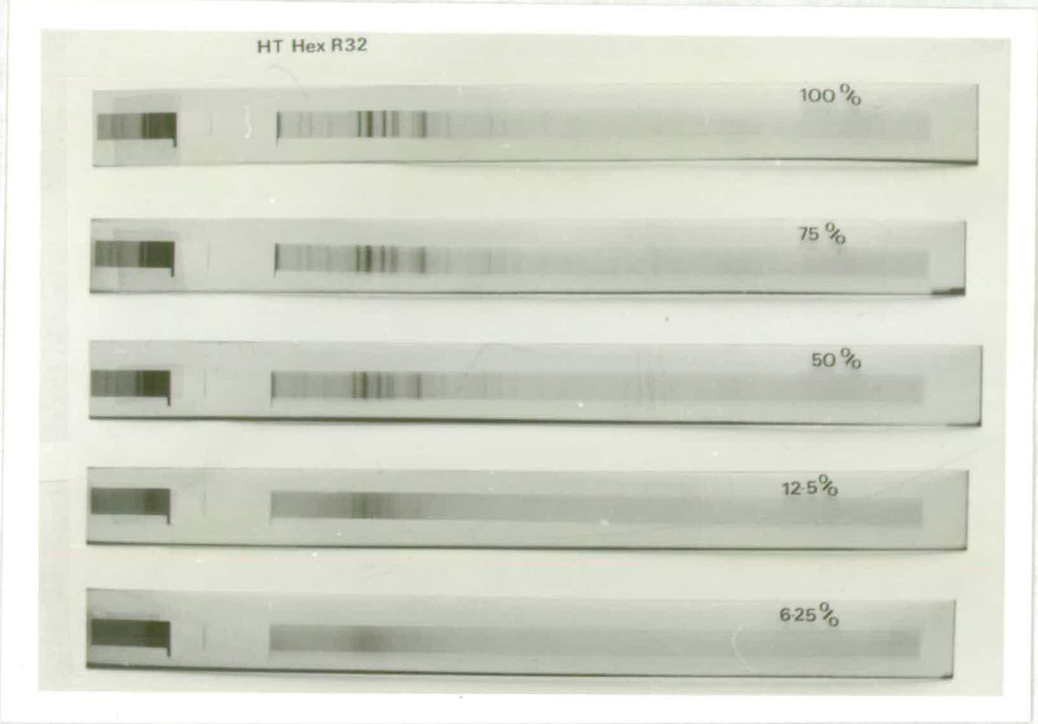


Plate 2.1

The output was analysed with a PW1390 channel control unit and fed to a PM8203 pen recorder (for continuous mode scanning). Samples were loaded by means of an automatic sample changer (PW1170) and scanning was controlled by a PW1394 motor control unit. No monochromator had been fitted consequently Cu $K\alpha_{1,2}$ radiation was used.

Quantitative information was obtained using the diffractometer from the peak intensities. The major disadvantages of the diffractometer were than the d-spacings were less precise, resolution was not as good as the Guinier-Hagg camera and larger samples (approximately 1 g) were required.

2.3 SCANNING ELECTRON MICROSCOPY

The scanning electron micrographs shown in this thesis were obtained with a Cambridge S150 instrument operated by Mr. J. Goodall of the Department of Electrical Engineering, University of Edinburgh.

The samples to be examined were dried overnight at 110°C then allowed to equilibrate with water by leaving the sample exposed to the atmosphere for several hours. The samples were then ground finely before being fixed to the aluminium "stubs" by double-sided adhesive tape. Care was taken to ensure that no air bubbles were trapped under the tape. Only a very small amount of sample (less than 1 mg) was used and this was spread as thinly as possible over the surface to prevent large agglomerates of crystals being present which can lead to charging (see later). Not all the adhesive tape was covered with sample, thus leaving an 'edge' along which the sample was so finely spread out that it was possible to examine single crystals. Part of the adhesive tape was removed to allow the sample to be coated with gold. This coating aids the conduction of electrons away from the surface and thus minimises the build-up of charge at the sample surface. "Charging" when it occurs prevents any resolution of individual crystals.

The electron micrographs were used to gain information on crystal size and shape and the distribution of sizes and "shapes" throughout a sample. Indeed it could be used to give a qualitative idea of sample homogeneity. To ensure that a representative sample was being examined the sample was mixed well before fixing to the stubs and at least three separate areas of the stub were examined.

The plates obtained from the SEM work can be seen throughout this work. The numbers on the bottom of the plates refer respectively to the scale, accelerating voltage, sample number and film number.

2.4 SORPTION[a]

The ability of dehydrated zeolites to sorb molecules with dimensions less than their pore size is a well known phenomena. Indeed sorption studies are one of the prime techniques used to characterise zeolites.

[a] The term sorption will be used throughout this work because it is not possible to differentiate between adsorption and absorption.

The purpose of the sorption studies carried out in this work was not to gain an exact measurement of the sorptive capacity of the material, instead it had two main functions:

a) To obtain an indication of the sorptive capacity and pore size of particular zeolites.

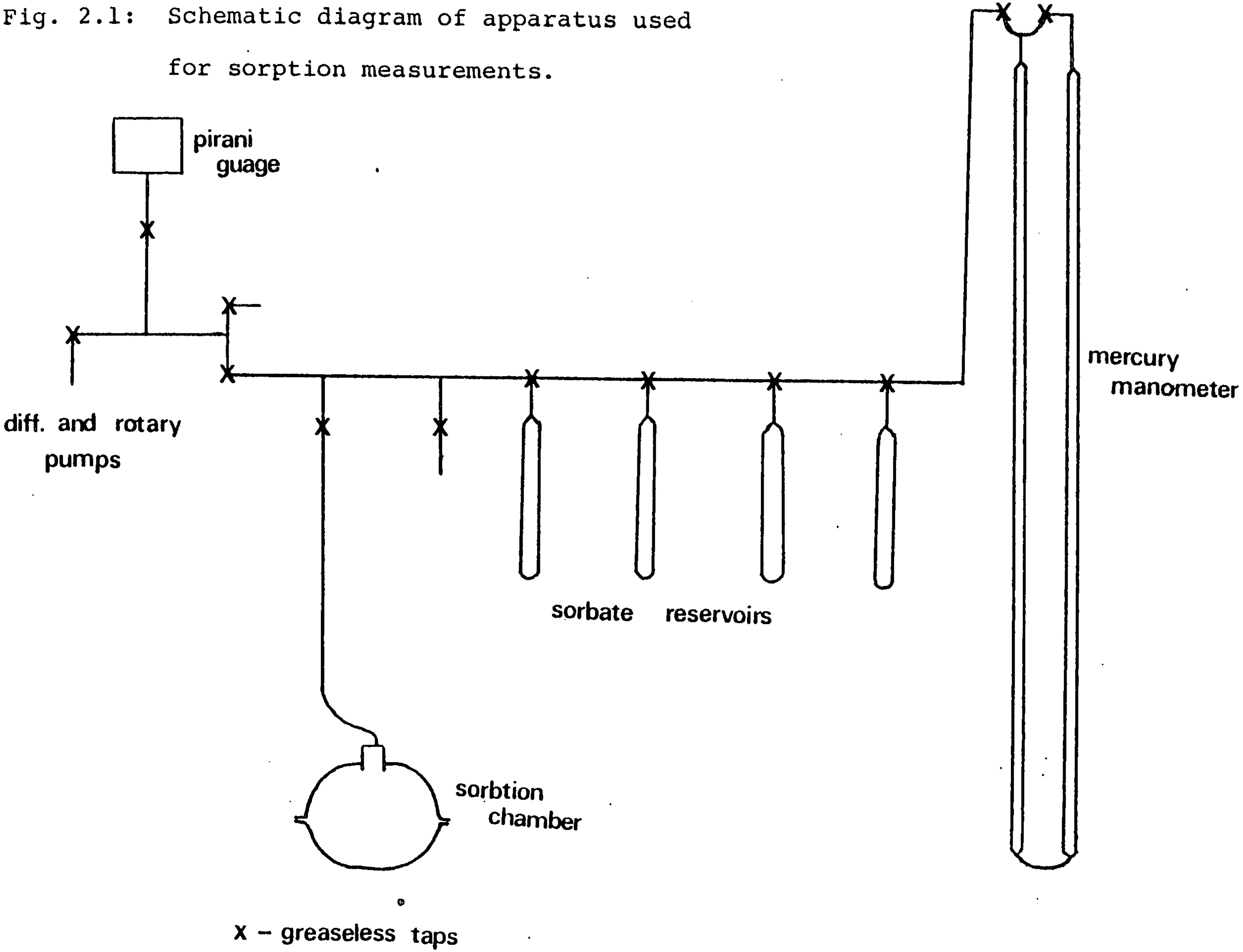
b) To follow the formation of zeolites (see chapter 4) by measuring the sorptive capacities of samples taken throughout the reaction.

Because of b) it was desirable to be able to examine several samples at one time.

Sorption studies were carried out using the apparatus illustrated in Fig. 2.1. This sorption apparatus was based on apparatus described by Landolt.

All taps were greaseless taps supplied by J.H. Young Ltd. Two sorption chambers were used, both were Jencons 6" desiccators one was a "dry-seal" type and the other a conventionally sealed desiccator. Both had advantages and disadvantages. The dry-sealed desiccator was much faster and simpler to use but did not give as good a seal as the ground-glass desiccator which required more time to obtain this good seal. A mercury manometer was used to measure the sorbate pressure which was controlled by operating with the sorbate at $0^{o}C$ obtained by surrounding the reservoir with ice stored in a thermos flask. Evacuation of the system to less than 10^{-3} torr was

Fig. 2.1: Schematic diagram of apparatus used for sorption measurements.



achieved using rotary and diffusion pumps. A pirani gauge and Pirani 6GB head were used to measure the pressure. The materials used in the sorption studies were purified before any sorption was carried out using the freeze-pump-thaw cycle technique.

Up to twenty samples could be examined at one time. These samples were left to equilibrate overnight with the sorbate vapour. Samples of approximately 0.5 to 1.0 g were used. Less sample than this could lead to problems in accurately measuring the weight increase while larger samples could have suffered from diffusion limitation problems. All sorption results are the average of at least two experiments. In those studies in which samples from throughout a run were examined a 'standard' sample of zeolite 13X was used. Only those 'runs' which gave maximum sorption of this 13X sample were used.

The samples studied which could have contained organic material were normally calcined at 450^{o}C for 70 hours although other conditions were used. Once calcined, samples were placed in a pre-weighed weighing bottle and dehydrated for several hours under vacuum using a Townsend and Mercer oven fitted with a rotary pump. The samples were cooled under vacuum over P_2O_5 before having the weighing bottle lids replaced, then the bottles and samples were weighed. The lids were removed and the samples placed in the sorption chamber. The system was evacuated then isolated from the pumps and the stable pressure noted. The required sorbate reservoir, which had been surrounded by ice for at least 1 hour before this, was then opened. Once the study was completed the pressure was noted and the sorbate reservoir closed. The system was brought up to atmospheric pressure, the lids were replaced on the sample bottles and re-weighed.

The amount of sorbate (x) taken up by 100 g of anhydrous material under study was as follows:

$$x = 100\,(wbss - wbs)/(wbs - wb)$$

where wb is the weight of the weighing bottle alone

wbs is the weight of the weighing bottle and anhydrous sample

wbss is the weight of the weighing bottle, anhydrous sample and sorbate.

Sorption results when quoted include the pressure noted, nature of sorbate and time for which the sorption was carried out.

Considerable problems were encountered trying to obtain reproducible results. Those results quoted were for at least two 'runs' which agreed, within experimental error. Many runs had to be discarded. It is believed that the two major sources of irreproducibility were due to leaks within the system and the samples "picking-up" moisture on being transferred to the sorption chamber. Obviously apparatus which used a micro-balance and furnace (to allow in situ dehydration) would have been more accurate, but even if these had been available such a system would not have allowed the examination of up to twenty samples in such a short period of time.

2.5 THERMAL ANALYSIS

2.5.1 BASIC PRINCIPLES

In thermal analysis studies, the way in which various parameters e.g. weight, temperature or dimensions vary as a sample is heated are measured.

The most common thermal analysis techniques (and the ones most applicable to zeolite studies/ characterisation) are thermal gravimetric analysis (tga) and differential scanning calorimetry (dsc) or differential thermal analysis (dta). The programmed rate of heating in both types of analysis is very important. Not only must it be reproducible but alterations in the heating rate can significantly alter the sensitivity or resolution obtained.

The first of these techniques, tga, measures the sample's weight loss as a function of temperature and is therefore very suitable for determining the water and/or organic content within the zeolite lattice. When both water and organic material is present it is important to use a fairly low heating rate if separation of both losses is to be achieved. Of course such a separation of losses may not be possible, however in general as low a heating rate as is practicable should be used.

In dsc and dta changes in the sample which require or release heat are monitored. In dta the sample temperature is measured relative to some reference material, subjected to the same programmed heating, and deviations from the reference material's temperature are recorded. In dsc both samples are maintained at the same temperature and the energy required to do this is monitored. Peaks corresponding to endothermic and exothermic processes can be clearly seen on both techniques. The heating rate is again very important here, because high heating rates give the best sensitivity. However, heating rates which are too large can, as with tga, cause several processes to overlap. All weight losses seen on tga traces are seen in dsc or dta traces, however, processes which involve no net weight loss can also be detected, for example, lattice collapse or transitions of one crystallographic form to another.

2.5.2 THERMAL GRAVIMETRIC ANALYSIS

Thermal gravimetric analysis was carried out using a Stanton-Redcroft TG770 instrument. Samples, approximately 5 to 10 mg, were ground finely then placed in the platinum sample holder and the furnace was raised. The heating rate (between 1°C/min and 50°C/min) was usually 10°C/min. The final temperature (up to 1500°C) was set as was the cut out/hold control. A twin channel Servoscribe chart recorder was used to monitor the sample temperature and weight. The sample weight, which was either recorded directly or as full-scale deflection (FSD), was set at 100%, 50% or 20% of the sample weight. Thus the percentage weight loss could be determined directly.

The balance was calibrated between runs using weights supplied by the manufacturers. The reference thermocouple was placed in a thermos flask filled with ice. The temperature was read from the chart in mV and converted to °C using the table provided. The instrument was always allowed a minimum of fifteen minutes to warm-up after being switched on.

Nitrogen or air could be passed over the sample although in this work air was used.

The normal operating conditions can be seen below:

Atmosphere/Flow rate	Air/4.5 mls/min
Chart speed	120 mm/hour
Sample weight	5-10 mg
Heating rate	10 °C/min
Temp (FSD)	20 mV
Weight (FSD)	50%.

2.5.3 DIFFERENTIAL SCANNING CALORIMETRY

A Du Pont 990 thermal analyser with a dsc cell was used in the differential scanning calorimetry studies. Samples, approximately 5 to 10 mg were placed in an aluminium crucible. An empty crucible was used as a reference. The heating rate normally used was 10°C/min. The maximum temperature was 550°C Samples were examined under flowing nitrogen.

2.5.4 DIFFERENTIAL THERMAL ANALYSIS

Dta studies were carried out using a Stanton-Redcroft 674 instrument. This instrument has a maximum temperature of 1500°C and was therefore more suitable, than the Du Pont instrument, for measuring the temperatures at which the collapse of alumino-silicate frameworks occur. Much larger samples were required for this instrument, approximately 50 to 100 mg, than for the Du Pont 990 dsc equipment. The reference used was alumina (Al_2O_3). A heating rate of 5°C/min was found to give the best combination of sensitivity, resolution and a stable baseline.

2.6 ANALYSIS

Analysis of samples by X-ray fluorescence to obtain information on framework composition was carried out using a Philips 1450 spectrometer[a]. While information on the Na_2O, SiO_2 and Al_2O_3 content was required this instrument also monitored the quantities of K_2O, Fe_2O_3, MgO, CaO, TiO_2, MnO and P_2O_5.

Samples, at least 1 g after removal of volatile species, were calcined at 1100°C for 30 minutes to remove any volatile species. A quantity of a lithium borate flux (5.3333 times the calcined sample's weight) was added and the mixture heated at 1100°C for a further 20 minutes. After cooling additional flux was added to make up to the original weight. The mixture was then heated over a meker burner and then poured into a graphite mould. After allowing to cool very slowly, so that the resulting glass disc did not

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[a] University of Edinburgh, Department of Geology.

crack, the discs were labelled and placed in the spectrometer. Normally several different sample discs were prepared simultaneously. The analysis was fully automated and results were produced as a computer print out. The results for SiO_2 content required correction since the spectrometer was calibrated for SiO_2 over the region 25% to 75%. Since the correlation is non-linear above 80% and most samples contained about 95% SiO_2 a correction factor was used. This was determined using a pure sample of SiO_2 (quartz).

Carbon, hydrogen and nitrogen analysis were carried out by the departmental analytical service.

2.7 pH MEASUREMENTS

pH measurements were carried out on some of the sodium silicate solutions studied in chapter 6, and also on samples taken throughout the course of zeolite synthesis reactions.

The instruments used were a Pye Unicam 290 pH meter and a Philips PW9409 digital pH meter. Because of the relatively high pH values being measured electrode lifetime was found to be a problem. Several electrodes were used but the best results and lifetime were obtained using an EIL plastic combination electrode.

The pH of the silicate solutions were measured in a conventional way. However, because it is believed that this is the first time that pH measurements have been shown to accurately follow the path of zeolite crystallisations more detailed information will be given.

Samples (5 to 20 cm^3) once taken were placed on sealed bottles and allowed to cool and equilibrate for at least 2 to 3 hours, but usually overnight. (It was found that if samples were kept in water-tight containers and re-examined several weeks later the same 'pattern' was obtained). pH measurements were made on the solid/liquid slurry, these results were more reproducible and consistent than for filtered solutions. The pH electrode was allowed to 'equilibrate' in the sample for at least 10 minutes. Longer 'response times' were noted as the electrode aged.

The pH meter was calibrated using buffer solutions of pH = 7.0 and pH = 9.2. When a series of samples was being measured the calibration was checked using the buffer with pH = 9.2 every three samples. Between samples the electrode was washed thoroughly using distilled water. Care was taken to ensure that water on the electrode was removed before insertion into the sample.

CHAPTER 3

LOW TEMPERATURE ZEOLITE CRYSTALLISATION IN THE PRESENCE OF MIXED BASES

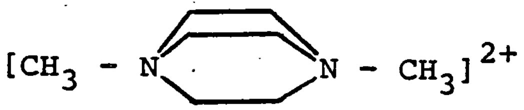
3.1 INTRODUCTION

It was shown by Barrer et al[1] that zeolite crystallisation can occur in the presence of more than one base to yield products which are not simply mixtures of those formed when only the single bases are present. The many possible combinations of two or more inorganic bases was first extended to include organic bases when tetramethylammonium was used in combination with sodium by Barrer and Denny[2]. Various workers have reported the formation of silica-rich analogues of known zeolites (e.g. sodalite[3,4] and A[2,3]) as well as novel zeolitic materials (e.g. ZSM-5, FU-1 and ZSM-11) using organic cations.

This work deals with zeolite crystallisation using the bis-quaternary ammonium compound hexamethonium.

$$\text{Hexamethonium} \equiv \text{HEX} \equiv [(CH_3)_3N\text{-}(CH_2)_6\text{-}N(CH_3)_3]^{2+}$$

Hexamethonium was chosen partly because previous work[5] had shown that hexamethonium produced a crystalline silicate in which the silicate unit, the double four-membered silicate ring, was the same as in crystalline tetramethylammonium silicate (see Chapter 6). Also, hexamethonium was one of several quaternary ammonium species the addition of which, it was claimed[6], increased the stability of aqueous alkali-metal silicate solutions. In addition there are several features of the structure of hexamethonium which make it an interesting species to use. The structure of hexamethonium is based on two tetramethylammonium units joined by a $-(CH_2)_4-$ chain. Tetramethylammonium, itself, has been used successfully in zeolite crystallisation and has produced several novel zeolites including NU-1[7] and FU-1[8] as well as 'high-silica' analogues of zeolites A[2,3] and sodalite[3,4] designated nitrogeneous A or N-A and N-HS. In addition hexamethonium is a bis-quaternary or doubly-charged species. Although several singly-charged quaternaries had been used when this work was first planned, bis-quaternaries had not received the same attention. The most notable success using a bis-quaternary was the synthesis of zeolites ZK-5[9,a] and ZSM-10[10]. The bis-quaternary used in the synthesis of both zeolites was 1,4-dimethyl-1,4-diazobicyclo[2,2,2]octane (DDO)[b]:



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[a] ZK-5 type species were formed by Barrer and Marcilly[11] in the absence of DDO. Instead barium salts were used. The species formed designated P and Q were formed using $BaCl_2$ and $BaBr_2$ respectively.

[b] DDO was used with sodium in the preparation of ZK-5 and with potassium in the preparation of ZSM-10.

Once the organic species (hexamethonium) had been chosen it was necessary to decide on the other reaction parameters e.g. other cation(s), compositions, temperature, reactors, reagents, etc. Reaction parameters were chosen, after examination of those used by other workers[3,9,10]. It was decided to study zeolite crystallisation from the system:

$$Na_2O - HEX\ O - SiO_2 - Al_2O_3 - H_2O$$

The range of compositions to be studied was changed several times before those in table 3.1 were decided upon.

TABLE 3.1 COMPOSITIONS TO BE STUDIED USING HEXAMETHONIUM

SiO_2/Al_2O_3	5	15	30	50
H_2O/SiO_2	40	60	80	100
$(Na_2O+HEX\ O)/Al_2O_3$	3	5	10	15
$Na_2O/HEX\ O$	1/0	7/3	5/5	3/7

The compositions set out in table 3.1 correspond to 256 reactions. However, some of these reactions could not be carried out because of the reagents used (see section 3.2). The range of compositions were chosen so that both low silica (SiO_2/Al_2O_3 = 5/1) and high silica (SiO_2/Al_2O_3 = 50/1) reactions could be studied.

3.2 EXPERIMENTAL

3.2.1 MATERIALS

Material	Source
Sodium hydroxide	B.D.H. Ltd.
Alumina ($Al_2O_3.3H_2O$)	B.A.C. Ltd.
Silica (CAB-O-SIL, M5)	B.D.H. Ltd.
Hexamethonium bromide	Koch-Light
Amberlite IRA 410	B.D.H. Ltd.
Zerolit FFIP	B.D.H. Ltd.

Distilled water was used in all reagent and reaction preparations.

Hexamethonium hydroxide was prepared from hexamethonium bromide by ion-exchange. Two ion-exchange columns were used, column A contained Zerolit FFIP anion-exchange resin (column volume 850 cm^3, exchange capacity 1.02 equivalents) and column B contained Amberlite IRA 410 resin (column volume 350 cm^3, exchange capacity approximately 0.5 equivalents). Since ion-exchange is an equilibrium process only one third of the possible exchange capacity of column A was used. Hexamethonium bromide, 350 cm^3 of 0.5 mol dm^{-3} solution, was passed through column A, then flushed through with distilled water until the solution leaving the column was neutral to litmus paper. This dilute solution (about 1 litre) was passed through column B. The resulting dilute hexamethonium hydroxide solution was concentrated by maintaining it at 60°C under partial vacuum. Once concentrated the quantity was measured and a portion titrated against 1 mol dm^{-3} hydrochloric acid. The amount of hexamethonium exchanged was calculated using the concentration and volume of the hexamethonium hydroxide solution. Exchanges of between 87% and 93% were obtained.

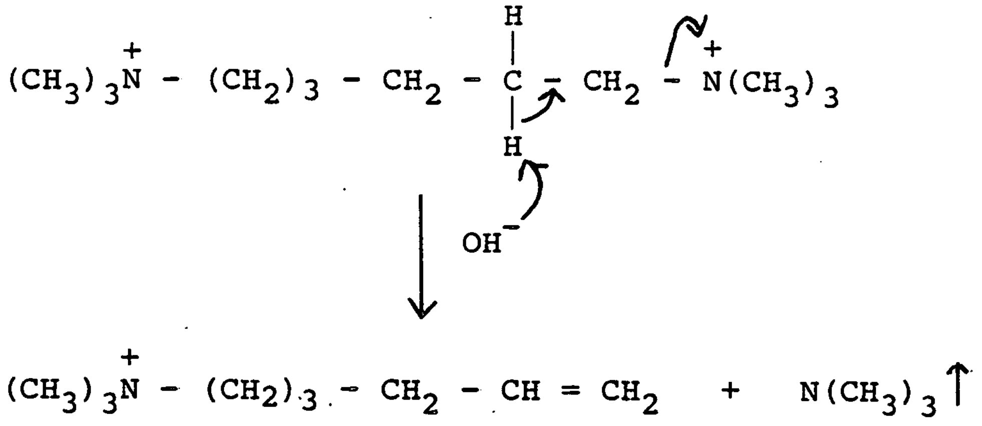
In table 3.1 it can be seen that although 'sodium only' reactions were planned, there were no equivalent 'hexamethonium only' reactions. This was because the aluminium source in these experiments was a sodium aluminate solution. In some preliminary experiments the aluminium source used was B.A.C. alumina tri-hydrate ($Al_2O_3.3H_2O$). The reaction compositions in this preliminary study was:

$$5SiO_2 - Al_2O_3 - 200H_2O - 2(Na_2O + HEX\ O)$$

The ratios of Na_2O/HEXO were:-

1/0 8/2 5/5 2/8 0/1

These five reactions were numbered (from left to right) HEX 1 to HEX 5. The procedure used to prepare the aluminate solution was to boil the alumina in the hydroxide solutions for approximately 30 minutes. For HEX 1 and HEX 2 the alumina dissolved fairly readily but in HEX 3, HEX 4 and HEX 5 the alumina did not dissolve. In addition, while boiling the alumina in the mixed hydroxide solution there was a strong smell of amines. It was presumed that the amines were generated by the action of the hydroxide ions on the hexamethonium in a Hoffmann degradation, producing trimethylamine.



$$(CH_3)_3\overset{+}{N} - (CH_2)_3 - CH_2 - \underset{H}{\overset{H}{C}} - CH_2 - \overset{+}{N}(CH_3)_3 \xrightarrow{OH^-} (CH_3)_3\overset{+}{N} - (CH_2)_3 - CH_2 - CH = CH_2 + N(CH_3)_3\uparrow$$

Because of this degradation of the hexamethonium and the poor solubility of the B.A.C. alumina in the hexamethonium hydroxide, it was decided to use a different source of aluminium. The source chosen was a stock solution of sodium aluminate. Although this meant that some reactions could not be carried out e.g. 'hexamethonium only' reactions, the use of the sodium aluminate solution was preferable to the addition of an alternative source of aluminium such as aluminium sulphate, since the addition of salts can affect zeolite crystallisation[11,12] and could mask effects due to the hexamethonium.

The stock solution of sodium aluminate was prepared by boiling the B.A.C. alumina in a 50% solution of sodium hydroxide for approximately 30 minutes. The ratio of Na_2O/Al_2O_3 was 1.5/1, so that the resulting solution had the composition:

$$1.5\ Na_2O - Al_2O_3 - xH_2O$$

After the solution had cooled additional distilled water was added to produce a solution of approximately 40% sodium aluminate. It was found that more concentrated solutions (approximately 50% $1.5\ Na_2O.Al_2O_3$) tended to be unstable and crystallised after several weeks.

The solution was stored in a glass reagent bottle although it is now believed that because the solution was very alkaline it would have been better to store it in a polypropylene bottle to avoid contamination of the sodium aluminate solution by silica[a]. However, over the range of reaction compositions studied in this work the amount of silica impurity added to the reaction mixture from the sodium aluminate solution is believed to have been insignificant.

3.2.2 EXPERIMENTAL DETAILS

Reaction mixtures were prepared using the following procedure: The water required was weighed into beaker A. The sodium hydroxide was weighed into beaker B and approximately 75% of the water from A added. The sodium hydroxide and water were stirred - using a magnetic stirrer - until all the sodium hydroxide had dissolved. The required amount of hexamethonium hydroxide solution was weighed and added with stirring to the sodium hydroxide solution. The silica was then weighed out and added to beaker B containing the mixed hydroxide solution. The beaker and contents were weighed and then placed in a water bath at 95°C for 10 minutes or until all the silica had dissolved. The beaker was removed from the bath cooled, weighed and any lost water replaced. In some reactions the alkali/silica

[a] The material that crystallised from the more concentrated sodium aluminate solution may have been an alumino-silicate.

ratio was so low that a clear solution was not obtained, instead, a cloudy solution resulted. In such systems it was likely that colloidal silica was obtained. No further attempt was made to dissolve the silica and the dispersion was used to prepare the reaction mixture. The sodium aluminate solution was weighed out and added with stirring to the remainder of the water in beaker A. The contents of beakers A and B were then mixed, to form a gel, which was then transferred to the reaction vessel.

The reaction vessels used were 'screw-top' polypropylene bottles of about 60 cm^3 capacity. Reactions were carried out without agitation in a water bath at 95°C. The water bath was fitted with a constant head device and its temperature controlled by a Fi-monitor (Fisons Ltd.). The sensitivity of the Fi-monitor was such that the temperature was maintained at $95 \pm 1^{\circ}C$.

Samples were normally taken after 1 day, 3 days, 7 days and if necessary (i.e. if the reaction had not crystallised) after 14 days. Samples (approximately 5 cm^3, were taken using a 5 cm^3 pipette with the end removed) were taken after the reactor had been removed from the water bath and shaken vigorously for about 15 seconds (to ensure that a representative sample could be taken). The samples were added to approximately 150 cm^3 of distilled water, filtered, washed with a further 150 cm^3 of distilled water then dried in an oven at 110°C for several hours. Before examination samples were equilibrated with water vapour by placing them in a desiccator over saturated sodium chloride solution in a water bath at 25°C, for 16 hours. Analysis of samples was restricted initially to examination by X-ray powder diffraction using a Guinier-Hagg powder camera. Both the quantity and type of material were determined by this technique. It has been pointed out in Chapter 2 that the Guinier-Hagg camera is not a reliable technique for quantitative analysis. However, in this case, quantitative information was restricted to determining whether there was a trace amount (approximately 10%) or a medium/major quantity (approximately 40 to 100%) of crystalline material in the product. Additional information was obtained by thermal analysis (dta and tga). These techniques have been described in Chapter 2 of this thesis.

In section 3.3, which deals with the results of these experiments, the effect of varying the water content of the reaction mixtures is discussed. One of the problems with the type of reaction vessel used in this work is that water vapour can be lost since the reactor is not completely sealed as in an autoclave. It was soon discovered that some of the polypropylene bottles did not seal very well. This was tested by placing the bottle (filled with the reaction mixture) in the bath at 95°C for about 30 minutes. If, after this period, the bottle had some pressure in it (due to expansion) the bottle was regarded as having a good seal. Those bottles which had lost pressure were removed and P.T.F.E. tape was wrapped around the threads on the bottle. These bottles were then replaced in the bath and the procedure was repeated. Bottles which did not seal after this were discarded. After reactions were completed, the bottles were emptied and washed. Care was taken to remove all crystalline material from the sides of the bottles. However, reactors were not washed with either acid or alkali which, it is now believed, is a very important stage in all zeolite synthesis studies (see Chapter 4).

3.3 RESULTS AND DISCUSSION

3.3.1 GENERAL REMARKS

Of the 256 possible reactions in table 3.1, 60 were carried out. The products obtained from these 60 reactions can be seen in table 3.2. The reactions in table 3.2 can be divided into two sections, section A, reactions HEX R1 to HEX R44 (table 3.3) and section B, HEX R45 to HEX R59 (table 3.4). Section A contains reactions with SiO_2/Al_2O_3 ratios of 5/1 while section B contains reactions with SiO_2/Al_2O_3 ratio of 15/1. The three rows in section A correspond to reactions with different ratios of H_2O/SiO_2. Comparison of the planned reactions in table 3.1 with those carried out (table 3.2) shows that one of the planned H_2O/SiO_2 ratios (H_2O/SiO_2 = 80/1) has been omitted. These reactions were not carried out because only small differences were found between the first two rows, with H_2O/SiO_2 ratios of 40/1 and 60/1.

The four columns in table 3.2 contain results of reactions which have different ratios of base/Al_2O_3. From left to right, the four columns correspond to

$(Na_2O+HEX\ O)/Al_2O_3$		3			5				10				15			
$Na_2O/HEX\ O$		1/0	7/3	5/5	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7
SiO_2/Al_2O_3 = 5,		H_2O/Al_2O_3 = 200,			H_2O/SiO_2 = 40											
Run No :	HEX R-	1	2	3	4	5	6	7	8	9	10	11	12	13	14	14a
S1	1d	X	(X)	Am	X+P1	X+P1	X+P1	Am	HS	HS	Am	Cn	HS	HS	Cn	CN
S2	3d	X+P1	P1+X	Am	X+P2	X+P2	P2+(X)	P1	HS	HS	Cn	Cn	HS	HS	Cn	-
S3	7d	P1+P2	P1+P2	P1	X+P2	X+P2	P2	P1+P2	HS	HS	Cn	Cn	HS	HS	Cn	CN^c
SiO_2/Al_2O_3 = 5		H_2O/Al_2O_3 = 300,														
Run No :	HEX R-	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
S1	1d	(X)	Am	Am	X	X	(X)	Am	X+A+(HS)	X+A+HS	X+A+HS	X+A	HS	HS	HS/CN^d	HS/CN^d
S2	3d	X+P1	(X)+(P1)	Am	X+P2	X+P2	X+P1	(P1)	-	-	-	-	-	-	-	HS/CN
S3	7d	X+P1	(P1)+(X)	X^b	P2+X	P2+X	P1+X	P1	X+A+HS	HS+(A)	HS+A	X+A+(HS)	HS	HS	HS/CN	HS/CN
SiO_2/Al_2O_3 = 5,		H_2O/Al_2O_3 = 500,			H_2O/SiO_2 = 100											
Run No :	HEX R-	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
S1	1d	Am	Am	Am	X^b	(X)	Am	Am	X+(P1)	X+(P1)	X+P1	(X)+(P1)	A+X+(HS)	HS+(A+X)	HS	A+HS
S2	3d	(X)	(X)	Am	$X+P2^b$	$X+P1^b$	X^b	Am	X+P1	X+P1	P1+X	P1+X	X+A+(HS)	HS	HS	HS
S3	7d	X+P1	X+P1	(X)	$X+P2^b$	$X+P2^b$	$X+P2^b$	Am	X+P1	X+P1	P1+X	P1+X	HS+X+(A)	HS	HS	HS
SiO_2/Al_2O_3 = 15,		H_2O/Al_2O_3 = 600,			H_2O/SiO_2 = 40											
Run No :	HEX R-	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59
S1	1d	Am	Am	Am	Am	Am	Am	Am	Y	Y	(Y)	Am	Y+P2	Y+P2	Y+P1	Y+P1
S2	3d	Am	Am	Am	Am	Am	Am	Am	Y+P2	Y+P2	Y+P1	P1	Y+P2	Y+P2	Y+P2	Y+P2
S3	7d	Am	Am	Am	Am	Am	Am	Am	Y+P2	Y+P2	Y+P1+P2	P1	Y+P2	Y+P2	Y+P2	Y+P2
S4	14d	Am	Am	Am	Am	Am	Am	Am	P2	P2+Y	Ps+Y	P1+P2	-	-	-	-

[a] Trace and minor quantities are enclosed in parenthesis. Am = amorphous, Cn = cancrinite, HS = hydroxysodalite or sodalite type. X = zeolite X, Y = zeolite Y, P1 = 'cubic' zeolite P, P2 = tetragonal zeolite P. When mixtures of zeolites are formed the dominant zeolite is given first.

[b] X-ray pattern contained some unidentified lines.

[c] Sample taken after 10 days.

[d] These species appear to be similar to both HS and CN - see text.

TABLE 3.3 - ZEOLITES CRYSTALLISED FROM STATIC REACTIONS AT 95°C - Section A, SiO_2/Al_2O_3 = 5/1

$(Na_2O$+HEX O$)/Al_2O_3$		3			5				10				15			
Na_2O/HEX O		1/0	7/3	5/5	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7
H_2O/Al_2O_3 = 200, H_2O/SiO_2 = 40																
Run No :	HEX R-	1	2	3	4	5	6	7	8	9	10	11	12	13	14	14a
S1	1d	X	(X)	Am	X+P1	X+P1	X+P1	Am	HS	HS	Am	Cn	HS	HS	Cn	CN
S2	3d	X+P1	P1+X	Am	X+P2	X+P2	P2+(X)	P1	HS	HS	Cn	Cn	HS	HS	Cn	-
S3	7d	P1+P2	P1+P2	P1	X+P2	X+P2	P2	P1+P2	HS	HS	Cn	Cn	HS	HS	Cn	CN^c
H_2O/Al_2O_3 = 300, H_2O/SiO_2 = 60																
Run No :	HEX R-	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
S1	1d	(X)	Am	Am	X	X	(X)	Am	X+A+(HS)	X+A+HS	X+A+HS	X+A	HS	HS	HS/CN^d	HS/CN^d
S2	3d	X+P1	(X)+(P1)	Am	X+P2	X+P2	X+P1	(P1)	-	-	-	-	-	-	-	HS/CN
S3	7d	X+P1	(P1)+(X)	X^b	P2+X	P2+X	P1+X	P1	X+A+HS	HS+(A)	HS+A	X+A+(HS)	HS	HS	HS/CN	HS/CN
H_2O/Al_2O_3 = 500, H_2O/SiO_2 = 100																
Run No :	HEX R-	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
S1	1d	Am	Am	Am	X^b	(X)	Am	Am	X+(P1)	X+(P1)	X+P1	(X)+(P1)	A+X+(HS)	HS+(A+X)	HS	A+HS
S2	3d	(X)	(X)	Am	$X+P2^b$	$X+P1^b$	X^b	Am	X+P1	X+P1	P1+X	P1+X	X+A+(HS)	HS	HS	HS
S3	7d	X+P1	X+P1	(X)	$X+P2^b$	$X+P2^b$	$X+P2^b$	Am	X+P1	X+P1	P1+X	P1+X	HS+X+(A)	HS	HS	HS

[a] Trace and minor quantities are enclosed in parenthesis. Am = amorphous, CN = cancrinite, HS = hydroxysodalite or sodalite. X = zeolite X, Y = zeolite Y, P1 = 'cubic' zeolite P, P2 = tetragonal zeolite P. When mixtures of zeolites are formed the dominant zeolite is given first.

[b] X-ray pattern contained some unidentified lines.

[c] Sample taken after 10 days.

[d] These species appear to be similar to both CN and HS - see text.

TABLE 3.4 - ZEOLITES CRYSTALLISED FROM STATIC REACTIONS AT 95°C[a] - Section B, SiO_2/Al_2O_3 = 15/1

$(Na_2O$+HEX $O)/Al_2O_3$		3			5				10				15			
Na_2O/HEX O		1/0	7/3	5/5	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7
		H_2O/Al_2O_3 = 600, H_2O/SiO_2 = 40														
Run No :	HEX R-	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59
S1	1d	Am	Am	Am	Am	Am	Am	Am	Y	Y	(Y)	Am	Y+P2	Y+P2	Y+P1	Y+P1
S2	3d	Am	Am	Am	Am	Am	Am	Am	Y+P2	Y+P2	Y+P1	P1	Y+P2	Y+P2	Y+P2	Y+P2
S3	7d	Am	Am	Am	Am	Am	Am	Am	Y+P2	Y+P2	Y+P1+P2	P1	Y+P2	Y+P2	Y+P2	Y+P2
S4	14d	Am	Am	Am	Am	Am	Am	Am	P2	P2+Y	P2+Y	P1+P2	-	-	-	-

[a] Trace and minor quantities are enclosed in parentheses. Am = amorphous, Cn = cancrinite, HS = hydroxysodalite or sodalite type. X = zeolite X, Y = zeolite Y, P1 = 'cubic' zeolite P, P2 = tetragonal zeolite P. When mixtures of zeolites are formed the dominant zeolite is given first.

ratios of $(Na_2O + HEX\ O)/Al_2O_3$ of 3/1, 5/1, 10/1 and 15/1. Within each column the ratio of $Na_2O/HEX\ O$ is varied from 1/0 ("sodium only" reactions) to 3/7. It should be noted that since the ratio of sodium to hexamethonium is given in terms of the oxides of both species the ratio represents the relative contributions of positive charges (or OH^- ions) to the reaction mixture by the inorganic and organic components. The mole ratio of Na/HEX is twice the oxide ratio.

In section 3.2.1 it was explained that because of the aluminium source being a sodium aluminate solution it was not possible to carry out "hexamethonium only" reactions. For a similar reason it was not possible to carry out some other reactions. These were reactions in which the ratio of $(Na_2O + HEX\ O)/Al_2O_3$ was 3/1 and the ratio of $Na_2O/HEX\ O$ was 3/7. This was because this required only 0.9 Na_2O to be added to the reaction although 1.5 Na_2O would have been added from the stock sodium aluminate solution.

As may be seen from table 3.2 these experiments produced six zeolites: X, Y, A, P (both P_1 and P_2), sodalite and cancrinite. Of these only cancrinite does not form readily in sodium systems. Zeolites X, Y, A and sodalite have a common structural unit, the sodalite or β-cage. This unit is a truncated octahedron. The structures of X (and Y), A and sodalite can be seen in fig. 3.1 along with that of the β-cage. In fig. 3.1 only the tetrahedral atoms (Si and Al) are shown, these occur at each of the vertices. The oxygen bridges between the tetrahedral atoms are not shown.

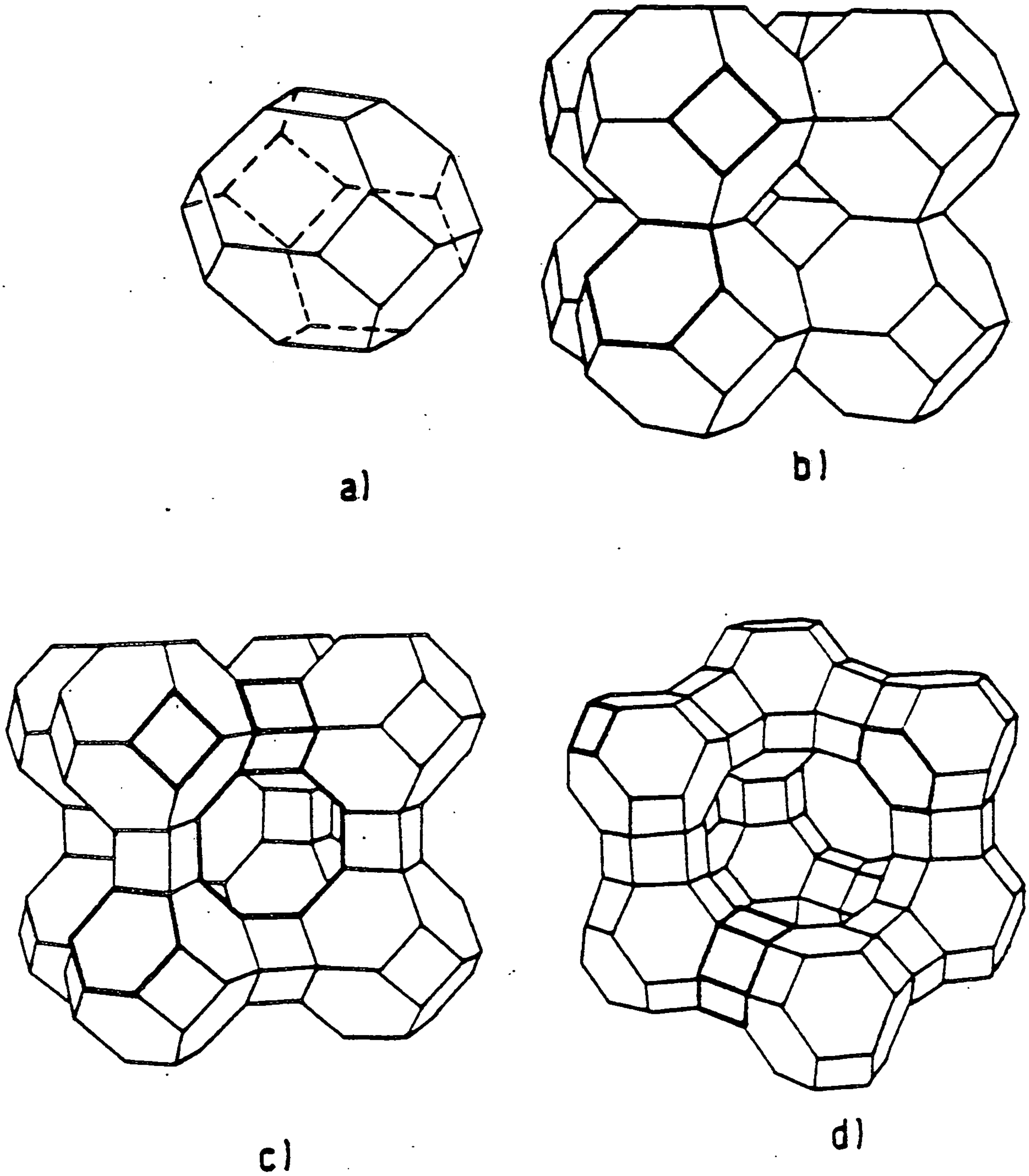


Fig. 3.1 Structures of a) β-cage, b) sodalite, c) zeolite A and d) Faujasite.

Both X and Y have the same structure as the rare mineral faujasite. This is based on β-cage units which are joined by oxygen bridges between the six-membered rings. It should be noted that the term six-membered and similar expressions refers to six tetrahedral atoms. Zeolites X and Y differ only in the SiO_2/Al_2O_3 ratios of their frameworks. In zeolite X the SiO_2/Al_2O_3 ratio is between 2 and 3 and in zeolite Y between 3 and 6[a]. Other differences between zeolites X and Y for example, unit cell parameter, are directly associated with the difference in the SiO_2/Al_2O_3 ratio.

Zeolite A was first synthesised by Milton[13]. No naturally occurring counterpart for zeolite A has been found. The structure of A is based on the β-cage but in this case the links are across the double four-membered ring, fig. 3.1c. The SiO_2/Al_2O_3 ratio of the framework is usually 2/1, however, more recently, using the tetramethylammonium cation zeolite A has been synthesised with higher SiO_2/Al_2O_3 ratios[2,3].

Sodalite is one of the most thermodynamically stable phases in the sodium system. Zeolite A in particular often transforms to sodalite. The structure of sodalite, like that of zeolites X and Y, is based on the β-cage (fig. 3.1b) however in this case they are packed together so as to occupy all the space available with each T-atom shared by four β-cages. Sodalite frequently contains occluded species such as water

[a] It is almost certainly possible to synthesise zeolite Y over a much wider range of SiO_2/Al_2O_3 ratios.

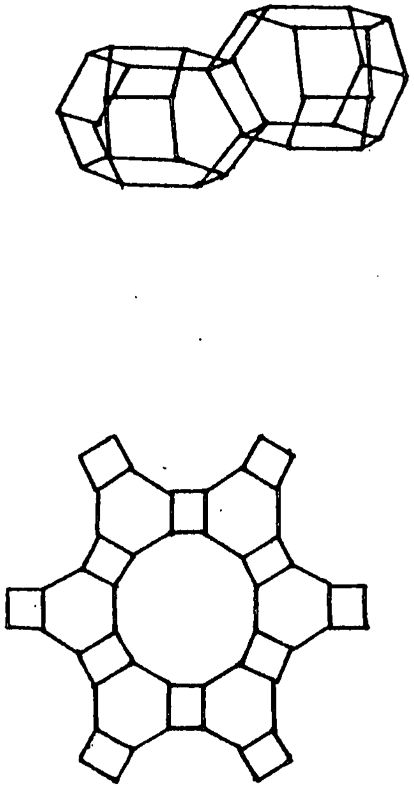
(sodalite hydrate), sodium hydroxide (hydroxy sodalite, HS), salts such as sodium chloride (naturally occurring sodalite) or quaternary ammonium species (N-sodalite).

Zeolite P or Linde zeolite B is actually a series of zeolites, two of which P_1 and P_2 have been formed in these experiments. P_1 and P_2 refer to the 'cubic' and 'tetragonal' forms of zeolite P. P_1 often transforms to P_2. Zeolite P has been shown[14] to have the same framework structure as gismondine whose structure can be seen in fig. 3.2b. It has been suggested[15] that zeolite P is an equilibrium phase. Zeolites A and X can both transform to zeolite P and in a stirred reactor pure samples of zeolite X can only be obtained by using an "active silicate"[16,17] as the silica source or by employing specific quiescent ageing steps. Zeolites X and Y were formed in these experiments because reactions were carried out without agitation.

Of the species formed in these reactions only cancrinite does not readily occur in the sodium system. Cancrinite formation normally requires either a high temperature (ca. 250°C) and a high concentration of sodium hydroxide (to produce hydroxy-cancrinite[18]) or lower temperatures (ca. 100°C) and a reaction mixture which contains salts such as sodium nitrate, chromate or molybdate which are occluded in the framework[19]. The structure of cancrinite is based on the 11-hedral cancrinite cage. The cancrinite cage and the way in which the cages are linked together can be seen in

Fig. 3.2

3.2a Cancrinite



3.2b Gismondine

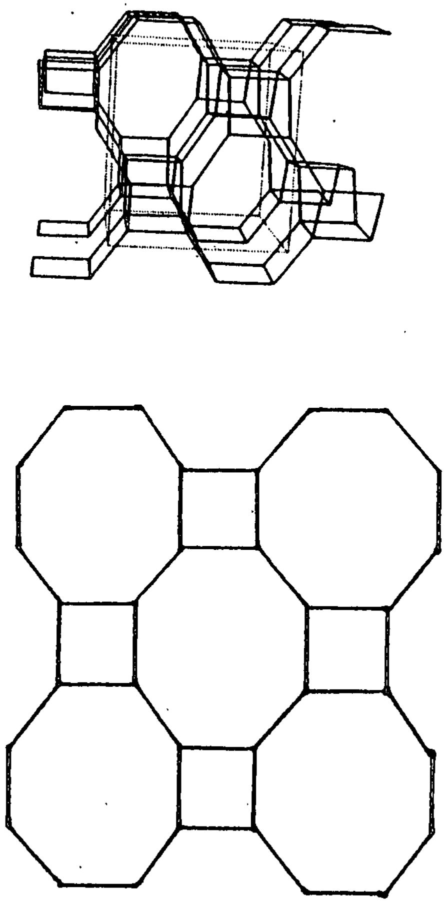


fig. 3.2a which also includes a schematic view of the main channel which is bounded by puckered twelve-membered rings.

The results of reactions HEX R1 to HEX R59 given in table 3.2 will be discussed in two parts:-

Part 1 (section 3.3.2)

This is concerned with the way in which changes in reaction composition affect the reactivity of the system. The reactivity was determined by comparing the quantity and type of material(s) obtained from reactions of different compositions. The combination of the amount and type of material allows relative reactivities to be determined. An example of this can be seen in the samples after 1 day of reactions HEX R1, R15 and R30 in which as the water content is increased the reactions produce zeolite X, trace zeolite X and amorphous. So that as the water content is increased the system becomes less reactive.

Part 2 (section 3.3.3)

This deals with how changes in reaction composition affect the type of material produced.

3.3.2 EFFECT OF REACTION COMPOSITION ON REACTIVITY

The effect of increasing the water content (H_2O/SiO_2 ratio) can be seen by looking at the columns in table 3.3. From top to bottom the H_2O/SiO_2 ratio increases from 40/1 to 100/1. Tables 3.5 and 3.6 also show the effect of increasing the water content, in the systems of compositions:

TABLE 3.5 - RELATION BETWEEN PRODUCTS AND WATER CONTENT FOR REACTIONS OF COMPOSITION: $5SiO_2 - Al_2O_3 - 5(Na_2O) + HEX\ O)\ xH_2O$

x = 200

$Na_2O/(Na_2O+HEX\ O)$	24	72	168
1.0	X+P1	X+P2	X+P2
0.8	X+P1	X+P2	X+P2
0.6	X+P1	P2+X	P2+X
0.4			
0.2	Am	P1	P1+P2

x = 300

$Na_2O/(Na_2O+HEX\ O)$	24	72	168
1.0	X	X+P2	P2+X
0.8	X	X+P2	P2+X
0.6	(X)[a]	X+P1	X+P2
0.4			
0.2	Am	(P1)	Am

x = 500

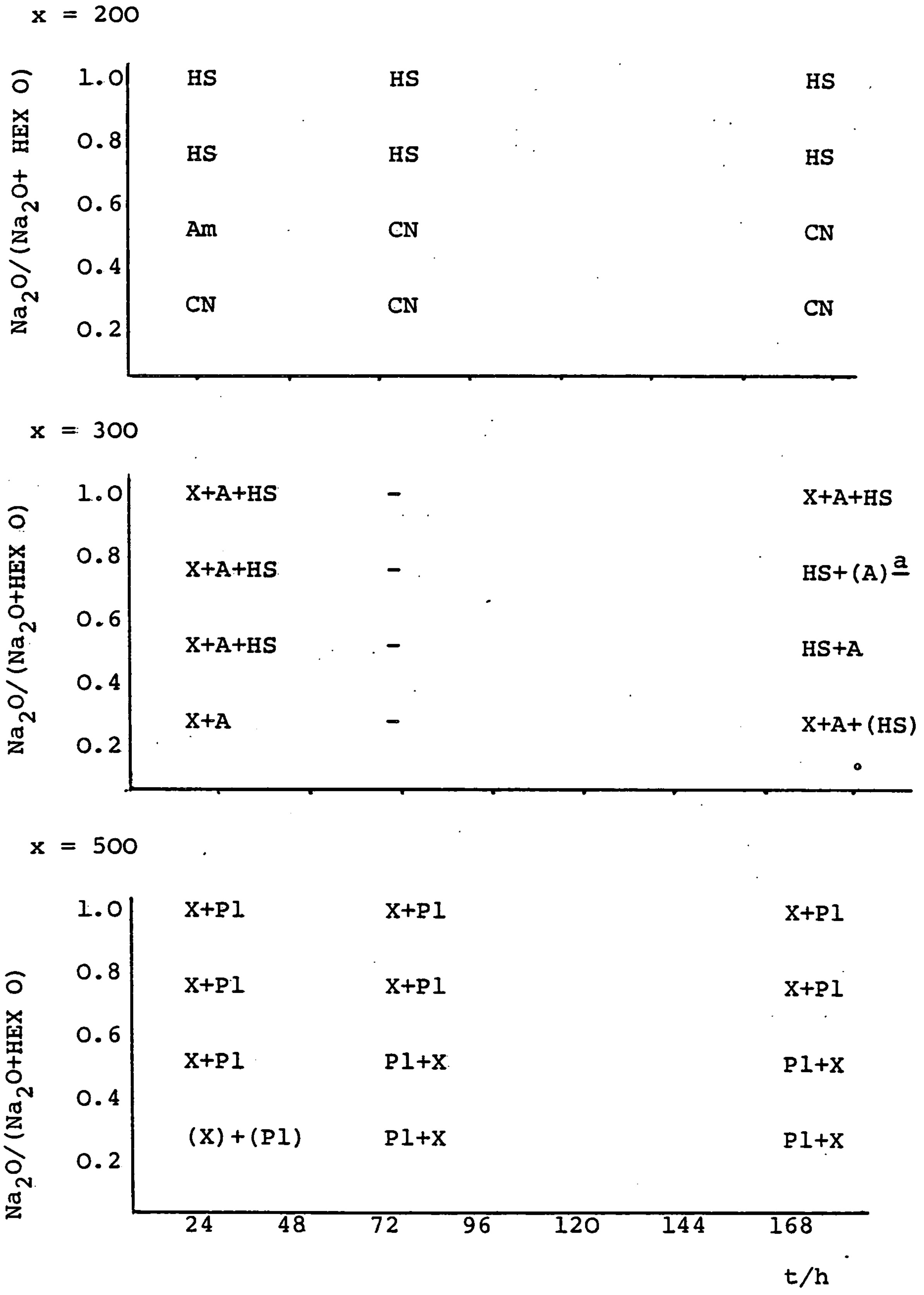
$Na_2O/(Na_2O+HEX\ O)$	24	72	168
1.0	X	X+P2	X+P2
0.8	X	X+P1	X+P2
0.6	(X)	X	X+P2
0.4			
0.2	Am	Am	Am

24 48 72 96 120 144 168

t/h

[a] Letters in parenthesis represent trace amounts.

TABLE 3.6 - RELATION BETWEEN PRODUCTS AND WATER CONTENT FOR REACTIONS OF COMPOSITION: $5SiO_2 - Al_2O_3 - 10(Na_2O + HEX\ O)\ xH_2O$



[a] Letters in parenthesis represent trace amounts

$5(Na_2O + HEX\ O) - 5SiO_2 - Al_2O_3 - xH_2O$ Table 3.5

$10(Na_2O + HEX\ O) - 5SiO_2 - Al_2O_3 - xH_2O$ Table 3.6

It can be seen from table 3.5 that as the quantity of water in the reaction mixture is increased then the systems become less reactive. So that reactions which produced zeolites X and P_1 after 1 day with x = 200, produced only zeolite X or a trace amount of zeolite X, when the water content was increased to x = 300 and 500. Furthermore the low sodium compositions which gave zeolite P_1 or $P_1 + P_2$ gave only traces of zeolite P or even failed to crystallise, at all, when the water content was increased. In table 3.6 the reactivity of the system can be seen to decrease as the water content increased. For reaction mixtures with H_2O/SiO_2 ratio of 40/1 sodalite and cancrinite were the only products formed, but, as the water content was increased to H_2O/SiO_2 ratio of 60/1 then zeolites X and A were formed in addition to sodalite. In the reactions with H_2O/SiO_2 ratios of 100/1 then only X and P were formed. It is believed that the effect of the water content on reactivity is due to the change in concentration of the reactants in particular the concentration of the bases (i.e. changes in pH).

Changes in the base/Al_2O_3 ratio $[(Na_2O + HEX\ O)/Al_2O_3]$ also effect the reactivity of the system. The effect of varying the base/Al_2O_3 ratio can be seen from examination of the columns in table 3.2 each of which has a different ratio of base/SiO_2. This is exemplified in tables 3.7 and 3.8 which show

TABLE 3.7 - EFFECT OF A CHANGE IN THE BASE/SiO_2 RATIO ON REACTIVITY

(Na_2O+HEX O)/SiO_2	Na_2O/(Na_2O+HEX O)	24	48	72	96	120	144	168
15	1.0	A+X+(HS)		X+A+(HS)				HS+X+(A)
	0.8	HS+(A+X)		HS				HS
	0.6	HS		HS				HS
	0.4							
	0.2	A+HS		HS				HS
10	1.0	X+(P1)		X+P1				X+P1
	0.8	X+(P1)		X+P1				X+P1
	0.6	X+P1		P1+X				P1+X
	0.4							
	0.2	(X)+(P1)		P1+X				P1+X
5	1.0	X		X+P2				X+P2
	0.8	(X)		X+P1				X+P2
	0.6	Am		X				X+P2
	0.4							
	0.2	Am		Am				Am
3	1.0	Am		(X)				X+P1
	0.8	Am		(X)				X+P1
	0.6	Am		Am				(X)
	0.4							
	0.2	-		-				-

t/h

TABLE 3.8 - EFFECT OF A CHANGE IN THE BASE/SiO_2 RATIO ON REACTIVITY

$(Na_2O+HEX\ O)/SiO_2$	$Na_2O/(Na_2O+HEX\ O)$	24	48	72	96	120	144	168
15	1.0	HS		HS				HS
	0.8	HS		HS				HS
	0.6							
	0.4	CN		CN				CN
	0.2	CN		CN				CN
10	1.0	HS		HS				HS
	0.8	HS		HS				HS
	0.6							
	0.4	Am		CN				CN
	0.2	CN		CN				CN
5	1.0	X+P1		X+P2				X+P2
	0.8	X+P1		X+P2				X+P2
	0.6							
	0.4	X+P1		P2+X				P2
	0.2	Am		P2				P1+P2
3	1.0	X		X+P1				P1+P2
	0.8	(X)		P1+X				P1+P2
	0.6							
	0.4	Am		Am				P1
	0.2	-		-				-

t/h

the results for a series of reactions with different ratios of base/Al_2O_3. It is important that reactions vary only on the ratio of base/Al_2O_3 and that in particular the ratio of $Na_2O/(Na_2O + HEX\ O)$ is kept constant. It can be seen from table 3.7 that as the ratio of base/Al_2O_3 decreases from 15/1 to 3/1 then the reactions produced zeolites A + X and a trace amount of sodalite after 1 day, then zeolites X and P_1, then a trace amount of zeolite X and finally only amorphous material with a base/Al_2O_3 ratio of 3/1 after similar lengths of time. Thus as the base/Al_2O_3 ratio increases the reactivity increases. Table 3.8 shows a changeover in the products obtained similar to that seen in table 3.6. In table 3.8 reactions which produced zeolites X and P with base/Al_2O_3 ratio of 3/1 and 5/1, produced sodalite (and cancrinite) when the ratio of base/Al_2O_3 rates increased to 10/1 and 15/1. The changeover from zeolites X and X + P to sodalite (and cancrinite) is similar to that which was seen in table 3.6. The similarity of the effects of varying the base/Al_2O_3 ratio and the $H_2O/Al2O_3$ ratio leads to a 'diagonal correlation' in table 3.2. Thus both an increase in the base/SiO_2 and a decrease in the H_2O/SiO_2 ratio increase the reactivity of the system, so that if the base/SiO_2 and the H_2O/SiO_2 ratios are both increased their effects should cancel each other to some extent. Indeed, this can be seen in table 3.9, where reactions HEX R1 to R3, HEX R18 to R21 and HEX R37 to R40 yield similar products, although reactions HEX R37 to R40 appear to be a little more reactive than the others in the 'diagonal'. This could

TABLE 3.9 - DIAGONAL CORRELATION FOUND WHEN BOTH THE RATIOS OF BASE/SiO_2 AND H_2O/SiO_2 ARE INCREASED

SiO_2/Al_2O_3 = 5/1 $(Na_2O+HEX\ O)/Al_2O_3$ Na_2O/HEX O	3			5				10			
	1/0	7/3	5/5	1/0	7/3	5/5	3/7	1/0	7/3	5/5	3/7
H_2O/SiO_2 = 40/1											
Run No : HEX R	1	2	3								
S1 1d	X	(X)	Am								
S2 3d	X+P1	P1+X	Am								
S3 7d	P1+P2	P1+P2	P1								
H_2O/SiO_2 = 60/1											
Run No : HEX R				18	19	20	21				
S1 1d				X	X	(X)	Am				
S2 3d				X+P2	X+P2	X+P1	(P1)				
S3 7d				P2+X	P2+X	P1+X	P1				
H_2O/SiO_2 = 100/1											
Run No : HEX R								37	38	39	40
S1 1d								X+(P1)	X+(P1)	X+P1	(X)+(P1)
S2 3d								X+P1	X+P1	P1+X	P1+X
S3 7d								X+P1	X+P1	P1+X	P1+X

be modified however by increasing the water content since if the H_2O/base ratio is examined it can be seen that in HEX R37 to R40 this ratio is lower than in HEX R1 to R3 or HEX R18 to R21. This correlation between reactivity and the concentrations of the bases present (pH) is very good considering that the concentration of the other reagents and the viscosity of the system are being changed quite markedly. The effect of pH (or concentration of the bases) on the reactivity of the system is probably related to the dissolution or rearrangement of the alumino-silicate gel which requires alkaline conditions.

The effect of changing the SiO_2/Al_2O_3 ratio can be seen in table 3.2 and by comparing tables 3.3 and 3.4. This increase in the ratio of SiO_2/Al_2O_3 has a profound effect on the reactivity of the system. Although this increase in the SiO_2/Al_2O_3 ratio decreases the reactivity of the system, two things should be noted:-

1) The SiO_2/Al_2O_3 has been trebled, from 5/1 to 15/1.
2) The 'constant' feature of the concentration of the alkali is the ratio of the base/Al_2O_3 not base/SiO_2.

Bearing 2) in mind it can be seen that while reactions HEX R45 to R51 did not crystallise, HEX R52 to R59 yielded similar products, in a similar time, to those formed in reactions HEX R1 to R7. There are obviously differences for example zeolite Y is found instead of zeolite X[a] and the reactivities are slightly different

[a] see section 3.3.3

but the fact that there is a similarity is most interesting. Previously it was mentioned that at a specific ratio of SiO_2/Al_2O_3 the important ratio (as far as reactivity is concerned) is the ratio of H_2O/base. In this case the ratio of base/H_2O is kept constant and the important feature is the ratio of base/SiO_2. Reactions HEX R1 to R3 (base/SiO_2 = 3/5) should be compared with reactions HEX R52 to R55 (base/SiO_2 ratio = 2/3) and reactions HEX R4 to R7 (base/SiO_2 = 1/1) with reactions HEX R56 to R59 (base/SiO_2 = 1/1). Such a comparison can be seen in table 3.10. One interesting feature is that in reactions with SiO_2/Al_2O_3 ratio of 5/1 (HEX R1-R7) the conversion of zeolite X to zeolite P (P_1 and P_2) proceeds much faster than in reactions with a SiO_2/Al_2O_3 ratio of 15/1 (HEX R52 to R59). It is suspected that this is due to the difficulty in forming zeolite P with a higher SiO_2/Al_2O_3 ratio.

From left to right within each of the four columns in table 3.2 the ratio of Na_2O/HEX O is varied from 1/0 to 3/7[a]. From examination of the columns in table 3.2 it can be seen that the replacement of Na_2O by HEX O tends to reduce the reactivity of the system. Thus in most reactions, those which produced cancrinite being notable exceptions (see section 3.3.3) the hexamethonium acts only as a source of hydroxide ions. This is similar to the reported formation of LOSOD[20]

[a] Except in the case when (Na_2O + HEX O)/Al_2O_3 ratio = 3/1, see section 3.3.1.

TABLE 3.10 Comparison of reactions with similar base/SiO_2 ratios.

$5\ SiO_2 - Al_2O_3 - 200\ H_2O$

$(Na_2O+HEX\ O)/SiO_2 = 3/5$

$Na_2O/(Na_2O+HEX\ O)$: 1.0, 0.8, 0.6, 0.4, 0.2

t/h	24	72	168
	X	X+P1	P1+P2
	(X)	P1+X	P1+P2
	Am	Am	P1

$(Na_2O+HEX\ O)/SiO_2 = 1/1$

t/h	24	72	168
	X+P1	X+P2	X+P2
	X+P2	X+P2	X+P2
	X+P1	P2+(X)	P2
	Am	P1	P1+P2

$15\ SiO_2 - Al_2O_3 - 600\ H_2O$

$(Na_2O+HEX\ O)/SiO_2 = 2/3$

$Na_2O/(Na_2O+HEX\ O)$: 1.0, 0.8, 0.6, 0.4, 0.2

t/h	24	72	168
	Y	Y+P2	Y+P2
	Y	Y+P2	Y+P2
	(Y)	Y+P1	Y+P1+P2
	Am	P1	P1+P2

$(Na_2O+HEX\ O)/SiO_2 = 1/1$

t/h	24	72	168
	Y+P2	Y+P2	Y+P2
	Y+P2	Y+P2	Y+P2
	Y+P1	Y+P2	Y+P2
	Y+P1	Y+P2	Y+P2

t/h: 24, 48, 72, 96, 120, 144, 168

which was said to proceed using the bulky quaternary ammonium species azonia-spiro[4.4]nonane only as a source of hydroxide ions. However the sodium content in the formation of LOSOD was very low (hence the name), approximately the same as the aluminium content. None of the quaternary ammonium compound was incorporated into the structure. In this study the organic content of species other than sodalite and cancrinite was not measured[a]. In the formation of LOSOD the quaternary ammonium species was too large to be incorporated into the structure, however, in this study, there is little doubt that hexamethonium could have been incorporated into zeolites X, Y and A. Although the ratio of base/SiO_2 is very important, the sodium content of the base is also important. There are several aspects of this. If one compares reactions HEX R15 and HEX R20 there are obvious similarities in their reactivities. The Na_2O content of HEX R15 is 3 and in HEX R20 it is 2.5 but in HEX R20 there are 2.5 'extra' hydroxide ions contributed by the hexamethonium but this does not have a major effect on the reactivity, except that zeolite P is formed. In HEX R17 a reaction which was amorphous after 3 days, produced zeolite X after 7 days, when one would expect P. However HEX R21 did produce zeolite P after a similar length of time. It is believed that the formation of zeolite P requires a higher concentration of base than zeolite X.

[a] see section 3.3.3

3.3.3 EFFECT OF REACTION COMPOSITION ON THE PRODUCT OBTAINED

The reaction parameters which when varied produced a change in the nature of the products formed, were:

SiO_2/Al_2O_3

$(Na_2O + HEX\ O)/H_2O$

$Na_2O/HEX\ O$

When the ratio of SiO_2/Al_2O_3 was changed from 5/1 to 15/1 the major effect on the type of product obtained was that zeolite Y was formed instead of zeolite X. Both zeolites X and Y have the same framework topology and differ only in the ratio of SiO_2/Al_2O_3 in the framework. Differences between X and Y are associated with the difference in lattice composition and stem from the change in the average T-O-T (where T is a tetrahedral atom, Si or Al) bond angle and length as aluminium atoms are replaced by silicon atoms. This results in a change in the unit-cell parameter a (there is only one cell constant since faujasite has cubic symmetry). Breck[21] first pointed out that for the cubic unit-cell the cell constant a varies with changes in the SiO_2/Al_2O_3 ratio and he stated that measurement of a could be used to determine the SiO_2/Al_2O_3 ratio of the framework. Wright et al[22] pointed out that within the compositional range studied by them (SiO_2/Al_2O_3 mole ratio of 2.44 to 4.93) a changes linearly with the change in the SiO_2/Al_2O_3 ratio.

Consequently they could find no reason to divide the compositional range at 3.0 and assign species with particular values of SiO_2/Al_2O_3 as being either zeolite X (SiO_2/Al_2O_3 ratio less than 3.0) or zeolite Y (SiO_2/Al_2O_3 greater than 3.0). Therefore they proposed that a uniform nomenclature whereby sodium zeolite X with a framework composition of 2.44 should be called: Faujasite, Na (2.44). More recent publications would not appear to have used the nomenclature proposed by Wright et al. Several workers[22,23,24] have reported a correlation between the cell constant a and the SiO_2/Al_2O_3 ratio of the framework. The data obtained by these workers was reviewed by Smith[25] who concluded that, because of conflicting reports, "The likelihood of a systematic experimental bias between the techniques for cell dimension measurement could only be tested by exchange of samples between various workers". In this study, it was decided to use the equation developed by Breck and Flanigen[24], equation 3.1.

$$R = \text{Si/Al ratio} = [(192 \times .00868)/(a - 24.191)] - 1 \quad (3.1)$$

In 3.1, a is the cell constant calculated from equation 3.2

$$a = [d^2(h^2 + k^2 + \ell^2)]^{\frac{1}{2}} \quad (3.2)$$

Using these equations the Si/Al ratio was determined for two samples from HEX R18 Si and HEX R53 Si. The lines in the powder diffraction patterns used in the calculation[26] were of the planes:

5	3	3			
6	4	2			
5	5	5,	7	5	1
11	9	3			
11	11	1			

The results can be seen in table 3.11. The results show that zeolite X was formed in HEX R18 and zeolite Y in HEX R53. It is assumed that the other faujasite samples in section A were zeolite X and those in section B were zeolite Y.

The formation of sodalite as the ratio of (Na_2O + HEX O)/H_2O was increased is not thought to have been an effect on the product type but a reflection on the reactivity of the system (see section 3.3.2). However there were differences between the sodalite samples formed. These were differences in their powder X-ray diffraction patterns. Such differences were noted by Barrer and White[18] who reported "... the X-ray powder reflections were extremely similar to those of natural sodalite .... yet small regular shifts in spacings occur". Naturally occurring sodalite is not a zeolite but a feldspathoid since it occurs with occluded sodium chloride which cannot be removed. Similarly hydroxy-sodalite, in which the occluded species is sodium hydroxide, is non-zeolitic. Apart from sodalite hydrate the only zeolitic forms of sodalite are those prepared with salts which can be removed by calcination. Sodalite has been synthesised in systems containing organic species, several times[4,2,3].

TABLE 3.11 CALCULATION OF THE SiO_2/Al_2O_3 RATIO OF FAUJASITE SAMPLES FROM THEIR CELL CONSTANTS

HEX R18 S_1

d/Å	a/Å	Average a/Å	SiO_2/Al_2O_3 (CALC)
1.595	24.86		
1.712	24.87		
2.871	24.86	24.86	2.98
3.319	24.84		
3.789	24.85		

HEX R53 S_1

d/Å	a/Å	Average/Å	SiO_2/Al_2O_3 (CALC)
1.590	24.79		
1.707	24.76		
2.863	24.79	24.79	3.56
3.313	24.79		
3.782	24.80		

Aiello and Barrer[3] reported that after removal of the organic species (tetramethylammonium) by calcination, the sodalite re-sorbed 17.9% w/w water[a]. Aiello and Barrer also stated that there was room for only one tetramethylammonium cation per 14-hedral cage. From the structure of hexamethonium it is difficult to see how it could be occluded into the zeolite framework. However, as mentioned in section 3.2.1, under alkaline conditions a strong smell of amines was noticed, produced by the Hoffmann degradation of hexamethonium. The trimethylamine so produced could be easily incorporated into the structure.

Whereas the variation in the cell parameter of faujasites is associated primarily with changes in the framework composition, in sodalites, the unit-cell parameter depends on the nature of the occluded species. Taylor[27] reported the relationship between cell-parameters and occluded species for a series of sodalites and sodalite-type species (noseans and hauynes) with Si/Al ratios of 1/1. Table 3.12 gives the cell parameters for a series of sodalite samples prepared both in this work and by other workers. Sodalite has cubic symmetry thus the cell constant a is calculated using equation 3.2. The lines used in the calculations were:

---

[a] On the basis of 4 water molecules per sodalite cage, the sample should have taken up 19.8% w/w.

2	2	2
3	2	1
3	3	0
4	1	1
4	3	1

These lines were chosen because low angle lines ($\theta = 14$ to 25) are very broad and have a large error associated with their positions. Although the error is smallest for $\theta = 90^{\circ}$ lines with θ larger than 60° tend to be quite faint. Consequently the lines chosen represent a compromise between intensity and accuracy. From table 3.12 it can be seen that the results obtained in this work are in close agreement with those obtained by other workers. Differences in the cell constant for the two 'sodium only' reactions, HEX R8 and HEX R12 can be attributed to both samples containing different amounts of sodium hydroxide. As the hexamethonium content of the reaction mixture increases the cell constant increases to 8.897, while the cell constant obtained by Barrer et al in systems containing both sodium and an organic cation is 8.92. However the organic content of the sample of sodalite synthesised by Barrer was approximately 16%. Thermal analysis (both tga and dta) of HEX R44 S_2 can be seen in fig. 3.3. Total weight loss was approximately 13%. From the tga curve it is difficult to determine the quantity of organic material in the framework. The dta curve however definitely shows that some organic material

TABLE 3.12 CELL PARAMETERS FOR A SERIES OF SODALITE SAMPLES

SAMPLE	OCCLUDED SPECIES	a/Å
Natural Sodalite[28]	2 Na Cl	8.88
Sodalite Hydrate[28]	8 H_2O	8.87
Hydroxy Sodalite	2 NaOH	8.86[a]
N - HS (Barrer and Denny[2])	Me_xN, Na[b]	8.93
N - HS (Aiello and Barrer[3])	Me_4N, Na	8.92
N - HS (Baerlocher and Meier[4])	Me_4N	8.975
<u>This work</u>:		
HEX R8	10 Na_2O[c]	8.875
HEX R12	15 Na_2O	8.868
HEX R13	10.5 Na_2O - 4.5 HEX O	8.876
HEX R9	7 Na_2O - 3 HEX O	8.883
HEX R44	4.5 Na_2O - 11.5 HEX O	8.897

[a] cell constant can vary depending on the quantity of NaOH and H_2O in crystals.

[b] Me_xN, x can be 1, 2, 3, 4.

[c] this is not the occluded species but refers to the composition of the reaction.

Fig. 3.3 Tga and dta for HEX R44 S_2

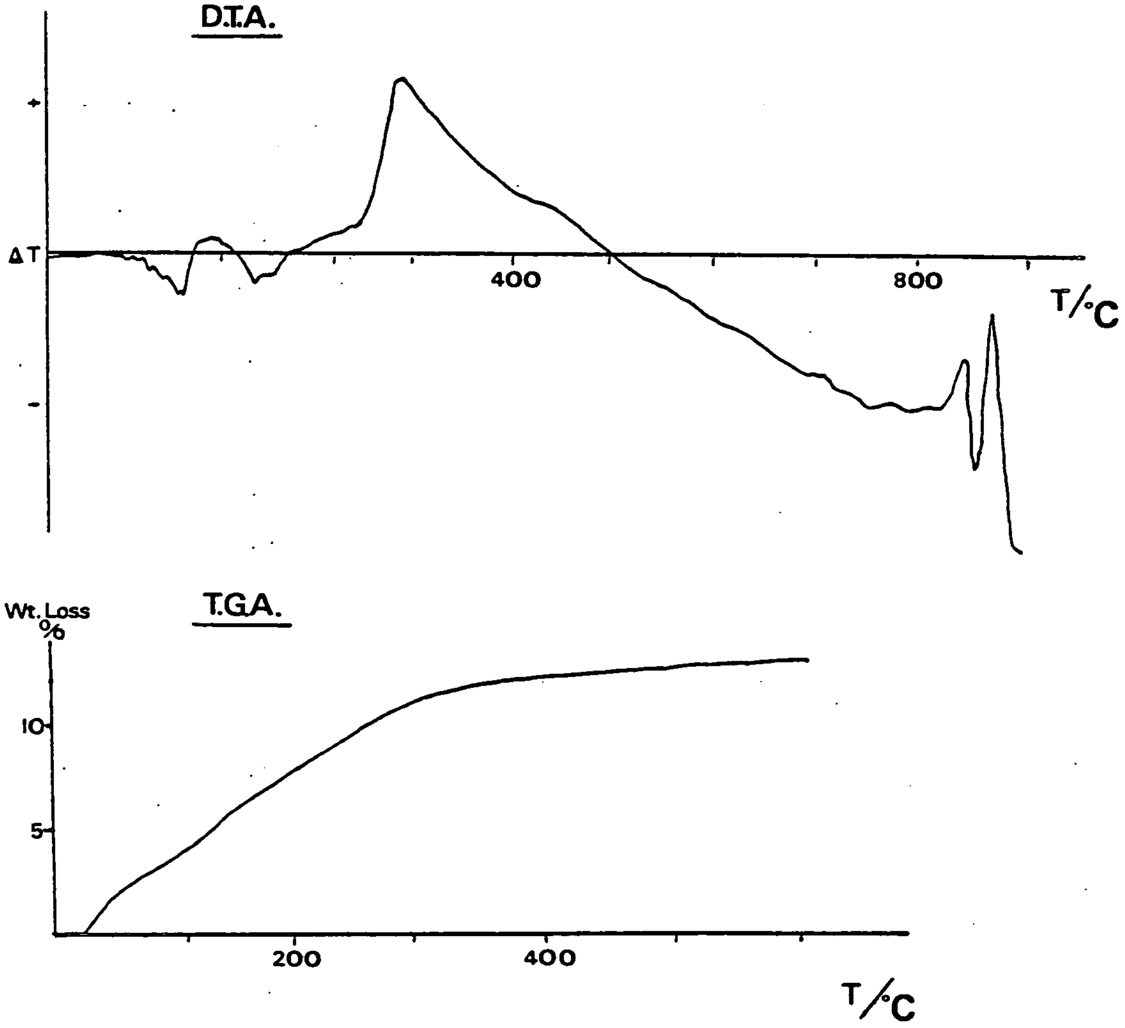


Table 3.13 Carbon, hydrogen and nitrogen analysis for HEX R44 S_2

Sample	% C	% N	% H	C/N
HEX R44 S_2	1.49	0.08	1.10	22/1

is present. The first two small endotherms are associated with the loss of water. The exotherm at about 300°C is believed to be associated with decomposition of occluded organic species since it occurs in a similar position to that noted for EU-1 (see Chapter 4). The broad endotherm and two sharp peaks at approximately 850°C are associated with the destruction of the lattice. Powder X-ray diffraction of the sample after dta showed that the sodalite had converted to nepheline (a sodium alumino-silicate with a tridymite type framework). The results of carbon, hydrogen and nitrogen analysis (C, H and N) can be seen in table 3.13. The results are inconclusive in that although they show that some organic material is present the C/N ratio of 22/1 does not allow its identification, however, the results may be inaccurate particularly with such a low level of organic material.

The formation of cancrinite (table 3.2) is a particularly significant result since all the other products are formed in both the 'sodium only' reactions and in the reactions containing hexamethonium. Cancrinite, however, requires the presence of hexamethonium and indeed is only formed when at least half the hydroxide is supplied by hexamethonium. According to Rollmann's[28] definition of a "template", hexamethonium was acting as a template in the formation of cancrinite. However the action of azonia-spiro[4,4]nonane in the formation of LOSOD[20], in which the quaternary ammonium species acts only as a source of hydroxide ions, could also be regarded as the action of a template (according to Rollmann). In

LOSOD the organic cation is not incorporated into the framework. Analysis (C, H and N) of the products of reactions HEX R10, HEX R11 and HEX R14 can be seen in table 3.14. It can be seen that the reaction in which the ratio of Na_2O/HEX O was lowest (HEX R11) contained the most organic material. In addition as the organic content increases then the C/N ratio decreases to 9.1, in hexamethonium the C/N ratio is 6/1. The results of tga of HEX R11 S_3 can be seen in table 3.15. It can be seen that the calcined sample of cancrinite could be a useful sorbent since it re-sorbed 6.5% water from the atmosphere in 2 hours.

Fig. 3.4 contains dta and tga of HEX R11 S_4. The dta of the cancrinite sample is very similar to that of sodalite (fig. 3.1). The initial endotherm at about 100°C is associated with water loss. The two exotherms at about 300°C and 500°C correspond to the loss of the organic material. Comparison of fig. 3.4 with the dta of a sample of EU-1 (Chapter 4) shows that the hexamethonium decomposes in two stages. The two sharp peaks at about 800°C are associated with the lattice collapse. Subsequent examination of the sample by powder X-ray diffraction showed that the sample had transformed to nepheline as had the sample of sodalite. Barrer[19] reported the transformation of cancrinite to nepheline at high temperatures.

Although the synthesis of cancrinite using hexamethonium hydroxide illustrated a possible route to a potentially useful sorbent the expense associated with the use of hexamethonium hydroxide is likely to be

TABLE 3.14

C, H and N analysis of cancrinite samples

Sample	% C	% N	% H	C/N[a]	% loss
HEX R10 S_3	2.24	0.04	1.05	64/1	15.0
HEX R11 S_3	4.27	0.55	1.38	9.1/1	17.4
HEX R14 S_4	1.76	0.15	0.68	13.7/1	10.8

[a] C/N for hexamethonium is 6/1.

TABLE 3.15

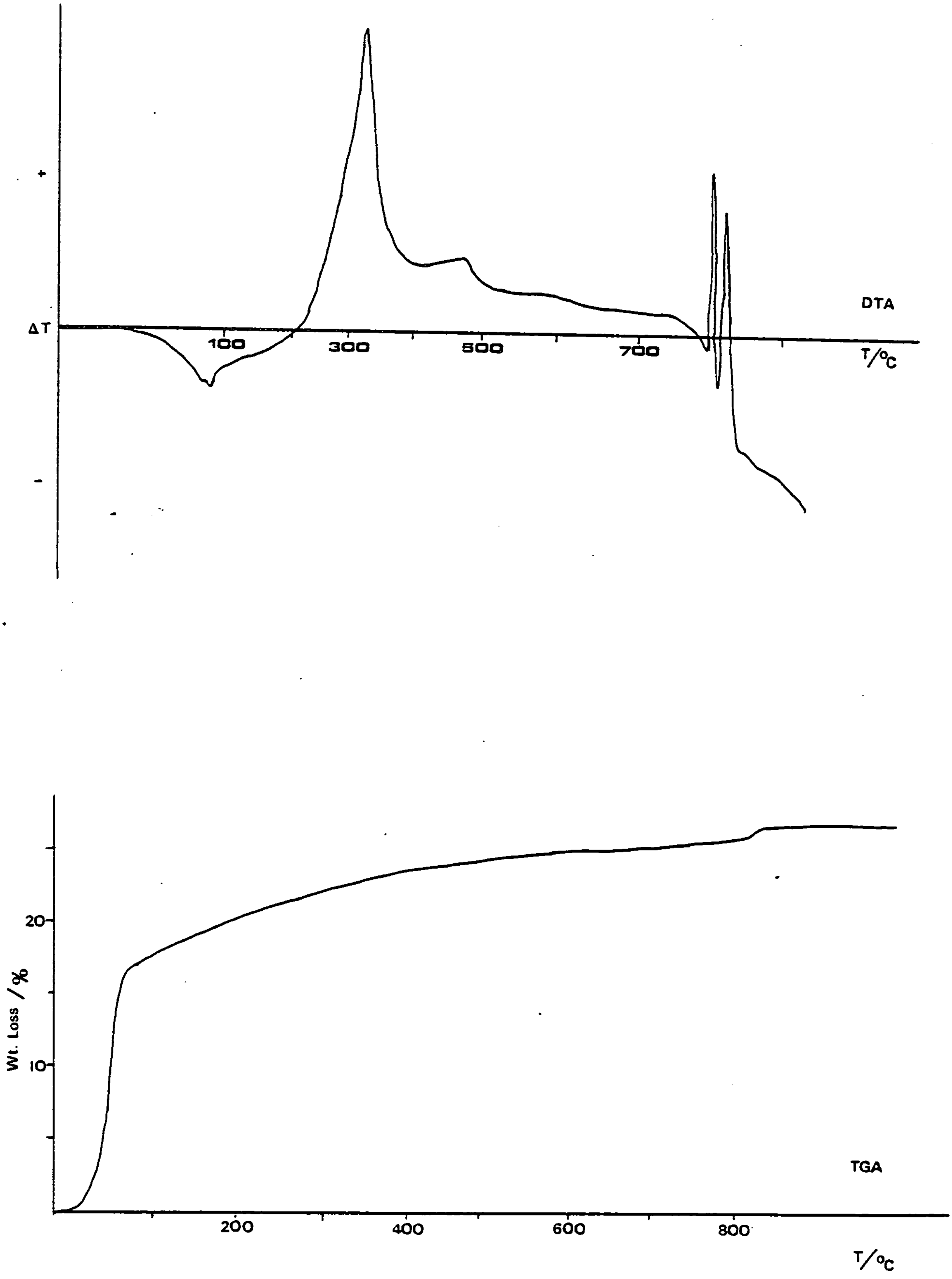
Tga[a] of HEX R11 S_3

Run	Temperature/°C	Weight loss/%	Weight Gain in Air/%
86	560	16±1	-
	730	16±1	-
	20	-	2.5 (1 hour)
87	350	13±1	-
	450	14±1	-
	20	-	6.5 (2 hours)

[a] Heating rate; 10°C/min. Atmosphere : dry air

Flow rate : 4.5 ml/min

Fig. 3.4 Dta and tga for HEX R11 S_4



prohibative. Consequently an attempt was made to prepare cancrinite using hexamethonium bromide and tetramethylammonium hydroxide (TMA OH). The results can be seen in table 3.16. From HEX R14b it can be seen that the replacement of $HEX(OH)_2$ by $HEX(Br_2)$ leads to the formation of sodalite. However, the production of a cancrinite like phase when the original concentration of hydroxide is restored (by sodium hydroxide) and $HEX(Br_2)$ added, suggests that both the pH and hexamethonium are necessary to form cancrinite. HEX R10b illustrates that a cancrinite like phase can be prepared by another quaternary, TMA.

The nature of the cancrinite-type phase formed in HEX R28, R29, R14c and R10b has not been resolved. Plate 3.1 shows the Guinier-Hagg films of samples of cancrinite (HEX R14a), sodalite (HEX R44) and the product from HEX R29. The variation can be seen to occur at the high angle lines. It seems likely that these variations are caused by some change in crystal symmetry.

Problems with the sorption apparatus (described in Chapter 2) together with a lack of time meant that a sorption study of cancrinite was not carried out. It is believed that such a study on a calcined sample of cancrinite is necessary to determine if the cancrinite produced was free from stacking faults and occluded salts both of which have restricted sorption by samples previously.

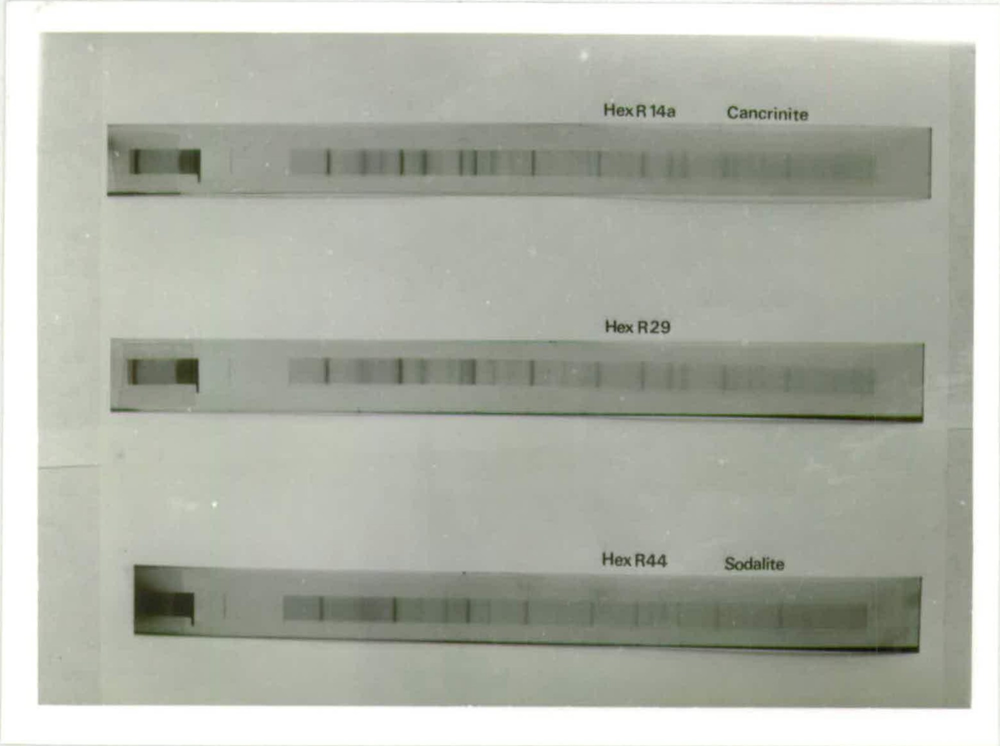
TABLE 3.16 SYNTHESIS OF CANCRINITE WITHOUT USING HEXAMETHONIUM HYDROXIDE[a]

Reaction No.	Composition	Time	Product
14b	5 SiO_2 - Al_2O_3 - 200 H_2O - 7.5 Na_2O - 7.5 HEX Br_2	S_1 1 day S_2 4 days S_3 7 days	HS
14c	5 SiO_2 - Al_2O_3 - 200 H_2O - 15 Na_2O - 7.5 HEX Br_2	S_1 3 days S_2 7 days	CN* [b]
10b	5 SiO_2 - Al_2O_3 - 200 H_2O - 5 Na_2O - 5 $(TMA)_2O$	S_1 1 day S_3 3 days S_4 10 days	CN* [b]

[a] Reaction conditions and preparation were the same as those outlined in section 3.2.2.

[b] This species is not identical to the cancrinite formed in HEX R11 etc., but is similar to the species in HEX R28 and HEX R29 all of which are similar to sodalite - see text.

PLATE 3.1



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CHAPTER 4

HIGH TEMPERATURE ZEOLITE SYNTHESIS

4.1 INTRODUCTION

Chapter 3 dealt with zeolite crystallisation, at 95°C, from the system

Na_2O - HEX O - SiO_2 - Al_2O_3 - H_2O
where HEX = hexamethonium = $[(CH_3)_3N-(CH_2)_6-N(CH_3)_3]^{2+}$

Table 3.1 in chapter 3 showed the compositions that were planned in the above system. However only about 25% of the reactions were carried out and none with SiO_2/Al_2O_3 ratio greater than 15/1. This was because the reaction mixtures became noticeably less reactive as the SiO_2/Al_2O_3 ratio was increased. It was reasoned that compositions with SiO_2/Al_2O_3 ratio of 30/1 and 50/1 would have been even less reactive[a] and therefore it was decided to carry out these reactions at higher temperatures using autoclaves. Further considerations led to the choice of 60/1 for the SiO_2/Al_2O_3 ratio and the use of HEX Br_2 instead of $HEX(OH)_2$. Thus it was decided not to carry out the systematic study set out in Table 3.1.

[a] Obviously this is not necessarily the case, since reactions with a different SiO_2/Al_2O_3 ratio could produce different products which could crystallise quite quickly. However investigations into the synthesis of ZSM-5 and FU-1[1] suggested that crystallisation at 95°C could take several weeks.

4.2 EXPERIMENTAL

4.2.1 MATERIALS

Reagent	Source
Sodium hydroxide	B.D.H. Ltd.
Potassium hydroxide	B.D.H. Ltd.
Ammonia (0.88)	Asschem Ltd.
Sodium aluminate	Nalfloc[a]
Alumina trihydrate ($Al_2O_3.3H_2O$)	BACO Ltd.
Silica:	
Cab-O-sil M5	B.D.H. Ltd.
KS300	Akzo Ltd.[b]
Colloidal silica	Monsanto (Syton x30)[c]
Zeolites:	
13X	B.D.H. Ltd.
Mordenite	[d]
Sodium bromide	Fisons Ltd.
Tetramethylammonium chloride	B.D.H. Ltd.
Tetramethylammonium bromide	B.D.H. Ltd.
Cetyltrimethylammonium bromide	B.D.H. Ltd.
Hexamethonium bromide	Fluorochem Ltd; Koch-Light Ltd.
Hexamethonium chloride	Fluorochem Ltd.
Propyltrimethylammonium bromide	[e]
Decamethonium bromide	Fluorochem Ltd.
Pyrrolidine	B.D.H. Ltd.
Hexamethylenediamine	B.D.H. Ltd.
Ethylenediamine	B.D.H. Ltd.
Hexanediol	Aldrich Ltd.
Decanediol	Aldrich Ltd.
Sodium adipate	[f]

[a] Analysis by I.C.I. Agricultural Division:
$1.25\ Na_2O.Al_2O_3.2H_2O$. Supplied by I.C.I. Agricultural Div.

[b] Analysis by I.C.I. Agricultural Division:
SiO_2-0.0116 Na_2O-0.00128 Al_2O_3-0.314 H_2O.

[c] Approximately 30% silica.

[d] Supplied as H-zeolon by I.C.I. Agricultural Division.

[e] See text for synthesis.

[f] Prepared from adipic acid and sodium hydroxide.

Propyltrimethylammonium bromide was synthesised according to the method of Smith and Franck[2]. The only modification to their procedure was that the reaction mixture was held in a round bottomed flask fitted with a cold finger condenser filled with dry-ice at -78°C rather than a stopper.

4.2.2 PROCEDURE

Reactions were carried out at two locations, at I.C.I. Ltd., Agricultural Division, Billingham and at Edinburgh University. Reactions were based on the 'standard' composition:

$$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

However the component ratios SiO_2/Al_2O_3, Na_2O/H_2O etc. were varied as was the choice of cations. For the reactions carried out at I.C.I. which used KS300[a] as the silica source, the procedure was as follows: the required sodium hydroxide was weighed into beaker A. Approximately 450 cm^3 of water was added with stirring until the sodium hydroxide had dissolved. The required amount of silica (KS300) was weighed and added with stirring to beaker A. The hexamethonium bromide was then dissolved in about 150 cm^3 water in beaker B. The required amount of sodium aluminate was dissolved in the remaining water

[a] The alumina, water and sodium content of KS300 were taken into account when the reagent quantities were calculated.

in beaker C. The solution in beaker C was then added to beaker A and finally the solution in beaker B was added whilst the resulting mixture was stirred. The gel produced by this procedure was then transferred to the autoclave.

For reactions in which the silica source was cab-o-sil the procedure was as follows: the required amount of sodium aluminate was dissolved in 200 g of water in beaker A. The required sodium hydroxide was dissolved in 400 g of water in beaker B. The required silica was added with stirring to the sodium hydroxide solution. The hexamethonium bromide was dissolved in the remaining water and added to the contents of beaker B. Finally the solution in beaker A was added, with stirring, to the mixture. The gel produced was then transferred to the autoclave.

For reactions carried out in Edinburgh the procedure was as follows: the required water was weighed into beaker A. The sodium hydroxide and sodium aluminate were weighed into beaker B and approximately 200 cm^3 of the water from beaker A were added to beaker B with stirring. The hexamethonium bromide was weighed into beaker C and the remainder of the water in beaker A added with stirring. The silica (cab-o-sil) was weighed into, the now empty, beaker A. The solution in beaker B was added with stirring and then finally the solution in beaker C. The resulting gel was transferred to the reactor[a].

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[a] In most reactions the gel was transferred to the liner of the autoclave. However the liner was later discarded because of corrosion problems and the gel was then transferred directly to the autoclave itself. (Runs HT HEX R150 and R151).

The above procedures although outlined for a particular standard reaction required trivial modification when a different organic species was used[a] or when different ratios of reactants were used. The addition of seed material - see section 4.8 etc. - was carried out after the gel had been transferred to the reactor. The seed material (details of its origin will be given in the appropriate tables and text) was ground finely before addition to the reaction mixture. In reaction HT HEX R14 potassium was used instead of sodium. For this reaction the alumina source was BACO Al_2O_3-$3H_2O$ which could not be dissolved completely in the potassium hydroxide solution. In this case the dispersion of alumina in the potassium hydroxide was treated as though a clear solution had been obtained.

4.2.3 LOW TEMPERATURE REACTIONS

Although this chapter is concerned primarily with zeolite crystallisation at high temperatures (above 100°C) some reactions were carried out at 95°C. Two types of reaction vessels were used.

Stirred reactions were carried out in a 50 cm^3 three necked, round bottomed Quickfit flask type FR500/3S/22P fitted with a reflux condenser and agitated by an electric stirrer (motor speed 150 r.p.m.) fitted with a glass shaft and a teflon paddle. The stirrer gland, supplied by Jencons Ltd. was a simple precision bore glass sleeve within which the glass stirrer rod fitted. The bearing

[a] Some of the organic materials used e.g. cetyltrimethylammonium bromide and decanediol were only slightly soluble at room temperature. In these cases a dispersion was prepared and used as outlined - see text and tables.

surfaces were lubricated with vaseline. The stirring rod was connected to the electric motor's shaft by means of a piece of rubber tubing about 5 cm in length. The connection was sufficiently flexible to prevent the glass stirrer rod from shearing if the assembly was not completely linear. The third port in the three necked flask was fitted with a stopper and was used to obtain samples.

Static reactions were carried out in a 500 cm^3 round bottomed Quickfit flask type FR500/2s fitted with a reflux condenser. To obtain samples the reflux condenser was first removed and replaced by a stopper and the flask was shaken for approximately 15 seconds to ensure that a representative sample could be taken.

The reaction vessels were partly immersed in a water thermostat bath which was maintained at 95^oC by a 'Fi-monitor' control unit. Two types of bath were used, a conventional water bath supplied by Towers and a larger water bath designed by Dr. B.M. Lowe and constructed at the University of Edinburgh. This bath was not as well thermostated as the conventional water bath because of faulty relays on the control unit. Consequently some of the initial reactions carried out in this bath were not reacted continuously at 95^oC. However reactions in which the rate of formation was followed, for example HT HEX R75, were thermostatically controlled at 95^oC.

4.2.4 HIGH TEMPERATURE REACTIONS

The high temperature reactions were carried out in a series of autoclaves at two locations, at Edinburgh University and in the laboratories of I.C.I. Ltd., Agricultural Division, Billingham.

Altogether 23 reactions were carried out at I.C.I., Agricultural Division, using 5 different autoclaves. All of the autoclaves were 1 litre in capacity, 2 were lined with titanium and the rest were lined with stainless steel. One of the 3 stainless steel autoclaves (situated in building 06, bay 2B) was used once only, run HT HEX R64. This autoclave unlike the others was not unbolted, to be cleaned, between runs but instead the autoclave was emptied by opening taps at the top and the bottom of the autoclave. Because the reaction mixture was poured in through the top tap it was essential that only thin mixtures were used. The silica source in HT HEX R64 was colloidal silica. The thermostat fitted to this autoclave differed from the others in that the heater was on continuously and the autoclave temperature was controlled by the flow of cooling water which was in turn controlled by a solenoid valve. The temperature profile of the autoclave[a] was that of a sinusoidal curve with an amplitude of 2°C and a wavelength of several minutes. The autoclave was stirred by a variable speed motor; the stirring speed could be controlled and monitored. Because this autoclave could not be easily cleaned and also because it could only be used with very thin gels it was used for only one reaction.

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[a] An almost continuous print-out was available, points being plotted approximately every 20 s.

The other four autoclaves were located in building L4, bays 11, 12, 13 and 14. The autoclaves were constructed by Autoclave Engineers Ltd. Apart from the difference in the lining materials the autoclaves were very similar to each other. Agitation was by magnetically driven stirrers. The stirring speed could be adjusted but it could not be measured, and so the same setting was used each time for each autoclave. To empty and clean each autoclave the top section (which included the stirrer) was removed. The reaction vessel itself could not be removed. To empty the vessel the slurry was syphoned into a beaker and any solid remaining in the autoclave was removed with a spatula. The autoclaves were cleaned using sodium hydroxide solution, at 150°C for 16 hours. The autoclaves were thermostatically controlled but the control thermocouples were placed in the heating elements rather than the reactor. This led to problems with fine temperature adjustment, long warm-up times[a] and reproducibility. A semi-continuous temperature read-out was available for some of the autoclaves[b] and examination of the traces suggested that the temperature was accurate to ±10°C (although individual reactions may have been more or less accurate).

Sampling from all of the autoclaves was attempted but there were considerable problems associated with the length and bore of the stainless steel tubing from the reactor to the sampling valve. This stainless steel line was constructed for hydrogenation experiments and was

[a] Since the reactions were concerned with the nature of the product obtained the variations in the warm-up period were thought to be unimportant.

[b] Bay 11 had a broken thermocouple during two reactions.

unsuitable for sampling slurries. When attempts to sample were successful the results have been included in the relevant tables.

The autoclaves used at Edinburgh University were designed and constructed by Baskerville and Lindsay Ltd. Initial experiments at Edinburgh (up to HT HEX R75) were carried out using a single autoclave. The original autoclave set-up can be seen in Plate 4.1. Later three other autoclaves were obtained (numbers 1, 2 and 3) and the original autoclave (number 4) was upgraded to the new specifications. Two of the three 'new' autoclaves were used in this work (autoclaves 2 and 3) as well as the upgraded autoclave, number 4. Autoclaves 2, 3 and 4 can be seen in Plate 4.1a.

The autoclaves had a capacity of 500 cm^3. All the autoclaves were agitated by magnetic stirrers and the stirring speed could be regulated and monitored from the individual control panels. Autoclaves 2 and 3 were constructed in stainless steel while autoclave 4 was constructed in stainless steel and inconel[a]. The temperature, of the original autoclave was controlled by a Pye-ether temperature controller. The temperatures of autoclaves 2, 3 and 4 were controlled by Guilton-West MC36 four-term temperature controllers. For all of the autoclaves the temperature of the reaction mixture was measured by a thermocouple situated in a thermocouple 'pocket' which projected into the reaction vessel. The thermocouple pocket can be seen in Plate 4.2 which shows the interior of the autoclave, from left to right the sampling pipe, stirrer and thermocouple pocket can be clearly seen.

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[a] A nickel-based alloy containing approximately 13% chromium, 6% iron and some manganese.

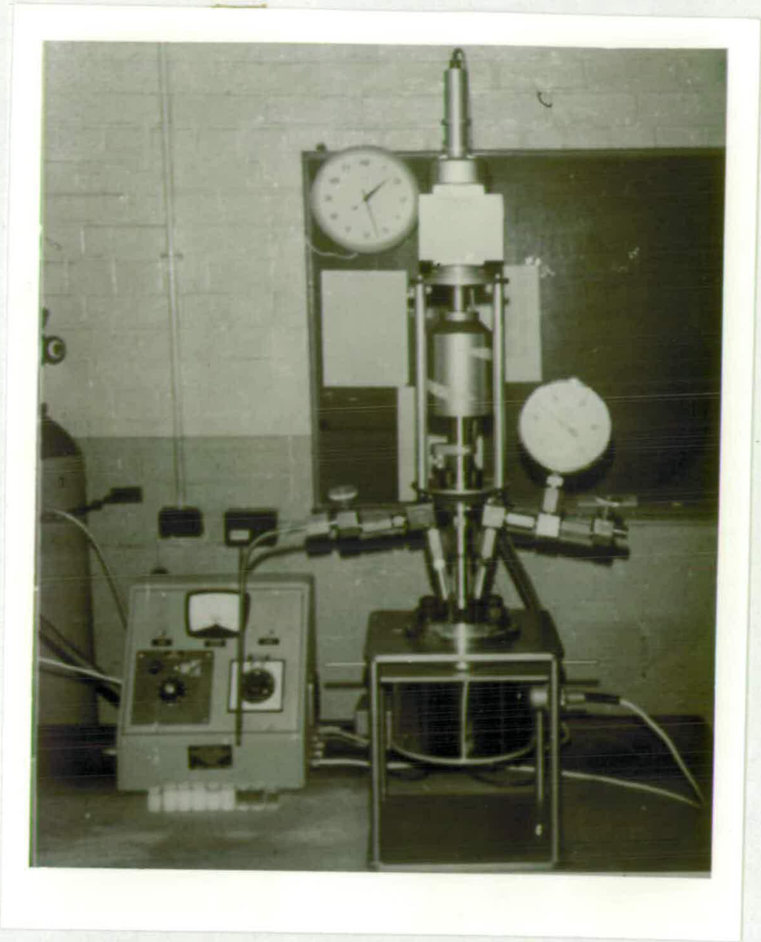


Plate 4.1

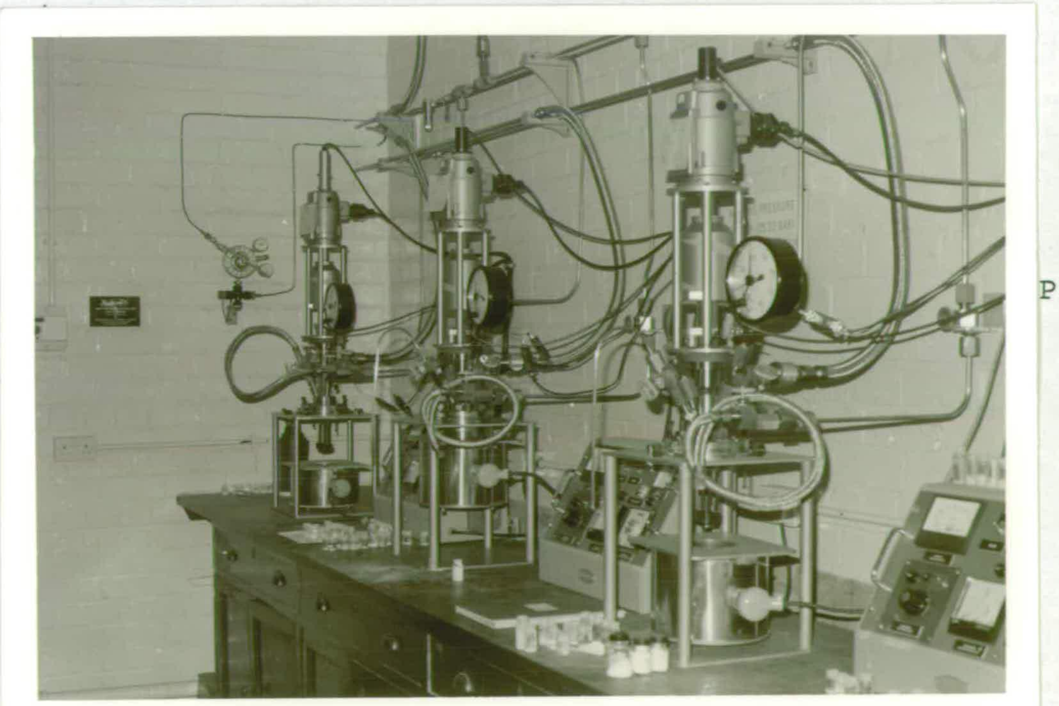


Plate 4.1a

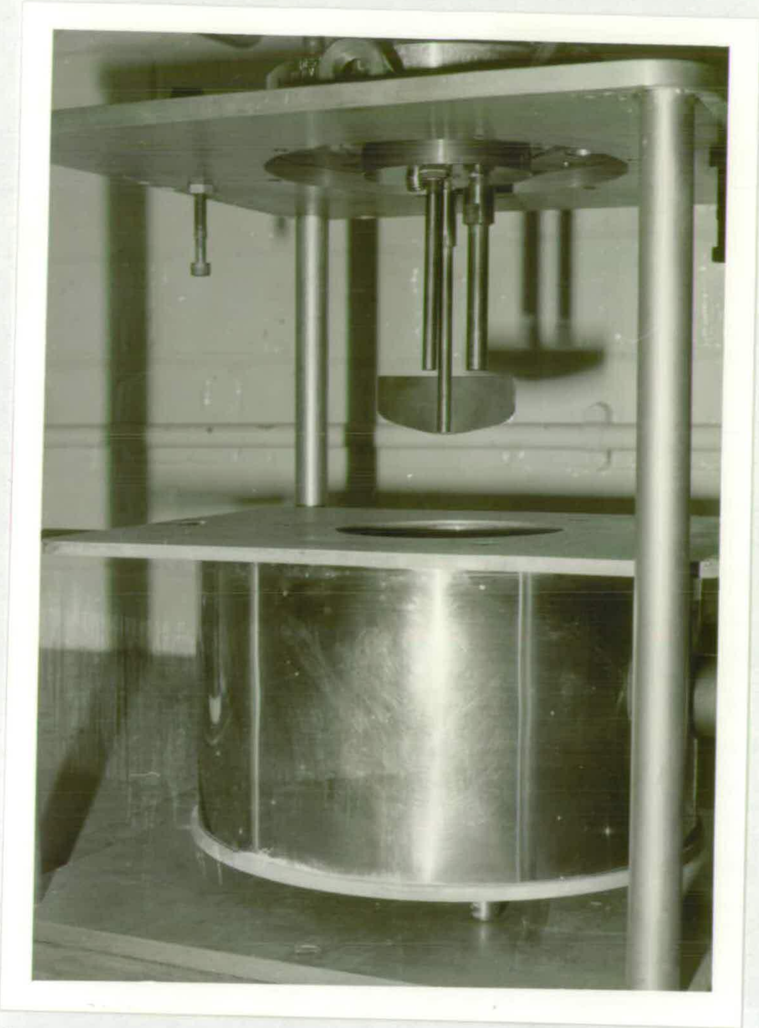


Plate 4.2

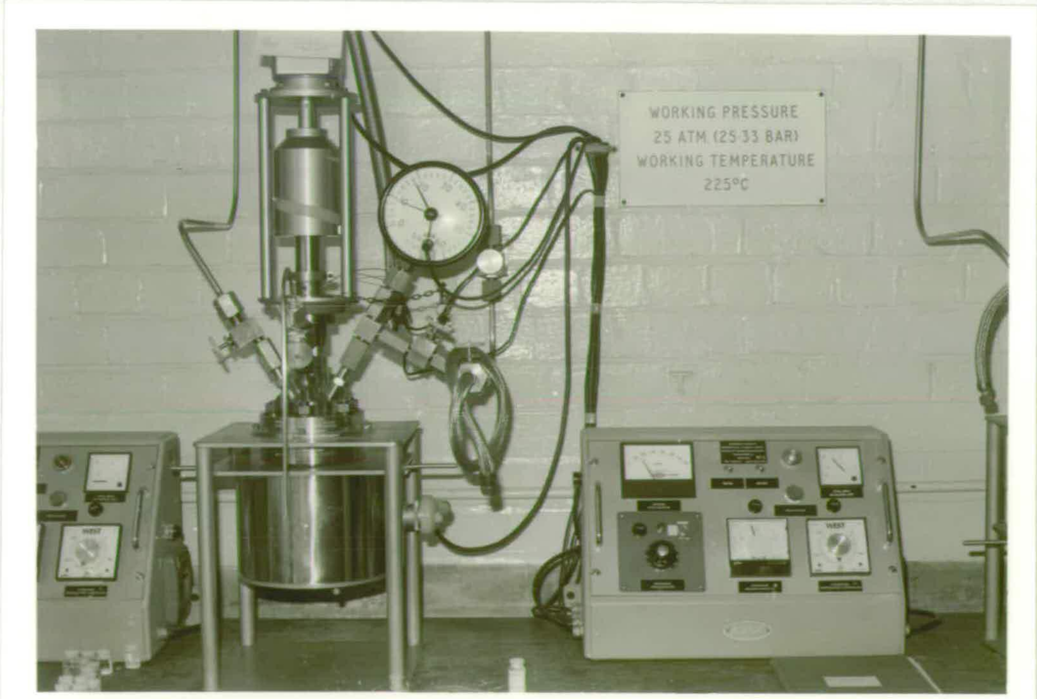


Plate 4.3

Although the Pye-ether controller was a simple on/off device, excellent thermostatting was obtained. The reproducibility of the operating temperatures was observed by comparing similar 'runs' and by observing the pressure of each reaction. The water vapour pressure changes rapidly with temperature between 180 and 220°C and changes in the working temperature are reflected in substantial pressure changes. The Gu lton-West controllers, although much more sophisticated than the Pye-ether device were, initially, not as satisfactory, since the autoclaves overshot the set-point temperature by several degrees and the temperature varied from one run to another by ±1.5°C. These problems were largely overcome by modifications to the relevant circuits by Gu lton-West engineers, however, they meant that it was very difficult to carry out experiments on the rate of zeolite formation (which is very sensitive to variations in temperature) on the 'new' autoclaves as initially set-up.

Plate 4.3 shows autoclave 3 and its control panel. Comparison of Plates 4.1 and 4.3 show the differences between the autoclaves and their control panels. Fig. 4.1 and 4.1a are schematic diagrams of the original and modified autoclave designs. The main difference is that the new autoclaves have a third 'pipe' entering the autoclave. This is the sampling valve. The valve on the lefthand side which was attached to the sampling in the original design is now a 'venting-off' valve. The difference in the angle of the side-arms of the original and new autoclaves (Plate 4.1 and Plate 4.3) is related

Fig. 4.1 Schematic diagram of the original autoclave

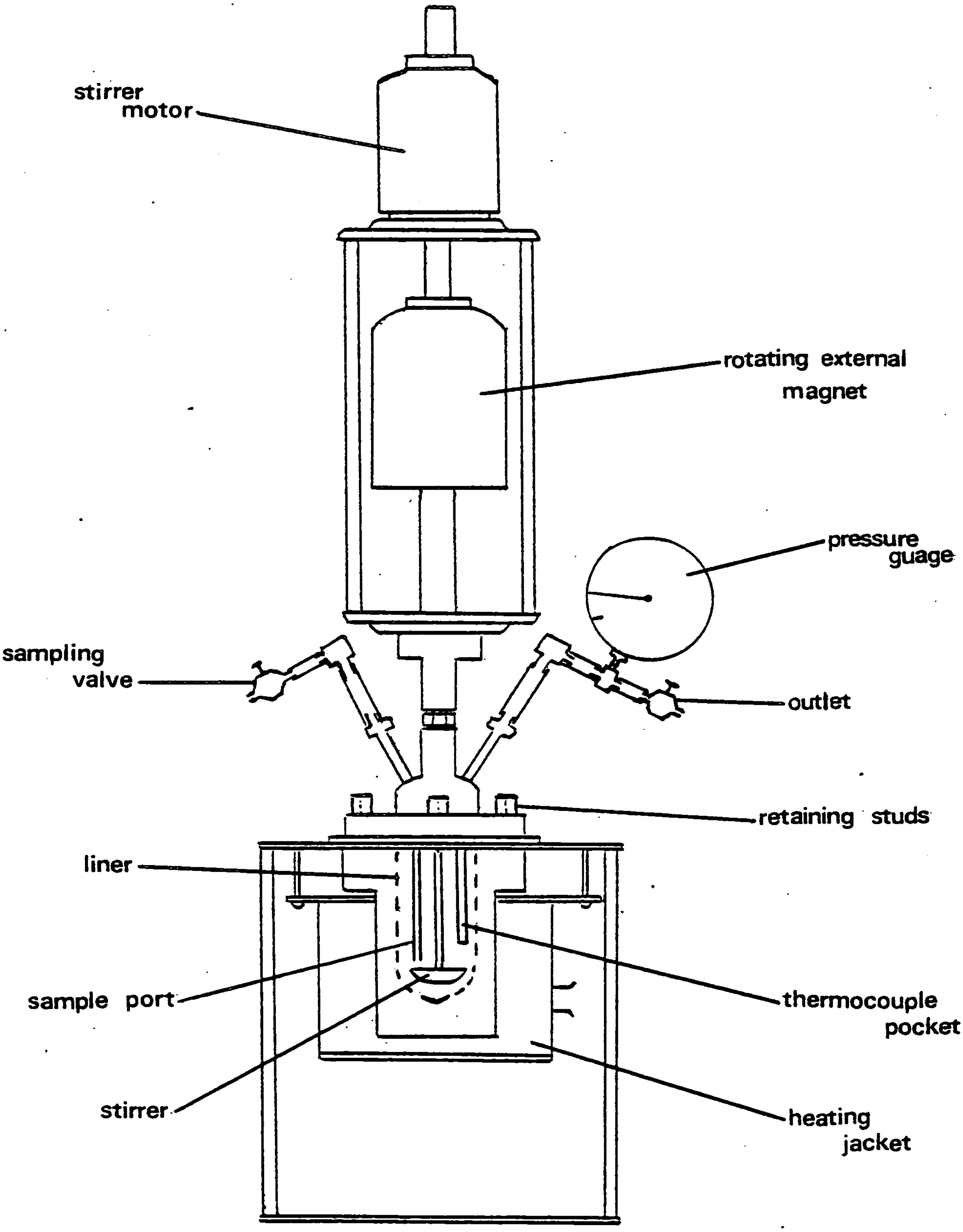
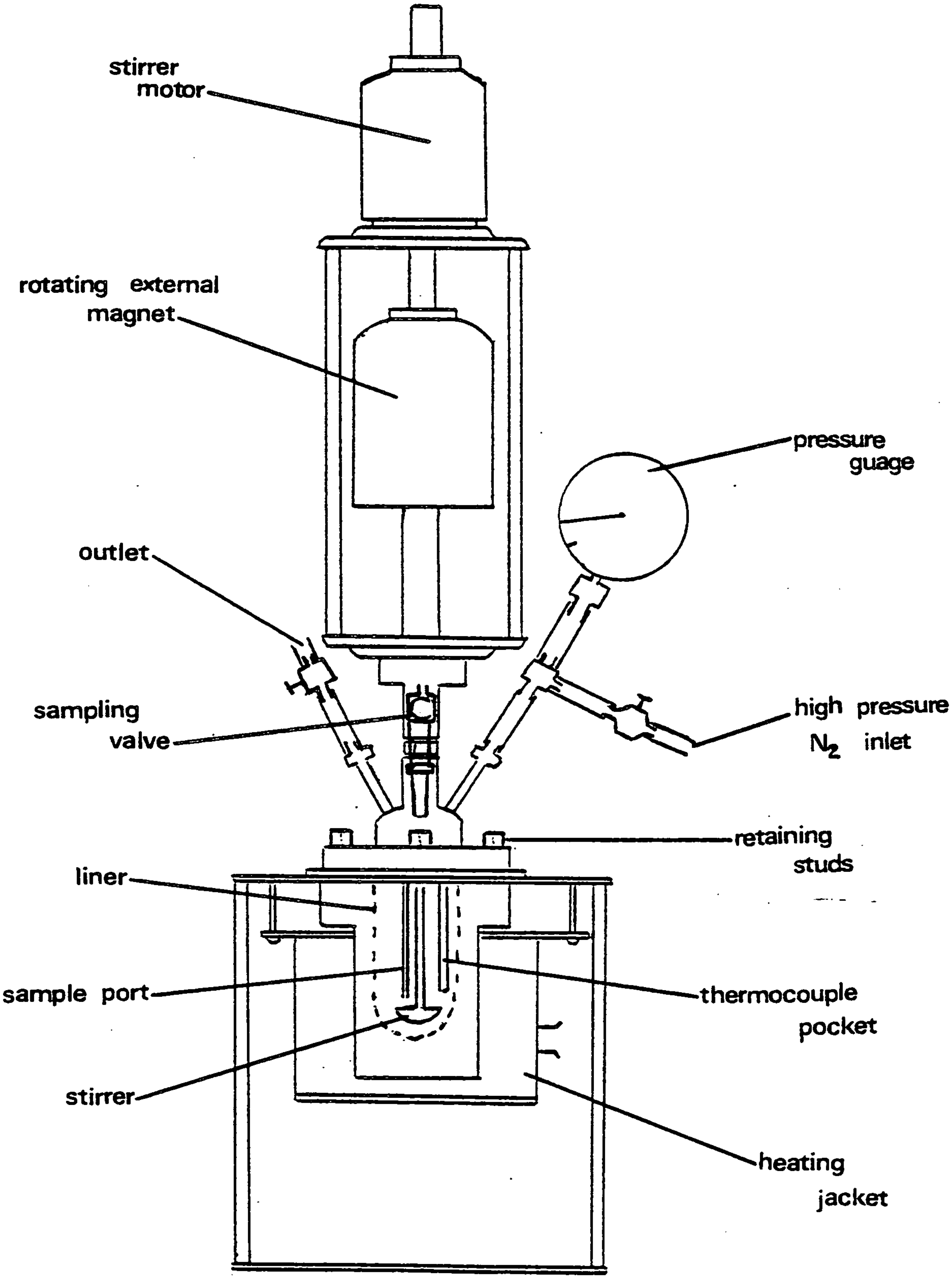


Fig. 4.1a Schematic diagram of the 'new' autoclave

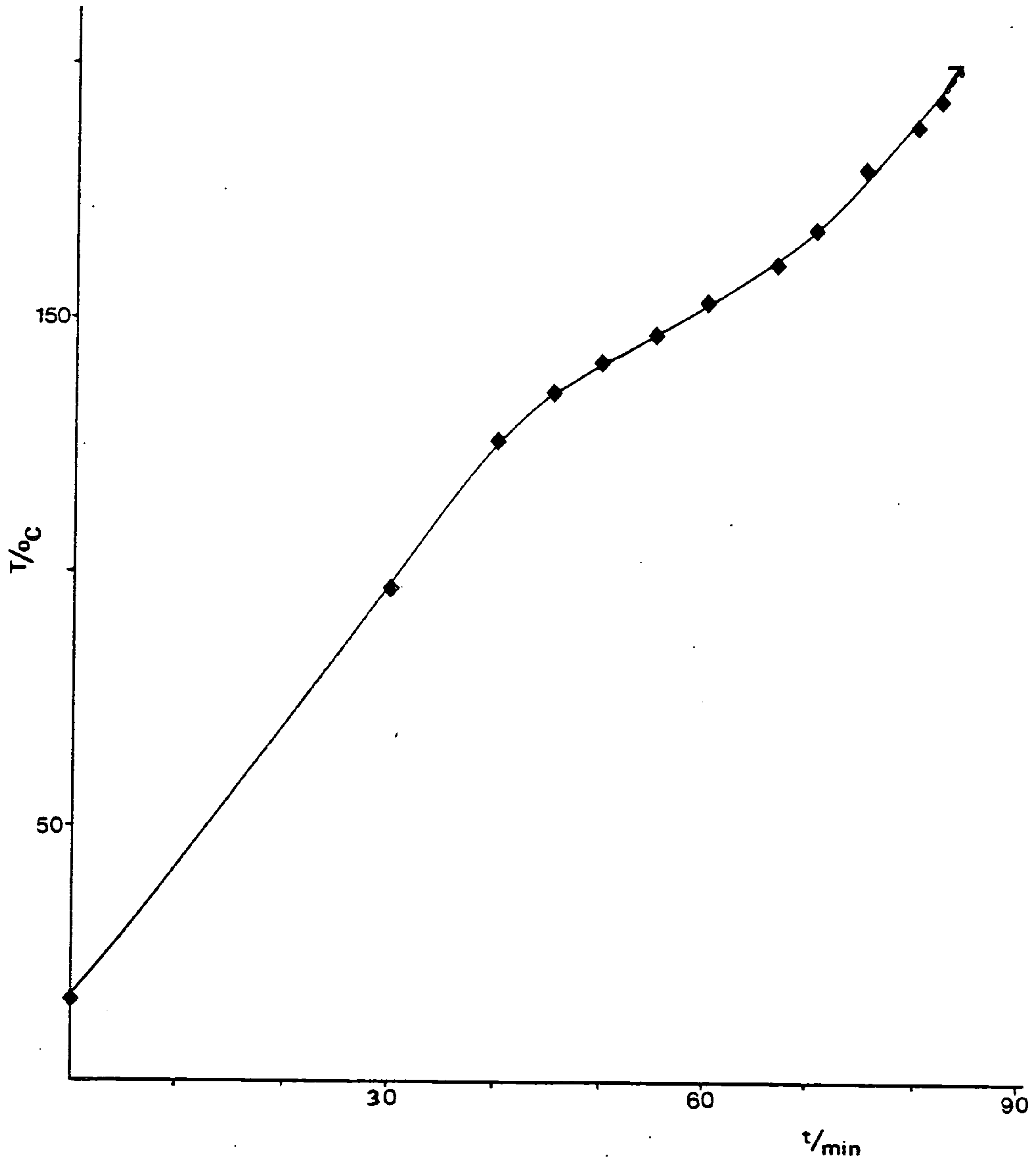


to problems encountered in the machining of inconel for the original autoclave. The pressure gauges on the new autoclaves differed from that on the original in that the new pressure gauges incorporated a reed switch which operated an 'over-pressure' trip. Thus if the pressure exceeded a particular pre-set value the heater was automatically switched off. The major feature of the control panels of the new autoclaves which are not present in those of the original are an ammeter and thermal cut-out control. The thermal cut-out was activated by a second thermocouple placed in the thermocouple pocket. The cut-out temperature was normally set 15 to 20°C above the reaction temperature (set-point temperature). Neither of these safety devices were fitted to the original autoclave but instead an external thermal cut-out was fitted. This was activated by the temperature of the external surface of the autoclave. This arrangement was unsatisfactory because of its relative insensitivity and because of the time lag between a temperature overshoot in the reaction vessel being reflected in an increase in the surface temperature. The ammeters in the control panels of the new autoclaves were used to monitor the current applied to the heaters. This was controlled by a Guilton-West MC36, four-term controller. The current supplied to the heaters was 'pulsed' from about 40°C below the set-point temperature. In theory this was to allow the temperature to increase gradually up to but not over the set-point temperature. As a consequence of this the new autoclaves took about 20 minutes longer than the original to warm-up to 200°C.

A typical warm-up curve for the original autoclave can be seen in Fig. 4.2. The warm-up period (up to 200°C) varied between 76 and 88 minutes, depending on ambient temperature. However in all cases the warm-up from 150°C was fairly uniform and reproducible to within 3 or 4 minutes. In all reactions the t_o time, i.e. the time at which reaction was considered to start, was taken as the time at which the autoclave reached set-point temperature. In the original autoclave the temperature warm-up was monitored by substituting a thermocouple connected to a Comark Thermometer for the thermocouple connected to the Pye-ether control. Heating was stopped about 6°C below set-point temperature to prevent 'overshoot'. In the new autoclaves the temperature was monitored using two thermocouples, one of which was situated in the thermocouple pocket and the other was in ice. These thermocouples were connected to a Solartron digital voltmeter.

Sampling was carried out extensively from the autoclaves at Edinburgh. Normal sample sizes ranged from 5 cm^3 to 20 cm^3. When a sample was required a stainless steel tube was connected to the sample valve and diverted into a glass sample bottle. The valve was then opened and closed several times. This procedure was found, by experience, to be the best method of sampling and was frequently used to release blockages in the sample pipe. The sample bottles were never filled completely from the autoclave, but instead a space of 2 or 3 cm^3 was left to accommodate the slurry remaining in the stainless steel tube,

Fig. 4.2 Typical warm-up profile for the original autoclave



which drained when the sampling pipe was disconnected. Care was taken to ensure that when a blockage occurred the sample valve was not opened by more than 'half a turn', since a sudden release of the blockage could result in a large amount of slurry being ejected from the sampling pipe before the valve could be closed. About 5 cm^3 of sample remained trapped within the sampling dip tube within the autoclave. In order to prevent this trapped slurry from contaminating the next sample it was normal practice to discard the first few cm^3 of sample. Alternatively, with the new autoclaves, the dip tube could be 'back flushed' with high pressure nitrogen. This technique was also used to release blockages. Inevitably the use of nitrogen to 'back flush' in this way caused a slight increase in the pressure inside the autoclave which in turn caused a slight temperature increase.

Although the autoclaves had a total volume of about 500 cm^3 it was important to leave room for expansion hence the volume of reaction mixtures never exceeded 400 cm^3. Often as much as 50% of the original volume was removed as samples. It was realised that the removal of such a large quantity of material could upset the rate of reaction, however, the results obtained were fairly reproducible. In many cases samples were taken merely to determine if the reaction had crystallised.

It was very important to clean the autoclaves very carefully between successive reactions (see section 4.8). The autoclaves were cleaned using a 4% (w/w) aqueous sodium hydroxide at a minimum of 150°C for 1 hour.

After this time the heater was switched off and at least 50 cm^3 of the caustic solution removed through the sampling valve. The autoclave, once cooled, was dismantled and washed. Scouring wire-wool pads, "Brillo-pads" were used to clean the autoclave. The side-arms were rinsed through with water or blown through with nitrogen. Occasionally the stirrer shaft was dismantled and on those occasions it was important that the grooves on its main bearing were kept free since this could lead to slurry being forced up around the armature and thus stopping agitation.

Two of the autoclave vessels developed cracks in their bases. The thickness of these bases was about 3.5 cm. The cracks occurred at 'corners' and at the apex of the base. Examination of both the failed autoclaves by Altrincham Laboratories[2a] revealed that they had undergone stress corrosion cracking. It was concluded that this was probably due to the concentration of halides and/or hydroxides on the surface of the autoclave bases. Several other contributing factors were also discussed in the report. Discussions with experts at I.C.I., Billingham suggested that the trouble arose because material became trapped between the liners and the vessel base and dried out on the surface. Therefore, it was decided to discontinue the use of liners. It was also decided that since the cracks arose from the apex of the base it would be better if future vessels had hemispherical bases.

4.3 SYNTHESIS AND CHARACTERISATION OF EU-1

4.3.1 INTRODUCTION

This section deals with the synthesis and characterisation of a novel zeolitic material from reaction mixtures based on the 'standard' composition:

$$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O.$$

The zeolite formed from these mixtures was named EU-1. The 'standard' reaction composition was based on the "high silica" reactions planned in Chapter 3 (see Table 3.1) and on conditions used to synthesise zeolites NU-1 and FU-1[1].

4.3.2 INITIAL EXPERIMENTS

The first experiment in this series, HT HEX R1, produced zeolite EU-1. The compositions, experimental conditions and results of some of the initial experiments can be seen in Table 4.1.

Reactions HT HEX R1 and R2 showed that EU-1 could be produced from reactions with different ratios of SiO_2/Al_2O_3 and HT HEX R6 illustrated that EU-1 could be formed with a different silica source. Reaction HT HEX R5 gave an indication about the time scale required to form EU-1, at 180°C. In addition, since samples containing medium EU-1, medium/major EU-1 and major EU-1 were examined by powder X-ray diffraction[a], the uniform increase in peak heights indicated that EU-1 was likely to be a single species since it is unlikely that two species would grow simultaneously at the same rate.

From Table 4.1 it can be seen that EU-1 was formed only over a limited range of SiO_2/Al_2O_3 ratios. Thus EU-1 was formed from a reaction with a SiO_2/Al_2O_3 ratio of 60/1,

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[a] I.C.I. diffractometer

TABLE 4.1 HIGH TEMPERATURE REACTIONS

Run No HT HEX	Reaction Mixture					Temp /°C	Sample No	Time /days	Product	Location	Notes
	SiO_2	Al_2O_3	Na_2O	HEX Br_2	H_2O						
R1	60	1	10	10	3000	180	S1 S2	7 8	MAJ EU1 MAJ EU1	I.C.I.	a
R2	86	1	10	10	3000	150	S1 S2	7 10	MAJ EU1 MAJ EU1	I.C.I.	a
R6	86	1	10	10	3000	180	S1 S2	1 5	Med EU1 MAJ EU1	I.C.I.	b
R5	86	1	10	10	3000	180	S1 S2 S3 S4	1 2 3 5	Med EU1 Med/MAJ EU1 MAJ EU1 MAJ EU1	I.C.I.	a
R8	30	1	5	5	1500	180	S1 S2 S3	1 2 5	Am Am Med EU1	I.C.I.	b
R28	60	0.5	10	10	3000	180	S1	4	Med EU1 + Med EU2	Edin.	b
R3	60	1	10	10	2000	180	S1	5	MAJ EU1	I.C.I.	a
R7	60	1	5	15	3000	180	S1 S2 S3 S4	1 2 3 5	Trace EU1 Med EU1 Med EU1 Med EU1	I.C.I.	b
R11	60	1	1.25	15	3000	180	S1	5	Am	I.C.I.	b
R14	60	1	10	10	3000	180	S1	5	Trace EU1	I.C.I.	b,c,d
R12	60	1	10	5	3000	180	S1	5	MAJ EU1	I.C.I.	b
R10	60	1	10	10	3000	180	S1	5	MAJ EU1	I.C.I.	b,e
R13	60	1	10	10	3000	180	S1	5	MAJ EU1	I.C.I.	b,f
R4	20	1	3.5	3.5	1000	95	S1 S2 S3 S8	3 4 5 12	Am Am Trace EU1 Trace EU1	I.C.I.	a,g,h

[a] Silica source was KS300.

[b] Silica source was CAB-O-SIL M5.

[c] Reaction mixture contained K_2O rather than Na_2O. For this reaction the alumina source was BACO Al_2O_3 $3H_2O$ which could not be dissolved completely before the reaction was placed in the autoclave. In all other reactions the aluminium source was sodium aluminate.

[d] Only a few faint diffraction lines were observed.

[e] This reaction used HEX Cl_2 instead of HEX Br_2.

[f] Quiescent reaction. All other reactions were agitated.

[g] Samples S_1 and S_2 were analysed by diffractometer (I.C.I.) and samples S_3 and S_8 with a Guinier-Hagg powder camera. The appearance of trace amounts of EU1 in samples S_3 and S_8 almost certainly reflects the higher sensitivity of the powder camera

however when the ratio of SiO_2/Al_2O_3 was increased to 60/0.5 or 120/1 (HT HEX R28) only a medium sample of EU-1 was obtained in addition to a second material. This second material was designated EU-2 - see section 4.4. As the SiO_2/Al_2O_3 ratio was decreased from 60/1 to 30/1 (HT HEX R8) only a medium sample of EU-1 was obtained after 5 days. (a pure sample of EU-1 was later obtained from a reaction with a SiO_2/Al_2O_3 ratio of 30/1, however in this case seed material was used).

A change in the H_2O/Al_2O_3 ratio from 3000/1 to 2000/1 (HT HEX R3) did not affect the product obtained although the rate of formation may have been affected.

A reduction in the Na_2O content of the 'standard' reaction mixture was found to have a marked affect on the reaction rate as can be seen by comparison of reactions HT HEX R1, R7 and R11. Reaction HT HEX R7 which contained 5 Na_2O only, produced medium EU-1 after 5 days and reaction HT HEX R11 which contained 1.25 Na_2O contained no crystalline material after a similar length of time. When K_2O replaced Na_2O (HT HEX R14) only a trace amount of EU-1 was obtained after 5 days[a].

In HT HEX R12 the Na_2O/Al_2O_3 ratio was kept constant but the ratio of HEX Br_2/Al_2O_3 was reduced from 10/1 (as in the 'standard' reaction) to 5/1. A major sample of EU-1 was obtained although as in HT HEX R3 the reaction rate may have

[a] It should be noted that in some high silica reactions the alkali metal cation can determine the final product. For example zK-5[3] can be prepared using DDO(1,4-dimethyl-1,4-diazoniabicyclo(2,2,2)octane) and sodium while ZSM-10 was prepared with DDO and potassium[4].

been affected. However the fact that a major sample of EU-1 was obtained using less HEX Br_2 may be of commercial interest because of the high cost of this reagent.

All the reactions in Table 4.1 - with the exception of HT HEX R13 - were carried out with agitation. Reaction HT HEX R13 was carried out under quiescent reaction conditions and although this did not affect the type of product obtained[a] it is likely that the rate of reaction was affected.

Although the reactions in Table 4.1 are headed "High Temperature Reactions", one reaction carried out at 95°C is included. This reaction HT HEX R4 was carried out in an attempt to find a low temperature route to EU-1. To help achieve this a quantity of 'seed' EU-1 was incorporated into the reaction mixture. The term 'seed', in this thesis, refers to some previously synthesised crystalline material which is added to the reaction mixture to aid in the nucleation process, this will be discussed in section 4.8. The quantity of 'seed' material corresponded to about 5% (w/w) of the silica in the reaction mixture. In HT HEX R4 the traces of EU-1 observed after 5 days probably corresponds to the original EU-1 seed and its detection reflects the superior sensitivity of the Guinier-Hagg camera over the diffractometer. Because of the considerable problems found in taking samples from the autoclaves at I.C.I. (see section 4.2) several other low temperature reactions were carried out. The compositions, conditions and products of these reactions are summarised in Table 4.2. The only crystalline material obtained from these experiments was an unknown material, which was

[a] It had been found[1] that zeolites FU-1 and NU-1 could be obtained from the similar reaction mixtures depending on whether the system was agitated or quiescent.

TABLE 4.2 LOW TEMPERATURE (95°C) REACTIONS[k]

Run No HT HEX	Reaction Mixture SiO_2	Al_2O_3	Na_2O	HEX Br_2	H_2O	Container[a]	Agitation	Seed[d]	Product[b]	Time /days[c]
R4	20	1	3.5	3.5	1000	GF	Yes	EU1	Am	12
R19	60	1	10	10	3000	GF	No	None	tr. EU3 type	118
R20	60	1	10	10	3000	GF	Yes	EU1	tr. EU3 type	110
R21	60	1	10	10[e]	3000	GF	Yes	EU1	Am	56[f]
R22	60[g]	1	19	20	3000	PB	No	None	Am	56
R23	60[h]	1	10	20	3000	PB	No	None	Am	56
R26	60	1	10	10	3000	GF	No	None	tr. EU3 type	73
R29	60	1	10	10	3000	GF	Yes	None	tr. EU3 type	<54[i]

[a] GF = glass flask; PB = polypropylene bottle.

[b] Products: Am = amorphous; EU3 denotes a new crystalline material; EU3 type refers to materials similar to EU3 but low intensity of diffraction lines makes positive identification difficult. Some samples show small shifts in line positions from those of EU3.

[c] The time given is either when reaction was stopped or when the first crystalline material was observed.

[d] Seed material used was "as synthesised" EU1. The amount used was about 5% (w/w) of the solid silica in the reaction.

[e] Reaction also contained 5 HEXO.

[f] Reaction boiled dry in about 60 days.

[g] Q79 used as sole silica source.

[h] Q79 used as sole silica source. The Q79 was treated with ion-exchange resin to reduce the sodium content to approximately 10 Na_2O.

[i] Reaction was treated to 200°C then cooled to 95°C. Sample taken after 20 days was amorphous but next sample after 54 days contained some EU3 type material.

[k] Reaction HT HEX R4 was carried out at I.C.I. All other reactions were carried out in Edinburgh.

designated EU-3. This material is discussed in section 4.5.

Both reactions HT HEX R19 and R20 which were based on the standard reaction composition of HT HEX R1 crystallised very slowly, both requiring more than 100 days to produce trace amounts of EU-3. The fact that EU-3 was formed not EU-1 was not thought to be too significant since most zeolites are metastable species and it was thought likely that EU-3 would ultimately transform to EU-1. However because of the time-scale of the reaction it was felt that compositional changes alone would not have a major effect on the reaction rate.

The crystallisation of zeolites can be regarded as taking place in two stages: nucleation and growth. Both are thought to require silicate and alumino-silicate species in solution. Nucleation involves the combination of silicate and alumino-silicate species to form the nuclei from which the zeolite grows. The growth stage requires a continual supply of nutrients from solution. Either stage can control the occurrence and rate of crystallisation and consequently attempts to increase the reaction rate at 95°C were aimed at both the nucleation and growth stages.

The addition of seed material (HT HEX R20) did not markedly affect the reaction rate and consequently other methods were used to reduce the rate determining step which it was then believed was associated with the depolymerisation of either the silica source or the alumino-silicate gel. Thus in reaction HT HEX R22 the silica source was changed from CAB-O-SIL to Q79 (a sodium silicate solution) which it was thought would remove the need to depolymerise the silica source. However HT HEX R22 contained 19 Na_2O (because of the Na_2O content of Q79) and this excess Na_2O could have upset the reaction. Consequently in HT HEX R23 the Q79 was pretreated with ion-exchange resin to remove the excess Na_2O. However neither system was significantly more reactive. The most significant result was obtained in reaction HT HEX R29. In this case the reaction mixture was heated to 200°C in an autoclave before being cooled and transferred to a glass reactor at 95°C. In this case EU-3 was produced more quickly but EU-1 was still not formed. Consequently it was decided that to study EU-1 formation it was essential to work above 95°C and consequently to use autoclaves.

4.3.3 CHARACTERISATION OF EU-1

The powder X-ray diffraction patterns for several samples of EU-1 can be seen in Table 4.3. The d-spacings are given for samples of EU-1 synthesised both at I.C.I. and at Edinburgh (HT HEX R1 was carried out at I.C.I.). The powder diffraction patterns of samples synthesised at different temperatures and with different ratios of SiO_2/Al_2O_3 have been included as well as the d-spacings of a calcined sample.

The diffraction pattern of EU-1 was found to have similarities with several of the "ZSM" series of zeolites including ZSM-5[5], ZSM-11[6], ZSM-12[7], ZSM-18[8], ZSM-23[9] and ZSM-34[10]. The zeolite found to be most similar to EU-1 was ZSM-23.

To further characterise zeolite EU-1, sorption studies were carried out. The results of two studies (one

TABLE 4.3 d-SPACINGS FOR EU1

Film	J403	J666	J665	J552	J667
HT HEX	R1	R51	R49	R32[a]	R52
T/°C	180	200	200	200	200
SiO_2/Al_2O_3	60	60	60	60	45
Error					
0.080	11.031 vs	11.111 vs	11.111 vs	11.111 vs	11.031 vs
0.065	10.096 vs	10.096 s	10.096 s	10.030 vs	10.096 s
0.062	9.716 m	9.839 w	9.777 m	9.777 w	9.716 w
0.037	7.690 m		7.729 vw	7.615 w	
0.030	6.843 w	6.813 w	6.902 w	6.843 m	6.843 w
0.025	6.213 vw			6.213 vw	
0.021	5.797 w	5.862 vw	5.840 w		5.862 vw
0.020	5.609 vw	5.712 vw		5.733 w	
0.015	4.712 vw			4.873 vw	
0.014	4.642 vs	4.655 s	4.655 s	4.601 vs	4.655 vs
0.012	4.286 vs	4.310 vs	4.298 vs	4.298 vs	4.310 vs
0.010	3.992 vs	4.002 vs	4.002 vs	3.972 vs	4.002 vs
0.009	3.799 s	3.808 m	3.818 s	3.772 s	3.818 s
0.009	3.701 s	3.719 s	3.701 m	3.710 w	3.710 s
0.008				3.625 vw	
0.007	3.428 w	3.443 m	3.436 w	3.421 m	3.443 m
0.007	3.342 m	3.370 m	3.370 w		3.377 m
0.007				3.334 m	
0.007	3.239 s	3.279 w	3.246 s	3.266 s	3.259 s
0.006				3.233 m	
0.006	3.143 vw		3.162 vw	3.149 w	3.162 vw
0.006	3.070 vw		3.094 vw	3.065 w	3.106 vw
0.005	2.930 vw	2.962 vw	2.946 vw	2.930 w	2.962 vw
0.005	2.694 vw	2.716 w	2.712 vw	2.685 w	2.712 vw
0.005				2.623 vw	
0.004	2.533 m	2.545 w	2.545 vw	2.569 vw	2.553 w
0.004			2.517 vw	2.510 w	
0.004	2.464 vw	2.486 vw		2.445 vw	2.483 vw
0.004	2.395 vw		2.413 vw	2.406 vw	2.420 vw
0.003	2.317 vw	2.304 vw	2.307 vw	2.317 vw	2.330 vw
0.003	2.291 vw			2.288 vw	2.304 vw
0.003	2.114 vw	2.128 vw	2.125 vw	2.112 vw	2.125 vw
0.002	1.991 vw				
0.002	1.942 vw				
0.002	1.907 vw				
0.002	1.873 vw				

[a] Sample had previously been calcined at 450°C for 40 hours.

carried out at I.C.I.[a] and the other at Edinburgh) can be seen in Table 4.4 and Table 4.5. Comparison of the results in these tables shows that the results for sample HT HEX R2 S2 are not in complete agreement. This is probably because the apparatus available for these studies in Edinburgh was less accurate than that used at Billingham. Whereas sorption of n-hexane and water by EU-1 was substantial, cyclohexane was barely sorbed and p-xylene was sorbed strongly. Comparison of the kinetic diameters of these molecules, Table 4.6, suggests that the pore size of EU-1 is between 5.85 Å and 6.00 Å. The hydrophobic nature of EU-1 can be seen in Table 4.4 in which the apparent voidage calculated for water is seen to be much less than that calculated for n-hexane and p-xylene. In addition it can be seen that the water sorption increases to 9.3 cm^3/100 g after 19 hours thus illustrating that the volume available to water was the same as that available to the organic species.

TABLE 4.6 KINETIC DIAMETER OF SORBED MOLECULES

sorbate	σ/Å
cyclohexane	6.00
p-xylene	5.85
n-hexane	4.30
water	2.65

---

[a] Results obtained by Mr. C. Howe, I.C.I. Agricultural Division, Billingham and (in part) by the author.

TABLE 4.4 SORPTION RESULTS FOR EU1[a]

Sorbate	Pressure mm Hg	Time h	% Weight[b] increase	Apparent[d] voidage $cm^3/100$ g
water	4.5	2	6.93	6.93
n-hexane	45.8	2	9.52	14.4
cyclohexane	27	2	1.12	-
m-xylene	1.6	2	2.30	-
		18.5	5.52	-
p-xylene	1.6	2	10.47	-
		18.5	10.78	12.5
water	4.7	2	3.86[c]	3.86
		19	9.34	9.34

[a] Results obtained at I.C.I. Ltd., Agricultural Division, Billingham, for the product from reaction HT HEX R2 S2 (SiO_2/Al_2O_3 = 76.8) which was calcined at 450°C for 40 hour. It is now believed that this sample may have contained some EU2.

[b] These results are an average for two samples.

[c] These results were obtained after the adsorption studies on the organic materials.

[d] This was calculated using the liquid densities of the sorbates.

TABLE 4.5 SORPTION RESULTS FOR EU-1[d]

	SORBATE		
Sample	water (p = 5.0 mmHg) (t = 17 hours) % sorbed (w/w)[a]	hexane (p = 51.0 mmHg) (t = 17 hours) % sorbed (w/w)[a]	cyclohexane (p = 26.1 mmHg) (t = 16.5 hours) % sorbed (w/w)[b]
HT HEX R2 S2[c]	6.88	7.80	2.37
HT HEX R6 S2[c]	7.09	9.26	2.56
HT HEX R1 S2	6.56	7.45	1.64

[a] Results are average of 3 experiments.

[b] Results are average of 2 experiments.

[c] It is now believed that these samples may have contained trace amounts of EU-2.

[d] Results obtained at Edinburgh.
Samples were calcined for 70 hours at 550°C.

Information about the thermal stability of EU-1, the amounts of water and organic materials occluded in its lattice, and the way in which these are removed by calcination was obtained by thermal analysis and the results can be seen in Fig.4.3. Both dta and tga results for sample HT HEX R77 have been included. The experimental conditions employed have been included in chapter 2. Tga of the sample shows that it contains less than 1.5% (w/w) of water and that this water is lost continuously at low temperature. Removal of the organic material begins at about 300°C and was almost completed at 700°C. The total decrease in weight above 700°C was about 0.5% (w/w). The dta trace of the same material shows a small endotherm below 100°C, corresponding to the water loss, then a large exotherm between about 300°C and 700°C corresponding to the decomposition of the organic material (hexamethonium). This can be seen to proceed in three stages, although the tga results appear to indicate that the organic loss is continuous. The dta trace between 700°C and 1100°C exhibits no transitions and the shift in the baseline is believed to be due to "machine effects". The baseline begins to change at about 1100°C and at about 1250°C there is a sharp endotherm associated with the destruction of the EU-1 lattice. After cooling, X-ray powder diffraction of the sample (using the Guinier-Hagg camera) showed that the EU-1 framework had indeed collapsed. A few feint diffraction lines were present, but these did not correspond to EU-1 and it appears that a trace of some other crystalline material was produced.

Analytical results for EU-1 can be seen in Tables 4.6 and 4.7. For all of the samples analysed the Na_2O/Al_2O_3

Fig. 4.3 Thermal analysis of EU-1, sample HT HEX R77

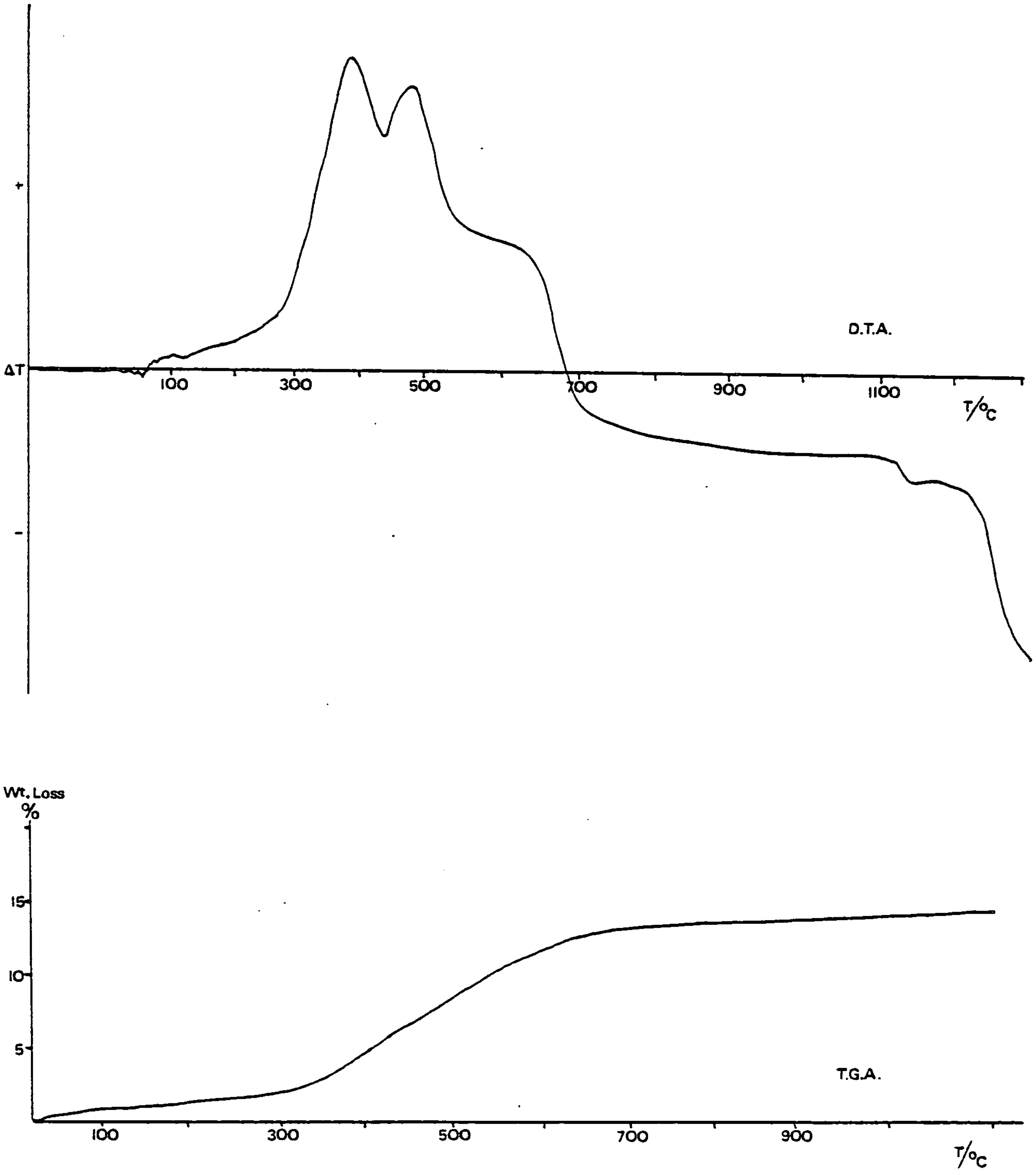


TABLE 4.6 PERCENTAGE COMPOSITION BY WEIGHT OF HIGH TEMPERATURE REACTION PRODUCTS

Sample HT Hex	Al_2O_3	SiO_2	Na_2O	C	H	N	HexO[a]	HexO[b]	HexO[c]	H_2O[d]	H_2O[e]	H_2O[f]	% Wt. Loss at 1000°C	Origin
R1 S1	3.0	80.7	0.49	6.8	-	1.7	10.30	13.25	11.78	4.03	3.12	3.58	14.9	ICI
R1 S1	-	-	-	6.81	1.50	1.38							-	Edin
R2 S1	1.9	80.3	0.74	6.9	-	1.7	10.45	13.25	11.85	5.21	4.35	4.78	16.2	ICI
R2 S1	-	-	-	7.24	1.73	1.45							-	Edin
R2 S1 TGA	-	-		0.17	0.56	0.20							-	Edin
R2 S2	1.8	81.4	0.60	7.1	-	1.6	10.76	12.47	11.62	4.58	3.58	4.08	15.2	ICI
R2 S2	-	-	-	7.45	1.71	1.45								Edin
R4 S	4.8	48.2	1.8	5.8	1.8	1.2	8.79	9.35	9.07	36.13	35.63	35.88	44.7	ICI
R6 S2	2.6	82.4	0.43	7.4	1.7	1.4	11.21	10.91	11.06	3.51	2.84	3.18	13.9	ICI
R8 S3	6.0	76.9	2.0	6.7	1.7	1.3	10.15	10.13	10.14	4.96	4.26	4.61	14.4	ICI
R77	2.78	81.9	0.33	-	-	-	-	-	12.5[g]	-	1.5	-	14.0	Edin
R81	5.90	93.7	0.52[h]	-	-	-	-	-	-	-	-	-	14.5	Edin

[a] Based on C, [b] Based on N, [c] Average.

[d] (100.0 - Sum of wt % oxides). [e] (Wt loss at 1000°C - wt % HexO[c]).

[f] Average wt. % H_2O. [g] Estimated from tga. [h] Framework composition only.

TABLE 4.7 MOLAR COMPOSITION OF HIGH TEMPERATURE REACTION PRODUCTS

Sample No HT Hex-	Product	Al_2O_3	SiO_2	Na_2O	HexO[c]	H_2O	Moles per mole $(Al_2O_3+SiO_2)$ Na_2O	HexO	H_2O	H_2O /Na_2O	C/N[a]	H/C[a]
R1S1	Maj. EU1	1	45.7	0.27	1.83	6.76	0.0058	0.0392	0.1448	25.0	4.7	-
R1S1	Maj. EU1										5.8	2.6
R2S1	Maj. EU1	1	71.7	0.64	2.91	14.25	0.0088	0.0400	0.1960	22.3	4.7	-
R2S1	Maj. EU1										5.8	2.9
R2S1 TGA	Maj. EU1[b]										1.0	39.5
R2S2	Maj. EU1	1	76.8	0.55	3.01	12.84	0.0077	0.0387	0.1650	21.4	5.2	
R2S2	Maj. EU1										6.0	2.8
R4S	Trace EU1	1	17.0	0.62	0.88	42.34	0.0344	0.0489	2.3522	68.4	5.6	3.7
R6S2	Maj. EU1	1	53.8	0.27	1.99	6.93	0.0049	0.0363	0.1265	25.8	6.2	2.8
R8S3	Med. EU1	1	21.8	0.55	0.79	4.35	0.0241	0.0346	0.1908	7.9	6.0	3.0
R77	Maj. EU1	1	50.5	0.23	2.11	3.06	0.0047	0.0410	0.0594	13.30	-	-
R81	Maj. EU1	1	27.0	0.14	-	-	0.0050	-	-	-	-	-

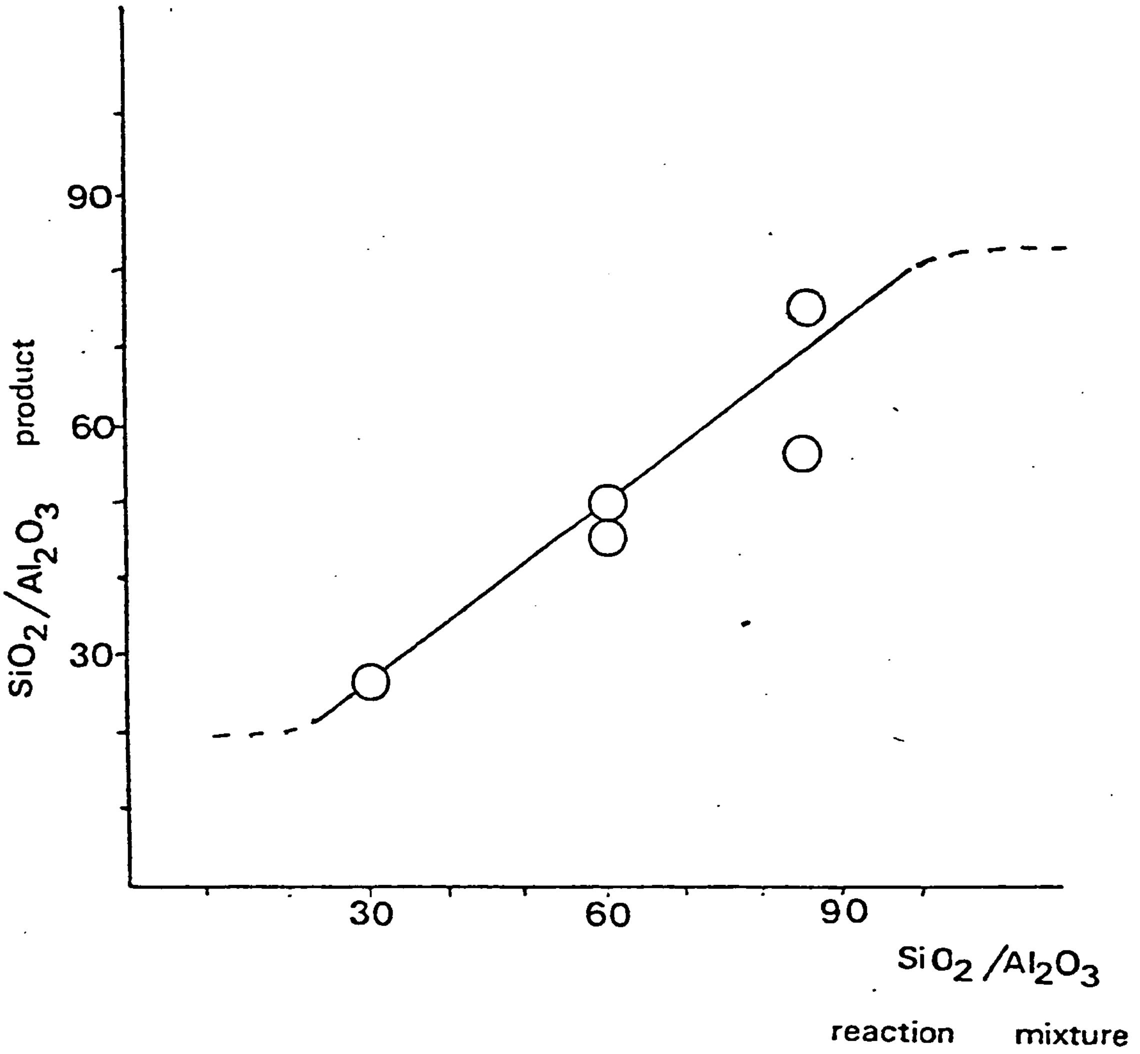
[a] For hexamethonium C/N = 6, H/C = 2.5.

[b] After tga to 600°C.

[c] Based on average value in Table 4.9.

ratio was less than unity and the $(Na_2O+HEXO)/Al_2O_3$ ratio ranges from 2/1 to 3.55/1. Although this "excess" hexamethonium has been assumed to be present as the hydroxide it is possible that the counter ion is actually bromide. The analysis of two samples of EU-1 from reaction HT HEX R2 suggested that the ratio of $(Na_2O+HEXO)/Al_2O_3$ stays constant but the proportions of SiO_2 and HEXO in the zeolite increase as the reaction proceeds. From the analysis of reactions which had not crystallised (HT HEX R4) or which had not fully crystallised (HT HEX R8), i.e. those which contained amorphous material, it can be seen that the proportions of Na_2O and HEXO are much greater than in the completely crystallised phase. This is as expected since in the final zeolitic product the only hydroxyl groups are those at the surface and at lattice defects. In the amorphous phase however there are alumino-silicate and silicate networks which contain many ionisable hydroxyl groups. Examination of the results on Tables 4.6 and 4.7 shows that the SiO_2/Al_2O_3 ratio of the product is always less than that of the reaction mixture. Indeed there appears to be a linear correlation between the SiO_2/Al_2O_3 ratios in the reaction mixture and product, as can be seen in Fig. 4.4. The dotted lines in this figure indicate that EU-1 was not synthesised over an indefinite range, and that, even with 'seeding' this range could only be slightly extended. So that a reaction with a SiO_2/Al_2O_3 ratio of 20/1 (HT HEX R96), even with seeding produced only a medium product of EU-1 and similarly a seeded reaction mixture with no added aluminium produced a mixture of EU-1 and EU-2. Thus there is a limited range over which EU-1 can be formed and even though

Fig. 4.4 Correlation between the SiO_2/Al_2O_3 ratios of the reaction mixtures and products.



<u>Note</u>: The products of reactions HT HEX R2 and R6 contained small amounts of EU-2 in addition to EU-1. In addition these reactions were carried out at different temperatures and it is not known if the differences in the SiO_2/Al_2O_3 ratios of their products reflects the effect of temperature on the ratio of EU-1/EU-2 or on the ratio of SiO_2/Al_2O_3 in the EU-1 formed.

this range could be extended by seeding it was not possible to make EU-1 with very high or very low ratios of SiO_2/Al_2O_3.

In principle there would appear to be no reason why a particular zeolite should not be synthesised over a very wide range of SiO_2/Al_2O_3 ratios. Since it would seem unlikely that a particular lattice would be unstable at a specific SiO_2/Al_2O_3 ratio, however, two things should be noted:

a) Since zeolites are metastable it may be that the rate of formation of a particular species could decrease considerably outwith a particular range of SiO_2/Al_2O_3 and another species could be formed more quickly.

b) Some structure types may be more susceptible to attack by alkali so that "silica only" analogues of, for example, zeolite A might not be stable above a pH of 12 at which it would be formed. Hence the structure would not crystallise.

Of the reactions carried out almost all were sampled either to determine how fast they were proceeding ("kinetics" experiments) or in the "synthesis only" experiments to determine whether the reaction mixture had crystallised. Consequently it was not possible to determine the yields of most of the reactions. However one experiment was carried out specifically to determine the yield of a standard EU-1 reaction (HT HEX R77). The details and results of this experiment are given in Table 4.8 and

TABLE 4.8 DETAILS OF REACTION HT HEX R77

Reaction No.	Temp/°C	Stirring Speed/R.P.M.	time/hours
HT HEX R77	200	300	14.5

Reaction composition:

$60\ SiO_2 \quad Al_2O_3 \quad 10\ Na_2O \quad 10\ HEX\ Br_2 \quad 300\ H_2O$

Quantities used:

24.04 g	silica (CAB-O-SIL)
1.437 g	sodium aluminate (NALFLOC - 1.25 $Na_2O.Al_2O_3.2H_2O$)
24.15 g	HEX Br_2
4.67 g	sodium hydroxide
358.6 g	water

Weight of product obtained = 20.875 g

% loss at 1000°C = 13.4%

(due to loss of H_2O and hexamethonium)

Framework composition:[a]

$50.5\ SiO_2 \quad Al_2O_3 \quad 0.226\ Na_2O$

Yield (%):

SiO_2	Al_2O_3	Na_2O
72	83.5[b]	2

[a] Determined by X.R.F., Dept. of Geology, Univ. of Edinburgh.

[b] Reliability of this is uncertain - see text.

analytical results for the product are included in Tables 4.6 and 4.7. As can be seen from Table 4.8 the yield with respect to aluminium was 83.5% and that based on the silicon added was 72%. Unfortunately the accuracy of the aluminium analysis is not known and it could be that all of the aluminium was consumed. However there is little doubt that almost 30% of the original solid silica added to the reaction mixture remains in solution or in a colloidal suspension, after the reaction has apparently reached completion. It could well be that while X-ray diffraction and sorption measurements suggest that the crystallisation has stopped, this may not be the case. Sorption and X-ray diffraction analyses only indicate whether the product is free from, or contains a constant amount, of solid amorphous material. If crystallisation was to continue from colloidal or solution species, this would not be detected by either sorption or X-ray diffraction studies. To test this it would be necessary to determine the yield at intervals after X-ray diffraction (or sorption) indicated that the reaction had finished. Detection of zeolite growth in the absence of amorphous material would go some way to showing that EU-1 crystals grow from solution species. The presence of about 30% of the silica in solution or colloidal form after all the amorphous solid has been consumed suggests that there is substantial amounts of silica in this form before the crystallisation begins, and it could be that nucleation occurs from solution species.

Several samples of EU-1 were examined by Scanning Electron Microscopy (SEM). Details of the samples and their preparation are given in Table 4.9. The SEM studies revealed that the EU-1 crystals were elipsoidal in shape and usually less than 4 μ in length and 3 μ in width. Plate 4.4 shows the distribution of particle sizes obtained from the standard reaction. Plates 4.5 and 4.6 show details of individual crystals formed in reaction HT HEX R108 and R30. Of particular interest are the small crystals which seem to 'grow' from the surface of the larger ones. It is believed that this reflects one aspect of zeolite crystallisation. The nucleation and growth of 'secondary' or 'daughter' crystals on the surface of the original crystals provides a mechanism by which the total number of crystals in the reaction mixture can increase without nucleation from the solution phase. As the 'daughter' crystals increase in size they break away from the surface of the original crystals and as they increase in size they, too, could produce 'daughter' crystals.

The initial formation of 'daughter' crystals takes place at lattice defects in the original crystals and the formation of crystals in this way is almost certainly easier than nucleation from solution/colloidal species. Although it is not clear why these 'daughter' crystals should break away from the original crystal it is believed that the process is assisted by mechanical agitation of the reaction mixture.

Although reaction HT HEX R80 was seeded with crystals of ZSM-5 the product (Plate 4.7) did not show any significant differences from those of unseeded reactions, Plates 4.4 to 4.6. It was not possible to detect the original ZSM-5

TABLE 4.9 SAMPLES USED IN SEM STUDY

	Sample Number		Reaction Conditions							
Plate Number	HT	HEX	Composition						Stirring speed	
			SiO_2	Al_2O_3	Na_2O	HEX Br_2	H_2O	Seed	/r.p.m.	Temp/°C
4.4	R108	S10	60	1	10	10	3000	-	300	200
4.5	R108	S10	60	1	10	10	3000	-	300	200
4.6	R30		60	1	10	10	3000	-	300	200
4.7	R80		60	1	10	10	3000	ZSM-5	300	200
4.8	R55		60	1	10	10	3000	-	750	200

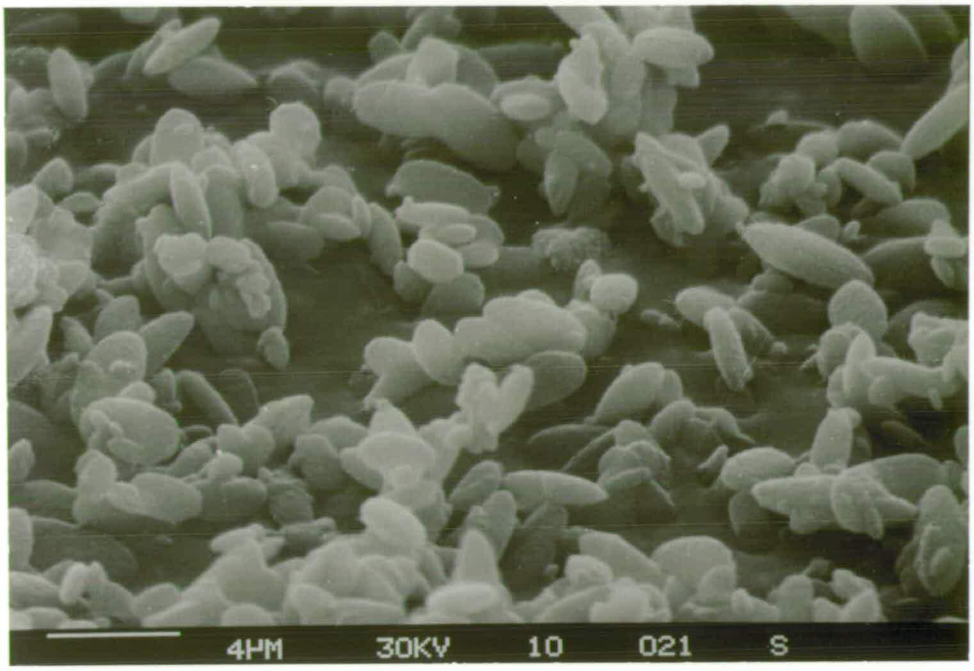


Plate 4.4

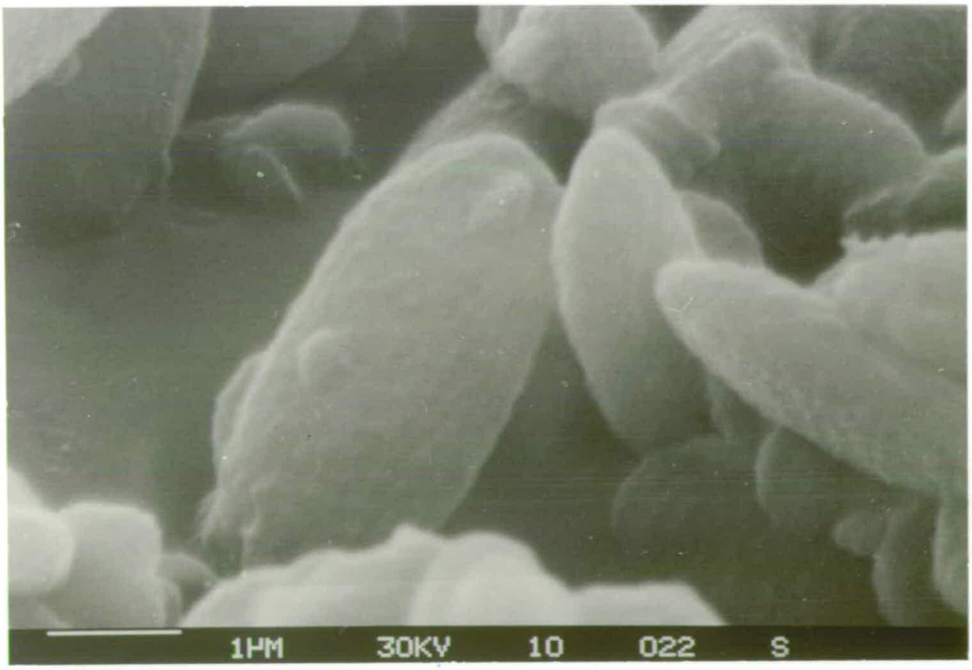


Plate 4.5

Plate 4.6

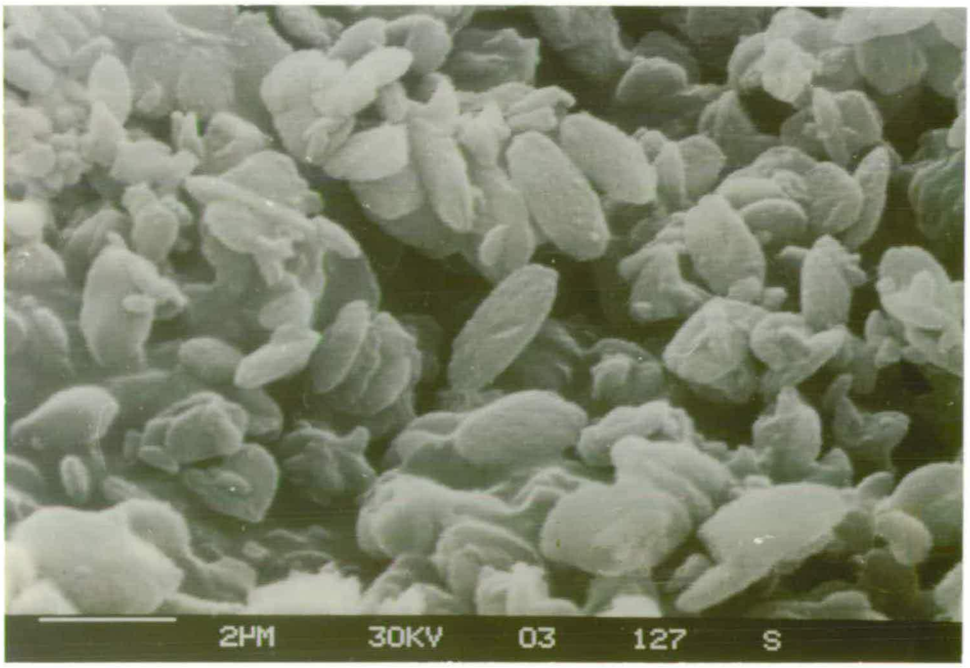


Plate 4.7

crystals by SEM or X-ray diffraction and it could be that they have dissolved in the reaction mixture. The crystals formed in reaction HT HEX R80 (Plate 4.7) may be slightly smaller and less regular in shape than those formed in the unseeded reactions thus reflecting the more rapid and less controlled growth, a consequence of the increased nucleation. The crystals obtained from HT HEX R55 (Plate 4.8), in which the stirring speed was 750 r.p.m., are not as regular as those obtained from reactions HT HEX R30 and 108. This is probably because the increased stirring speed increases the rate of transfer of nutrients to the growing crystal to such an extent that growth is more rapid and less even.

Although EU-1 was found to resemble several of the "ZSM" series of zeolites it was most similar to the zeolite ZSM-23. A comparison of the d-spacings for EU-1 and ZSM-23 can be seen in Table 4.10. There are obvious similarities and differences between the two powder X-ray diffraction patterns. It should be noted that several lines classed as being diagnostic of ZSM-23 (i.e. they are used in Table 1 of the G.B. patent[9]) do not occur in the EU-1 pattern. The sorption properties of EU-1 and ZSM-23 are compared in Table 4.11, from which it can be seen that EU-1 is a better sorbent for water and n-hexane than ZSM-23 and indeed the sorptive capacity of EU-1 is double that of several samples of ZSM-23. The wide variation in the sorption properties of the samples of ZSM-23 in Table 4.11 suggests that the inventors found it difficult to synthesise a pure sample of ZSM-23. Several of the synthesis examples

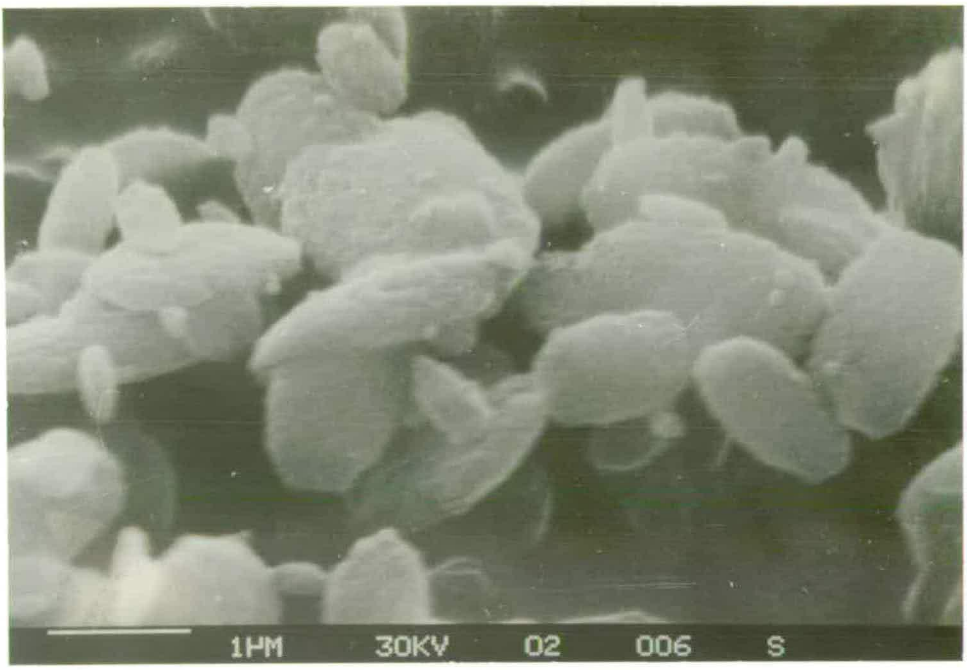


Plate 4.8

TABLE 4.10 COMPARISON[a] OF DIFFRACTION LINES FOR ZSM23 AND EU1

ZSM23[b]		EU1[c]	
11.19	m	11.03	vs
10.07	w	10.10	vs
-		9.716	m
9.51	w	-	
7.86	w	-	
-		7.69	m
7.50	w	-	
-		6.84	w
6.40	w	-	
-		6.21	vw
6.15	w	-	
6.03	w	-	
5.71	w	5.80	w
5.58	w	5.61	vw
5.44	w		
5.16	w		
5.00	w		
4.91	w		
-		4.71	vw
4.54	s	4.64	vs
4.45	w	-	
4.37	w	-	
4.27	vs	4.29	vs
4.17	w	-	
4.12	w	-	
4.07	m	-	
-		3.99	vs
3.90	vs		
3.83	m	3.80	s
3.73	vs	3.70	s
3.63	vs	-	
3.54	m	-	
3.45	s	3.43	w
3.37	w	3.34	m
3.32	w	-	
-		3.24	s
3.17	w	3.14	vw
3.06	w	3.07	vw
2.996	w	-	
2.956	w	2.93	vw
2.851	w	-	
2.787	w	-	
2.732	w	2.69	vw
2.640	w	-	
2.609	w	-	
2.537	m	2.533	m
2.495	w		
2.472	w		
-		2.464	vw
2.445	w	-	
2.401	w	2.395	vw
2.344	w	-	
2.316	w	2.317	vw

[a] Only diffraction lines which agree to within ±0.5 are shown on the same line.

[b] The diffraction lines for ZSM23 were taken from Table 2, U.K. Patent 1,491,398. The values of d which are underlined are those which correspond to those in Table 1, U.K. Patent 1,491,398.

[c] The sample of EU1 is HT HEX R1, film J403.

TABLE 4.11 COMPARISON OF ADSORPTION BEHAVIOUR OF EU1 AND ZSM23

	Results for EU1				Results for ZSM23[a]								
	Sample HT Hex R2S2[b]			Example No.	1	2	3	4	5	6	7	8	9
	SiO_2/Al_2O_3 = 76.8			SiO_2/Al_2O_3	60.6	63.3	67.3	63.4	66.8	55.1	67.9	101	217.1
Adsorbate	P mmHg	Time h	% Weight increase	P mmHg	Percentage Weight Increase								
Water	4.5	2	6.93	12	5.5	6.2	4.0	4.2	3.2	5.1	5.0	4.6	2.3
	4.7	2	3.86										
		19	9.34										
n-hexane	45.8	2	9.52	20	5.3	5.6	5.6	5.7	5.4	4.5	5.1	6.1	2.0
cyclohexane	27	2	1.12	20	1.4	1.7	1.3	1.0	1.7	2.2	1.4	2.1	1.2

[a] Examples 1-9 taken from UK Patent 1491 398. Adsorption times did not exceed 8 hours. Calcined at 540°C for 16 hours.

[b] Calcined at 450°C for 40 hours - results taken from Table 4.4.

described in the patent[9] report the formation of impurities such as ZSM-5, α-crystobalite and an unidentified material. In addition a line at d = 4.26 Å which occurs in the X-ray diffraction patterns of all the examples was not included in the Table 1 lines of the patent. Since α-quartz has a major line at d = 4.26 Å, their samples of ZSM-23 may all have contained α-quartz in addition to the impurities mentioned above. Although it was believed that EU-1 and ZSM-23 were different materials several attempts were made to synthesise ZSM-23 in order to compare the materials directly. The results of these attempts are given in Table 4.12. At no stage was ZSM-23 synthesised. Attempts by T.V. Whittam[1] at I.C.I. Agricultural Division also failed to produce ZSM-23.

4.3.4 RATE OF FORMATION OF EU-1

The experiments used to study EU-1 formation were of two types, those concerned with the product obtained from the reaction and those specifically concerned with the rate of reaction. In both types of experiment it was important to follow the reaction by the examination of samples taken during the reaction. Four different methods were used to examine these samples and hence to follow the crystallisation; these were as follows:

a) Visual examination

This method relies on the relative sedimentation rates of amorphous and crystalline materials. The sedimentation of amorphous material can take several weeks whereas the crystalline zeolite sediments

TABLE 4.12 ATTEMPTS TO SYNTHESISE ZSM23

Run No	Composition					T/°C	t/d	Product
	SiO_2	Al_2O_3	Na_2O	PYR[a]	H_2O			
ZSM23 Ex 1[b,c]	59.1	1	1.45	19.41	602.3	180	11	tr/MED mordenite + α Q [g]
ZSM23 Ex 2[b,d]	59.2	1	1.42	37.37	707.6	180	11	tr ZSM5
ZSM23 Ex 3[e]	124.6	1	1.57	36.9	2935.2	180[h]	3	FU6[f]
ZSM23 Ex 4[e]	124.6	1	1.57	36.9	2935.2	175	4	FU6[g]
HT HEX R62[b]	60	1	5	20	2000	180	[i]	-
HT HEX R65[b]	60	1	5	20	2000	180	5	Med ZSM5 + α Q

[a] PYR = pyrrolidine.

[b] Reaction carried out at ICI Agricultural Division, Billingham.

[c] Example 1 (179°C, 7d) U.S. Patent 4,104,151.

[d] Example 3 (177°C, 11d) U.S. Patent 4,104,151.

[e] Example 1 (177°C, 3d) U.S. Patent 4,160,788

[f] FU6 feldspathoid type material synthesised and characterised by T.V. Whittam, Agricultural Duvision.

[g] X-ray diffraction pattern also contains a few unidentified lines.

[h] Temperature overshot by about 15°C. Reaction was repeated (ZSM23 Ex 4) since increase in temperature may have caused formation of FU6.

[i] Bursting disc failed.

very rapidly. The rate of sedimentation depends primarily on the size of the zeolite crystals and the nature of the reaction liquor. Although large differences in the sedimentation rates of different zeolites were found, zeolite EU-1 was observed to settle out, normally, under 30 minutes. Plate 4.9 shows this for samples taken from reaction HT HEX R52. Note Plate 4.9 can be compared with the results of pH and n-hexane sorption studies in Fig. 4.6. This technique has been noted by several other workers and Breck[14] includes a photograph which shows the separation of zeolite X from its mother liquor in successive samples taken during its crystallisation. In the present study the method was used solely to determine if the reaction mixture had crystallised.

b). X-ray powder diffraction

This is the method most widely used to follow zeolite crystallisation. Unfortunately it could not be used for most of the present investigation since a suitable X-ray powder diffractometer was not available at Edinburgh. Successive samples from reactions were analysed by the Guinier-Hagg camera but only when it was believed that some transition was occurring, or, when a mixture was obtained

Plate 4.9 Samples taken from Run HT HEX R52 at hourly intervals

and it was necessary to determine which species had formed first. It is important to realise that X-ray diffractometry can only be used to study the rate of zeolite growth when the zeolite crystallises in the presence of some amorphous material, since the method depends on the changes in peak height which is a consequence of the proportion of zeolite (by volume) in the sample. It cannot be used to study crystallisation from a solution free from amorphous material or as suggested in section 4.3.3 the zeolite continues to crystallise from colloidal or solution species once all the amorphous material has been used up.

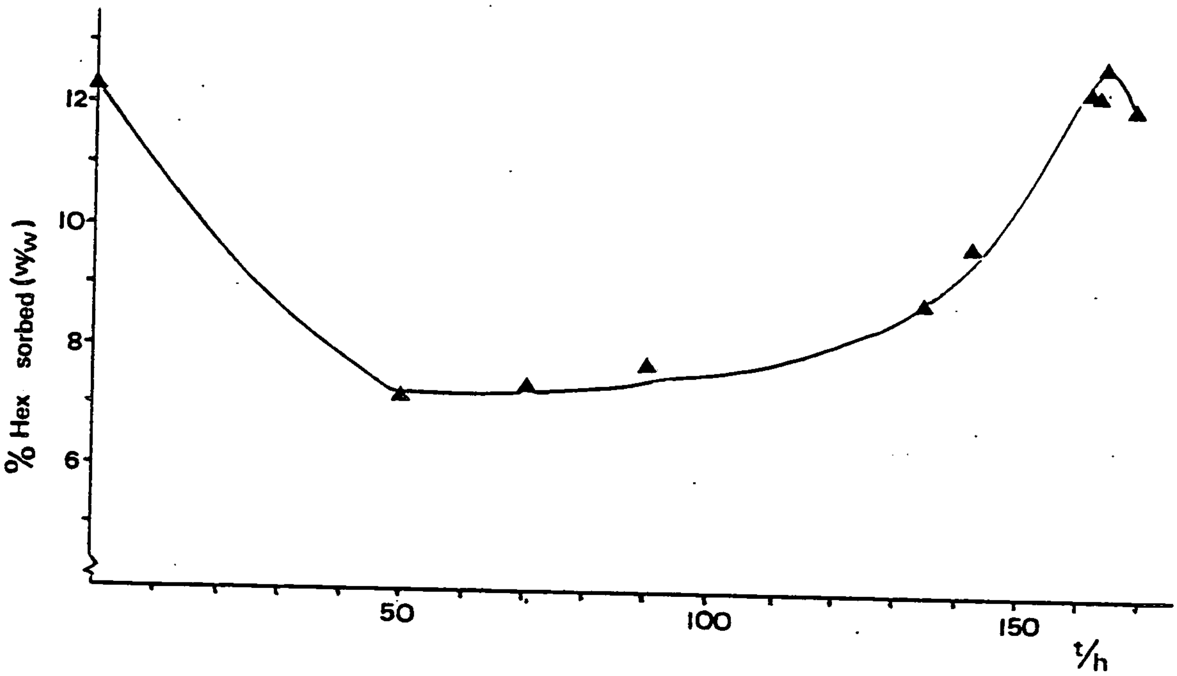
c) Sorption

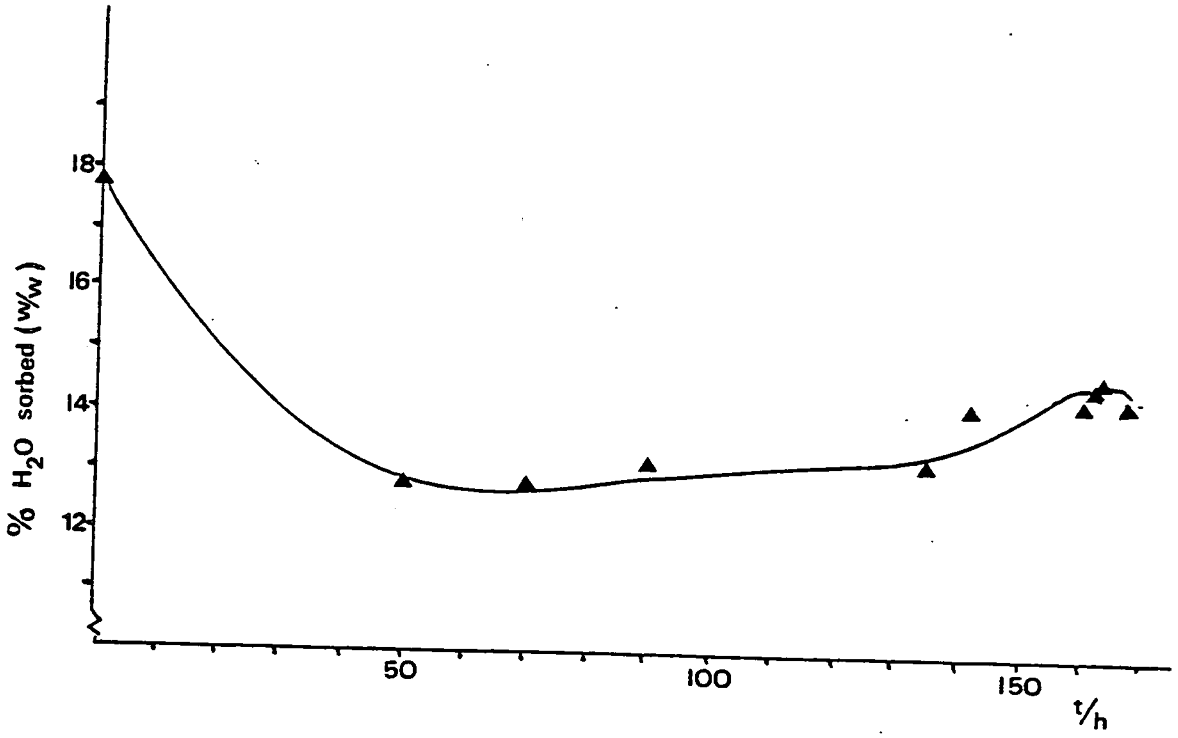
The use of sorption to follow a zeolite crystallisation requires the amorphous and crystalline materials to have different sorption properties. Examination of Fig. 4.5 shows that for EU-1, n-hexane sorption fills this requirement whereas water sorption does not. The use of sorption to follow a reaction has similar problems to those outlined above for X-ray diffraction.

d) pH measurements

It was found that the pH of samples taken from "medium" and "high silica" zeolite reaction mixtures once cooled to room temperature (but unfiltered) reflected the progress of

Fig. 4.5 n-hexane and water sorption of samples from run, HT HEX R25





crystallisation. Fig. 4.6 shows pH and sorption data for run HT HEX R52. Comparison with Plate 4.9 shows that all three techniques give a reliable indication of the onset of zeolite crystallisation. Fig. 4.7 gives sorption, pH and X-ray powder diffraction data for run HT HEX R30 and illustrates that both pH and sorption give a reliable indication of the onset of crystallisation as shown by X-ray diffractometry. In "low silica" zeolite crystallisation e.g. in the synthesis of zeolites X, P etc., this change in pH cannot be monitored by conventional techniques[12] since initial pH values tend to be around 14.0 and the detection of a small pH change in this region by conventional glass electrodes is difficult. By comparison the initial and final pH values in the "medium" and "high silica" zeolite reactions were in the range pH = 11.0 to pH = 12.5 and changes were easily detected. Note it is believed that this is the first time zeolite crystallisation has been followed by the associated pH change.

In section 4.3.3 the results of SEM studies of EU-1 were discussed. In addition to those "final product" investigations, the technique of SEM was also used to examine changes in the solid phase which occurred during reaction HT HEX R108. The growth curve for this reaction as followed by changes in pH can be seen in Fig. 4.8 (in which the position of sample S4 was estimated). Samples

Fig. 4.6 pH and sorption studies of samples from reaction HT HEX R52

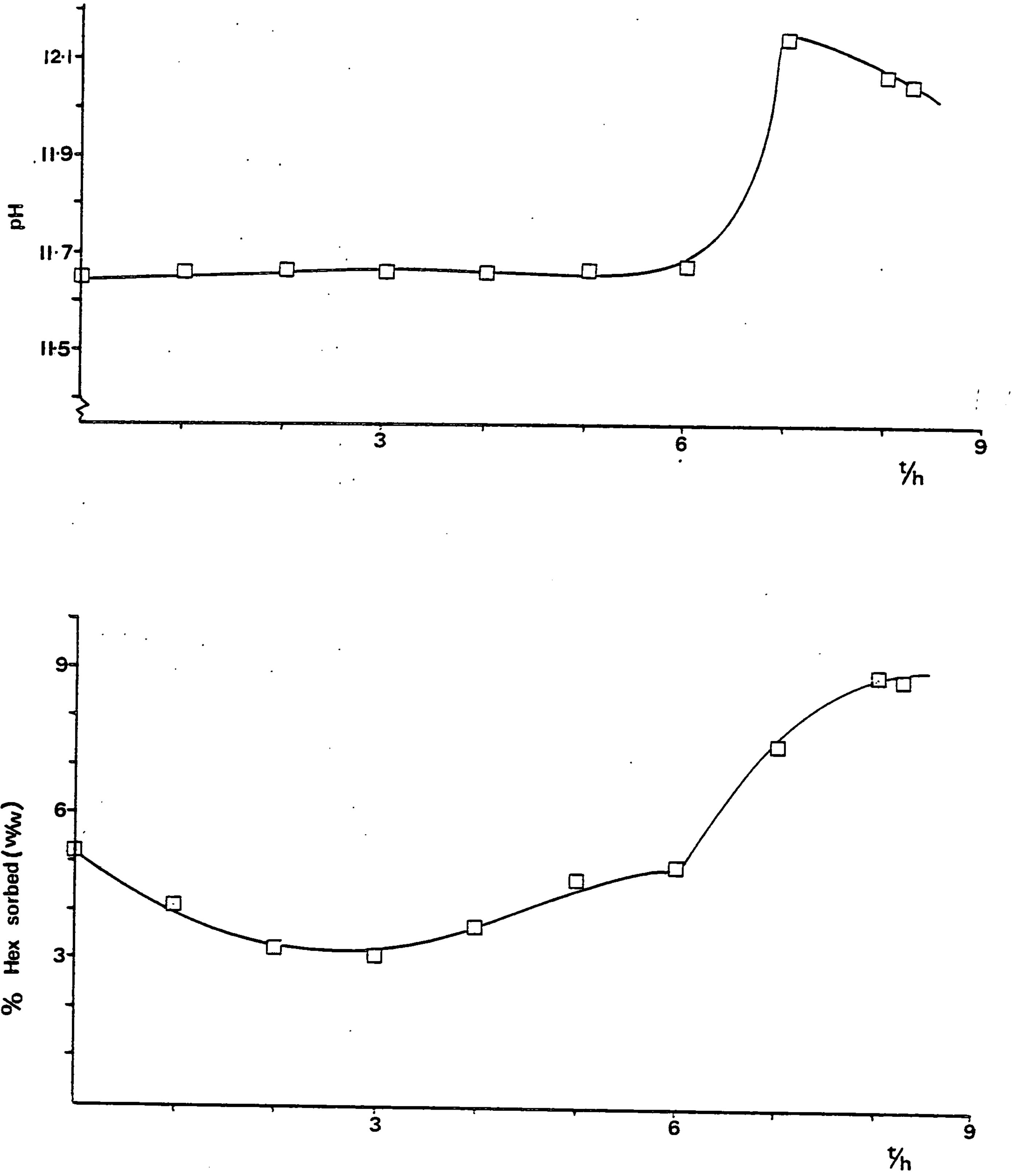


Fig. 4.7 pH, sorption and XRD studies of samples from run, HT HEX R30

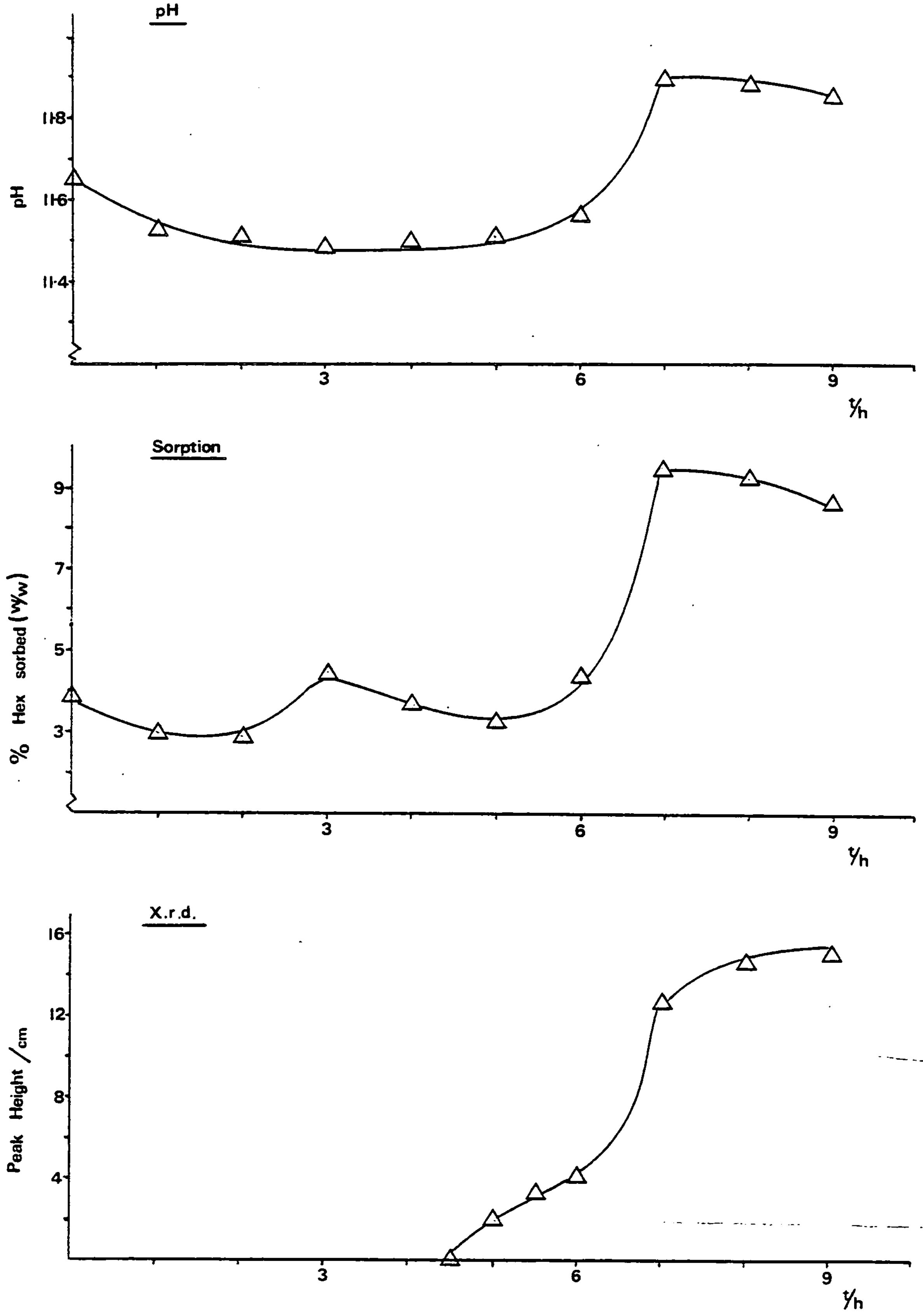
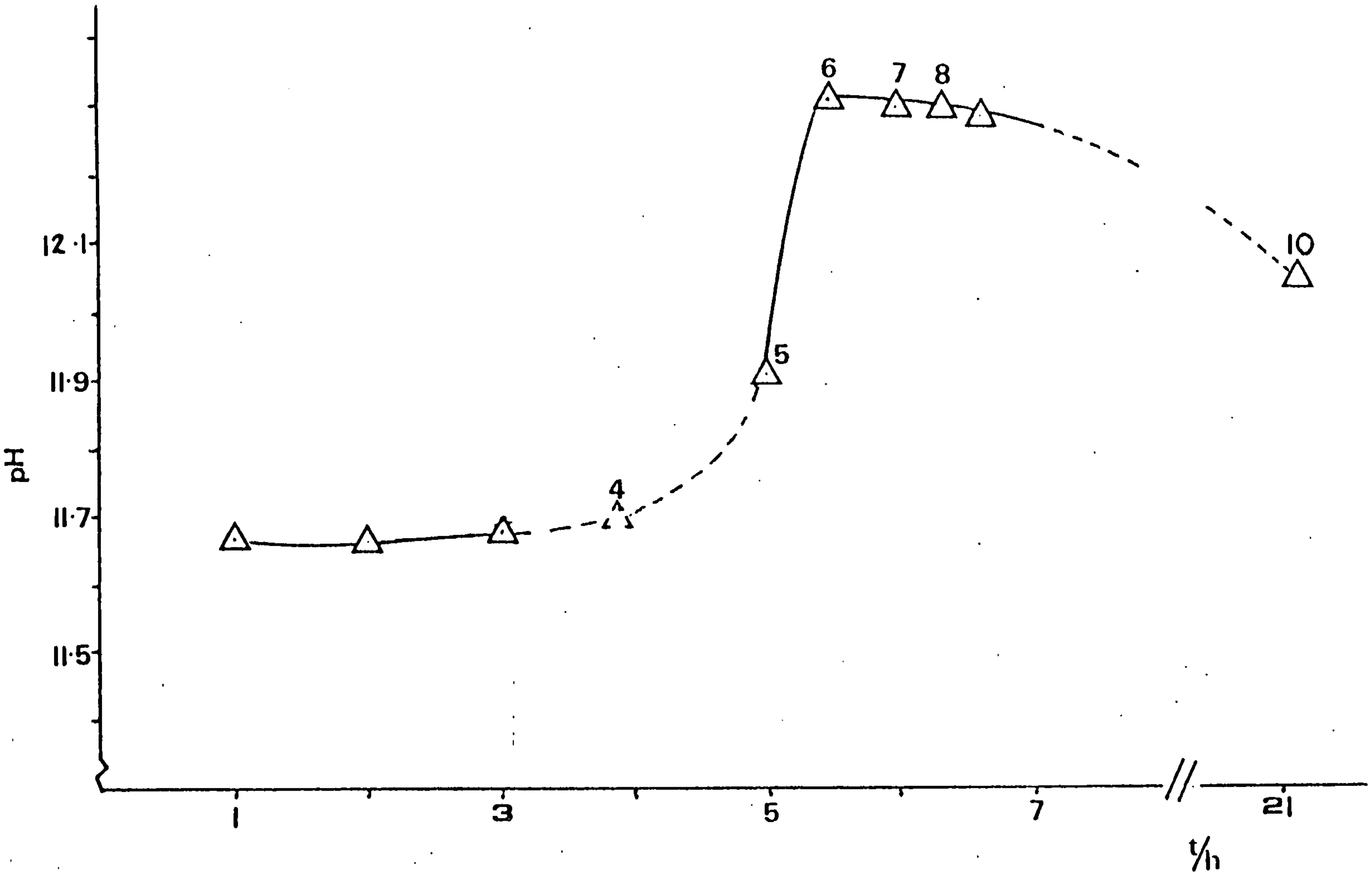


Fig. 4.8 pH studies of samples taken from run HT HEX R108



4,5,6,7,8 and 10 were examined by SEM. It is of particular interest that the crystals in sample 10, Plate 4.15 are similar in size and size distribution to those in samples 5,6,7 and 8 (Plates 4.11, 4.12, 4.13 and 4.14 respectively). This suggests that nucleation occurs continuously in the EU-1 system. Plates 4.10 and 4.11 show that the reaction mixture when it is still amorphous (Plate 4.10) and when a major part of the amorphous material had been converted to EU-1 (Plate 4.11). What is particularly significant and can be seen in several of the micrographs, particularly those of samples 5 and 6 is the growth of "secondary" crystals from the surface of the crystals already present. This was discussed in section 4.3.3. The formation of these "secondary" or "daughter" crystals on the surface of larger growing crystals provides a mechanism for the continuous nucleation required to explain the constant size distribution. The "secondary" crystals probably grow at defects in the lattice and as the external surface area increases, the number of defects, and hence the number of daughter crystals also increases. Growth of the original crystals ceases when the growth of "secondary" crystals uses up all the nutrients available to the total surface. Once a "secondary" crystal has broken off from the surface another may begin to grow at the same place. Thus there are two types of nucleation; the first, is responsible for the production of the "initial" nuclei which start off the reaction and the second method of nucleation is provided by the secondary "crystals" previously described. The production of the "initial" nuclei could occur by the

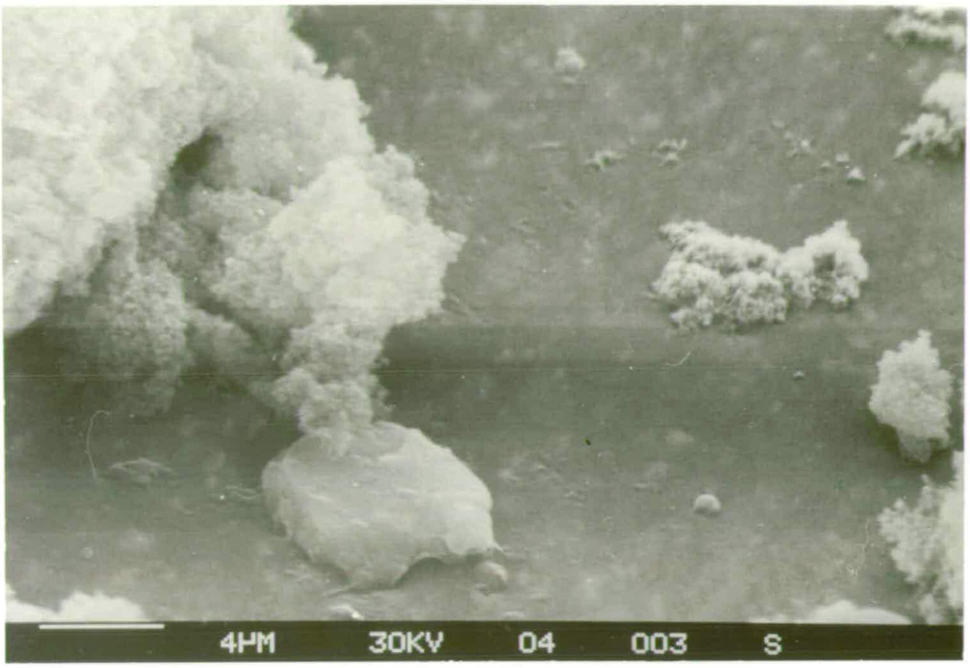


Plate 4.10
HT HEX R108
S4

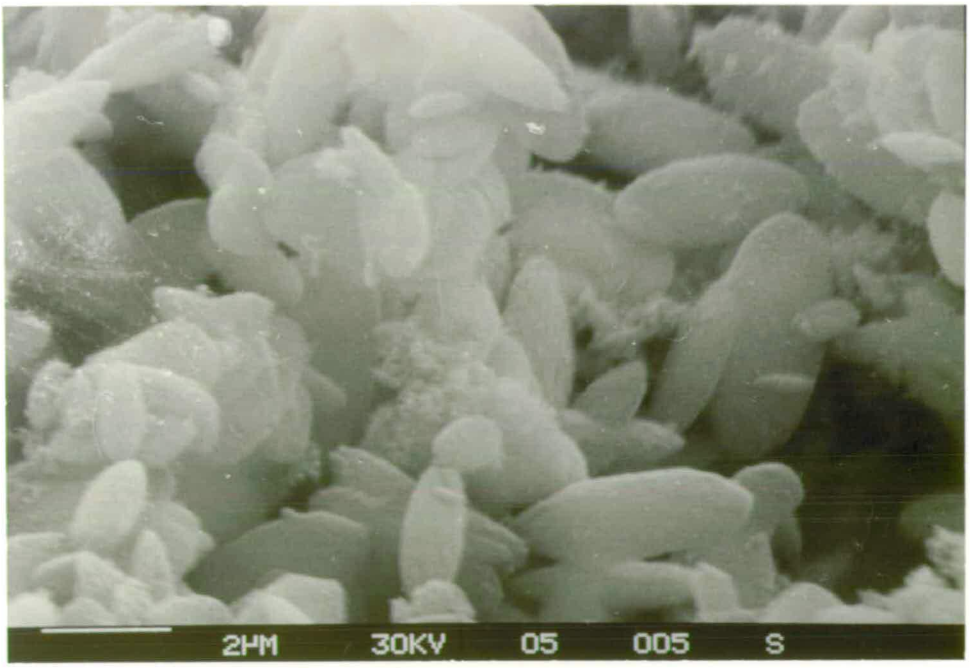


Plate 4.11
HT HEX R108
S5

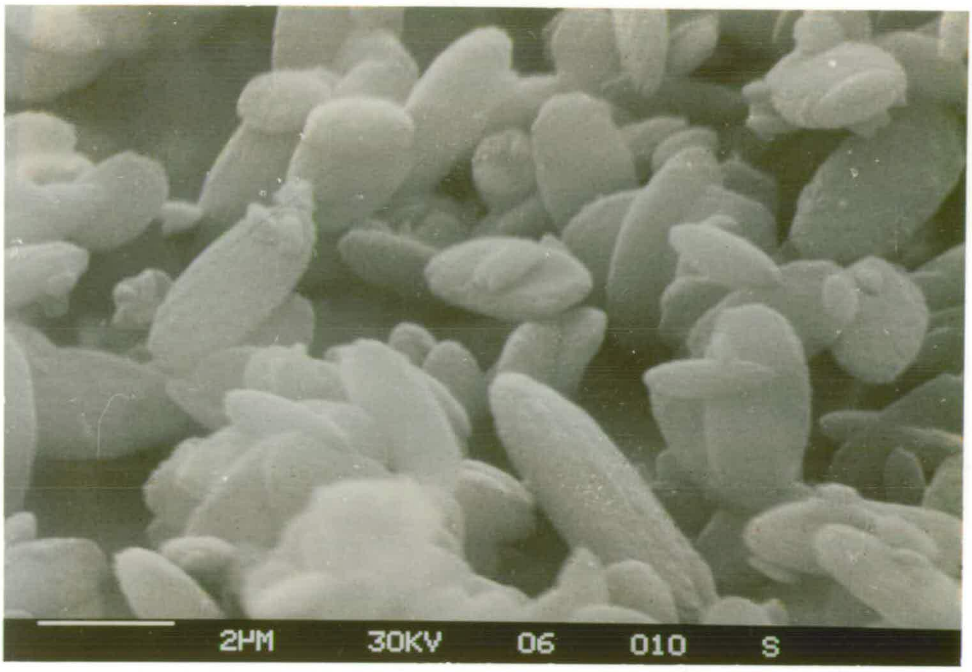


Plate 4.12
HT HEX R108
S6

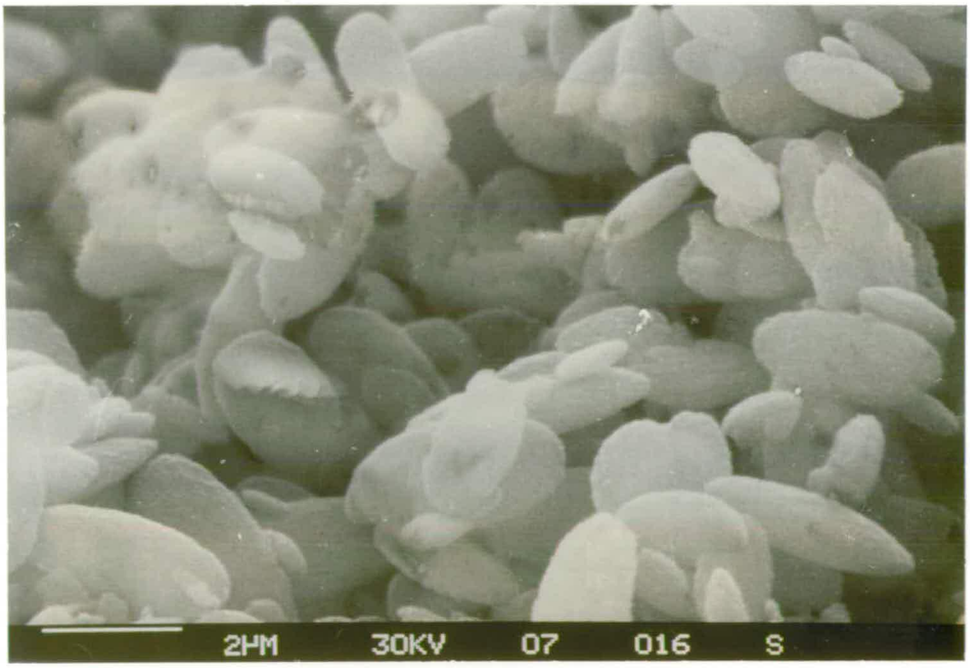


Plate 4.13
HT HEX R108
S7

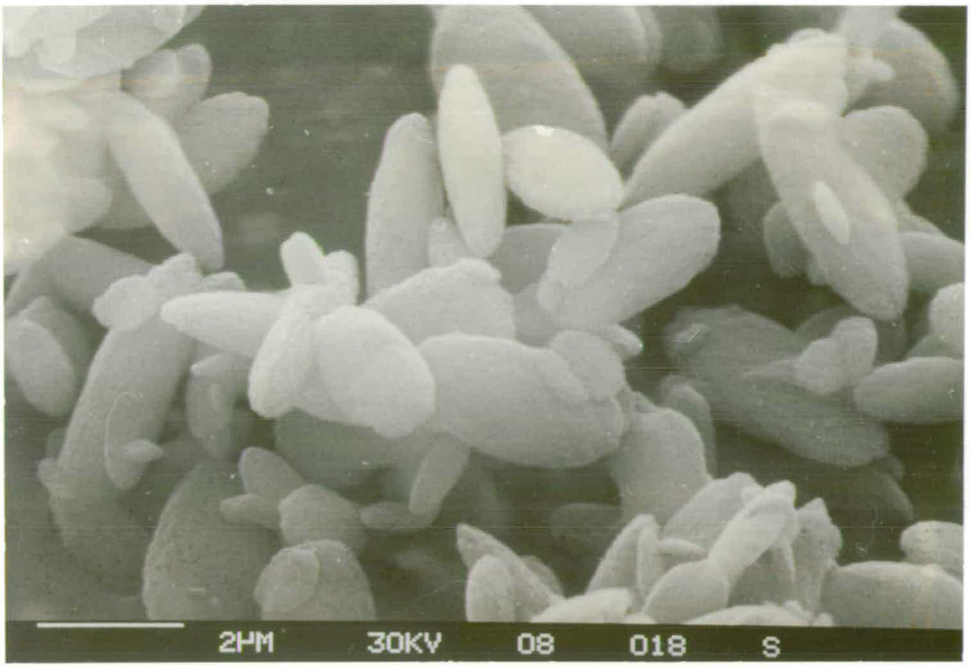


Plate 4.14
HT HEX R108
S8

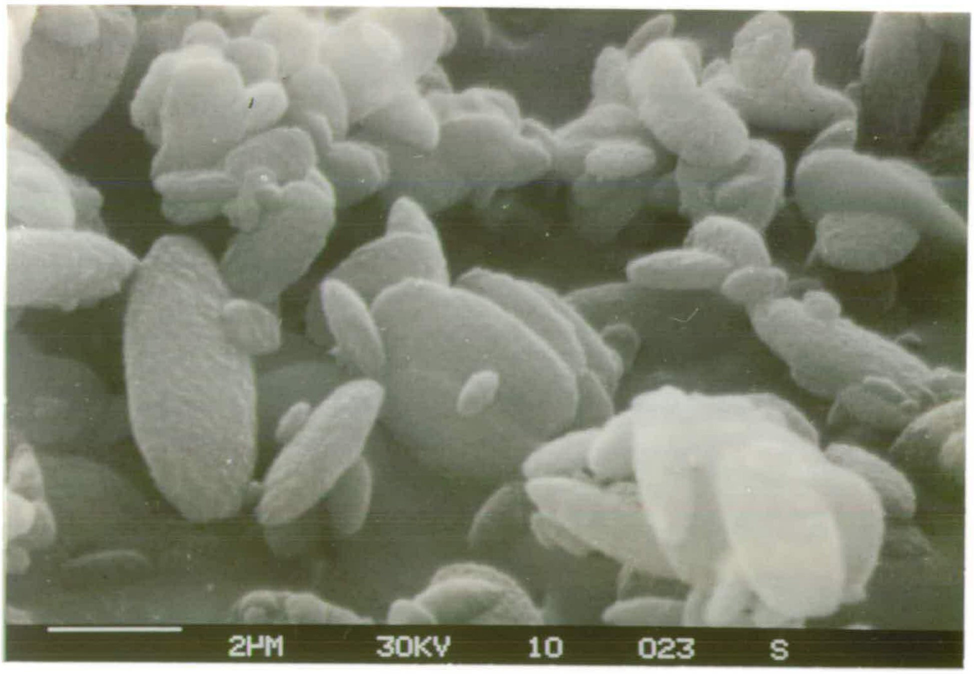


Plate 4.15
HT HEX R108
S10

flocculation of colloidal alumino-silicate units (originally formed from solution species) or directly by the condensation of solution species. Once the "initial" nuclei have been formed and growth begins it is likely that the solution species are then used in growth and further production of the "initial" nuclei ceases. Further "growth centres" are then only produced by the "secondary" crystal method.

In systems in which the growth of the "initial" nuclei is slow (at lower temperatures or in reactions of different compositions) larger crystals may be produced. This is because a decreased growth rate leads to more perfect crystals i.e. ones with a smaller number of defects and thus there are fewer "secondary" crystals produced. Thus the nutrients are transferred to a smaller number of "growth centres" which would lead to the production of larger crystals. In a system in which the growth of the "initial" nuclei is very fast a change in the number of "initial" nuclei would have little effect on the size of the crystals produced. A decrease in the number would lead to a relative abundance of nutrients and growth would occur very quickly producing "secondary" crystals. A very large number of "initial" nuclei would rapidly remove the nutrients from the solution but in such a case it would be likely that the nutrients would be depleted before large crystals were produced. It was suggested above that "initial" nucleation would occur by condensation of colloidal species. Further evidence for this is given in a paper by Sand and Culfaz[13] who reported that the addition of NaCl to a reaction mixture had little effect on the activation energy for growth (compared with the reaction without NaCl) but had a marked effect on the activation energy for nucleation. The growth rate however was decreased by more than two-fold. This was attributed to an increase in the viscosity of the solution. However the effect on NaCl on the activation energy for nucleation was not discussed. It is possible that the reduction in the activation energy brought about by the addition of salt is associated with the increase in ionic strength of the medium and the consequent increase in the flocculation rate. It should also be noted that NaCl could produce a "salting out" of sodium alumino-silicate species from solution. Both of these effects could increase the rate of nucleation and both could also reduce the crystal growth rate by limiting the amount of nutrients in solution. A combination of these two effects could lead to the formation of larger crystals as reported in a paper by Barrer and Cole[17] in which they state that ".... salt inclusion generally improved the quality of sodalite and cancrinite microcrystalline powders. ... this salt encapsulation has generally increased the size and quality of the crystals." Although Barrer referred to encapsulated salts it could be that the observed effect could have been obtained in the way described above.

4.3.5 EFFECT OF TEMPERATURE ON EU-1 FORMATION

Although attempts to synthesise EU-1 at 95°C were unsuccessful and instead of EU-1 a new species, EU-3 (section 4.3.2) was formed, there was no evidence for the formation of EU-3 as an intermediate in a 150^{o}C, EU-1 reaction (see for example HT HEX R25, Fig. 4.5). This will be discussed further in section 4.5, and it is sufficient to note that the formation of EU-3 as an intermediate does not complicate the analysis of results obtained by the study of EU-1 formation at different temperatures.

Fig. 4.9 shows growth curves for EU-1 formation in the temperature range 180-220^{o}C. The reactions were followed by the amount of n-hexane sorbed by the calcined samples. It was possible to calculate an apparent activation energy for the formation of EU-1. To do this a measure of the rate of EU-1 formation was required. The value chosen was t_r^{-1}, in which t_r, the reaction time, represents the time required to complete the crystallisation of EU-1 (t_r was measured from t_o, that is, from when the reaction mixture reached the chosen reaction temperature). An Arrhenius plot based on the equation,

$$t_r^{-1} = A \exp ({}^{-Er}/_{RT})$$

was constructed and this can be seen in Fig. 4.10. Values of t_r, observed and calculated, are given in Table 4.12. The apparent activation energy of the reaction Er = 109.1 kJ mol^{-1} and the pre-exponential factor A = 1.77×10^{11} h^{-1}. Several workers have reported activation energies for the formation of low silica zeolites such as X, A and Mordenite[13,14,18,19]. Activation energies for A, X and Mordenite although different were all in the range 10 to 15 k cal mol^{-1}. It should be noted that although most activation energies reported are for zeolite growth,

Fig. 4.9 Growth curves for EU-1 crystallisation at 150, 180, 200 and 220°C

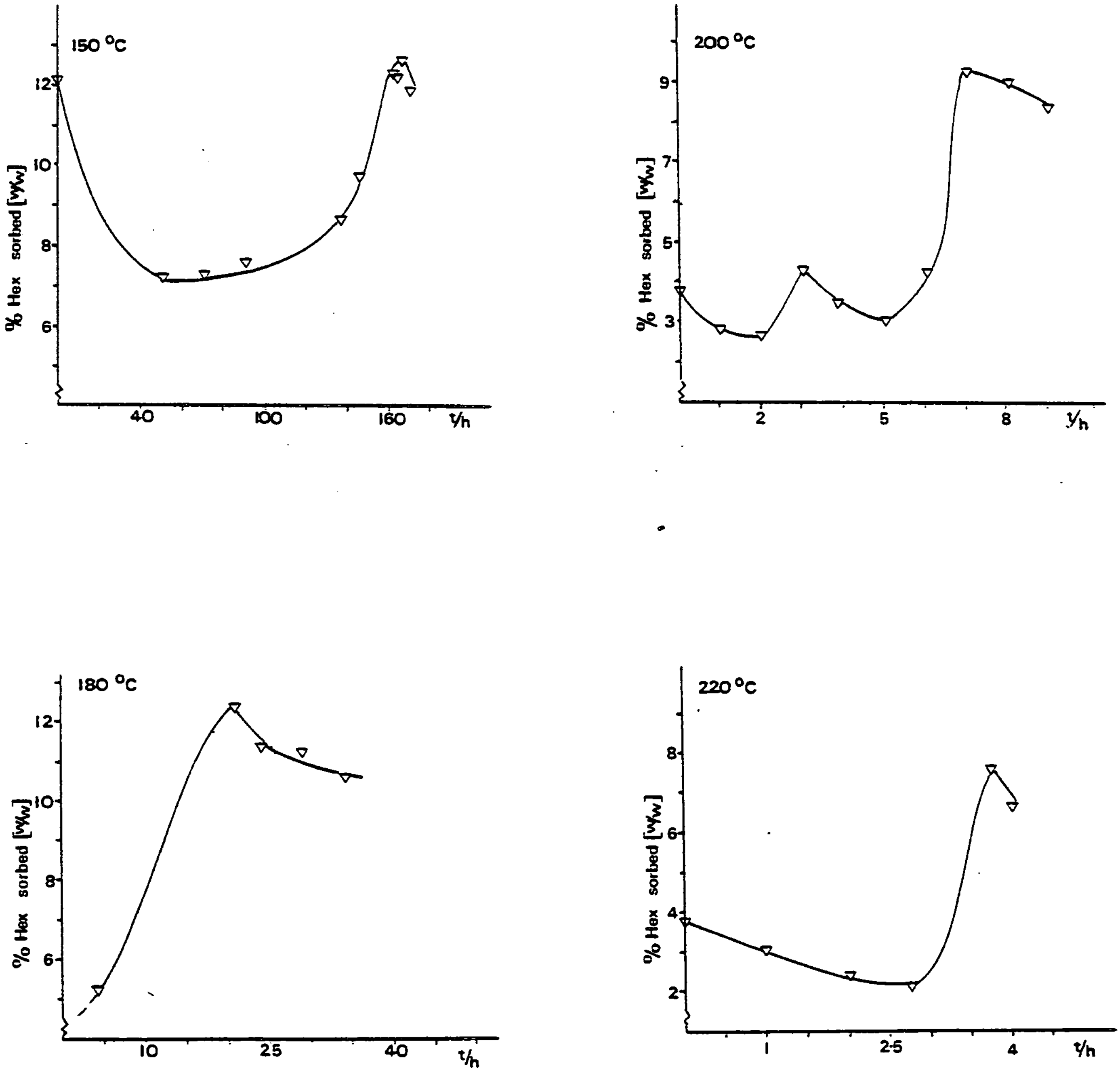


Fig. 4.10 Plot of $\ln(tr^{-1})$ against $1/T$ for EU-1

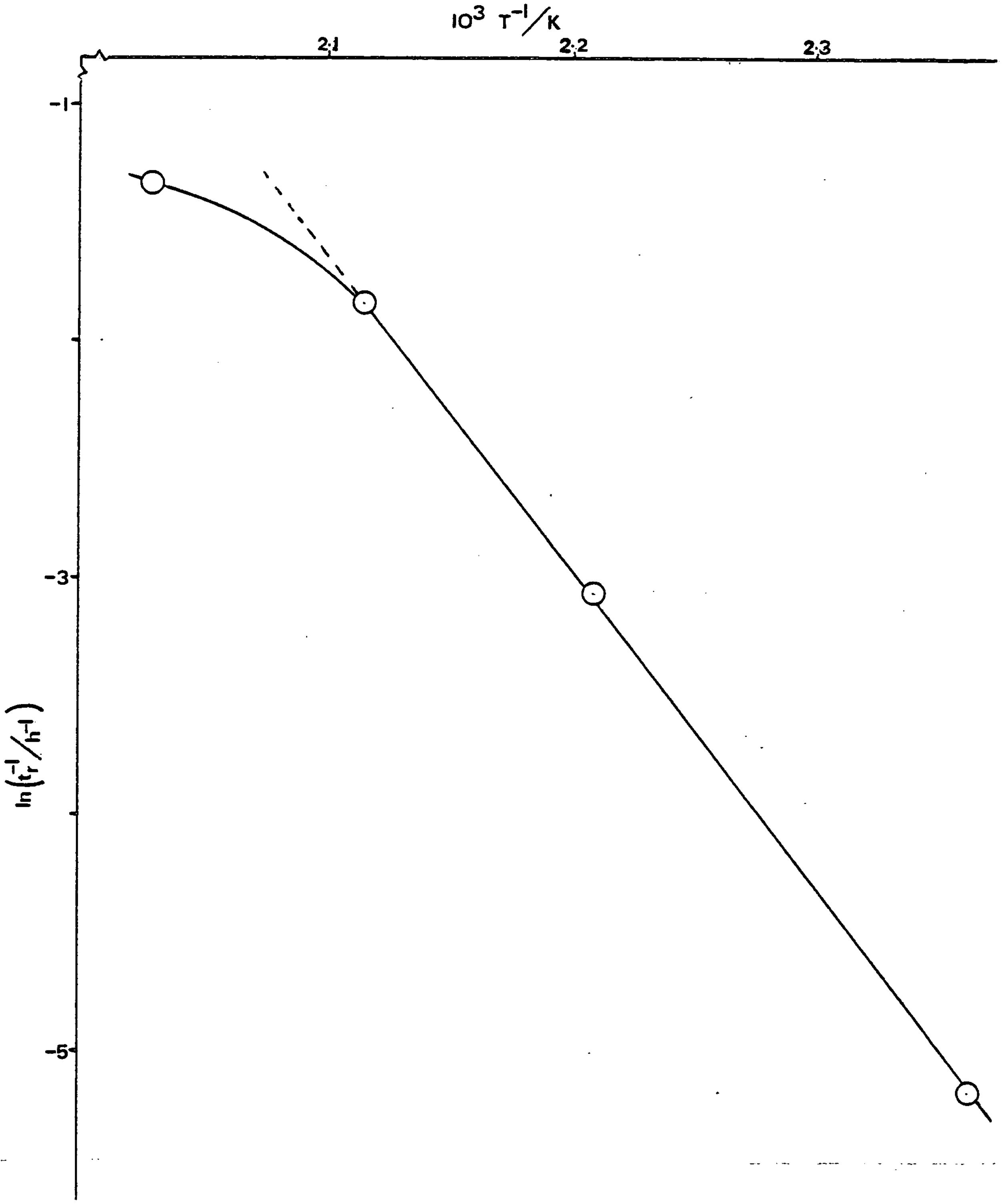


TABLE 4.12 EFFECT OF TEMPERATURE ON THE TOTAL TIME REQUIRED FOR THE STANDARD EU-1 REACTION[a]

Run No HT HEX	Temperature T/°C	 T/K	Time, t_r/h Obs.	 Calc.[b]
R25	150	423	165	167.8
R24	180	453	21	21.5
R30	200	473	6.25	6.32
R50	220	493	3.75	0.49
-	135	408	-	525.0 (= 21.9 d)
-	95	368	-	17316.2 (= 721.5 d)

[a] Standard reaction mixture 10 Na_2O - 10 HEX Br_2 - Al_2O_3 - 60 SiO_2 - 3000 H_2O; stirred; no seed.

[b] Calculated with $t_r^{-1} = A \exp(-E_r/RT)$ using $E_r = 109.1$ kJ mol^{-1} and $A = 1.77 \times 10^{11}$ h^{-1}.

Çulfaz and Sand[13] reported separate activation energies for both nucleation and growth. In the present study it was believed that there was insufficient experimental data to allow separate calculations for nucleation and growth and the value obtained was for the whole process. Breck[14], stated that it was difficult to assign a physical significance to the activation energy for zeolite crystallisation because it is not usually clear which process is rate determining in the nucleation and growth processes. Although he considers the similarity between the few available activation energies and that reported by Greenberg[15] for the dissolution of silica (apparent activation energy, 21.5 k cal mol^{-1} [a]) to be significant.

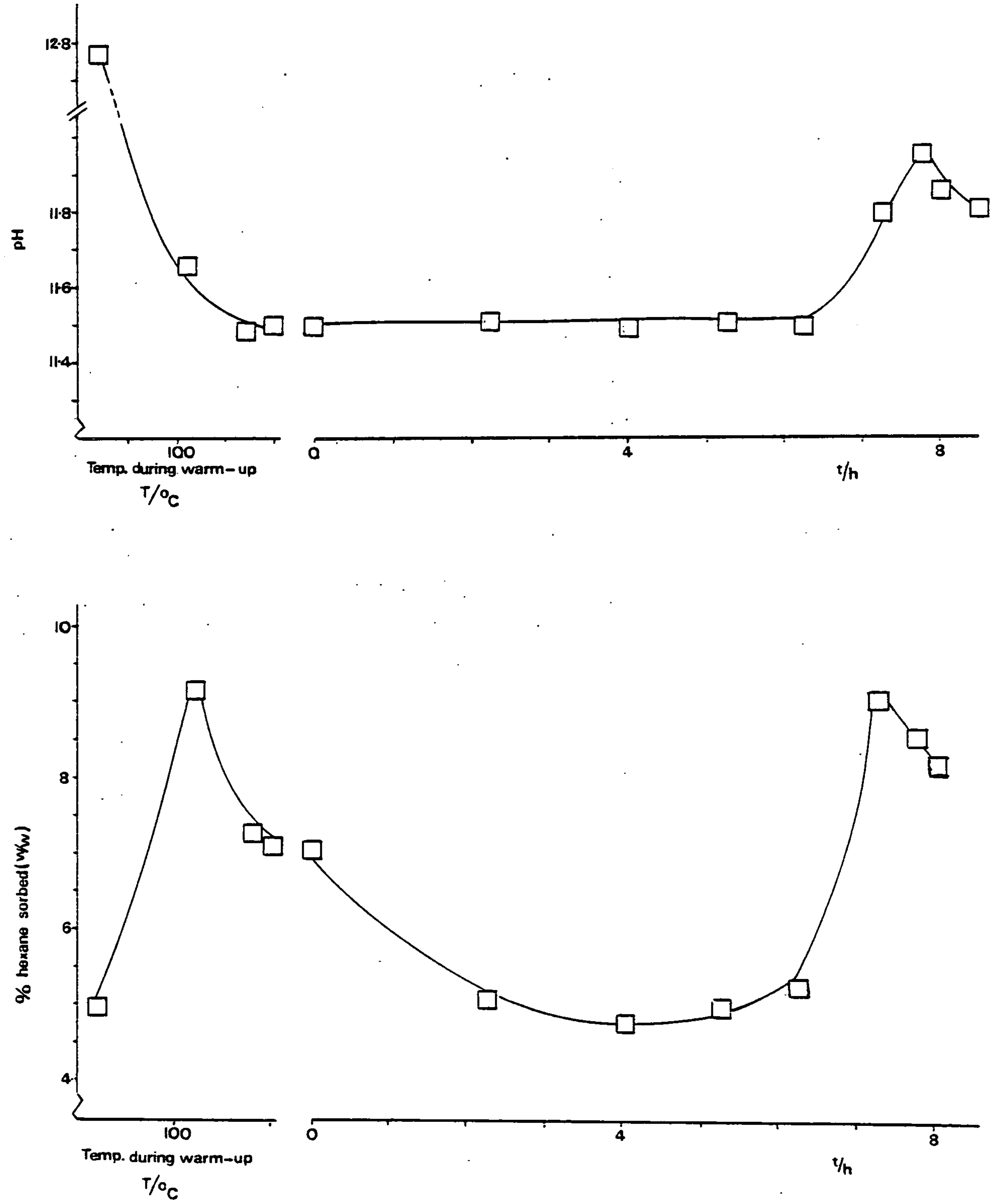
It would have been instructive to have carried out activation energy determination for a series of EU-1 reactions seeded in such a way that the induction period was eliminated, as was done by Culfaz and Sand for zeolite Mordenite. However this was not possible as the addition of seed material did not remove the induction period but merely reduced it (see section 4.3). The effect of seeding on the values of Er and A may have given a clue as to their physical significance. For example if their Er is primarily associated with depolymerisation of the silica and alumino-silicate species it would be unchanged by seeding. The value of A may be associated with the nucleation stage and would be expected to be quite different for the seeded reactions.

[a] Greenberg[15] also reports the effect of pH, stirring speed and surface area on the dissolution rate of silica.

The calculated values of t_r in Table 4.12 illustrate why EU-1 was not formed readily at 95°C. They also show that the only reaction which did not fit the empirical Arrhenius equation was that carried out at 220°C. This is also apparent from Fig. 4.10. The reason that this reaction was slower than expected is probably because the value of t_r^{-1} represents not one but several processes, the main ones being nucleation and growth. The failure of the empirical equation to represent the result for the 220°C run probably reflects the fact that the rate controlling process for this reaction is different to that in the other reactions.

Changes in pH and sorptive capacity during 'warm-up' were also monitored. Fig. 4.11 contains pH and n-hexane sorption results for samples from HT HEX R48 taken during warm-up and crystallisation. The pH, as expected, decreases during warm-up, as the silica dissolves. A minimum value is reached and there is little deviation from this until crystallisation begins. The n-hexane sorption of the calcined samples, however, is quite different. Sorption of n-hexane maximises during warm-up at about 115°C then decreases to 200°C. The decrease in sorption capacity continues throughout the reaction before increasing as crystallisation begins. Two things should be noted, firstly, considerable rearrangement of the amorphous material occurs before the onset of crystallisation which involves no net change in the hydroxide ion concentration. Secondly, the change in the sorption capacity of the amorphous materials may reflect their relative thermal stabilities rather than their porosities.

Fig. 4.11 pH and n-hexane sorption for reaction HT HEX R48

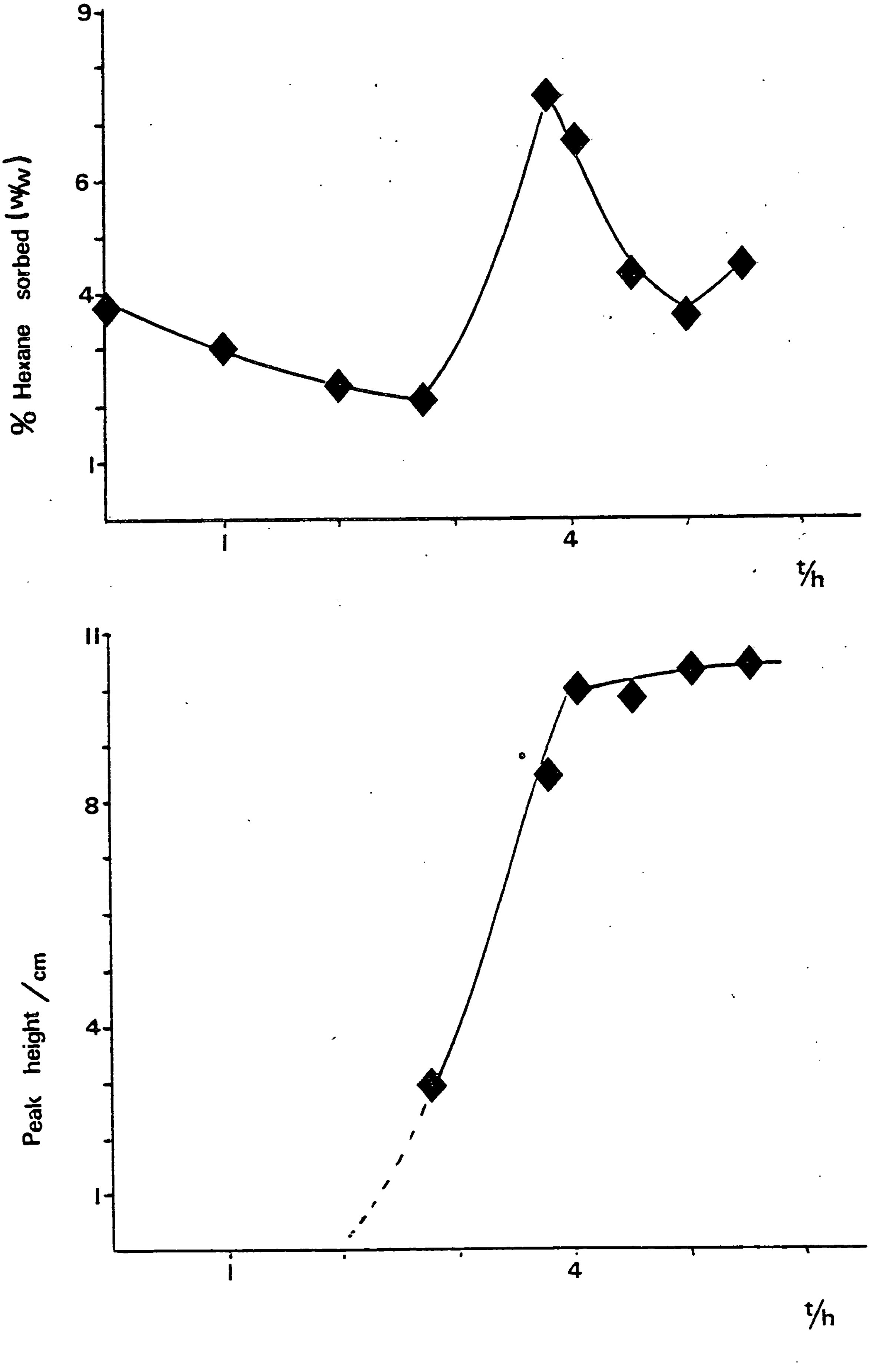


It was observed that both the pH and n-hexane sorption capacity both decreased after EU-1 had crystallised (see Fig. 4.11). This occurred in all of the reactions monitored but was largest for the reaction carried out at 220°C, HT HEX R50. Only part of the n-hexane sorption curve for HT HEX R50 is shown in Fig. 4.9. The complete curve of n-hexane sorption against time for HT HEX R50 can be seen in Fig. 4.12. In addition the results of analysis by powder X-ray diffraction using a diffractometer have been included. It can be seen that the decrease in sorptive capacity is not mirrored in the X.R.D. results which show a continuous increase in crystallinity with time. There are at least two possible explanations for this:

(1) As crystallisation occurs and the pH increases, a stage is reached at which the zeolite is just soluble in the alkaline liquor. The resulting dissolution and disruption of the outer layers of the zeolite affects its sorption properties but its X.R.D. pattern remains unchanged. As the zeolite dissolves the pH decreases and dissolution ceases.

(2) In the final stages of crystal growth either salts (e.g. sodium silicate) are occluded into the lattice or defects occur in the outer layers of the zeolite crystals, possibly by the action of sodium hydroxide. Either process would affect the sorption properties of EU-1 but not its X.R.D. pattern.

Fig. 4.12 n-hexane sorption and peak height from X.R.D. analysis against time for reaction HT HEX R50



One further point should be noted, that is, that the sorption capacity is always largest for the EU-1 samples synthesised at lower temperatures, see Fig. 4.9. It is believed that whatever process causes the decrease in sorption occurs more quickly at higher temperatures and thus it is more difficult to obtain the "best" sample of EU-1 for runs carried out at higher temperatures. The conclusion must be that to synthesise EU-1 with maximum sorptive capacity low temperatures should be used. It should also be noted that the samples of EU-1 used in the sorption study (section 4.3.3) almost certainly did not reflect the best possible sorption of EU-1.

4.3.6 EFFECT OF COMPOSITIONAL CHANGES ON EU-1 FORMATION

Some of the initial experiments described in section 4.3.2 involved changes in the standard reaction composition:

$$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

They showed that EU-1 could be made from a range of compositions. This section deals with how changes in the reaction composition affect the type of product obtained and its rate of formation.

The range of SiO_2/Al_2O_3 ratios over which EU-1 can be synthesised can be seen in Table 4.13. It is interesting that at high SiO_2/Al_2O_3 ratios another material EU-2 was formed in increasingly larger amounts until at a SiO_2/Al_2O_3 ratio of 300/1 only EU-2 was formed. However as the ratio of SiO_2/Al_2O_3 was decreased from 60/1 to 30/1 the decrease in the amount of EU-1 formed was not accompanied by the formation of another material.

TABLE 4.13 PRODUCT OBTAINED FROM REACTIONS OF DIFFERENT SiO_2/Al_2O_3 RATIOS

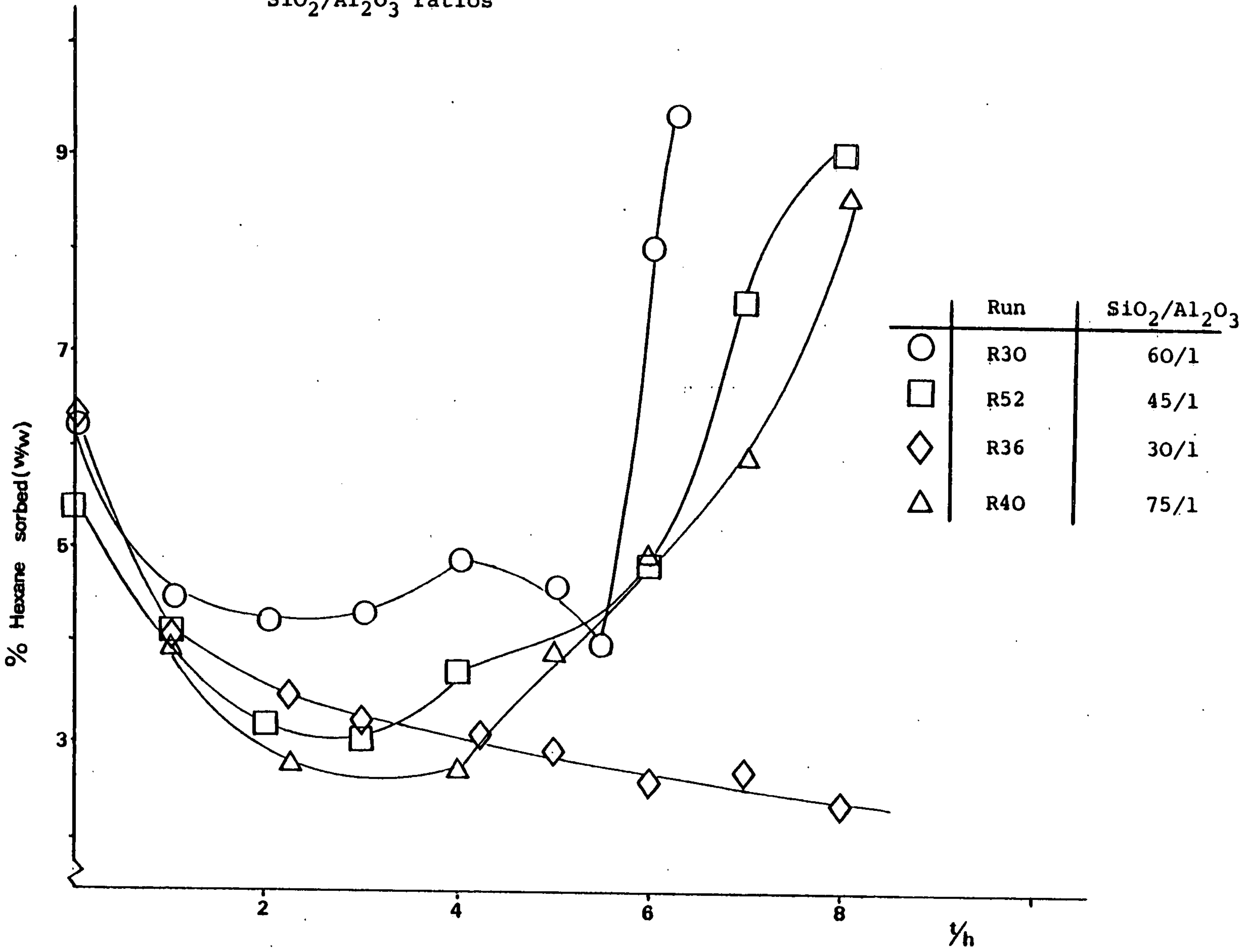
$60\ SiO_2 - x\ Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$

HT HEX	x	SiO_2/Al_2O_3 Ratio	Product
R94	2	30/1	Med EU-1
R52	1.333	45/1	Maj EU-1
R30 R32	1	60/1	Maj EU-1
R40	0.8	75/1	Maj EU-1
R38	0.667	90/1	EU-1 + tr. EU-2
R28	0.5	120/1	Med EU-1 + Med EU-2
R18	0.4	150/1	EU-2 + tr. EU-1
R17	0.2	300/1	EU-2[a]

[a] Sample may contain some EU-1 see section 4.4

The failure to synthesise a material from a particular reaction composition usually arises when its rate of formation is so slow that another material is formed more quickly. Thus any investigation into the phases formed from a particular reaction should be accompanied by kinetic studies. Fig. 4.13 shows the growth curves for EU-1 synthesised from reaction mixtures containing different ratios of SiO_2/Al_2O_3, but which were otherwise identical. These growth curves were obtained by measuring the quantity of n-hexane sorbed by the calcined samples. It appears from these results that a SiO_2/Al_2O_3 ratio of 60/1 is the optimum for the formation of EU-1. The rates of formation of EU-1 from reactions with SiO_2/Al_2O_3 ratios of 45/1 and 75/1 appear to be very similar, while the reaction mixture (HT HEX R36) with a SiO_2/Al_2O_3 ratio of 30/1 did not produce any EU-1 within the time allowed for the experiment (8 hours). The limitations of the sorption method for the determination of the nucleation time and the rate of zeolite crystallisation are clearly illustrated by the results in Fig. 4.13. It is difficult to assess the relative contributions of the nucleation and growth rates to the overall result, and the only way in which this could be resolved reliably would be by X-ray diffraction studies. Unfortunately time and facilities did not permit such a study. However, in both reactions HT HEX R52 and HT HEX R40, EU-1 appeared to grow more slowly than in HT HEX R30. It is believed that in the course of reaction HT HEX R52 the rate controlling process was the depolymerisation of the relatively alumina-rich alumino-silicate gel. Although the alumino-silicate units

Fig. 4.13 Growth curves for EU-1 reactions of different SiO_2/Al_2O_3 ratios



would be likely to produce nuclei fairly quickly, since it is believed that aluminium plays a very important role in this process, the supply of nutrients requires the depolymerisation of the alumino-silicate gel, and thus it is going to become more difficult when the SiO_2/Al_2O_3 ratio is low. In reaction HT HEX R40 the depolymerisation of the alumino-silicate gel is likely to proceed more readily but the more soluble alumino-silicate (more silica rich) units would be less likely to produce stable nuclei.

One interesting feature of the reactions carried out with different SiO_2/Al_2O_3 ratios was that the pH, as measured when the reactions had reached reaction temperature (i.e. at time t_o), was not constant but decreased as the SiO_2/Al_2O_3 ratio increased. This can be seen in Fig. 4.14. The pH decreases sharply as the SiO_2/Al_2O_3 ratio increases from 30/1 to 150/1 and then levels off. This change in the pH is believed to be associated with the pK_a values of the alumino-silicate species. As the quantity of aluminium is increased the alumino-silicates are less likely to be attacked by the alkali. With this in mind it was decided to alter the Na_2O content of a reaction mixture which had a SiO_2/Al_2O_3 ratio of 75/1 from 10 Na_2O to 12 Na_2O. This was carried out since there could be a correlation between the pH of the reaction and the rate of crystallisation. This reaction, HT HEX R73 had the composition:

$$60\ SiO_2 - 0.8\ Al_2O_3 - 12\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

The pH curve for this reaction can be seen in Fig. 4.15 along with the corresponding curve for the reaction HT HEX R30 of composition:

Fig. 4.14 pH of reaction mixtures as a function of their SiO_2/Al_2O_3 ratios

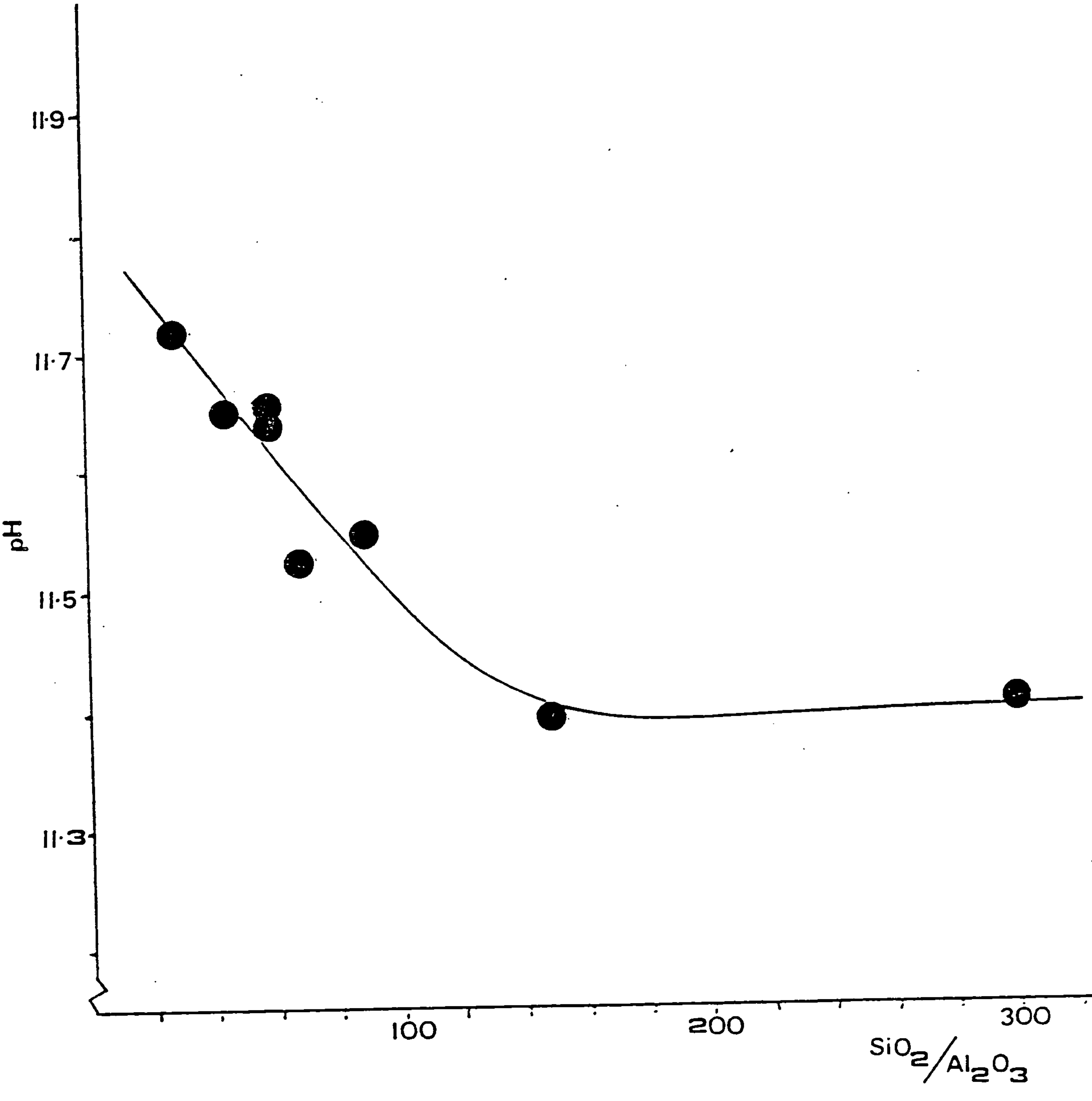
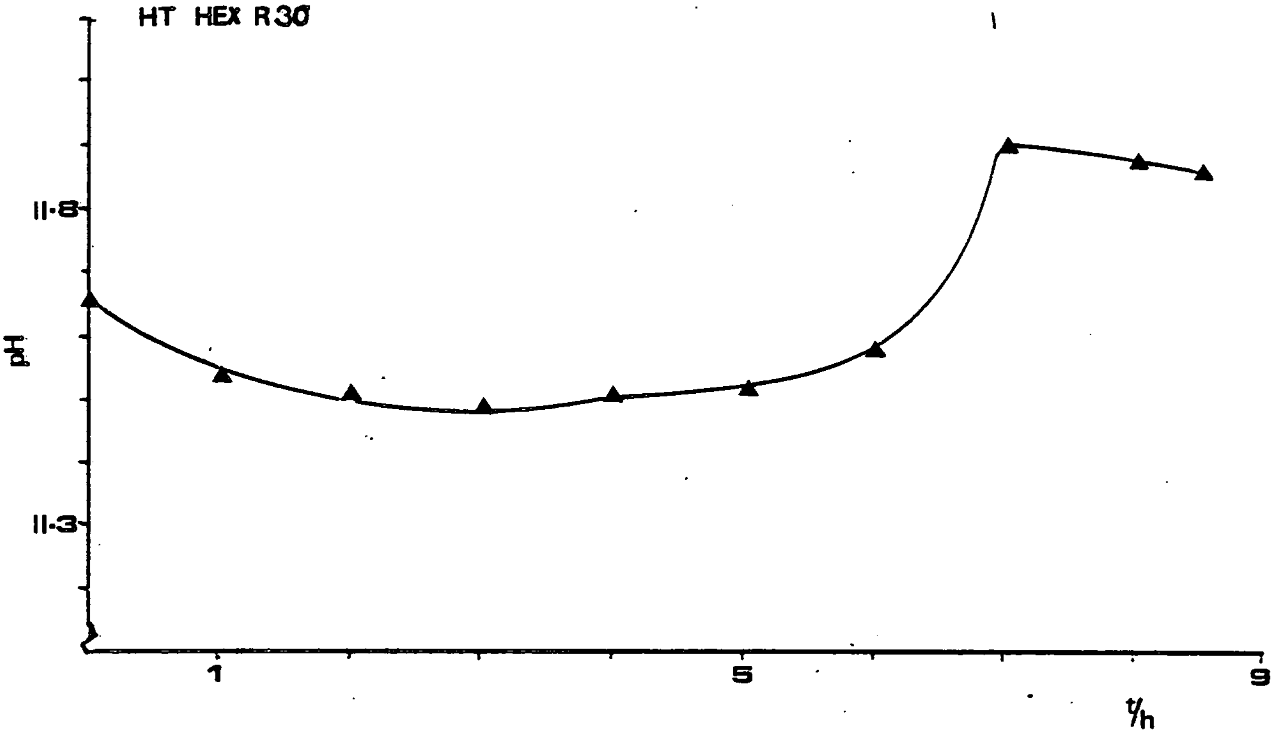
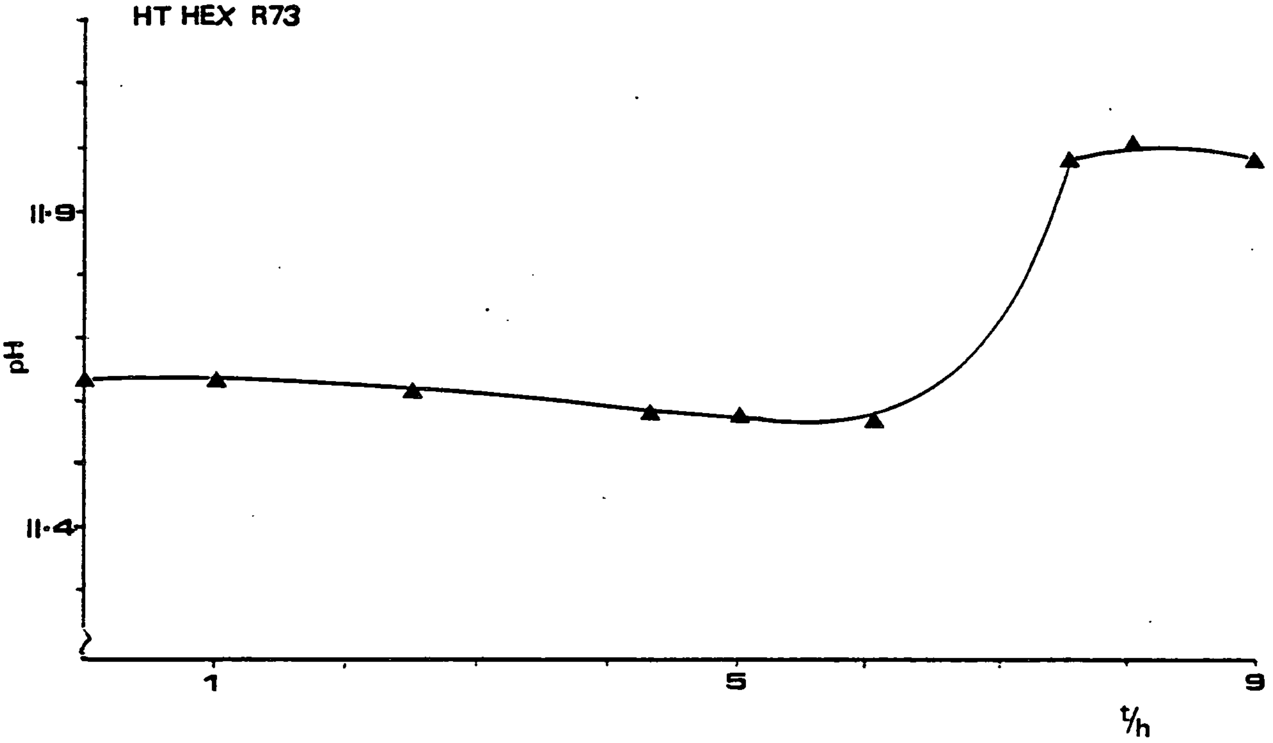


Fig. 4.15 Growth curves as followed by changes in pH for reactions HT HEX R30 and R73





$$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

It was not possible to sample HT HEX R73 between 6 hours and 7.5 hours due to a blocked sampling valve and consequently it was difficult to determine if the reaction rate had been increased. However the pH at t_o was similar to that for reaction HT HEX R30. It is considered that the idea of altering both the SiO_2/Al_2O_3 ratio and Na_2O content should be pursued.

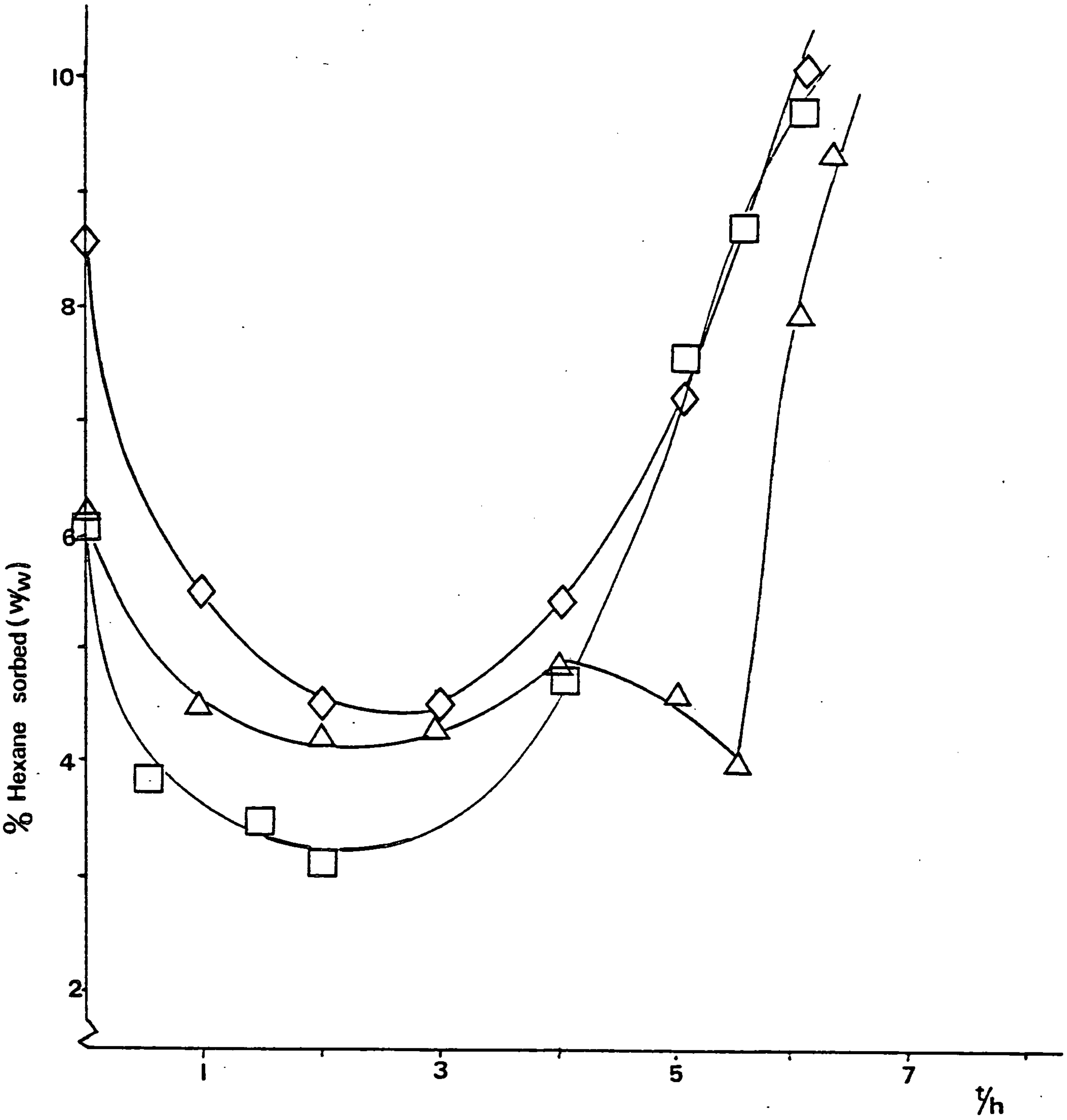
4.3.7 EFFECT OF SEED ON THE FORMATION OF EU-1

For the purposes of this section 'seed' will be regarded as already crystallised zeolitic material. The addition of seed to EU-1 reactions had two major effects; firstly, it increased its rate of formation and secondly it led the production of major (i.e. amorphous free) samples of EU-1 from a reaction which would not otherwise produce major samples of EU-1.

The effect of seed material on the rate of formation of EU-1 can be seen in Fig. 4.16. Two types of seed material were used, EU-1 and ZSM-5 type organosilicate[a]. The quantity of seed material used corresponded to about 5% (w/w) of the silica used in the reaction. Both types of seed, EU-1 and the ZSM-5 type organosilicate[20], increased the rate of formation of EU-1 significantly. The overall reaction times were very similar to each other thus indicating that both seed materials act in a similar way. It is believed that

[a] Supplied by Miss U. Lindsay, Dept. of Chemistry (sample K/2).

Fig. 4.16 Effect of seed on the rate of formation of EU-1



Reactions were carried out at 200°C. Mixtures had composition: 60 SiO_2 Al_2O_3 10 Na_2O 10 HEX Br_2 3000 H_2O

△ R30 - no seed
□ R35 - EU-1 - seed
◇ R44 - ZSM5 - organosilicate seed

they act either as nucleation centres or as centres from which "secondary crystals" can form - see section 4.3.4. It should be noted that the inducation period although reduced is not eliminated and this suggests that the length of the induction period is not simply related to the time required to form suitable nuclei. The growth rates of both reaction HT HEX R35 and R44 appear to be less than that of HT HEX R30. It appears that although nucleation occurs sooner, the growth rate is limited by the supply of nutrients. These growth units are no doubt produced by rearrangement of the alumino-silicate gel during the induction period, and if this is reduced by seeding it could be that growth is limited due to the lack of nutrients. It could be suggested that the "aluminium free" ZSM-5 type organosilicate (silicalite) will not redirect the reaction to ZSM-5, whereas ZSM-5 itself would. To check this ZSM-5 synthesised with a SiO_2/Al_2O_3 ratio of 60/1 was used as seed in a reaction similar to HT HEX R44. This reaction, HT HEX R80, again produced zeolite EU-1. It should also be noted that SEM analysis of HT HEX R80 (section 4.3.3) showed that only EU-1 crystals were present and that there was little difference between the size of these crystals and those from unseeded reactions.

The addition of seed material also allowed the synthesis of EU-1 from reaction mixtures with a much wider range of SiO_2/Al_2O_3 ratios. Results of these experiments can be seen in Table 4.14. The results of the reaction with $SiO_2/Al_2O_3 = 30/1$, HT HEX R81 is unambiguous in that analysis (see section 4.3.3) indicated that the SiO_2/Al_2O_3

TABLE 4.14 PRODUCTS OBTAINED FROM SEEDED REACTIONS WITH DIFFERENT SiO_2/Al_2O_3 RATIOS

$60\ SiO_2 - x\ Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$[a]

HT HEX	x	SiO_2/Al_2O_3 ratio	Product
R96	3	20/1	med. EU1
R81	2	30/1	major EU1
R37	0.4	150/1	major EU1
R90	0	1500/1[b]	med. EU1 + med. EU2

[a] All of the reactions contained EU1 seed. The weight added was approximately 5% (w/w) of the silica added.

[b] Estimated. The aluminium is present only in the seed material and as an impurity in the other components.

ratio of the product was 27/1. However in reaction HT HEX R90 a significant amount of aluminium was added in the 'seed' material. Since only a medium sample of EU-1 was obtained it is possible that the product EU-1 contained a significant amount of aluminium, even though the addition of seed certainly led to the production of EU-1 with a much higher than usual SiO_2/Al_2O_3 ratio.

The addition of seed material allowed EU-1 to be synthesised from a reaction mixture which contained a much smaller amount of HEX Br_2 - see Table 4.15. When HEX Br_2 was completely replaced by NaBr only a trace amount of EU-1 was found and this is believed to be the original seed material.

Further experiments concerned with seeding will be discussed in section 4.8.

4.3.8 EFFECT OF STIRRING SPEED ON EU-1 CRYSTALLISATION

All of the previous experiments on the rate of EU-1 formation described so far were carried out using the original autoclave. The experiments discussed in this section, however, were carried out in autoclave No. 4. The problems associated with the thermostating of the 'new' autoclaves by means of the Gulton-West temperature controllers, were described in section 4.2. In these experiments the reaction temperature was monitored using a pair of thermocouples (one on ice and the other in the reactor) and a digital voltmeter (Solartron). Only reactions which had similar temperature profiles were used. For example reaction HT HEX R108 previously described (section 4.3.4) was not considered

TABLE 4.15 PRODUCTS OBTAINED FROM SEEDED REACTIONS CONTAINING DIFFERENT AMOUNTS OF HEX Br_2

HT HEX	Composition	Seed[a]	T/°C	t/h	Product
R93	60 SiO_2 Al_2O_3 10 Na_2O 2 HEX Br_2 3000 H_2O	None	200	15	med EU1
R97	60 SiO_2 Al_2O_3 10 Na_2O 2 HEX Br_2 3000 H_2O	EU1	200	15	major EU1
R92	60 SiO_2 Al_2O_3 10 Na_2O 20 NaBr 3000 H_2O	EU1	200	14.5	tr. EU1[b]

[a] Weight of seed used was approximately 5% (w/w) of the silica added to the reaction mixture.

[b] This EU1 is believed to be the added seed.

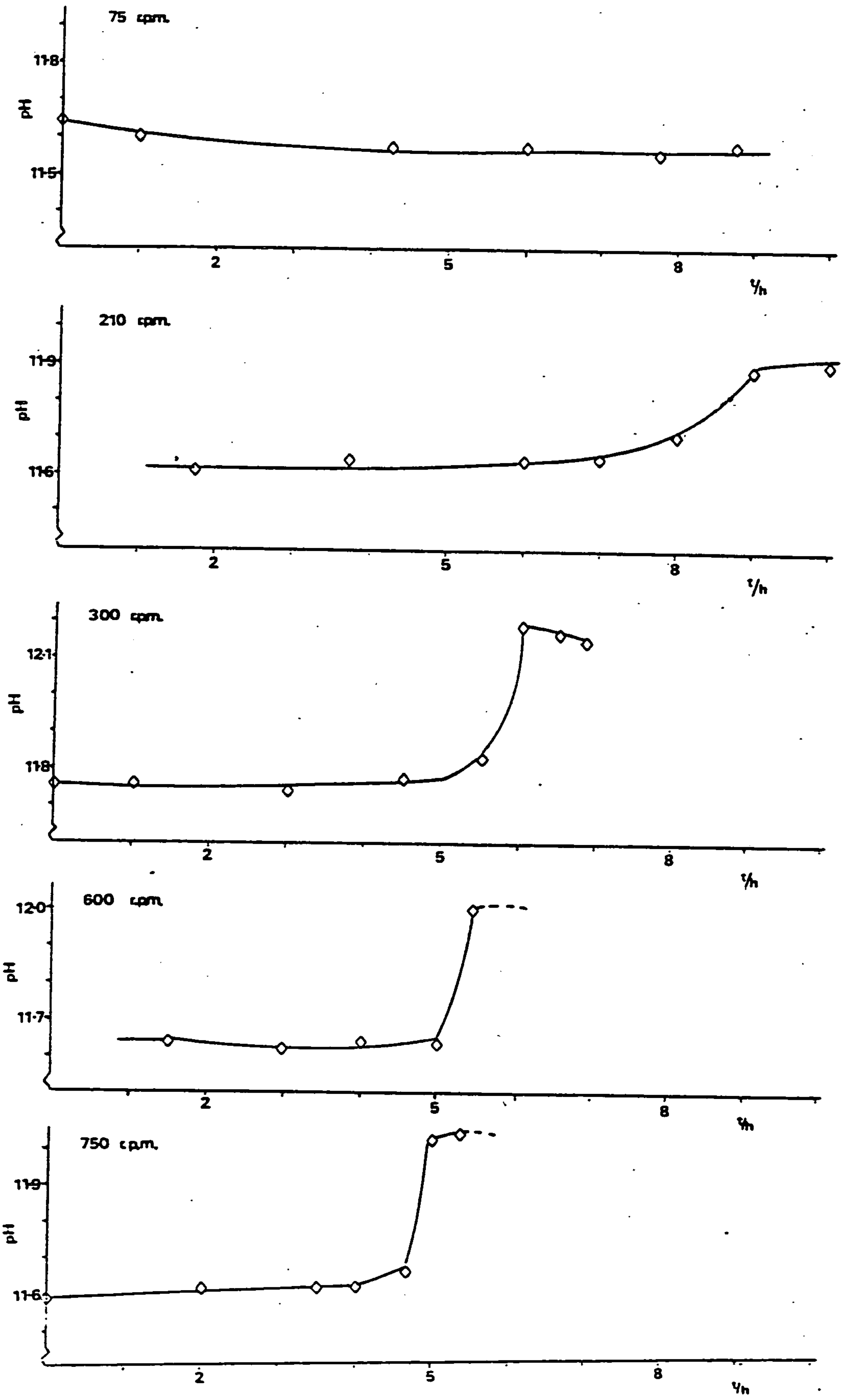
good enough to be included because of an 'overshoot' in temperature mid-way through the reaction.

The effect of stirring speed on the formation of EU-1 from reaction mixtures of composition:

$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$

at 200°C can be seen in Fig. 4.17 and Fig. 4.18. It is clear from these results that agitation has a very important effect on the rate of EU-1 formation. Similar effects of agitation have been observed by other workers for other zeolites. The most thorough study is that of Freund[19] on the effect stirring on the rate of formation of zeolite X. Freund reported that an increase in stirring speed had three effects: firstly the reaction profile was altered, secondly the overall crystallisation rate increased and thirdly the yield of zeolite X obtained, decreased. Examination of Fig. 4.17 showed that the first two of Freund's observations occurred here, since the induction period decreased and the growth rate increased, i.e. the pH againt time curve became steeper. The increase in the growth rate is likely to be due to the increased rate of transfer of nutrients to the growing crystals. This increase in the growth rate also leads to an increase in the rate of formation of 'secondary crystals' or in Freund's[19] terminology an increase in collision breeding and this in turn gives a further increase in growth rate. For such fast growth to occur a high concentration of nutrients is essential. It is possible that the increased stirring speed increases the rate of dissolution of the silica and alumino-silicate gel thereby not only supplying nutrients for growth but also decreasing the time required

Fig. 4.17 The effect of stirring speed on the formation of EU-1



for nucleation. The effect of the stirring speed on the rate of EU-1 formation (= $1/t_r$, where t_r is the reaction time) can be seen in Fig. 4.18. It is expected that at the lower end i.e. stirring speeds less than 150 r.p.m. that the reaction rate would 'tail-off' and that the formation of EU-1 from unstirred reactions would be very slow.

4.3.9 PRODUCT FORMATION FROM REACTIONS INVOLVING DIFFERENT ORGANIC SPECIES

The experiments in this section were carried out in an attempt to find a route to EU-1, other than those based on hexamethonium. The organic species used in these reactions were chosen because of their structural similarities with the hexamethonium ion. The compounds used and the products obtained from these reactions can be seen in Table 4.16.

EU-1 was not formed in any of the reactions, however, two related species were formed. The first of these EU-4 was formed using PTMBr (propyltrimethylammonium bromide) which corresponds to exactly half a hexamethonium unit. This zeolite and its similarity with EU-1 will be discussed in section 4.6. The second material was formed from reaction mixtures which contained decamethonium (HT HEX R63 and R76). This material was not characterised and further work is required before it could be regarded as a novel species. The reaction profile for reaction HT HEX R63 obtained by pH measurements, can be seen in Fig. 4.19. Although the final product from this reaction contained some α-quartz the sample marked S9 in Fig. 4.19 did not. The X-ray powder diffraction pattern obtained

Fig. 4.18 Correlation between the stirring speed and rate of formation of EU-1

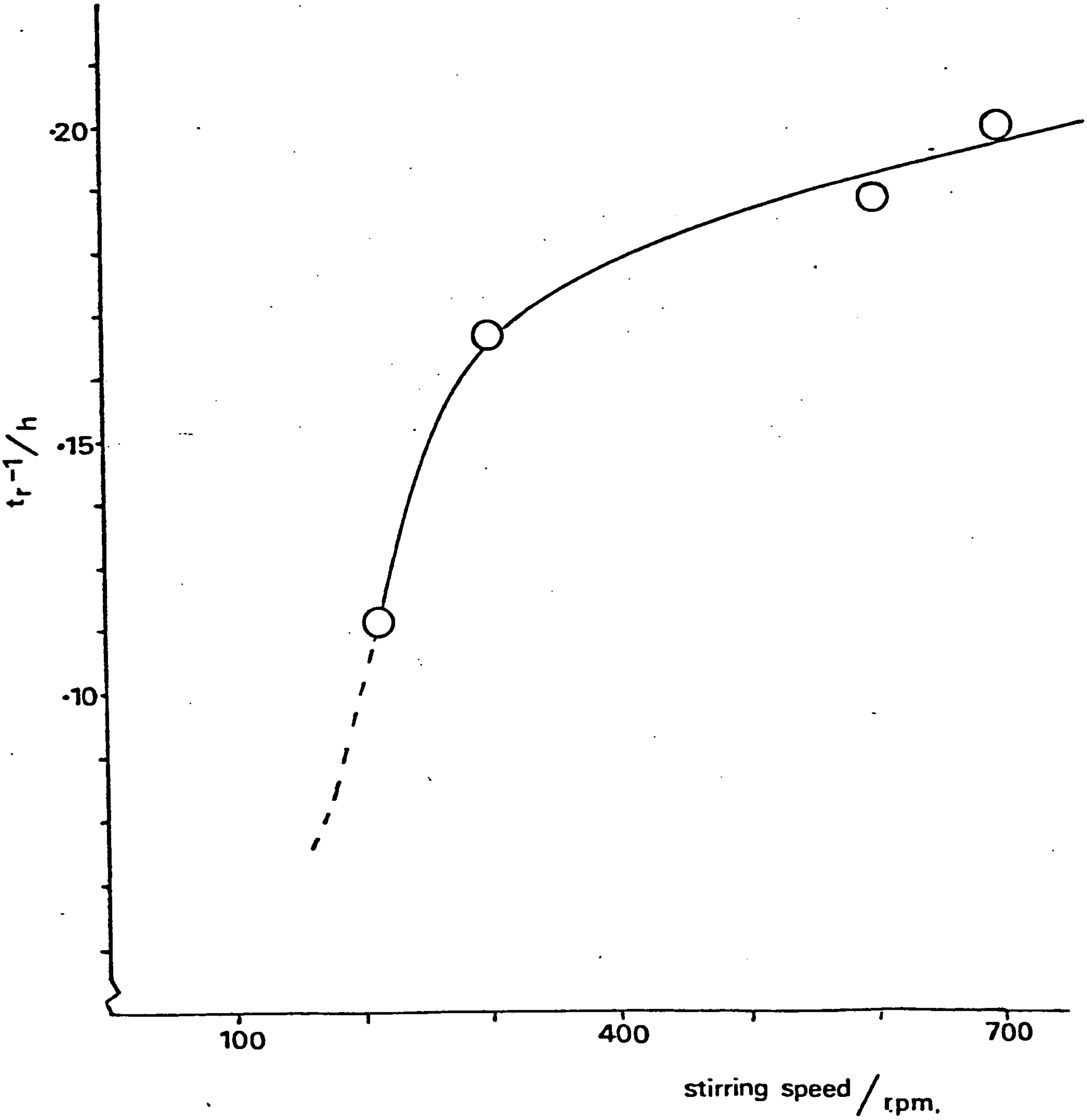


TABLE 4.16 REACTIONS USING DIFFERENT ORGANIC SPECIES

HT HEX	Structure	Name	Composition SiO_2	Al_2O_3	Na_2O	R_2O	H_2O	Product
R30	$(CH_3)_3N-(CH_2)_6-N(CH_3)_3$	Hexamethonium	60	1	10	10	3000	EU1
R79	$CH_3(CH_2)_2-N(CH_3)_3$	PTM = propyltrimethylammonium	60	1	10	20	3000	EU4[a]
R63	$(CH_3)_3N-(CH_2)_{10}-N(CH_3)_3$	Decamethonium	60	1	10	10	3000	[b] + α Q
R76								[b] + FU6
R66	$CH_3-N(CH_3)_3$	TMA	60	1	10	20	3000	NU1 + α Q
R87	$CH_3(CH_2)_{15}-N(CH_3)_3$	CETAB = Cetyltrimethylammonium	60	1	10	5	3000	Med ZSM5[c]
R65		Pyrrolidine	60	1	10	5	3000	ZSM5 type[c] + α Q
R91	$H_2N-(CH_2)_6-NH_2$	Hexamethylenediamine	60	1	10	10	3000	ZSM5[c]
R67	$H_2N-(CH_2)_2-NH_2$	Ethylenediamine	60	1	10	10	3000	ZSM5[c]
R116	$HO-(CH_2)_6-OH$	Hexanediol	60	1	10	10	3000	ZSM5[c]
R140	$HO-(CH_2)_{10}-OH$	Decanediol	60	1	10	10	3000	ZSM5[c] + [d]
R125	$^{-}O_2C-(CH_2)_4-CO_2^{-}$	Sodium Adipate	60	1	10	10	3000	ZSM5[c]

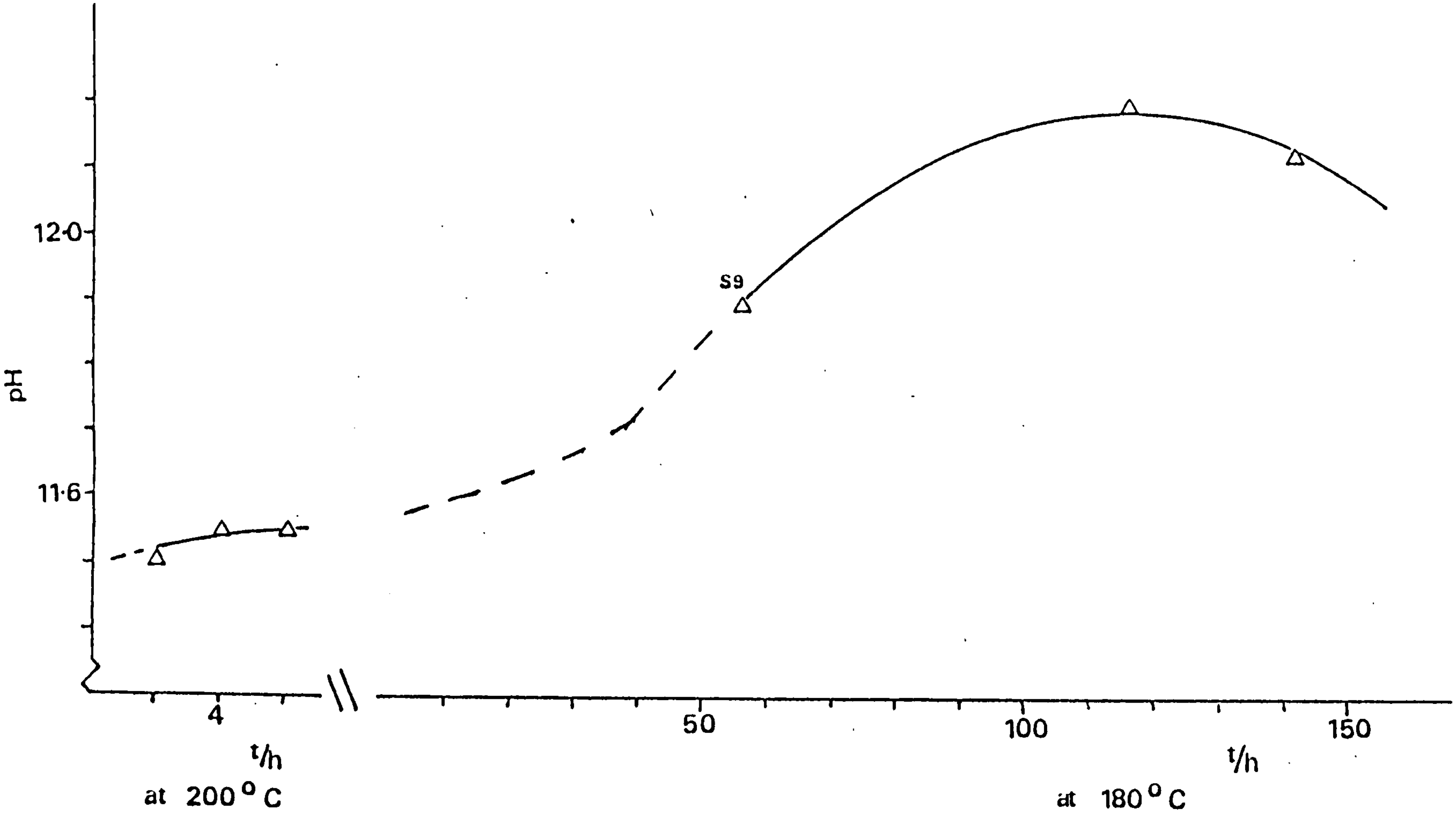
[a] See section 4.6.

[b] This material had a similar X-ray diffraction pattern to EU4, although it may be a new material. Insufficient time and the expense of the reagent prevented further study.

[c] See section 4.7.

[d] This product also contained some additional lines. The lines could correspond to decanediol itself, since it was a fairly insoluble species.

Fig. 4.19 Growth curve for reaction HT HEX R63



for this sample is given in Table 4.17.

With the exception of TMA (tetramethylammonium) which produced NU-1 (a known TMA zeolite) all the other organic species produced ZSM-5. The synthesis of ZSM-5 will be discussed in section 4.7.

TABLE 4.17 d-SPACINGS FOR THE PRODUCT OBTAINED WITH DECAMETHONIUM BROMIDE (HT HEX R63 S9)

d/Å	Intensity
12.71	m
11.07	vs
10.54	s
10.03	vw
8.35	m
6.84	m
6.53	w
5.81	vw
5.50	vw
5.29	vw
5.05	vw
4.59	vs
4.40	m
4.29	vs
4.23	m
4.17	m
4.06	m
3.97	vs
3.93	s
3.822	w
3.688	s
3.604	w
3.410	s
3.388	vw
3.359	vw
3.263	s
3.236	vw
3.153	vw
3.073	vw
2.900	vw
2.854	vw
2.523	s
2.458	m
2.383	m
2.315	vw
2.097	w

Note:

Line positions were not drastically altered by calcination at 500°C for 21 hours.

4.4 SYNTHESIS AND CHARACTERISATION OF EU-2

4.4.1 INTRODUCTION

The co-crystallisation of EU-1 and a species designated EU-2 from reaction HT HEX R28 of composition:

$$60\ SiO_2 - 0.5\ Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

was discussed in section 4.3. However EU-2 was first crystallised from reaction HT HEX R9 which was carried out at I.C.I. Ltd., Agricultural Division, Billingham. The composition of HT HEX R9 was:

$$60\ SiO_2 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

This reaction was carried out in an attempt to produce a "silica only" analogue of EU-1 analogous to silicalite[20] and silicalite-2[21]. Although EU-1 was not formed in this reaction the species EU-2, which was, is itself, another member of the series of "hydrophobic crystalline silica molecular sieves" described by Flanigen et al.[20].

4.4.2 SYNTHESIS OF EU-2

Table 4.20 contains the compositions, reaction details and results of experiments carried out to synthesise EU-2. Individual aspects of these results will be discussed later. All the reactions included, except HT HEX R27, were carried out in autoclaves at temperatures between 180°C and 200°C. HT HEX R27 was carried out at 95°C. As with other reactions carried out at 95°C and described in section 4.3 the aim was to synthesise EU-2 at low temperature. However, in all cases the product obtained was a new species designated EU-3 (see section 4.5).

TABLE 4.20 RESULTS OF EU-2 SYNTHESES

HT HEX	Composition					T/°C	Agitation/ r.p.m.	t/h	Product
	SiO_2	Al_2O_3	Na_2O	HEX Br_2	H_2O				
R9	60	-	10	10	3000	180	[a]	48 120 (S3)	Med EU-2 Major EU-2
R15	60	-	10	10	3000	180	300	48 120	Med EU-2 Major EU-2 + α Q
R16	60	-	10	10	3000	180	300	96	Major EU-2
R17	60	0.2	10	10	3000	180	300	24 48 72 96 (S4)	Med EU-2 Major EU-2 Major EU-2
R18	60	0.4	10	10	3000	180	300	24 48 72	tr EU-1 + tr EU- tr EU-1 + tr EU- Med EU-2 + tr EU-
R28	60	0.5	10	10	3000	180	300	90	EU-1 + EU-2
R34	90	1	10	10	3000	200	300	9	EU-1 + tr EU-2
R38	60	0.667	10	10	3000	200	300	9	EU-1 + tr EU-2
R41	60	0.2	10	10	3000	200	300	9	EU-2
R68	60	0.2	2	10	3000	200	300	55	Am
R72	60	0.2	2	10	3000	200	300	120	tr EU-2
R112	60	0.2	3	10	3000	200	300	312	EU-2
R78	60	0.2	10	10	3000	200	300	16	EU-2
R101	60	0.2	10	10	3000	200	300	9	EU-2
R104	60	0.2	10	10	3000	200	750[b]	9	EU-2
R106	60	0.2	10	10	3000	200	300	9	EU-2
R109	60	0.2	10	10	3000	200	900[c] ↓ 600	6	EU-1 + EU-2
R138	60	-	10	10	3000	200	300	16	EU-2
R27	60	-	10	10	3000	95	-	35 days	tr EU-3
R124	60	-	10	10	3000	95-200	150-300	-	EU-2[d]

[a] This reaction was carried out at I.C.I. Ltd., Agricultural Division, Billingham. All other reactions were carried out at Edinburgh.

[b] Stirrer stopped and jammed, result was not used.

[c] Stirrer speed adjusted from 900 r.p.m. to 600 r.p.m. after about 30 minutes.

[d] This reaction will be described in section 4.5.

4.4.3 CHARACTERISATION OF EU-2

The X-ray powder diffraction pattern of EU-2 can be seen in Table 4.21. Results are included for samples synthesised with no added aluminium (HT HEX R9, R15) and for one, HT HEX R78 produced from a reaction mixture with SiO_2/Al_2O_3 ratio of 300/1. HT HEX R15 S2C represents a sample calcined at 600°C for 12 hours.

Examination of the lines for EU-2 in Table 4.21 and comparison with those of EU-1 (Table 4.3), shows that the samples of EU-2 may be contaminated with EU-1. This can be seen from lines which are strong in EU-1, for example at $d = 10.2$ Å, 4.3 Å and 3.8 Å which also occur in the EU-2 patterns as weak/medium lines. Changes in synthesis conditions, discussed later, failed to produce any samples of EU-2 which did not contain some lines which could correspond to EU-1. Products obtained from reactions in Table 4.20 were labelled EU-2 although they could contain some EU-1. The intensities of the lines which could correspond to EU-1 were so low that it was not possible to resolve this problem in the time available. The co-crystallisation of EU-1 and EU-2 has been noted in the relevant tables in these cases for which the intensities of the EU-1 lines were such that it could be positively identified.

Results of sorption studies can be seen in Table 4.22 and Table 4.23. The results in Table 4.22 were obtained in Edinburgh and those in Table 4.23 by workers at I.C.I. Ltd., Agricultural Division, Billingham. Table 4.23 was taken from British Patent application number 80 19211[22] and the sample

TABLE 4.21 DIFFRACTION LINES FOR EU-2

Reaction	HT HEX R9 S3	HT HEX R15 S1		HT HEX R15 S2C[a]	HT HEX R78	
Film	J429	J438		J445	J757	
Error	d/Å	d/Å	Int.	d/Å	d/Å	Int.
0.09	11.88	11.79	m	11.61	11.78	vs
0.08	11.11	11.19	vw	-	11.02	vw
0.07	10.23	10.23	m	10.06	10.23	m
0.05	9.84	-		-	-	
0.03	-	-		-	7.23	w
0.03	6.30	6.33	vw	6.12	6.24	vw
0.02	5.86	5.85	vw	5.82	5.86	s
0.01	4.67	4.67	m	-	4.67	vw
0.01	4.31	4.33	m	-	4.35	vw
0.01	4.18	4.18	vs	4.19	4.17	vs
0.01	3.90	3.89	vs	3.87	3.87	vs
0.01	3.85	3.86	s	-	[b]	
0.01	3.69	3.69	m	-	3.71	vw
0.01	-	-		-	3.61	m
0.01	-	-		3.36	3.39	m
0.01	-	3.29	vw	-	3.26	vw
0.01	-	-		-	3.11	vw
0.01	2.85	2.85	m	2.84	2.85	s
0.01					2.64	w
0.01					2.47	w
0.01					2.39	w
0.003					2.353	w
0.003		2.09	w		2.096	m

[a] Sample was calcined at 600°C for 12 hours.

[b] Line at 3.87 Å was so broad that a second line could have been hidden.

TABLE 4.22 SORPTION OF EU-2

HT HEX[a]	Water (g/100 g) p = 4.8 mmHg t = 17 hours	n-hexane (g/100 g) p = 50.6 mmHg t = 17 hours	cyclohexane (g/100 g) p = 27.2 mmHg t = 16.5 hours
R9 S3	2.93	3.05	1.34
R17 S4	3.06	4.46	1.38

[a] Samples were calcined at 550°C for 70 hours.

TABLE 4.23

Sorption at 25°C p/po = 0.5[b]

Sorbate	Kinetic diameter[a] σA	Time/min	Wt sorbed g/100 g	Voidage available cc/100 g
Water	2.7	10	0.1	Negligible
		120	0.2	
		1440	0.5	
n-hexane	4.3	10	5.9	8.9
		60	6.4	9.7
		120	6.7	10.2
p-xylene	5.85	10	5.7	7.6
		60	7.6	10.1
		120	7.6	10.1
m-xylene	6.8	10	3.8	5.0
		60	5.7	7.5
		120	5.7	7.6
cyclohexane	6.0	10	3.2	4
		60	3.5	4.4
		120	3.9	4.9
Symm trimethyl benzene	7.6	10	0.1	Negligible
		1440	0.3	

[a] Lennard Jones Kinetic Diameter[14]

[b] Sample was calcined at 450°C for 48 hours

used in the study was prepared from a reaction of composition:

$$60\ SiO_2 - 0.1\ Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

carried out at 180°C for 16 hours. The samples used to obtain the results given in Table 4.22 were taken from HT HEX R9 and HT HEX R17. The compositions and reaction conditions of these syntheses can be seen in Table 4.20.

It is noticeable that, as with EU-1, the sorption capacities obtained at Edinburgh are not as high as those measured at I.C.I. It is believed that this reflects the more accurate apparatus used at I.C.I. However two things can clearly be seen, firstly, EU-2 is not as good a sorbent as EU-1 and secondly EU-2 is very hydrophobic.

Thermal analysis of a sample of EU-2, taken from reaction HT HEX R78 can be seen in Fig. 4.20. From the tga curve in Fig. 4.20 it can be seen that the total weight loss of EU-2 was about 10.5%, of which about 2% was water. So while the water content of EU-2 was similar to that of EU-1, EU-2 contained considerably less organic material which is consistent with EU-1 having a larger internal volume. Dta of EU-2 shows a small endotherm at about 100°C corresponding to water loss. The exotherm at about 300°C must be associated with the decomposition of the hexamethonium ion. As with EU-1 (Fig. 4.3) while the tga suggests the organic material is lost in a single continuous process, the dta reveals that three stages are involved. In the dta of EU-2 there is no large endotherm corresponding to lattice collapse as seen with EU-1. Instead a sharp transition occurs at about 950°C, followed by other changes at about

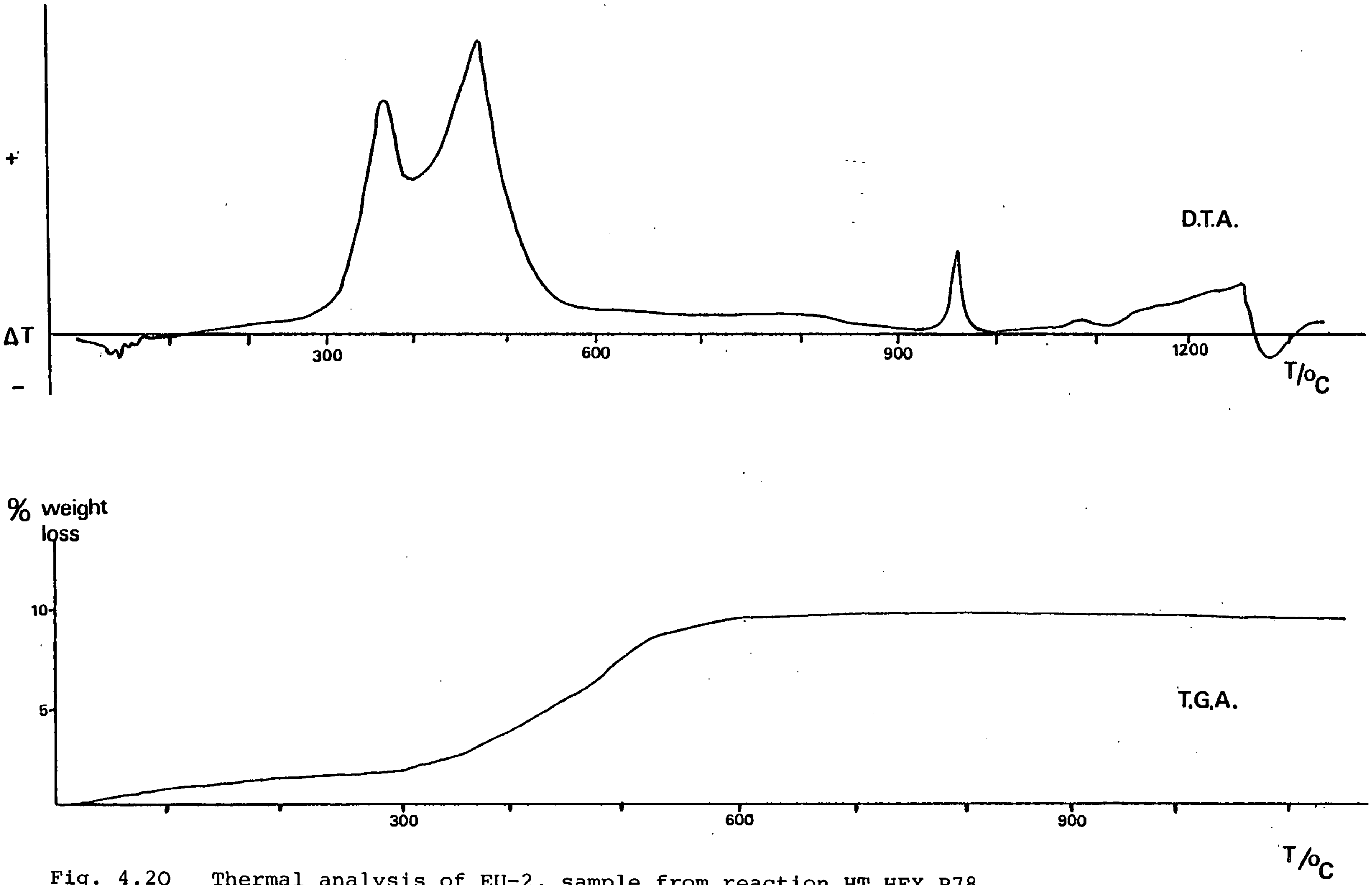


Fig. 4.20 Thermal analysis of EU-2, sample from reaction HT HEX R78.

1300°C. It is not known if the transition at about 950°C is reversible. Once the sample had cooled, analysis of the sample by X-ray diffraction indicated that the EU-2 framework had indeed collapsed. The resulting crystalline material was identified as α-cristobalite[a].

Analytical results for EU-2 are given in Tables 4.24 and 4.25. From Table 4.25 it would seem that for reactions with added aluminium (HT HEX R78 and R112) the SiO_2/Al_2O_3 ratio of the product is less than that of the reaction mixture. However reactions HT HEX R9 and R138 were synthesised from reactions with no added aluminium. The quantity of aluminium in the silica source, CAB-O-SIL M5, was less than 10 p.p.m.[b]. Thus the aluminium in the silica and in the other reagents must be selectively incorporated into the product.

From the analytical results it can be seen that the C/N ratio is fairly close to 6/1, thus the organic material is present largely as hexamethonium. The Na_2O content of EU-2 varies considerably (it can be reduced by reducing the quantity in the reaction mixture) but the consistent feature is that it exceeds the aluminium content. Thus both the sodium and hexamethonium must be present almost entirely as the hydroxide or halide. Since zeolite EU-2 appears to have a fairly compact structure it is possible

[a] A crystalline silica polymorph. It exists in two forms α-, the low temperature species and β-, the form above about 300°C.

[b] Analysis of CAB-O-SIL M5 was supplied by the manufacturers Cabot Corp.

TABLE 4.24 PERCENTAGE COMPOSITION BY WEIGHT OF EU-2 SAMPLES

Sample HT HEX	Al_2O_3	SiO_2	Na_2O	H_2O[a]	C	H	N	% wt loss at 1000°C	Origin
R9 S3	0.149	98.93	0.919	3.20	5.7	1.4	1.2	12.2	I.C.I.
R78	0.776	98.14	2.899	2.00	-	-	-	10.5	Edin.
R112	0.623	97.73	0.493	-	-	-	-	10.80	Edin.
R138	0.106	97.90	1.391	-	-	-	-	10.95	Edin.
R15 S2	-	-	-	-	4.98	1.28	0.94	9.2	Edin.

TABLE 4.25 MOLAR COMPOSITION OF SAMPLES OF EU-2

Sample HT HEX	Al_2O_3	SiO_2	Na_2O	$Na_2O/(Al_2O_3+SiO_2)$	C/N[a]	H_2O/Na_2O
R9 S3	1	1127.2	10.14	0.0090	4.8	12.00
R78	1	214.7	6.15	.0285	-	2.37
R112	1	266.3	3.67	.0137	-	-
R138	1	1568.0	21.59	.0138	-	-
R15 S2	-	-	-	-	6.2	-

[a] C/N for hexamethonium is 6/1.

that salts such as NaBr and NaOH, occluded during synthesis might not be removed by washing. This could have a profound effect on the reproducibility of, and values obtained in, sorption studies.

Although only two values for the H_2O/Na_2O ratio were determined, it would seem that the water is not only associated with the sodium ions but may be present as a separate occluded species as in sodalite. That is, there may be only a specific number of sites for hexamethonium salts, sodium salts and water. A combination of all three species occupies the zeolite, but if one is present to a larger extent then there is correspondingly less of the other two. However, such a possibility requires further study.

SEM studies of zeolite EU-2 were carried out. The samples examined were from reaction HT HEX R78 (Plate 4.16) and the final product from reaction HT HEX R124 (Plate 4.17). It is clear from the electron micrographs that these products have different morphologies. The sample from HT HEX R78 contains large amounts of amorphous material and the EU-2 crystals are almost spherical. However the crystals in Plate 4.17 are quite different and appear to be aggregates of much smaller crystals (c.f. zeolite P). Also there are some crystals (indicated by arrows in Plate 4.17) which are very similar to those of zeolite EU-1. This reinforces the earlier suggestion that samples of EU-2 are contaminated with small quantities of EU-1.

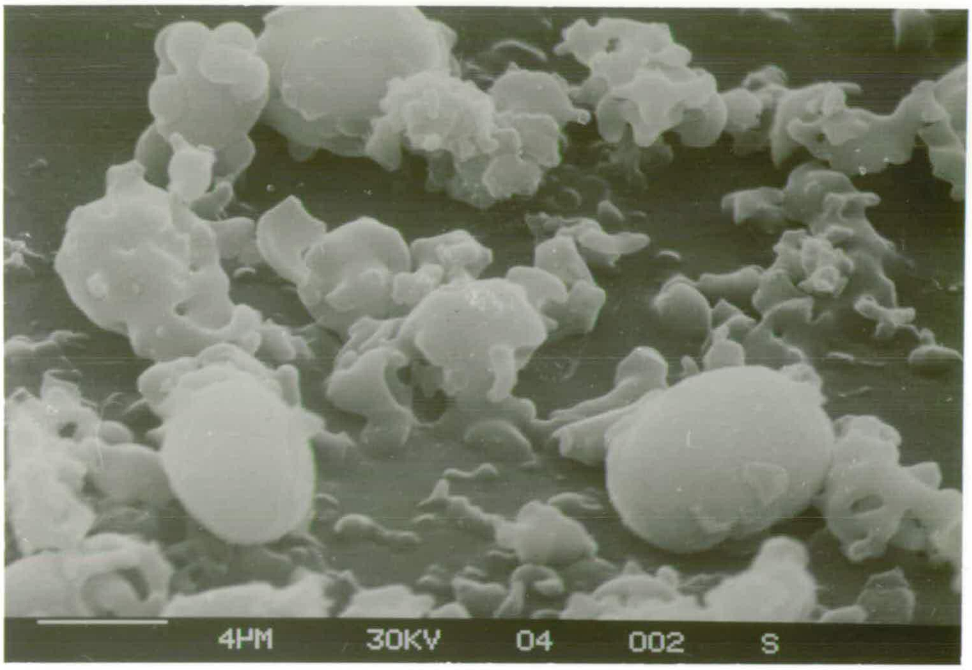


Plate 4.16
HT HEX R78

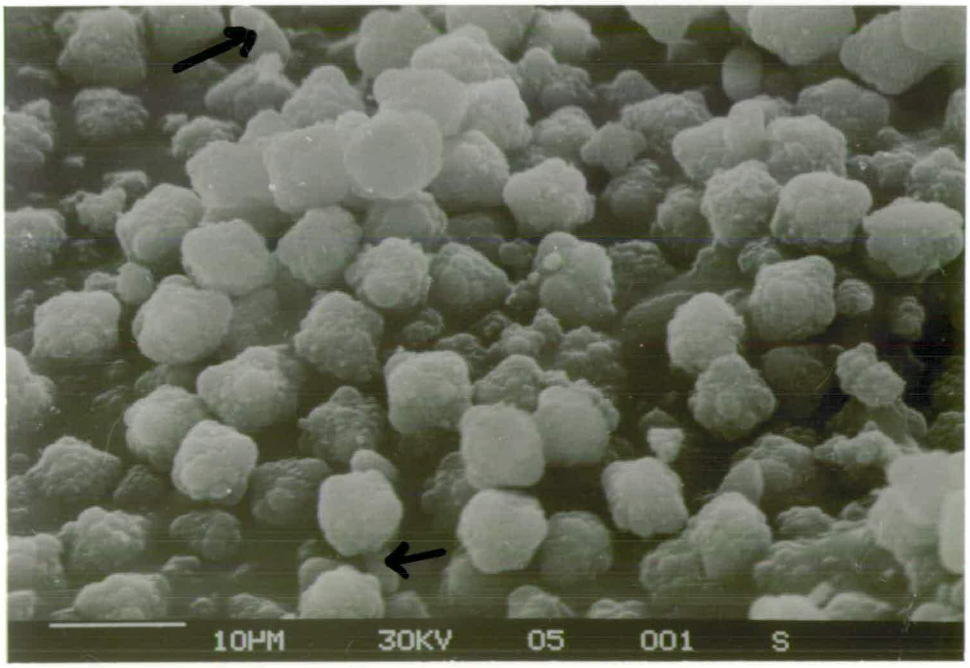


Plate 4.17
HT HEX R124

4.4.4 EFFECT OF COMPOSITIONAL VARIATIONS ON EU-2 FORMATION

EU-2 can only be formed over a limited range of SiO_2/Al_2O_3 ratios. As the values of SiO_2/Al_2O_3 are decreased from 300/1,EU-2 co-crystallises with increasingly larger amounts of EU-1. This can be seen in Table 4.26. It is believed that this reflects the relative rates of formation of these species from reaction mixtures with different ratios of SiO_2/Al_2O_3. The addition of 'seed' EU-2 did not extend the range, as can be seen in Table 4.27, indeed the only effect it had was to increase the rate of formation of EU-1 in reaction HT HEX R39. However the addition of seed EU-2 had a profound effect on the rate of EU-2 formation. Fig. 4.21 contains the growth curves of EU-2 for reactions HT HEX R41 and R101, both of which had a SiO_2/Al_2O_3 ratio of 300/1. Growth curves were followed by pH measurements. The effect of EU-2 seed material can be seen in Fig. 4.22, which is of reactions HT HEX R101 and R111. Reaction HT HEX R111 had the same composition as HT HEX R101 but contained some crystalline EU-2 corresponding to about 5% (w/w) of the solid silica added.

It was noted in section 4.3.8 that an increase in stirring speed decreased the time required to form EU-1. To see if this also applied to EU-2 formation, reaction HT HEX R109 was carried out. However the product obtained was a mixture of EU-1 and EU-2. It is believed that this happened because the change in stirring speed increased the rate of formation of EU-1 to such an extent that it 'offset' the decrease in rate due to the high SiO_2/Al_2O_3 ratio.

TABLE 4.26 PRODUCTS FORMED FROM REACTIONS WITH DIFFERENT SiO_2/Al_2O_3 RATIOS

For reactions of general composition:

$$60\ SiO_2 - x\ Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

Reaction HT HEX	x	SiO_2/Al_2O_3	Temp/°C	Products
R15	0	>1000/1	180	EU-2
R17	0.2	300/1	180	EU-2
R18	0.4	150/1	180	Med EU-2 + t_r EU-1
R28	0.5	120/1	180	Med EU-1 + Med EU-2
R38	0.667	90/1	200	EU-1 + t_r EU-2

TABLE 4.27 PRODUCTS OBTAINED FROM REACTIONS CONTAINING 'SEED' EU-2

Reaction HT HEX	Composition SiO_2	 Al_2O_3	 Na_2O	 HEX Br_2	 H_2O	Seed[a]	Product
R30	60	1	10	10	3000	-	EU-1
R39	60	1	10	10	3000	EU-2	trace EU-1[b]
R28	60	0.5	10	10	3000	-	EU-1 + EU-2
R139	60	0.5	10	10	3000	EU-2	EU-1 + EU-2

[a] The quantity of seed material added corresponded to about 5% (w/w) of the silica added.

[b] The addition of EU-2 also increased the rate of formation of EU-1 to a similar extent as EU-1 seed or ZSM-5 seed - see section 4.3.7.

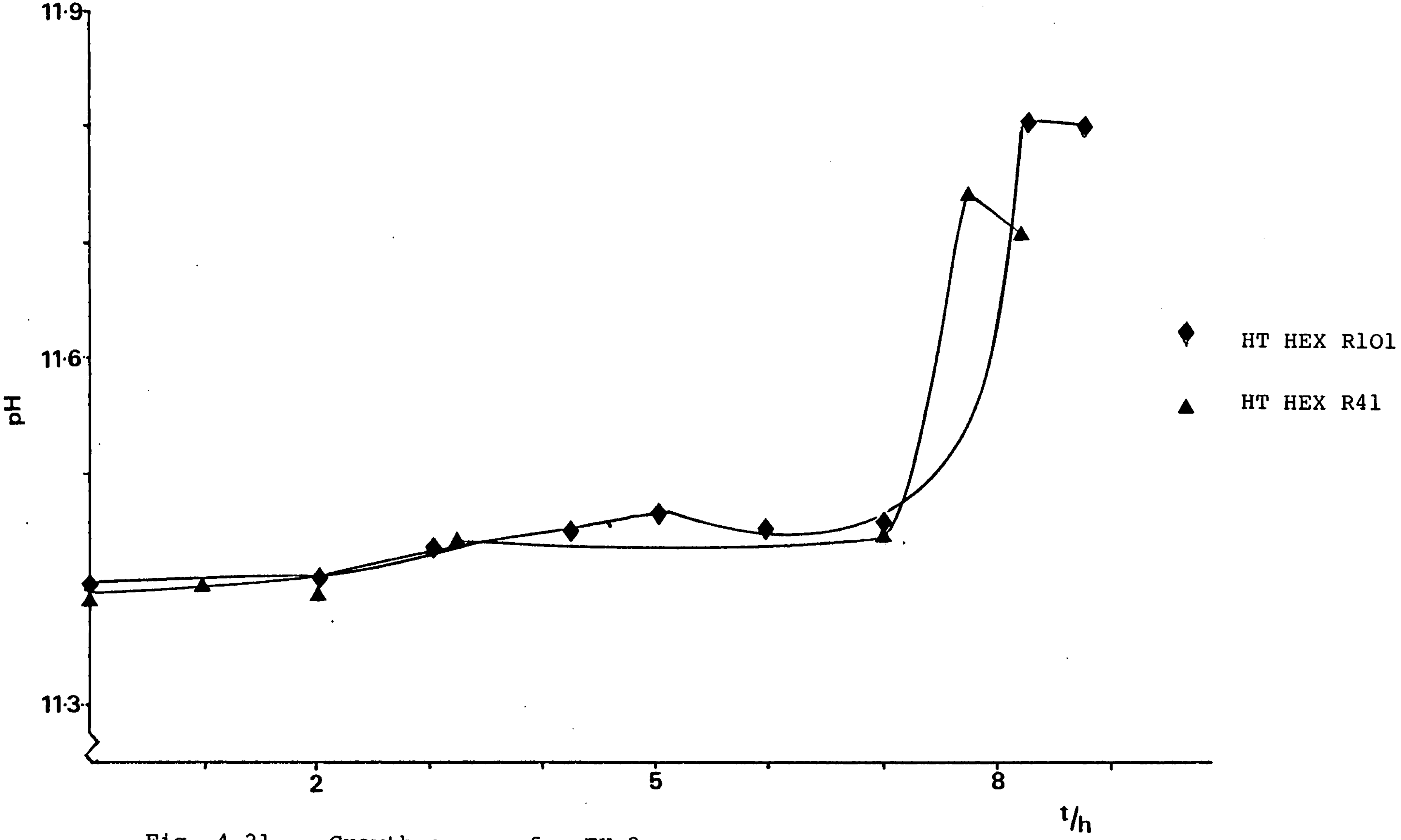


Fig. 4.21 Growth curves for EU-2.

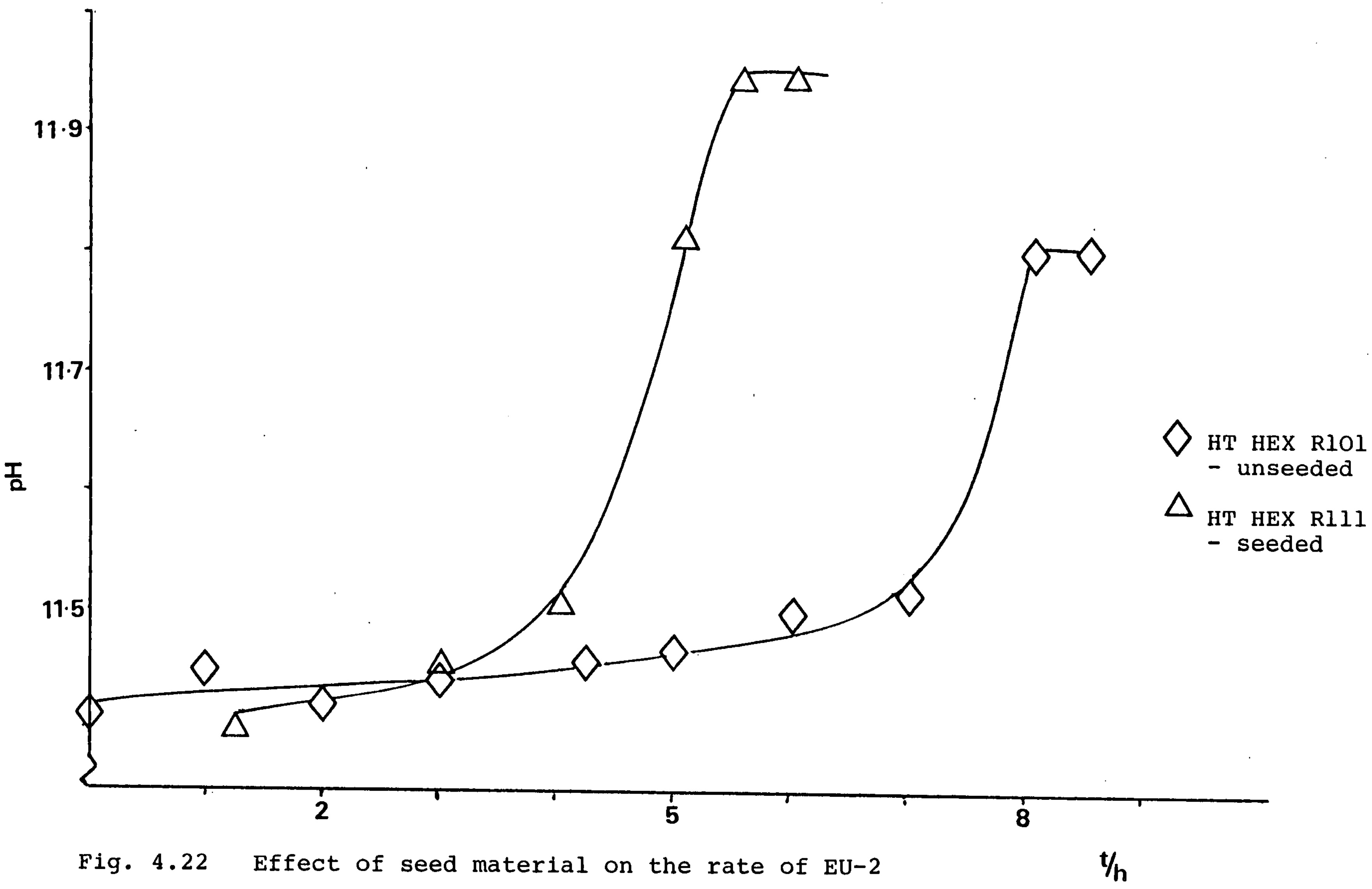


Fig. 4.22 Effect of seed material on the rate of EU-2 formation.

Thus EU-1 and EU-2 were formed. It is not known if slight increases in stirring speed would increase the rate of EU-2 formation without EU-1 being formed.

The possibility that EU-2 was always contaminated with EU-1 has been mentioned several times previously. It was thought that by seeding the crystallisation a pure of EU-2 could be obtained. However this was not the case. Other experiments that were designed to produce a pure EU-2 sample involved reducing the Na_2O content of the reaction mixture. The results of these experiments, reactions HT HEX R68, R72 and R112 are included in Table 4.20. The samples of EU-2 formed in reaction HT HEX R112 still appeared to contain some EU-1. Although no further experiments were carried out it is believed that reducing the stirring speed could lead to the preparation of a pure/purer sample of EU-2.

4.5 SYNTHESIS AND CHARACTERISATION OF EU-3

4.5.1 INTRODUCTION

The species EU-3 was formed from reactions carried out at 95°C. The reaction mixtures which produced EU-3 gave either zeolites EU-1 (e.g. HT HEX R1 - see section 4.3) or EU-2 (e.g. HT HEX R9 - see section 4.4) when carried out under autoclave conditions.

It was decided to investigate this species since it could be a precursor of zeolites EU-1 and EU-2.

4.5.2 SYNTHESIS OF EU-3

Table 4.28 contains the results of experiments carried out to synthesise EU-3. It can be seen that EU-3 is formed more quickly from reaction mixtures which do not contain aluminium (HT HEX R27) than from those which do (HT HEX R19). It can also be seen that EU-3 crystallises more rapidly from an agitated system (e.g. HT HEX R60) than from a static one (HT HEX R27).

The pH profile for reaction HT HEX R75 is shown in Fig. 4.23. It can be seen that the pH change (c.a. 0.15 units) is not as large as for EU-1 or EU-2. This could be due to the reaction being incomplete since it was observed that the quantity of EU-3 increased for up to about 104 days, i.e. about 3 times longer than the induction period. However it is much more likely that the small pH change is related to the fact that EU-3 is not a tectosilicate.

TABLE 4.28 SYNTHESIS OF EU-3[c]

HT HEX	Composition					Agitation[a]	t/d[b]	Product
	SiO_2	Al_2O_3	Na_2O	HEX Br_2	H_2O			
R19	60	1	10	10	3000	x	118	t_r EU-3
R27	60	-	10	10	3000	x	35	t_r EU-3
R60	60	-	10	10	3000	✓	7	med EU-3
R74	60	-	10	10	3000	✓	7	med EU-3
R75	60	-	10	10	3000	✓	6	med EU-3

[a] Reactions which were agitated were stirred at 150 r.p.m.

[b] The time given corresponds to when first crystalline material was observed.

[c] Reactions were all carried out in glass reactors at 95°C.

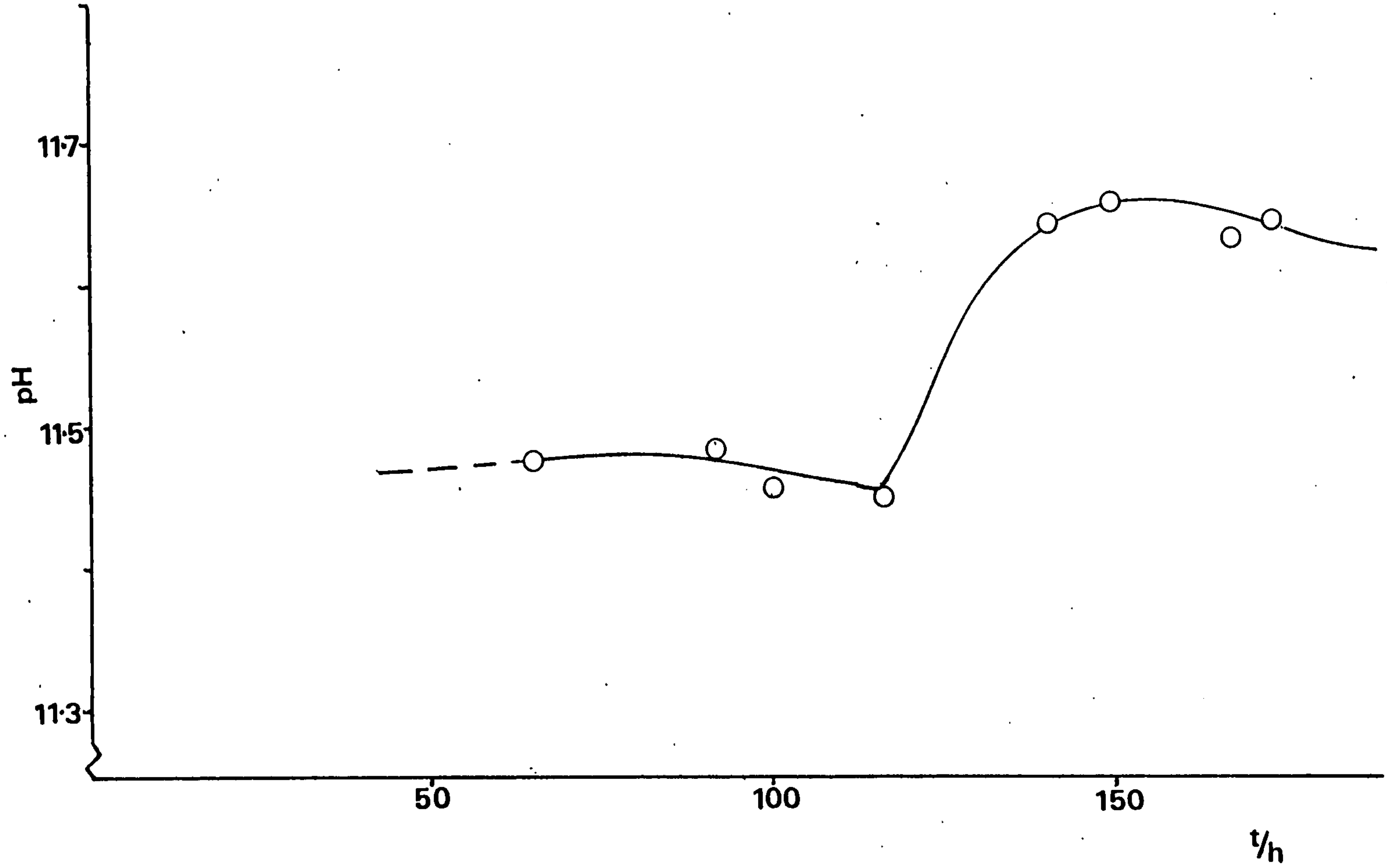


Fig. 23 Growth curve for EU-3, reaction HT HEX R75.

4.5.3 CHARACTERISATION OF EU-3

The X-ray powder diffraction pattern of EU-3 has been included in Table 4.29. The error in the line positions is likely to be up to 3 times the tabulated error because many of the lines are broad and/or feint. This was especially true of the first line the most intense in the diffraction pattern which was very broad. In addition it was noted that its position varied depending on how the sample was treated. When samples were allowed to dry at ambient temperature rather than in an oven this variation was reduced considerably.

Attempts to further characterise EU-3 from its sorptive properties were unsuccessful since although the product of calcination (sample was calcined at 450°C for 70 hours) did sorb significant amounts of water and n-hexane it was found to be amorphous to X-rays.

Thermal analysis of EU-3 was carried out. Fig. 4.24 contains the results of DSC[a] and tga of EU-3 sample, HT HEX R60. The major feature of the DSC trace is an endotherm, due to water loss, at about 50°C. However there is also a small endotherm at about 280°C followed immediately by a large exotherm. It is believed that these correspond to structural collapse and decomposition of the hexamethonium ion. X-ray diffraction of an EU-3 sample after it had been analysed by DSC showed that the crystalline structure had indeed collapsed and the resulting material was amorphous. The tga trace of EU-3 shows that three weight losses occur. The first at below 100°C must correspond to the loss of water. This is quite sharp, much more so than for EU-1 or EU-2 and it would appear that all the water is lost in

[a] Differential scanning calorimetry carried out using the DuPont instrument - see chapter 2.

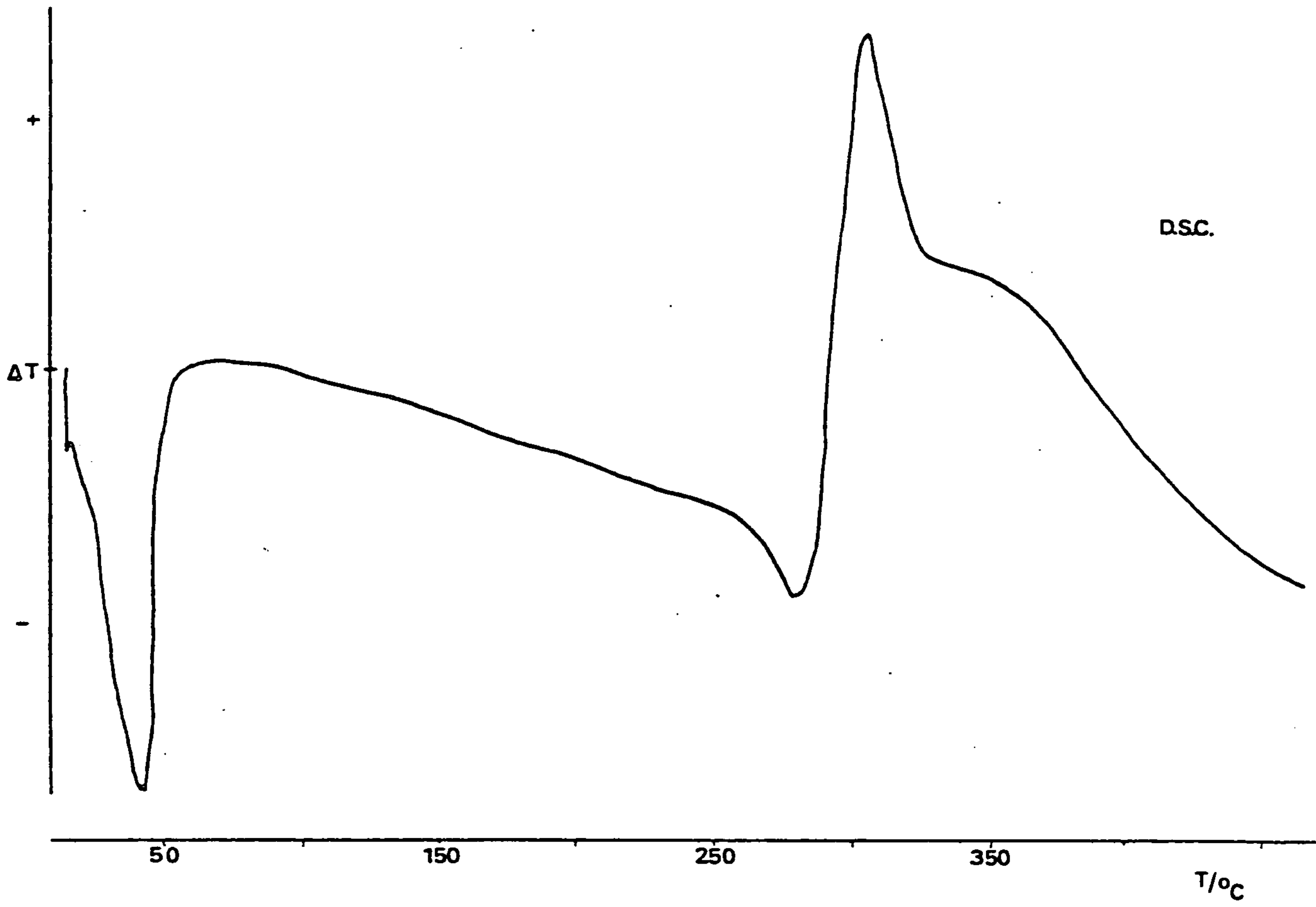
TABLE 4.29 X-RAY DIFFRACTION LINES FOR EU-3[a]

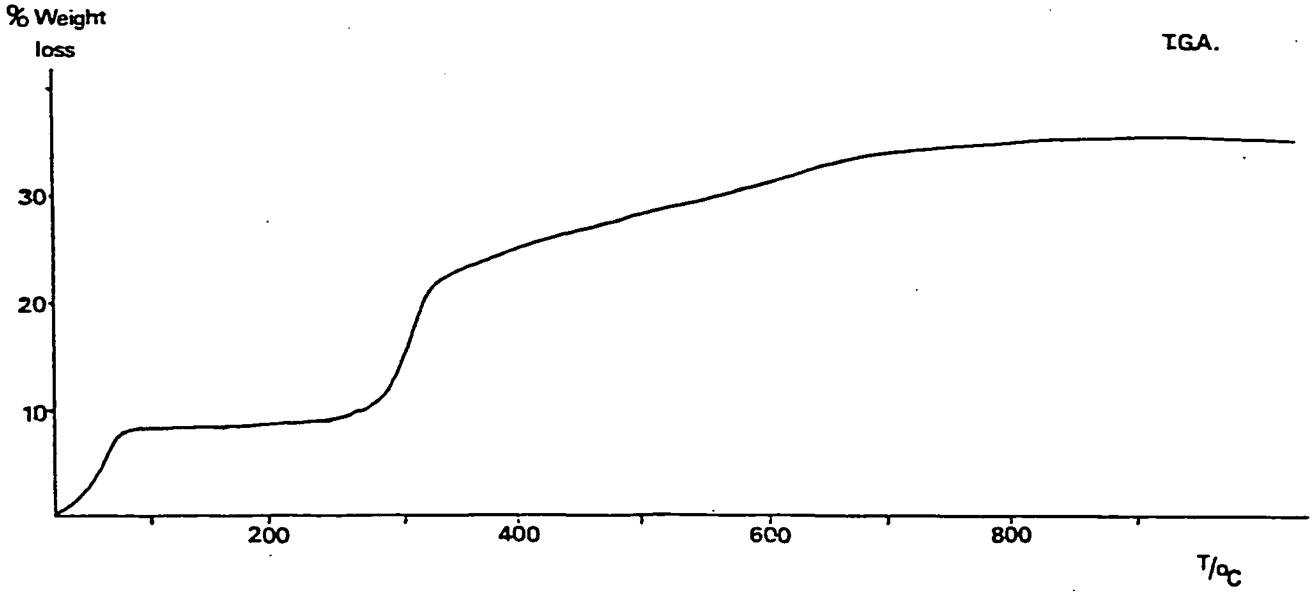
Line	d/Å	Error[b] in d
1	14.560 vs	0.167
2, 6	8.350 s, 8.395 s	0.047
3, 7	7.964 vw, 8.047 vw	0.042
4, 8	6.840 m, 6.810 m	0.030
5, 9	6.579 vw, 6.551 vw	0.027
10	5.609 vw	0.020
11	5.322 vw	0.018
12	5.063 vw	0.016
13	4.642 m	0.014
14	4.419 m	0.012
15	4.310 s	0.012
16	4.183 vw	0.011
17	4.023 vw	0.010
18	3.874 m	0.010
19	3.675 s	0.009
20	3.600 vw	0.008
21	3.536 w	0.008
22	3.428 s	0.007
23	3.175 w	0.006
24	3.076 vw	0.006
25	3.035 vw	0.006
26	2.877 vs	0.005
27	2.806 vw	0.005
28	2.730 m	0.005
29	2.449 vw	0.004
30	2.409 vw	0.004
31	2.367 vw	0.003
32	2.217 vw	0.003
33	2.156 s	0.003

[a] Guinier Film CJ553. Sample taken from run HT HEX R27, 55 days.

[b] These errors are based on the precision of the scale readings. Many of the lines are broad and/or feint and the uncertainty in the d-spacings may be up to 3 times the tabulated error.

Fig. 4.24 DSC and TGA of EU-3, reaction HT HEX R60.





one process since there is no further loss in weight until about 275°C. This is quite unusual and in marked contrast to the behaviour of high silica zeolites for which water loss tends to continue, albeit very slowly, up to the temperature at which the loss of the occluded organic species occurs. The second and third weight losses for EU-3 are probably part of the same process and correspond to the decomposition of the hexamethonium ion. The second loss is quite sharp while the third (which corresponds to an endotherm in the DSC trace) occurs more slowly.

The low thermal stability of EU-3 together with its destruction at about the same temperature as the organic material decomposes suggests that EU-3 is not a zeolite. Whilst its insolubility in water indicates that it is unlikely to contain discrete silicate anions, since simple sodium and quaternary ammonium silicates are usually fairly soluble. The shifts in the X-ray diffraction line positions caused by different drying conditions suggests that EU-3 is a smectite[a]. This is strongly supported by the increase in some of the d-spacings which occurred when a sample of EU-3 was slurried with ethanediol for about 2 hours. The major change was in the position of the most intense line for which the d-spacing increased from 14.30 Å to 16.07 Å. It is believed that this line corresponds to the basal spacing in the material. Since it is well known that smectites can undergo ion-exchange attempts were made to

[a] Smectites are layer-structured materials of which the clay minerals are typical examples. These materials can take up water and/or organic molecules between their layers and thus they exhibit 'swelling' which can be detected by X-ray diffraction.

exchange the interlayer cation(s) for the tetramethylammonium (TMA) and sodium ions. DSC traces of the resulting materials can be seen in Fig. 4.25. The TMA exchanged material showed two endotherms at similar positions to those observed for the synthesised sample. The first endotherm corresponds to water loss and the second is believed to be associated with loss of surface hydroxyls (as water) rather than complete structural collapse. This behaviour is commonly observed for smectites and is consistent with a small endotherm. The exotherm due to organic decomposition was shifted to a higher temperature. The material after sodium exchange only showed an endotherm due to water loss. Examination of the ion exchanged samples by X-ray diffraction showed that the sodium exchanged material had broken down and was completely amorphous whereas the TMA exchanged sample was still crystalline but the line positions, particularly the line corresponding to the basal spacing, had shifted. The inter-lamellar distance was observed to have increased which was surprising since the TMA ion is not as bulky as the HEX ion. However tga of the TMA -EU-3 showed that it contained considerably more water (approximately 20% of the total sample weight) which may account for the measured 'swelling' of the inter-lamellar distance.

SEM studies of EU-3 show that it has platey crystals consistent with a layered structure. Plate 4.18 is of HT HEX R74 and Plate 4.19 is of HTHEX R124 S8. It can be seen that EU-3 consists of clusters of thin plates which are about 6 to 7 μ in length and less than 0.1 μ thick. The large clusters appear to have many plates stacked

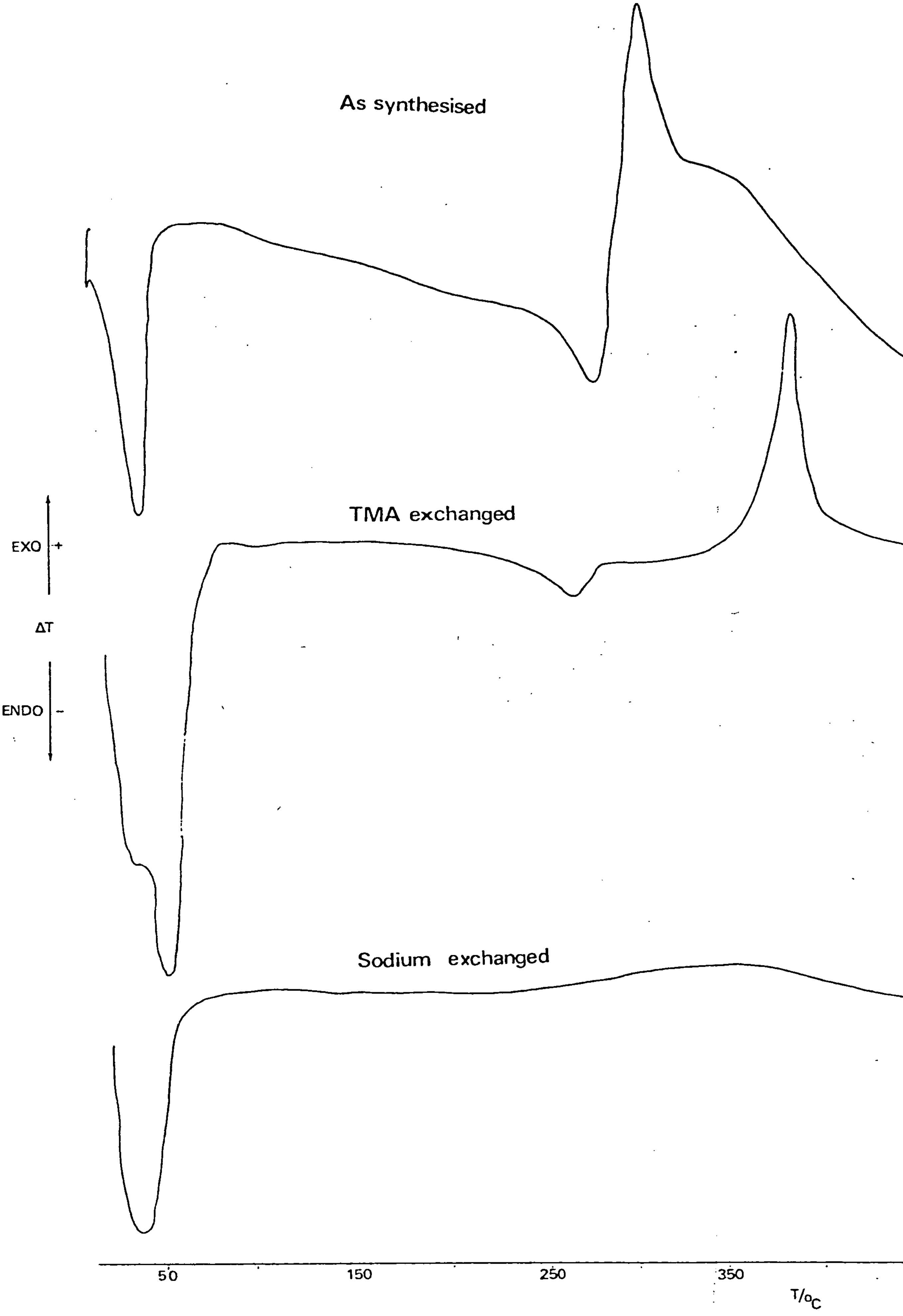


Fig 4.25 DSC of EU-3 samples.

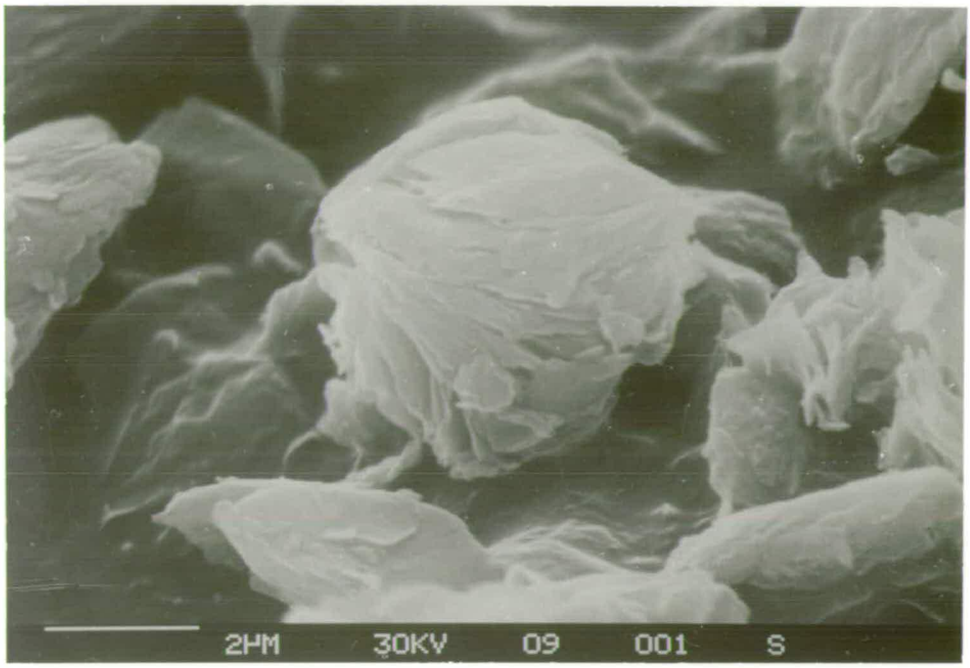


Plate 4.18
HT HEX R74

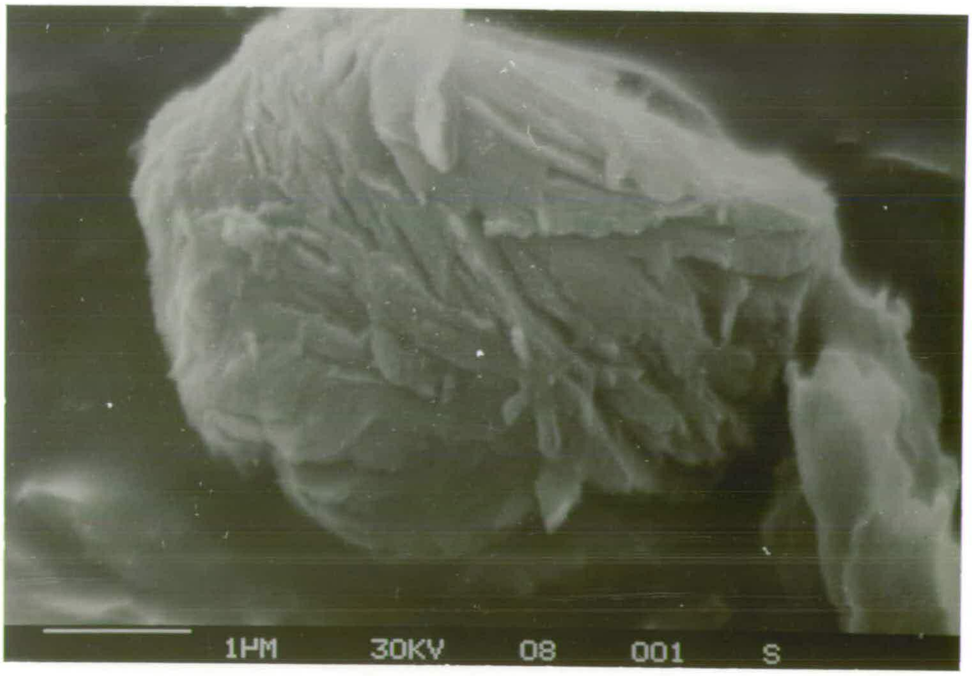


Plate 4.19
HT HEX R124

together into a near spherical shape.

The analysis of EU-3, sample HT HEX R60 can be seen in Table 4.30. Although the reaction was carried out in a glass reaction vessel the SiO_2/Al_2O_3 ratio is as high as those obtained for EU-2 reactions carried out in autoclaves. No sodium was detected thus the 'framework' is composed almost entirely of silica. The inter-lamellar species comprise about 34% of the material's weight. However it is not known if the hexamethonium is present as the cation or as a salt (either halides or hydroxide). Both are possible depending on whether the silica layers are neutral or are charged (i.e. silicates).

4.5.4 INVESTIGATION OF EU-3 CONVERSION TO EU-2

EU-3 was formed at 95°C from reaction mixtures which at higher temperatures yielded either EU-1 or EU-2. Aiello, Barrer and Kerr reported the formation[24] of small smectite materials from clear aluminosilicate solutions which eventually yielded zeolites and it was thought possible that a similar process could occur in high silica zeolite formation. Thus reaction HT HEX R124 was carried out. The reaction mixture HT HEX R124 had the composition:

$$60\ SiO_2 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000\ H_2O$$

and was allowed to react at 95°C until EU-3 had been produced (188 hours). It was then transferred to an autoclave which was heated to 200°C. The progress of these reactions can be seen in Fig. 4.26. The growth of EU-3 at 95°C can clearly be seen in section A. In section B the pH decreases as the EU-3 framework collapses. While in section C, EU-2

TABLE 4.30 COMPARISON OF EU-3 HT HEX R60

Percentage composition by weight of HT HEX R60

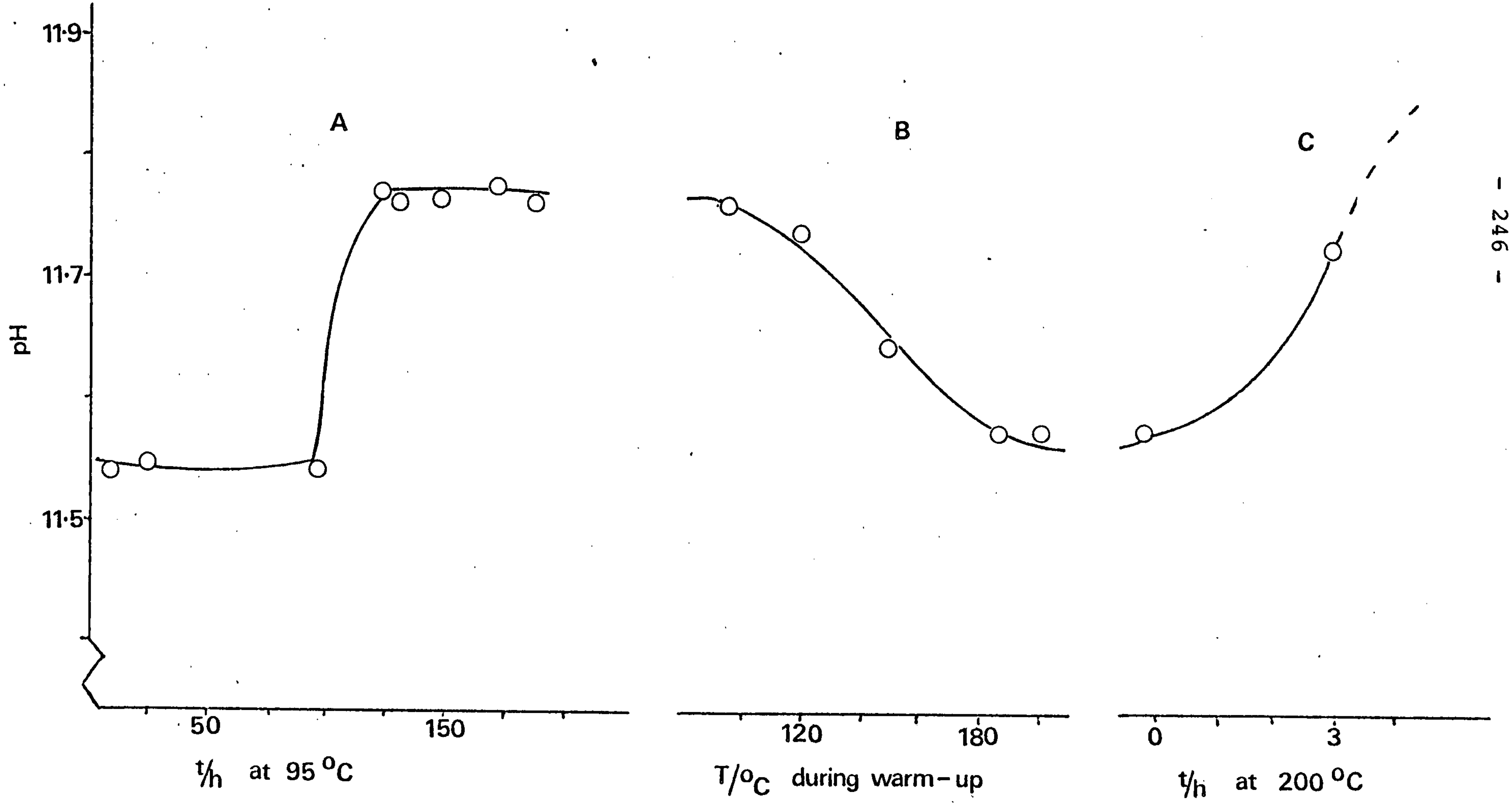
SiO_2	Al_2O_3	Na_2O	% loss at 1000°C	H_2O	HEX[a]
98.92	0.128	0	34.4	8	26

Molar composition of HT HEX R60

SiO_2	Al_2O_3	Na_2O
1312	1	0

[a] It is not known if this is present as the salt or in the cationic form - see text.

Fig. 4.26 pH changes observed throughout reaction HT HEX R124.



begins to crystallise after about 3 hours. Analysis of samples by X-ray diffraction confirmed that the three sections did indeed correspond to formation of EU-3, destruction of EU-3 and growth of EU-2. However it was noted that the EU-3 lines disappeared not gradually as suggested from pH measurements but almost in one step, between 150°C and 180°C. It would seem likely that EU-3 is unstable under such a combination of pH and temperature. However, the instability of EU-3 above 180°C coupled with the 'time lag' between EU-3 destruction and EU-2 growth suggests that EU-3 is not a precursor for EU-2 but a separate species.

4.6 SYNTHESIS AND CHARACTERISATION OF EU-4

4.6.1 INTRODUCTION

The zeolitic species EU-4 was synthesised from the system:

$SiO_2 - Al_2O_3 - Na_2O$ - PTMBr - H_2O

where PTM represents the propyltrimethylammonium cation:

$[CH_3 \cdot CH_2 \cdot CH_2\ N(CH_3)_3]^+$

This cation was chosen because it corresponds to exactly half of the bis-quaternary ion, hexamethonium, which was used in the synthesis of EU-1 and EU-2. It was thought that the use of PTM could provide an alternative (and cheaper) route to both of these species. However PTM produced an unidentified material which was designated EU-4.

4.6.2 SYNTHESIS OF EU-4

The syntheses carried out using PTMBr are summarised in Table 4.30. It can be seen that EU-4 can be synthesised over a wide range of SiO_2/Al_2O_3 ratios and indeed it was possible to synthesise an "aluminium free" version of EU-4 from reaction HT HEX R136. Of the novel materials formed in this work EU-4 was the only one which could be formed over the range of SiO_2/Al_2O_3 ratios from 60/1 to 60/0.

The rate of formation of EU-4 increased as the quantity of aluminium decreased, so that a reaction with no added aluminium (HT HEX R136) required 19 hours at 180°C to produce a major sample of EU-4. While reaction

TABLE 4.30 HIGH TEMPERATURE REACTIONS USING PTMBr[a]

HT HEX	SiO_2	Al_2O_3	Na_2O	PTMBr[a]	H_2O	T/C	t/h	Product
R79	60	1	10	20	3000	180	90	EU-4
R86	60	0.2	10	20	3000	200	16	EU-4 + α Q
R89	60	0	10	20	3000	200	17	EU-4 + α Q
R99	60	1	3	20	3000	180	170	EU-4
R133	60	1	10	20	3000	180	-	b
R134	60	0	10	20	3000	180	65	α Q + minor EU-4
R135	60	2	10	20	3000	180	268	minor EU-4[c]
R136	60	0	10	20	3000	180	19	EU-4
R137[d]	60[d]	2	10	20	3000	180	144	EU-4[c]
R144	60	0.667	10	20	3000	180	72	EU-4

[a] PTMBr = propyltrimethylammonium bromide. PTMBr was synthesised according to the method of P.A.S. Smith and S. Frank (J. Amer. Chem. Soc., 1952, 74, 509). The reaction mixture was held in a conical flask fitted with a cold finger condenser filled with dry-ice at -78°C rather than a stopper.

[b] Fault developed in autoclave.

[c] These samples of EU-4 are different from the others and are similar to EU-1 and EU-4; see text.

[d] Reaction carried out with added EU-4 seed in the as synthesised form obtained from HT HEX R79. The amount of seed added corresponded to about 5% of the weight of silica added.

HT HEX R79 with a SiO_2/Al_2O_3 ratio of 60/1 required about 90 hours at 180°C to produce a major sample of EU-4. Furthermore reaction HT HEX R135 with SiO_2/Al_2O_3 ratio of 60/2 (30/1) only produced a minor EU-4 type product after 268 hours at 180°C. This behaviour is quite different to that encountered in the formation of EU-1 (see section 4.3) but shows similarities with the synthesis of EU-2 (see section 4.4). Additional compositional changes, for example, decreasing the Na_2O content from 10 Na_2O (HT HEX R79) to 3 Na_2O (HT HEX R99) caused a large decrease in the reaction rate, with the time required for EU-4 formation increasing from 90 hours (HT HEX R79) to 170 hours (HT HEX R99).

The rate of formation of EU-4 was increased by the addition of 'seed' material. Thus reaction HT HEX R137 which was seeded, with an "as synthesised" sample of EU-4 from reaction HT HEX R79, produced a major product in 144 hours, whereas an identical mixture (HT HEX R135) without the 'seed' gave a minor product in 268 hours. It should be pointed out however that the products obtained from reactions HT HEX R135 and R137 were not identical with other samples of EU-4 (e.g. HT HEX R79, R99 and R136). Thus it may not be possible to extrapolate the effect of seeding in these reactions to reactions which produce the 'standard' EU-4. The similarities and differences of these samples will be discussed in section 4.6.3.

4.6.3 CHARACTERISATION OF EU-4

Table 4.31 contains the results of X-ray powder diffraction for a series of samples of EU-4, synthesised from reactions with different ratios of SiO_2/Al_2O_3. It can be seen that there is little difference between the samples obtained from reactions with SiO_2/Al_2O_3 ratio of 60/1 (HT HEX R79, R99) and 60/0 (HT HEX R136). Although it was observed that the sample obtained from reaction HT HEX R136 was of a superior quality, since the lines obtained from the Guinier-Hagg camera were much sharper than those from reactions HT HEX R79 and R99. It should also be noted that HT HEX R99 was synthesised over a much longer period than HT HEX R79 yet their X-ray diffraction patterns are very similar. The sample obtained from HT HEX R137 however was in many ways quite different from those obtained in reactions HT HEX R79, R99 and R136. The major differences are associated with lines at d = 10.06, 5.905 and 3.835 although it contains several other lines which are not present in the 'standard' EU-4 pattern. It was noted that the product from HT HEX R137 while different from that of the 'standard' EU-4 was in many ways similar to EU-1. A comparison of the 'd-spacings' for EU-4 (HT HEX R136), EU-1 (HT HEX R1) and the product from HT HEX R137 can be seen in Table 4.32. Although it appears that the product from HT HEX R137 contains some lines from both EU-1 and EU-4 it is not believed to be a mixture of the two species. Instead it is believed that it may be a species intermediate between EU-4 and EU-1. This is possible since EU-1 is predominantly a 'low silica' species while EU-4 is a 'high silica' species. So as the SiO_2/Al_2O_3 ratio of the EU-4 reaction mixture is decreased the EU-4 begins to crystallise as a species closer in structure to EU-1. The similarities between the species can best be seen in Plate 4.20 which shows the films of the X-ray powder diffraction patterns of the three samples. Comparisons between other properties of EU-4 and the product from HT HEX R137 were carried out.

Table 4.33 contains a comparison of d-spacings' for 'as synthesised' and calcined samples of EU-4, from reaction HT HEX R79 and R99. It can be seen that calcination does not significantly alter the X-ray diffraction pattern of EU-4.

Analysis of samples of EU-4 from reactions HT HEX R79 and HT HEX R99 have been included in Table 4.34a and Table 4.34b. In both cases the SiO_2/Al_2O_3 ratios of the products are less than that of the reaction mixtures and the Na_2O content is less than unity. These features are similar to those found for EU-1. The difference between the Na_2O contents of the two products reflects the difference in the Na_2O content of the reaction mixtures. Indeed the relative amounts of Na_2O in reaction mixture and product are almost identical. The quantity of PTM in the samples was much larger than required to satisfy the aluminium content. The question of whether this 'excess' organic cation is present as the hydroxide or halide was not resolved as analyses for halide were not carried out. However molar compositions for both possibilities are

Plate 4.20

TABLE 4.31 d-SPACINGS FOR "AS SYNTHESISED" EU-4

Run HT HEX	R137	R79	R99	R136
Film	J848	J758	J797	J847
SiO_2/Al_2O_3[a]	60/2	60/1	60/1	60/0
	11.111	11.071	11.067	11.031
	10.063			
	9.224	9.224	9.224	9.196
				7.615
			7.559	
		7.522		
	6.873	6.828	6.828	6.873
	6.260	6.276	6.276	6.289
		5.963	5.986	5.975
	5.905			
		5.829	5.829	5.840
	4.655	4.594	4.594	4.628
	4.482	4.450	4.450	4.469
	4.333	4.292	4.280	4.286
	4.002	3.967	3.967	3.982
	3.835			
				3.799
		3.768		3.754
	3.710		3.723	
		3.688	3.671	3.675
	3.600	3.571	3.563	3.584
	3.458			
	3.436			
		3.425	3.417	3.421
	3.363			
		3.338	3.338	3.342
	3.279			
		3.269	3.263	3.266
	3.259			
			3.223	3.226
	3.168			
		3.128	3.116	3.106
	3.106			
		3.073	3.079	3.076
		3.027	3.021	3.001
	2.996	3.004	2.993	2.979
	2.945			
		2.854	2.839	2.846
		2.780	2.780	
		2.746	2.742	2.749
	2.707			
		2.687	2.678	2.635
	2.589			
		2.571		2.561
	2.537			
		2.511	2.511	
	2.483			
		2.458	2.458	
		2.440	2.432	
	2.406			
		2.393	2.390	
	2.337			
	2.307	2.299	2.292	
	2.243	2.236	2.236	
	2.169			
	2.117	2.113	2.110	
	2.003		1.973	
	1.951	1.943	1.941	
	1.920			

[a] SiO_2/Al_2O_3 of reaction mixture

TABLE 4.32 COMPARISON OF d-SPACINGS FOR EU-1, EU-4 AND PRODUCT FROM RUN R137

Phase	EU-4	EU-4(?)	EU-1
Run HT HEX	R136	R137	R1
SiO_2/Al_2O_3[a]	60/0	60/2	60/1
Film	J847	J848	J403
Error	d/Å	d/Å	d/Å
0.079		11.111 vs	
0.079	11.031 vs		11.031 vs
0.066		10.063 w	10.096 vs
			9.716 m
0.055	9.196 vs	9.224 w	
0.037	7.615 m		7.690 m
0.030	6.873 m	6.873 m	6.843 m
0.025	6.289 m	6.260 vw	6.213 vw
0.023	5.975 m		
0.023		5.905 w	
0.023			5.797 w
0.022			5.609 vw
0.016			4.712 vw
0.014		4.655 vs	4.642 vs
0.014	4.628 vs		
0.013	4.469 s	4.482 w	
0.012		4.333 vs	
0.012	4.286 vs		4.286 vs
0.010	3.982 vs	4.002 vs	3.992 vs
0.010		3.835 vw	
0.009	3.799 w		3.799 s
0.009	3.754 m		
0.009		3.710 s	3.701 s
0.009	3.675 s		
0.008		3.600 w	
0.008	3.584 s		
0.008		3.458 m	
0.007	3.421 m	3.436 m	3.428 w
0.007		3.363 s	
0.007	3.342 s		3.342 m
0.007	3.314 w		
0.007	3.266 s	3.279 vs	
			3.239 s
0.007	3.226 m		
		3.168 vw	3.143 vw
0.006	3.106 w	3.106 w	
0.006	3.076 w		3.070 vw
0.006	3.001 vw	2.996 m	
0.006	2.979 vw		
		2.945 vw	
			2.930 vw
0.005	2.846 w		
0.005	2.749 w		
		2.707 w	
			2.694 w
0.004	2.685 m		
0.004	2.561 w	2.589 vw	
0.004	2.532 w	2.537 w	2.533 m

[a] SiO_2/Al_2O_3 ratio of reaction mixture

TABLE 4.33 d-SPACINGS FOR CALCINED EU-4 SAMPLES

Reaction	HT HEX R79	HT HEX R79	HT HEX R99	HT HEX R99
Treatment	As Synthesised	Calcined in air 650°C, 40 h	As Synthesised	Calcined in air 650°C, 40 h
Film	J758	J887	J797	J838
	d/Å	d/Å	d/Å	d/Å
	11.071	11.031	11.067	11.111
	9.224	9.115	9.224	9.196
	7.522		7.559	7.504
	6.828	6.813	6.828	6.813
	6.276	6.238	6.276	6.263
	5.963	5.952	5.986	6.021
	5.829	5.797	5.829	5.840
		5.510		5.589
	4.594	4.601	4.594	4.628
	4.450	4.457	4.450	4.482
	4.292	4.286	4.280	4.322
	3.967	3.962	3.967	4.002
	3.768	3.753	3.723	3.763
	3.688	3.693	3.671	3.719
	3.571	3.567	3.563	3.592
	3.425	3.413	3.417	3.436
	3.338	3.342	3.338	3.349
	3.269	3.259	3.263	3.273
	3.128	3.226	3.223	3.252
		3.100	3.116	3.181
	3.073	3.082	3.079	3.094
	3.027	2.041	3.021	3.041
	3.004	2.990	2.993	3.001
	2.854	2.851	2.839	2.862
	2.780	2.782	2.780	2.787
	2.746	2.744	2.742	2.758
	2.687	2.698	2.678	2.694
	2.571			
	2.511		2.511	2.619
	2.458		2.458	
	2.440		2.432	
	2.393		2.390	

TABLE 4.34a QUANTITATIVE ANALYSIS OF EU-4

Sample	Percentage Composition by Weight[a]					
HT HEX	Al_2O_3	SiO_2	Na_2O	Organic[b,c]	H_2O[b]	Total
R79	2.92	84.53	0.986	∿8.2	3.2	99.84
R99	2.60	84.41	0.324	∿8.25	3.75	99.33

[a] The non-volatile oxides were determined by X-ray fluorescence of the calcined material; the values for R79 and R99 were respectively Al_2O_3 : 3.301, 2.957; SiO_2 : 95.41, 95.95; Na_2O : 1.113, 0.368; total 99.824, 99.245%.

[b] The water and 'organic' values are based on the low and high temperature weight losses determined by TGA.

[c] CHN values not available.

given in Table 4.34b. The quantity of water in the samples did not reflect the Na_2O content and indeed in reaction HT HEX R99 the lower amount of Na_2O was 'balanced' by an increase in both the water and PTM contents. Similar behaviour was observed for EU-2.

The results of sorption measurements on samples of EU-4 calcined at 450°C and on the same samples after further calcination at 550°C are given in Table 4.35. None of the samples exhibit a significant sorption capacity. However two things can be seen, firstly, the sample from HT HEX R136 sorbs virtually nothing and secondly, the sorption capacity of the sample from HT HEX R137 is much higher than that of samples from HT HEX R79 and R99. This provides further evidence that HT HEX R137 is not a typical sample of EU-4. It should also be noted that the samples from HT HEX R79, R99 and R136 were not white after calcination suggesting that some organic material remained inside. This may be the cause of their low sorption capacity.

DTA results for three samples of EU-4 are shown in Fig. 4.27. The three samples compared are from reactions HT HEX R137, R79 and R136. All three show two small endotherms at low temperatures which are probably due to the loss of water. In addition they all contain several exotherms at higher temperatures related to the decomposition of the organic material. At very high temperatures (>800°C) samples from HT HEX R137 and R79 give endotherms due to the collapse of the lattice. No corresponding endotherm was observed for the sample from

TABLE 4.34b MOLAR COMPOSITION OF EU-4

Since a full elemental analysis was not carried out it is not possible to give a molar composition without making certain assumptions. If the samples do not contain any Br^- and if all the organic material is present as the PTM^+ cation then the molar compositions are:-

R79: 0.56 Na_2O 0.44 PTM_2O Al_2O_3 49.1 SiO_2 6.2 H_2O 1.65 PTMOH
R99: 0.22 Na_2O 0.78 PTM_2O Al_2O_3 55.1 SiO_2 8.2 H_2O 1.38 PTMOH

or in oxides

R79: 0.56 Na_2O 1.27 PTM_2O Al_2O_3 49.1 SiO_2 7.03 H_2O
R99: 0.22 Na_2O 1.47 PTM2O Al_2O_3 55.1 SiO_2 8.89 H2O

Alternatively if all the excess organic is present as PTMBr the molar compositions are:

R79: 0.56 Na_2O 0.44 PTM_2O Al_2O_3 49.1 SiO_2 6.2 H_2O 1.08 PTMBr
R99: 0.22 Na_2O 0.78 PTM_2O Al_2O_3 55.1 SiO_2 8.2 H_2O 0.90 PTMBr.

TABLE 4.35 SORPTION BY EU-4[a,d]

Sample HT HEX	After Calcination at 450°C for 70 h	After Calcination at 550°C for 20 h
Sorption of water P = 6 mmHg, t = 16 h		
R137(60/2)[c]	5.27	4.37
R79 (60/1)	0.78	0.72
R99 (60/1)	0.68	0.54
R136(60/0)	0.04	0.05
Sorption of hexane P = 49 mmHg, t = 17 h		
R137(60/2)	3.48	4.13
R79 (60/1)	1.96	1.46
R99 (60/1)	1.54	2.33
R136(60/0)	0.09	0.08
Sorption of cyclohexane P = 27.6 mmHg, t = 18 h		
R137(60/2)	1.93	3.21
R79 (60/1)	1.76	1.27
R99 (60/1)	0.91	3.13
R136(60/0)	0.11	1.36
Sorption of water[b] P = 5.8 mmHg, t = 20 h		
R137(60/2)	4.17	4.05
R79 (60/1)	0.93	0.85
R99 (60/1)	0.74	0.87
R136(60/0)	0.12	0.10

[a] Increase in weight per 100 g of dry zeolite

[b] These results were obtained after sorption studies with the organic sorbates

[c] SiO_2/Al_2O_3 ratio of reaction mixture

[d] Results were obtained in Edinburgh.

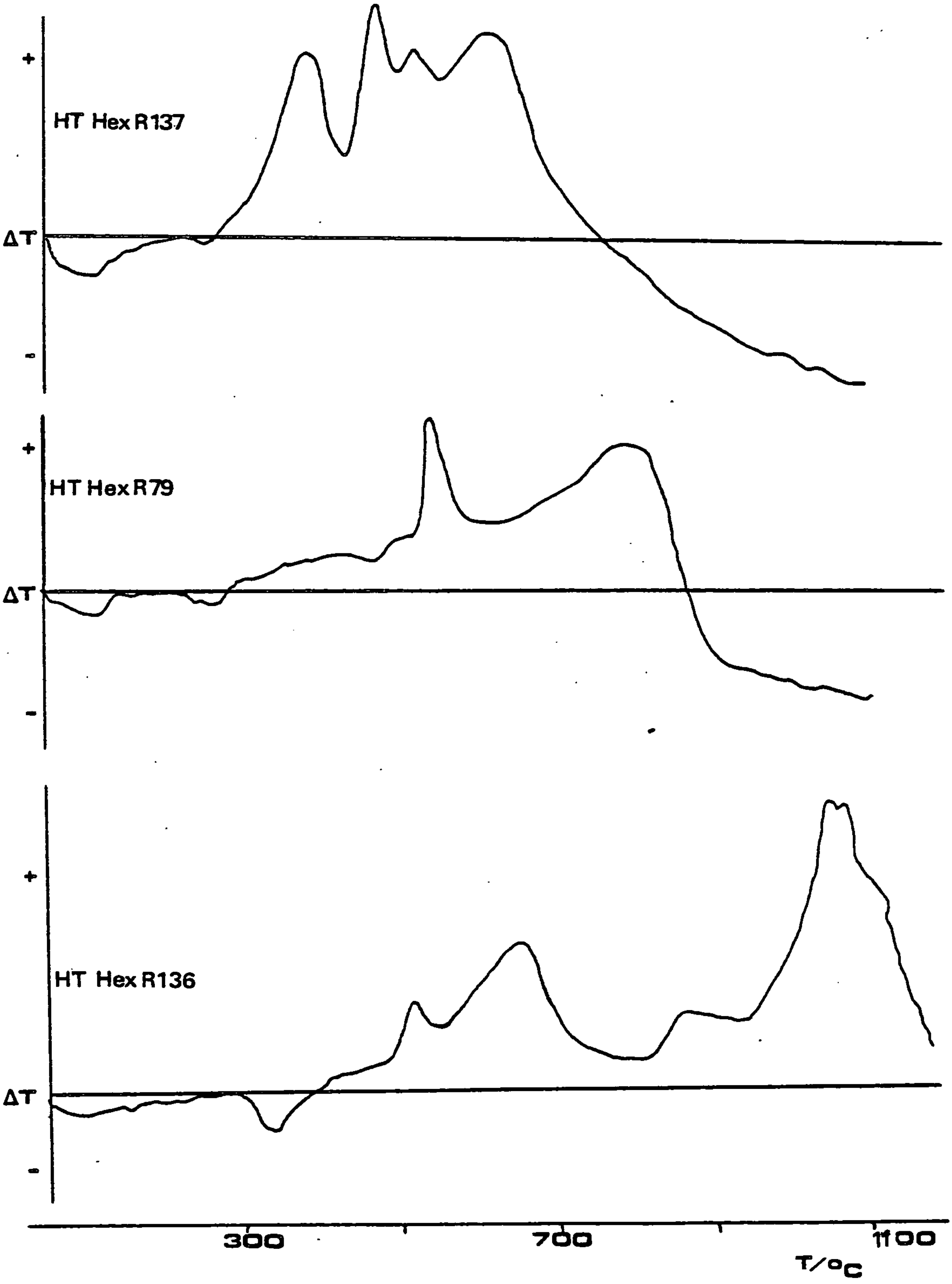


Fig. 4.27 DTA of EU-4 samples from reactions HT HEX R137, R79 and R136.

HT HEX R136 even though subsequent analysis of the material showed that it too had broken down. It is likely that in this case the exotherm due to the break up of the organic material masks the endotherm caused by the collapse of the lattice. It can be seen that the temperature at which the organic material decomposes and the lattice collapses both increase when the SiO_2/Al_2O_3 ratio is increased. The relationship between the SiO_2/Al_2O_3 ratio of a framework and its thermal stability is well known. However, much less is known about the temperature at which the occluded organic material decomposes and about the way in which this process depends on the SiO_2/Al_2O_3 ratio of the framework. It could be that the ease with which organic material trapped within the lattice breaks down is related to the catalytic action of the zeolite. Thus materials with extremely high SiO_2/Al_2O_3 ratios (e.g. 60/0) cannot readily catalyse the decomposition of the trapped organic material, and consequently the exotherm in their DTA trace occurs at much higher temperature than it does for corresponding zeolites with lower SiO_2/Al_2O_3 ratios.

X-ray powder diffraction analysis of the samples remaining after DTA investigations showed that all three had converted to α-cristobalite. However only a very small amount was found for the product of reaction HT HEX R137 once again illustrating that the material differs from the high silica samples of EU-4.

Fig. 4.28 contains both TGA and DTA traces for the sample from reaction HT HEX R79 (SiO_2/Al_2O_3 ratio of 60/1). The way in which the weight losses correspond to the exotherms and endotherms in the DTA trace can clearly

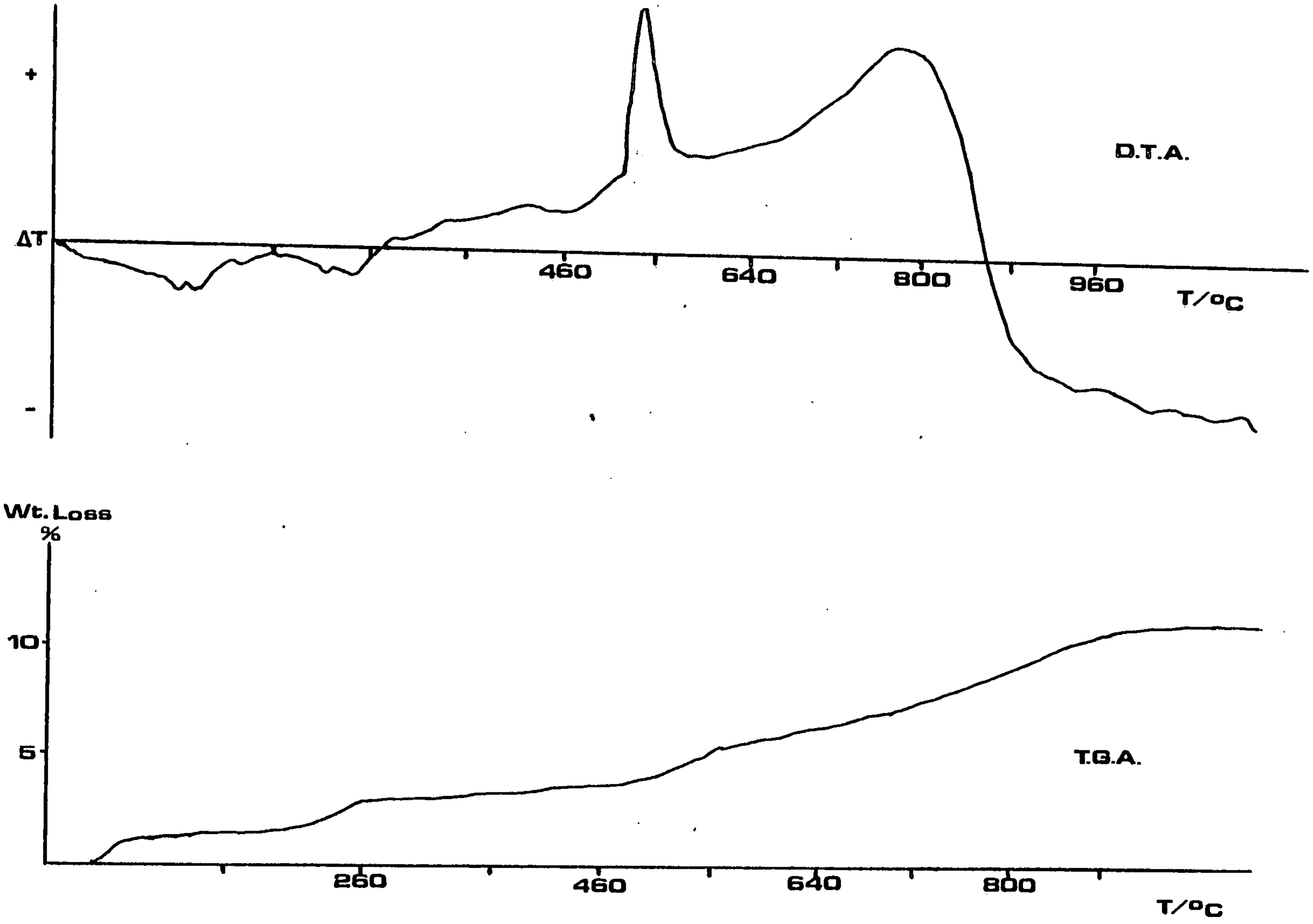


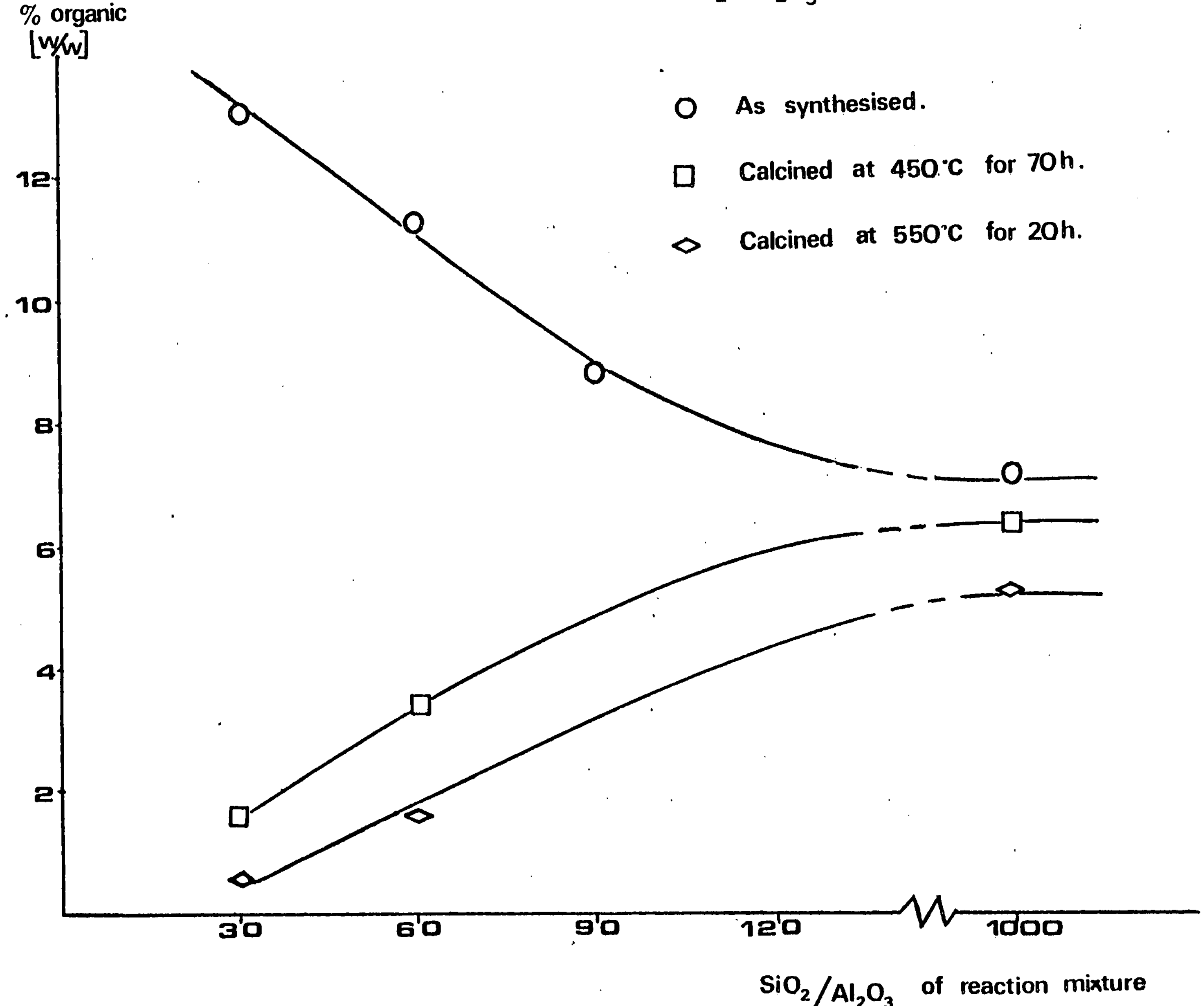
Fig. 4.28 TGA and DTA of EU-4, reaction HT HEX R79.

be seen. Also, it is apparent that the organic material continues to be lost up to almost 1000°C. Now while prolonged calcination at a lower temperature may remove more of the organic material than suggested by the TGA trace it is unlikely that all the organic material would be removed.

This is confirmed in Fig. 4.29 which shows the quantity of organic material present in the as synthesised samples, and in the samples calcined at 450°C and 550°C as a function of the SiO_2/Al_2O_3 ratio of the reaction mixture. It can clearly be seen that the amount of organic material incorporated into the zeolite decreases as the SiO_2/Al_2O_3 ratio of the reaction mixture is increased. In addition Fig. 4.29 shows that the organic material is most easily removed from the product of reaction HT HEX R137 (SiO_2/Al_2O_3 of 30/1) and that it becomes progressively more difficult to remove the organic material as the SiO_2/Al_2O_3 ratio of the zeolite increases.

SEM studies on three samples of EU-4 were carried out. There were samples from HT HEX R79 (SiO_2/Al_2O_3 = 60/1), HT HEX R137 (SiO_2/Al_2O_3 = 60/2) and HT HEX R136 (SiO_2/Al_2O_3 = 60/0). This can be seen in Plates 4.21, 4.22 and 4.23 respectively. It can be seen that whereas the X-ray diffraction pattern of HT HEX R137 differs from those of HT HEX R136 and R79, there are marked similarities between the electron micrographs of R79 and R137, and in this case it is the product of the high silica (60/0) reaction R136 which is different from the others. The crystals in R79 and R137 (Plates 4.21 and 4.22) are very

Fig. 4.29 Quantity of organic material in EU-4 samples as a function of their SiO_2/Al_2O_3 ratios.



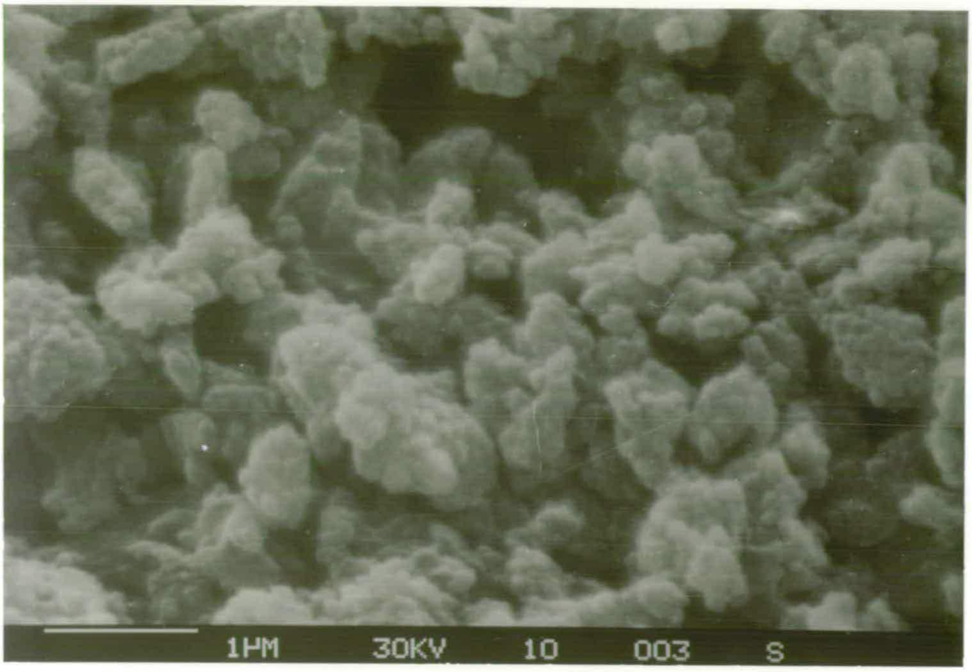


Plate 4.21
HT HEX R79
SiO_2/Al_2O_3 = 60/1

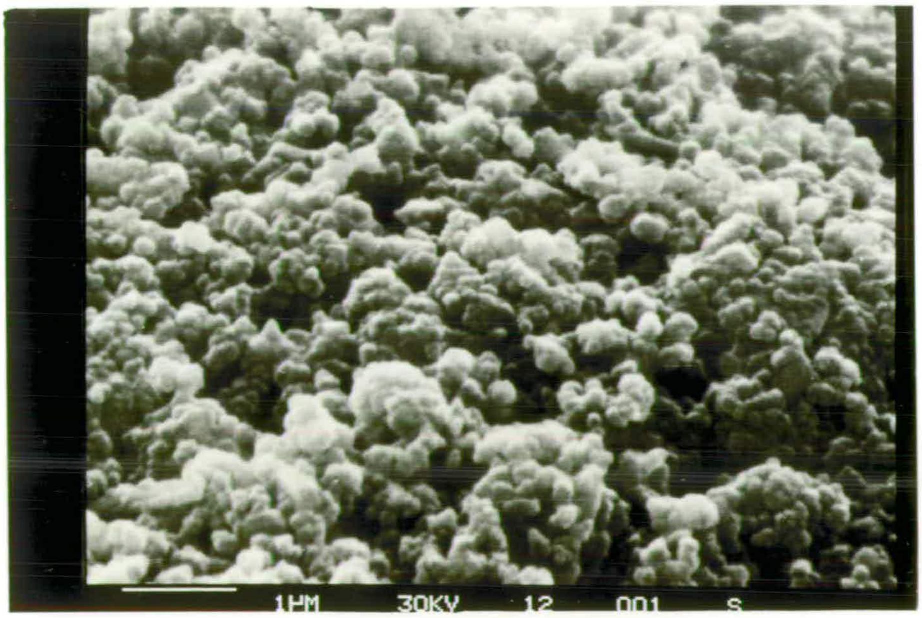
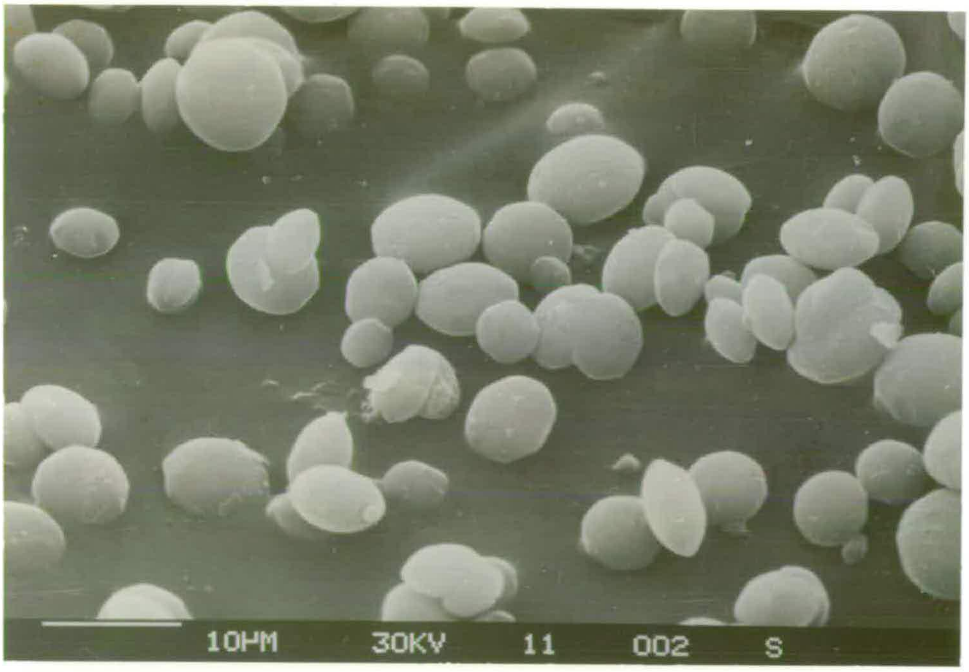


Plate 4.22
HT HEX R137
SiO_2/Al_2O_3 = 60/2

Plate 4.23
HT HEX R136
SiO_2/Al_2O_3 = 60/0



small and like EU-2 (see section 4.4) appear to be aggregates of very small crystals (cf. zeolite P). The crystals from reaction HT HEX R136 are very large, indeed some are almost 10 μ in diameter. These are some of the largest zeolitic crystals seen in any of these studies. It is worth mentioning that these large crystals are similar in shape to those seen for EU-2, synthesised in a reaction (HT HEX R78) with SiO_2/Al_2O_3 ratio of 300/1, see Plate 4.16 (section 4.4.3). The crystal size of the EU-4 samples increases with their SiO_2/Al_2O_3 ratio and it could be that the difficulty experienced in removing the organic material from high SiO_2/Al_2O_3 ratio samples is related, in part, to their large crystallite size.

Zeolite EU-4 appears to be 'unique' amongst the novel zeolitic materials discovered in this work, in that it can be synthesised over such a wide range of SiO_2/Al_2O_3 ratios. Of the zeolites so far reported in the literature the one which bears most resemblence to EU-4 is zeolite ZSM-34[25], which was synthesised using choline ($(CH_3)_3\overset{+}{N}CH_2CH_2OH\ X^-$). EU-4 is also similar to EU-1 and EU-2, the resemblence to EU-1 increases as the SiO_2/Al_2O_3 ratio is reduced and is most marked when the ratio is 30/1. The sorption capacity of EU-4 is apparently very low but this is almost certainly because the organic material occluded in the structure is not easily removed by calcination. Indeed unless some way can be found to remove the organic material without disrupting the lattice it is unlikely that EU-4 could be used as a sorbent or catalyst. Although the low aluminium content and the large crystal size may contribute to the difficulty experienced in removing from high silica EU-4 they are not the major cause of the problem since similar difficulties are not found with EU-2 or ZSM-5 organosilicate species. The reason is almost certainly associated with the EU-4 framework which is perhaps such that the cavities containing the organic species are linked by narrow channels, alternatively the problem could be due to stacking faults or intergrowths. This will only be resolved by work in the structure of EU-4 and by continuing experiments on its synthesis.

4.7 SYNTHESIS OF ZSM-5

4.7.1 INTRODUCTION

The synthesis of ZSM-5 from systems containing the tetrapropylammonium cation is the subject of several patents by the Mobil Oil Corporation. The publication of later patents[26] and abandonment of several of the earlier ones reflects the early problems in the synthesis and characterisation of this material. The synthesis of ZSM-5 from systems which contain hexamethylenediamine[27] and alcohols[28] instead of the tetrapropylammonium species has also been patented. The widespread interest in ZSM-5 has led to the publication of several reports on its synthesis and structure[29-33]. The interest in ZSM-5 is based on its use as a catalyst in which it can be used to produce gasoline[34] from methanol as well as applications in xylene isomerisation and toluene disproportionation[35,36]. There is also interest in ZSM-5, because it has been shown[20] to be possible to synthesise a "silica-only" version of ZSM-5, known as silicalite.

4.7.2 SYNTHESIS OF ZSM-5

In this work it was found that ZSM-5 could be synthesised using many different substances as the organic component. As can be seen in Table 4.36 the organic species which are effective in this reaction can be of widely differing structures. Furthermore it was found after these reactions had been completed that it was possible to synthesise ZSM-5 from reaction mixtures

TABLE 4.36 SYNTHESIS OF ZSM-5

HT HEX	Organic species	Composition					Product(s)
		SiO_2	Al_2O_3	Na_2O	R	H_2O	
R87	CETAB Cetyltrimethylammonium	60	1	10	5	3000	Med. ZSM-5 type[a]
R65	Pyrrolidine	60	1	10	5	3000	Med. ZSM-5 type[b] + α Q
R91	Hexamethylenediamine	60	1	10	10	3000	ZSM-5
R67	Ethylenediamine	60	1	10	10	3000	ZSM-5
R116	Hexane-1,6-diol	60	1	10	10	3000	ZSM-5
R140	Decane-1,10-diol	60	1	10	10	3000	Med. ZSM-5 + c
R125	Sodium Adipate	60	1	10	10	3000	tr./med. ZSM-5
R146	Organic free	60	1	10	0	3000	Med. ZSM-5[d]

[a] The reaction mixture was very viscous and this could have reduced the reaction rate.

[b] ZSM-5 type means product had a similar pattern to ZSM-5 but had lines shifted. It is possible that the pattern would revert to a 'standard' ZSM-5 after calcination.

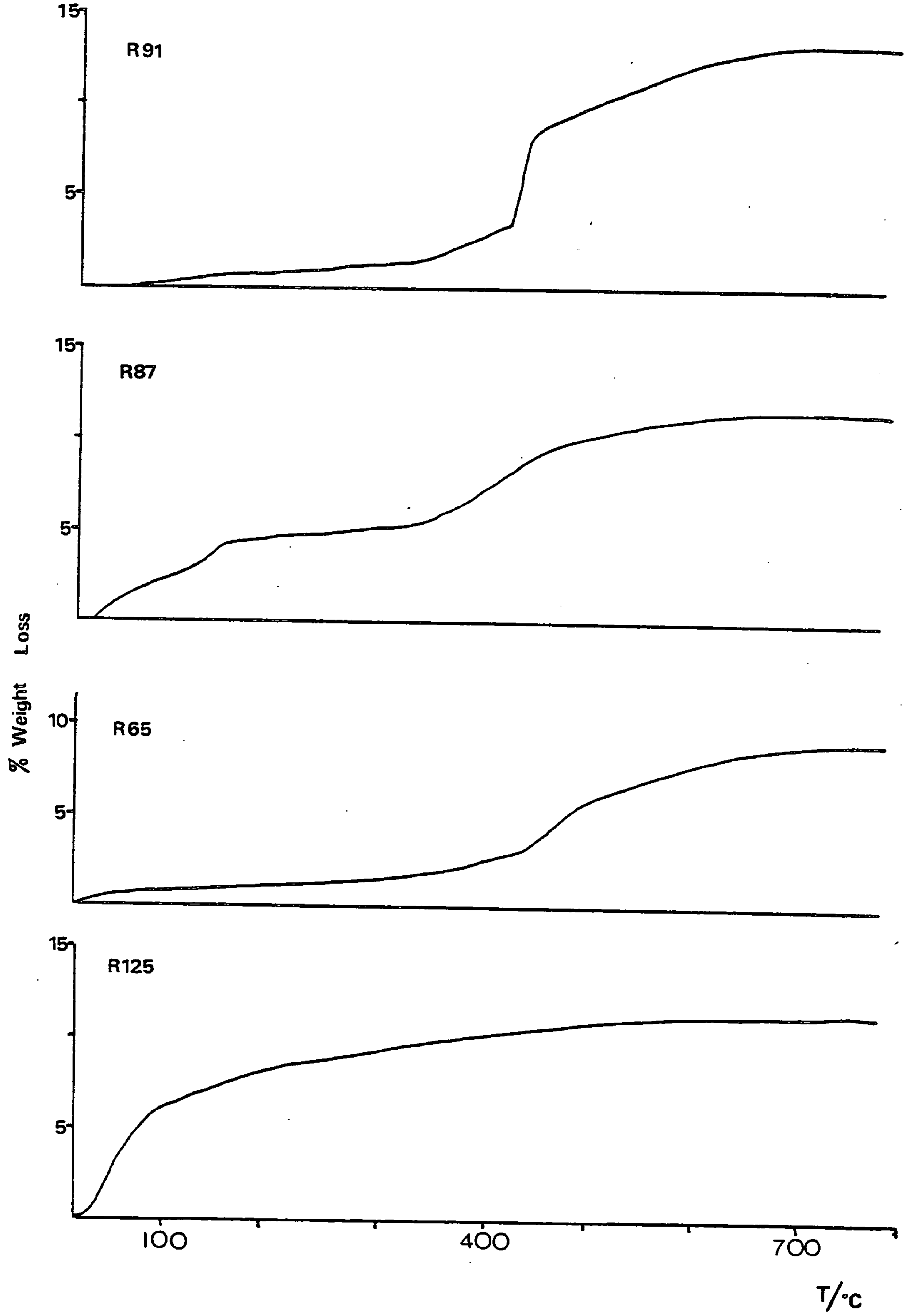
[c] The product's X-ray pattern also contained a few unidentified lines, possibly due to the decane-1,6-diol itself.

[d] This reaction contained no organic material at all. The ZSM-5 product may have been 'seeded' in some way - see text and section 4.8.

which contained no organic component. An example of one of these reactions has been included in Table 4.37 (HT HEX R146). It should be noted that although several organic free reactions were carried out, the quantity of ZSM-5 formed (as estimated by the Guinier-Hagg camera) varied considerably from trace amounts to medium/major amounts. Whether this material formed as a 'genuine' product or as a consequence of the autoclaves being contaminated with ZSM-5, was not resolved. The possibility of such a reaction being 'seeded' will be discussed in section 4.8.

The synthesis of ZSM-5 using hexamethylenediamine is a patented process and consequently it is not surprising that reaction HT HEX R91 produced ZSM-5. However the small species, ethylenediamine which has been reported[37] to produce ZSM-21, from high silica reaction mixtures, was found in the present work to produce ZSM-5 as a major product. The formation of 'medium' samples of ZSM-5 from reactions containing CETAB (R87), pyrrolidine (R65) and sodium adipate (R125) could be either because the reactions were genuinely slow or because the organic species had no effect and the reactions proceeded as if no organic material was present (e.g. R140). TGA traces for the products from reactions HT HEX R91, R87, R65 and R125 can be seen in Fig. 4.30. The largest amount of organic material was found in sample HT HEX R91 which was synthesised using hexamethylenediamine. Although the products from reactions HT HEX R87 (CETAB) and R65 (pyrrolidine) did not contain as much organic material as R91 the fact

Fig. 4.30 TGA of ZSM-5 samples from reactions HT HEX R91, R87, R65 and R125



that they contained some organic material suggests that these organic species were involved in the crystallisation process. The ZSM-5 synthesised in reaction HT HEX R125, however, contained almost no organic material and therefore it would seem that the sodium adipate did not take part in the crystallisation. However it is believed that the use of salts of organic acid such as sodium adipate could be useful in the preparation of high silica zeolites. It is known that the addition of salts to low silica zeolite reaction mixtures can affect both the rate of formation of the product[13] and the morphology of the crystals[17]. It is believed that despite the unpromising result of reaction HT HEX R126 negatively charged hydrophobic species could play a useful role in high silica zeolite synthesis. The problem which arises when inorganic salts are used is that it is not always possible to remove the salts from the product zeolite by washing. However, with organic salts such as sodium adipate the salt could be removed by calcination and washing.

The occlusion of the cetyltrimethylammonium cation in ZSM-5 (R87) is surprising since CETAB is not very soluble in water and indeed because of its surface active properties the concentration of monomeric (as opposed to micellar) CETAB is in the millimolar region at room temperature[38]. While temperature, pH and ionic strength can change the C.M.C. (critical micelle concentration) their effects are not very large and it is interesting that so much cetyltrimethylammonium was incorporated into the framework, despite the low monomer concentration in the reaction mixture.

The use of alcohols in the synthesis of ZSM-5 has been reported by T.V. Whittam[28]. However the use of hexane-1,6-diol in the synthesis of ZSM-5 is of particular note because it produced a major product of ZSM-5 very quickly. Although the course of reaction was not monitored in detail there is little doubt that it was significantly faster than any of the other reactions in Table 4.36. The advantage of using hexanediol (or any alcohol) is that it should be possible to wash the alcohol out of the zeolitic framework thus avoiding the expensive calcination stage. Conversion of the sodium zeolite into the catalytically active H-form could then be carried out after the organic species had been removed or indeed the washing out of the organic and exchange of hydrogen for sodium could be combined into a single process. The TGA curves of the hexane-1,6-diol ZSM-5 (R116) in its as synthesised and modified forms can be seen in Fig. 4.31. The modifications involved heating to 180°C under vacuum and washing. The washing stage was carried out by warming 2 g of the product from R116 in 200 g of water in an autoclave to 180°C. It can be seen that the washing stage has indeed removed some of the hexane-1,6-diol (about half), although the heating under vacuum did not remove any of the hexane-1,6-diol.

The results of analysis of the products from HT HEX R87 and R116 can be seen in Table 4.37.

Fig. 4.31 TGA curves for reaction HT HEX R116 in its as synthesised and modified forms.

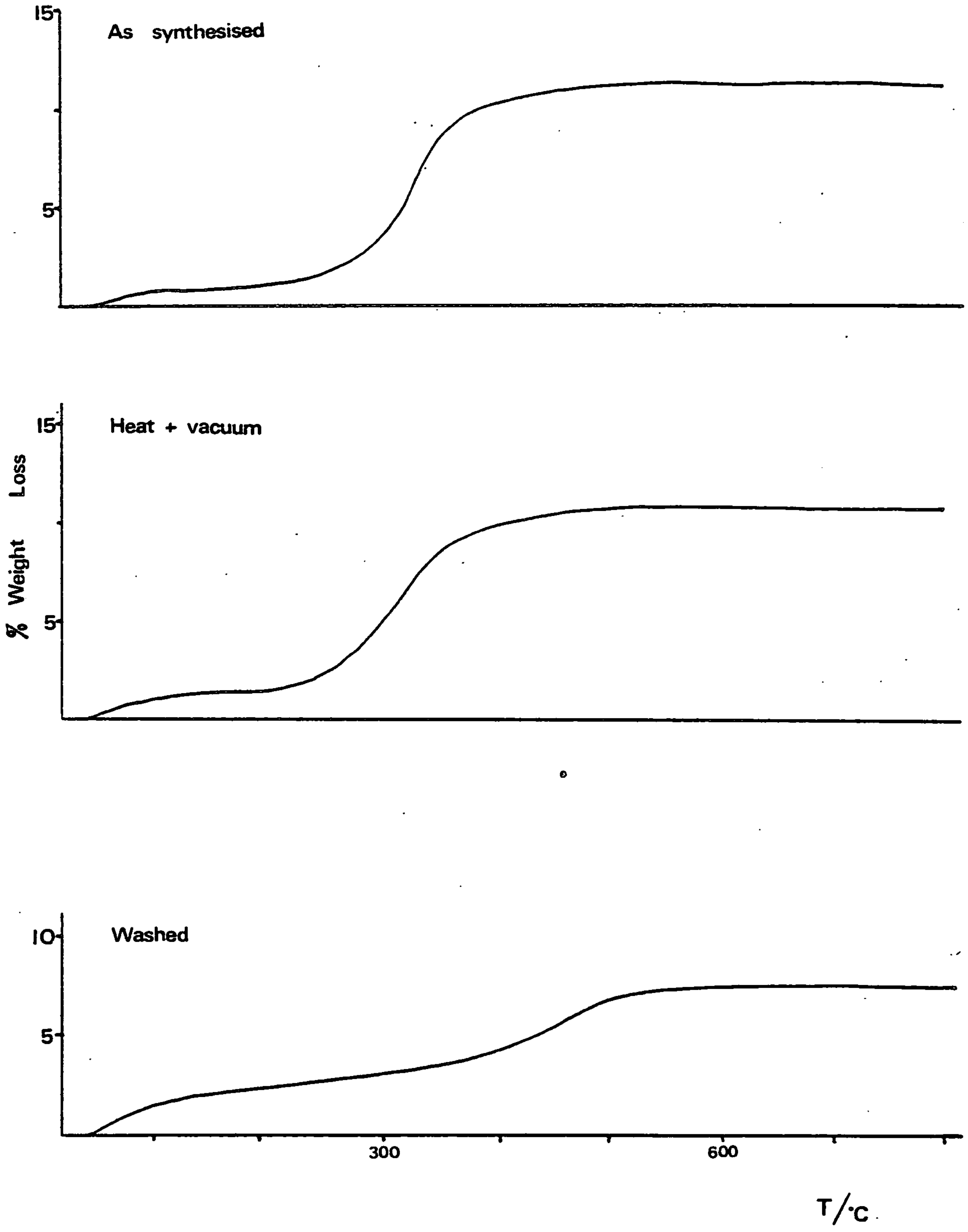


TABLE 4.37 MOLAR COMPOSITION OF ZSM-5 FRAMEWORK

	Composition		
HT HEX	SiO_2	Al_2O_3	Na_2O
R87	46.82	1	0.69
R116	45.29	1	1.04

The SiO_2/Al_2O_3 ratios of these products are very close to those which would be expected for a reaction mixture with SiO_2/Al_2O_3 = 60/1 (see Fig. 4.4). However, although the SiO_2/Al_2O_3 ratios of the products are very similar, the Na_2O/Al_2O_3 ratios are quite different. The Na_2O/Al_2O_3 ratio for sample HT HEX R87 shows that some of the CETAB in the framework is there as the free cation and not as the salt or the hydroxide. In HT HEX R116 however the Na_2O/Al_2O_3 ratio is 1.04/1 which reflects the fact that the only available cation in the reaction mixture was sodium. That there is not much 'excess' sodium also shows that the hexanediol must play an important role in the formation of ZSM-5.

It was noted in Table 4.36 that several samples of the ZSM-5 produced were identified as ZSM-5 type materials, that is their X-ray diffraction patterns had lines shifted from that of a standard ZSM-5. Whether their X-ray diffraction patterns would indeed revert to that of a standard ZSM-5 after calcination is not known. However in view of a recent patent[39] by Mobil in which a material was described which has a structure intermediate between ZSM-5 and ZSM-11 it may be that some of the samples synthesised here were not ZSM-5 but some intermediate species. It is believed that this should be investigated more fully.

4.8 THE ADDITION OF 'SEED' TO HIGH SILICA ZEOLITE REACTION MIXTURES

4.8.1 INTRODUCTION

The 'seed' material added to some of the reactions referred to previously in this work was exclusively zeolitic in nature. The 'seed' zeolite was normally used in its "as synthesised" state (i.e. not calcined) and the only prior treatment, after filtration from its mother liquor was to dry it overnight at 110°C. The purpose of these 'seed' additions was to aid the nucleation process which was believed to be one of the slow steps in the crystallisation process. Little work has been published on the addition of seed material to high silica zeolite reaction mixtures, the majority of studies have dealt with zeolites A, X, Y and mordenite.

The autocatalysis of zeolite A was studied by Kerr[40] by a procedure in which an additional 'batch' of amorphous substrate was added to a batch of reaction mixture which had already crystallised. Although Kerr reported that the second crystallisation had no nucleation period there are obvious problems in the interpretation of his results. For example the increase in zeolite A from 50% to 100% as followed by X.R.D. could actually be due to a decrease in the amorphous material as it dissolves. In addition there may be other species in the mother liquor which catalyse the conversion of amorphous substrate to crystallise zeolite other than the crystals of zeolite A. A more comprehensive study of the effect of seed material on zeolite crystallisation was carried out by Culfaz and Sand[13]. These workers added zeolite seed crystals of various sizes to reaction mixtures which produce mordenite, X and A and they were able to show unambiguously that the rate of crystallisation could be increased and the induction period reduced by this procedure. The chief aim of the present work was to establish whether the addition of seed crystals could determine which zeolite would form from a given reaction mixture.

4.8.2 RESULTS AND DISCUSSION

It was noted in section 4.3.7 that the addition of zeolite in seed quantities to EU-1 reactions increased the rate of formation of EU-1 from the 'standard' reaction mixture and caused the formation of major samples of EU-1 from systems which either gave only small amounts of EU-1 or EU-1 in combination with a second crystalline material (EU-2). All of these observations can be explained in terms of the seed material increasing the rate of formation of EU-1. A possible mechanism for the action of the seed was suggested in section 4.3.7. However it was found that the addition of other zeolites could also have a 'seeding' effect (e.g. the addition of ZSM-5 organosilicate to a standard reaction mixture HT HEX R44 also enhances the rate of formation of EU-1). Table 4.38 contains the results of a variety of reactions in which different seed materials were used. It can be seen that EU-1 was produced regardless of the nature of zeolite seed material used. The effect of the addition of zeolite seed on the products obtained for

TABLE 4.38 PRODUCTS OBTAINED FROM SEEDED EU-1 REACTIONS

Reactions had composition:

$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 10\ HEX\ Br_2 - 3000$

HT HEX	Seed[a]	Product
R44	ZSM-5 organosilicate	EU-1
R80	ZSM-5[b]	EU-1
R39	EU-2	EU-1
R56	13X[b]	EU-1

[a] The quantity of seed added corresponded to about 5% of the silica added.

[b] It is not known if the reaction rate was affected in these reactions.

reactions containing different organic species can be seen in Table 4.39. These reactions were carried out to see if the nature of the seed could determine which type of zeolite would be formed. The results in Table 4.39 should be compared with those in Table 4.16. This comparison shows that in most cases the same products were obtained irrespective of whether zeolite seed was added to the reaction mixture. The exceptions (reactions HT HEX R82 and R149) produced zeolite FU-6 rather than NU-1 + α-quartz which was formed in the unseeded reaction (HT HEX R66). The formation of FU-6[a] is common in the "over run" of NU-1 reactions, and thus its production here could represent an enhanced rate caused by the addition of zeolite seed. It was shown in Table 4.36 that ZSM-5 could be prepared from reactions which did not contain an organic species. The reaction mixture for these reactions had the composition:

$$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 3000\ H_2O.$$

This reaction was carried out several times (Table 4.40) and on each occasion ZSM-5 was prepared although in different quantities (as determined using the Guinier-Hagg camera). It was believed that the formation of ZSM-5 from an inorganic reaction mixture was unlikely and that its formation must be due to residual seed ZSM-5 or traces of organic material in the autoclaves. The autoclaves were always cleaned very carefully after each

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[a] FU-6 was first formed using TMA: synthesis and characterisation by T.V. Whittam.

TABLE 4.39 PRODUCTS OBTAINED FROM SEEDED REACTIONS

HT HEX	Organic (R)	SiO_2	Al_2O_3	Na_2O	R	H_2O	Seed	Product
82	TMA Br[a]	60	1	10	20	3000	EU-1	FU-6
149	TMA Cl[b]	60	1	10	20	3000	ZSM-5	FU-6
88	CETAB[c]	60	1	10	5	3000	EU-1	ZSM-5
95	Pyrrolidine	60	1	10	20	3000	EU-1	ZSM-5
115	Hexanediol	60	1	10	10	3000	EU-1	ZSM-5

[a] Tetramethylammonium bromide

[b] Tetramethylammonium chloride

[c] Cetyltrimethylammonium bromide

TABLE 4.40 PRODUCTS OBTAINED FROM INORGANIC REACTIONS

Reactions had the composition:

$60\ SiO_2 - Al_2O_3 - 10\ Na_2O - 3000\ H_2O$

HT HEX	Seed	Product
R127	None	ZSM-5
R128	None	ZSM-5
R145	None	ZSM-5
R146[a]	None	ZSM-5
R147	EU-1	ZSM-5
R150	Mordenite[b]	Mordenite + α Q

[a] The autoclave had been washed with 1 M HNO_3 after the 1M NaOH - see text.

[b] Hydrogen exchanged zeolon.

reaction as described in section 4.2, and it seems unlikely that a high silica zeolite which had adhered to the reactor walls would remain stable after the treatment with hot sodium hydroxide solution. However it was reasoned that if in the formation of the initial nuclei the aluminium content was not uniform but concentrated in the centre of the crystal then while the outside of the crystal would dissolve the "high alumina" part might remain stable. Reaction HT HEX R146 was designed to investigate this possibility. In this reaction (see Table 4.40) the autoclave was washed with 1 M HNO_3 at 95°C for about 1 hour after being washed - as usual - with 1 M NaOH. The purpose of the "acid-wash" was to dissolve the proposed "high alumina" part which may have seeded the ZSM-5 formation. However as can be seen from Table 4.40, ZSM-5 was obtained despite the acid treatment, and in the succeeding reaction (HT HEX R147) the addition of seed EU-1 again led to the production of ZSM-5. The addition of mordenite (reasoned to be the most likely zeolitic product for the organic free reaction mixtures) led to the production of mordenite and α-quartz (HT HEX R150). Although this reaction may represent a genuine "seeding" effect it could be that the formation of mordenite was due to the increase in the aluminium content of the reaction mixture as the mordenite dissolved. The dissolution of the added seed zeolite in the reaction mixture before zeolite growth began was observed in several cases, but in most of these the high silica zeolite seed was unlikely to have a significant effect on the composition of the reaction mixture.

In conclusion it would appear that in high-silica zeolite synthesis the addition of any high-silica zeolitic seed leads to the production of that species which would be formed if no seed was present, provided that the addition of seed does not change the stoichiometry of the system so as to make the formation of that species no longer favourable. The formation of ZSM-5 from an inorganic reaction may be the result of 'seeding' however the seed in this case is likely to be quite different from that of added zeolite crystals.

This area of high silica zeolite synthesis, more than any other, requires a great deal of additional work. Amongst the aspects which should be examined are the rates of 'dissolution' of different 'seed' zeolites, under alkaline conditions, the types of alumino-silicate species these zeolites form in solution, the effect of seed crystallite size on the reaction rate and induction period and the production of ZSM-5 from inorganic reaction mixtures.

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CHAPTER 5

REACTIONS CONTAINING ETHYLENE GLYCOL

5.1 INTRODUCTION

This section deals with experiments which were carried out using ethylene glycol as a major component of the reaction mixture. Organic solvents have been used previously[1,2,3] in zeolite synthesis. The first recorded instance is that of Barrer and Denny[1], who used methanol in their study of nitrogenous aluminosilicates in the belief that the methylammonium bases under study would hydrolyse to methanol and less substituted methylammonium species. The addition of the methanol appeared to make no difference to the products but this could be because it was added in small quantities (approximately 13% w/w of the water added). The use of alcohols in the synthesis of ZSM-5 was reported by T.V. Whittam[2] and has been mentioned briefly in section 4.7. However in this case the use of alcohols was restricted to their use as replacements for the organic cation in high silica zeolite synthesis. The purpose of the work described in this chapter was to replace the water in zeolite reaction mixtures by ethylene glycol. While in practice there may not have been a great deal of difference between the quantities of alcohol added in this and other work, the principle was quite different. It was reasoned that the solvation of sodium by ethylene glycol would lead to a species of a different shape from that when water was the solvent and therefore might lead to the formation of a novel zeolitic species.

5.2 EXPERIMENTAL

MATERIALS

REAGENT	SOURCE
Cabosil-MS	B.D.H.
Sodium metasilicate pentahydrate	B.D.H.
Sodium aluminate	B.D.H.
Sodium hydroxide	B.D.H.
Ethylene glycol	B.D.H.

All reactions were based on the composition

$$5.15\ Na_2O - Al_2O_3 - 4\ SiO_2 - (242-x)\ H_2O - x\ (CH_2OH)_2$$

The procedure employed was as follows. The required amount of water was weighed into beaker A. The sodium metasilicate pentahydrate (or when CAB-O-SIL was used, the CAB-O-SIL and the sodium hydroxide) was weighed into a beaker (B) and half the water from beaker A was added. This was stirred until a clear solution resulted. The sodium aluminate was weighed into beaker C and the remainder of water from A added with stirring until all the sodium aluminate had dissolved. The sodium aluminate solution from C was added with stirring to the sodium silicate solution (B) in about 15 to 30 seconds. Stirring was continued for about a minute. Finally the required amount of ethylene glycol was added with further stirring. The resulting gel was transferred to the autoclave. When the mole fraction of ethylene glycol was increased above 0.47 it became increasingly difficult to dissolve the silicate and aluminate species. At the limit (i.e. mole fraction of ethylene glycol 0.95 to 1.00) the reagents were added as solid to the reactor. Obviously there was some water present in the sodium aluminate source and sodium hydroxide and thus strictly speaking even when pure ethylene glycol was used as the solvent, the mole fraction was not 1.00 but probably of the order 0.99.

All the reactions were carried out in the autoclave (original) described in section 4.2. It should be noted that these reactions were the first carried out at Edinburgh using the autoclave and they were used in part to gain experience in its operation.

5.3 RESULTS AND DISCUSSION

The results of these experiments are given in Table 5.1. It can be seen that only well established zeolitic products were obtained from these reactions. The reactions carried out at 105°C with the mole fraction of ethylene glycol in the solvent of 0.19 and 0.37 both produced analcite and this shows that in this case the reaction product is determined by the composition of the solvent. However the observed results are most likely to be due to an increase in the viscosity of the gel rather than a specific chemical effect associated with the organic component. The species formed in the corresponding water only reaction were as expected zeolites X, P1, HS and analcite. The formation of analcite is fairly common at high temperatures and under alkaline conditions[4]. As the mole fraction of ethylene glycol is increased it is believed that the increased alkalinity leads to the production of analcite. However, when almost all the water is replaced by ethylene glycol the only product of zeolitic nature which is formed is HS. Now HS is

TABLE 5.1 - ZEOLITES CRYSTALLISED FROM REACTION MIXTURES CONTAINING ETHYLENE GLYCOL*

Temp. °C	Silica Source	Mole fraction of ethylene glycol in the solvent used to prepare the reaction mixture					
		0.0	0.19	0.37	0.47	0.95	1.00
105	S5	X,Hs	An	An	An,(Pl)	By	-
105	S5		X,An,HS+	An,HS,(X)+			
125	S5	X,HS,Pl	An	An	An	Am(1d) HS(3d)	By(3d)
125	Cabosil	Pl,An	An	An	An	Am(3d)	
150	S5					HS	HS(3d)
150	Cabosil						(HS)(5d)‡

* Stirred reactions. Overall mixture composition 5.15 $Na_2O.Al_2O_34SiO_2(242-x)H_2OxGlycol$.

S5 = sodium metasilicate pentahydrate. X = zeolite X, Pl = zeolite Pl, HS = hydroxysodalite, An = analcite, Am = amorphous, By = bayerite. Products are those obtained in 1 day except where otherwise indicated. Trace quantities shown in parenthesis.

\+ In these reactions water corresponding to the ethylene glycol was omitted from the reaction mixture but glycol was not added.

‡ Water completely excluded from the reaction mixture.

often formed[5,6,7] with occluded salts such as NaCl and NaOH within the framework and it is believed that in these cases the sodalite was formed with ethylene glycol within the framework. None of the samples obtained were analysed or characterised in any way other than identification by x.r.d. It would have been instructive if some of the samples particularly those of sodalite had been analysed to see if they contained occluded ethylene glycol or sodium hydroxide.

Obviously with so few syntheses (and no product analyses) it is difficult to draw any conclusions from this work. However it is hoped that the deficiencies in these experiments at least show how future work should be carried out. In particular it is believed that higher temperatures should be employed, i.e. above the boiling point of the organic solvent. In addition much higher ratios of SiO_2/Al_2O_3 should be employed and reactions in which there is no added aluminium component should also be carried out. The use of ethylene glycol should be pursued but other solvents such as methanol and ethanol should also be investigated. The problem of solvating the silica in the organic solvent and allowing the necessary condensation reactions to proceed could be overcome by using bases such as sodium methoxide in methanol. It is believed that such an approach although very different from the type of experiments which have been carried out before to synthesise zeolites is one which is likely to produce zeolites which are chemically and structurally different to those currently available.

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CHAPTER 6

NUCLEAR MAGNETIC RESONANCE STUDIES OF AQUEOUS SILICATE SOLUTIONS

6.1 INTRODUCTION

Previous chapters in this thesis have described the synthesis of zeolites and investigations into the mechanism of crystallisation, in which information was obtained by varying various physical and chemical parameters and observing how these control the reaction. In these studies no attempt was made to identify any of the silicate or alumino-silicate species taking part in the crystallisation. Studies[1] of aqueous aluminate solutions e.g. sodium aluminate have shown that only one species is present in solution, that is the $[Al(OH)_4]^-$ ion. However, several species are known to be present in silicate solutions, thus it would seem likely that the nature and distribution of the silicate anions will influence not only the alumino-silicate gel formed initially but also the zeolite ultimately produced. Therefore it is important to obtain as much information as possible about the structure and distribution of the silicate species present in solution and the parameters which can alter the distribution.

Several techniques have been used by previous workers, to examine the species present in aqueous silicate solutions, these include infra-red[2] and Raman spectroscopy[2a], paper chromatography[3], trimethylsilylation[4,5] and ^{29}Si nuclear magnetic resonance (n.m.r.) spectroscopy[6,7]. The techniques of infra-red and Raman spectroscopy only give limited information about the polynuclear species present in silicate solutions. More complete information concerning the silicate species can be obtained by paper chromatography and by trimethylsilylation, followed by separation and identification of the derivatives by gas-liquid chromatography (g.l.c.). However, both methods of analysis involve, as part of their procedure, an acidification stage, during which there may be some rearrangement of the silicate anions present in the original solution[8]. In the present work analysis of silicate solutions was carried out by ^{29}Si n.m.r. spectroscopy since it provides a more direct method of examining the silicate anions than any of the other methods. Its chief disadvantage is that with present techniques (Fourier transform n.m.r.) it still requires runs of several hours to obtain spectra with reasonable signal/noise ratios.

Organic species, in particular quaternary ammonium compounds have been used extensively in zeolite synthesis. However, their action during crystallisation has not been fully established, although quaternary ammonium silicate solutions are known[9] to have properties (e.g. viscosity, stability towards precipitation of colloidal silica, etc.) which differ from those of alkali metal silicate solutions. These differences have never been correlated with the anions present in the silicate solutions.

The aim of the present investigation was to examine the way in which organic species influence the type and distribution of the silicate anions found in their aqueous solutions.

6.2 NOTATION

The notation used here to describe the silicate species follows that used by Engelhardt[10] and is analogous to that used to describe siloxane structures. In this notation the silicate anions are referred to by the 'Q-notation' in which Q refers to the SiO_4 tetrahedra under examination and the superscript to the number of other silicon atoms it is bonded to through oxygen bridges. A subscript can be used to denote the number of equivalent Q-units in one structure. Thus the cyclic trinuclear species or three-membered ring[a] can be described by:

$$\overline{Q^2 \quad Q^2 \quad Q^2} \qquad \text{or} \qquad Q^2_3$$

The extent of ionisation of the silicate species is ignored. Examples of the notation and of the types of structures present in silicate solutions can be seen in Fig. 6.1. All species are written as silicic acids.

6.3 PREVIOUS WORK

Various techniques have shown that aqueous silicate solutions can contain a variety of anionic species

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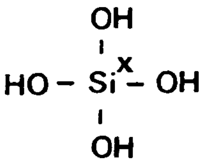
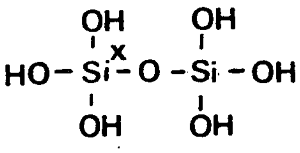
[a] Three-membered ring and similar terms, refer to rings containing three tetrahedral units. That is, not three atoms but three silicon atoms and three oxygen atoms.

Fig. 6.1 Examples of silicate species found in aqueous silicate solutions.

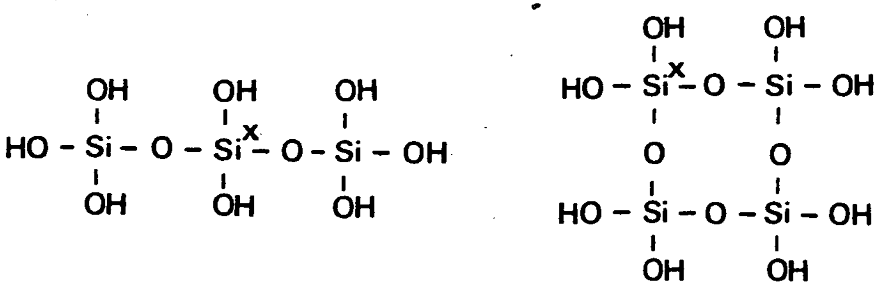
Q^0



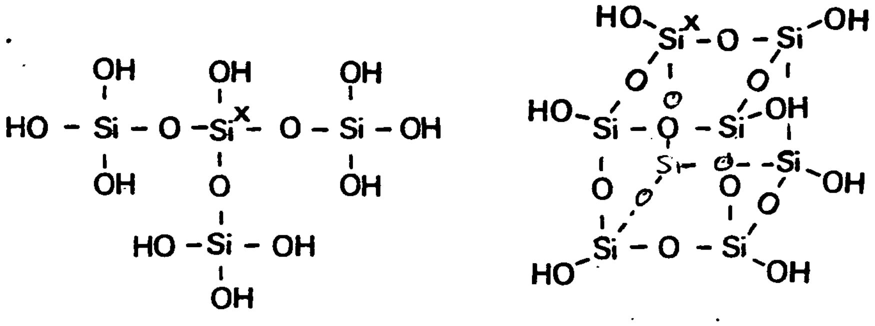
Q^1



Q^2



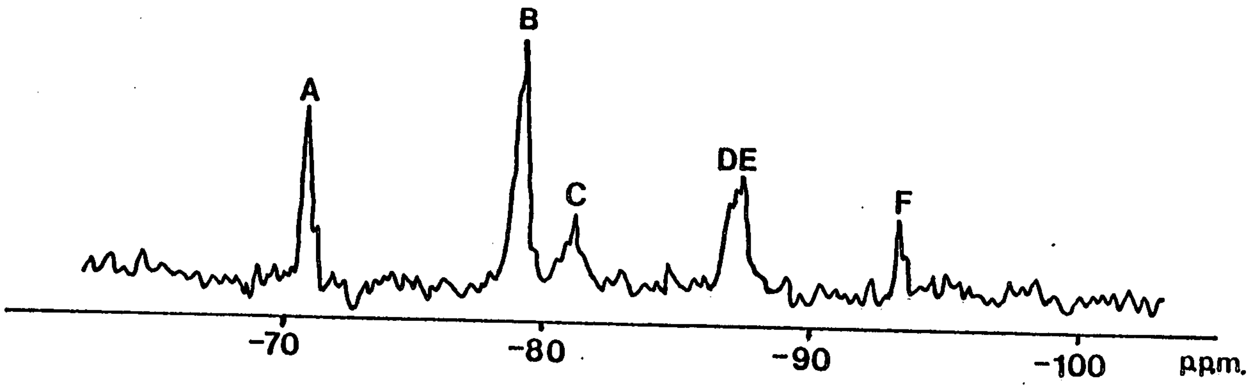
Q^3



including linear and branched chains, cyclic and cage type units. Indeed the species present in silicate solutions are analogous to those found in aqueous solutions of phosphates[12]. With the introduction of pulsed and Fourier transform methods, ^{29}Si nuclear magnetic resonance spectroscopy has recently achieved prominence in the study of silicate solutions. Initial work produced spectra with peaks corresponding to silicon atoms in a variety of environments which showed beyond doubt that many different anions are present in solution. The distribution of anions in these solutions was shown by MacGilp[13] to be dependent on the ratio of silica to base. However, MacGilp also stated that "... the variation of relative peak area with concentration is almost insignificant in comparison with the effect of changes in r". ($r = SiO_2/Na_2O$). As part of the present investigation this observation was reinvestigated and, as described later, found to be incorrect.

A ^{29}Si n.m.r. spectrum for an aqueous sodium silicate solution ($Na_2O/SiO_2 = 1/1$; $[SiO_2] = 1.3$ mol dm^{-3}), can be seen in Fig. 6.2. The principal features of the spectrum have been labelled alphabetically, following the scheme used by Marsmann[14], since the labels involve no assumptions as to the assignment of the resonances. Various assignments[7,14,15] of similar spectra have been carried out, and several species have been suggested for peaks C and E. However, it is generally agreed that peaks A, B, D and F form a regular sequence Q^0, Q^1, Q^2 and Q^3 respectively. The most detailed analysis of a silicate solution was presented by Harris and Newman[11].

Fig. 6.2 ^{29}Si n.m.r. spectrum of an aqueous sodium silicate solution.
(Na_2O/SiO_2 = 1/1 : $[SiO_2]$ = 1.3 mol dm^{-3})



A

$\underline{Q}^0$

B

$\underline{Q}^1Q^2\underline{Q}^1$

$\underline{Q}^1\underline{Q}^1$

$\underline{Q}^1\overline{Q^3Q^2Q}^2$

D

$Q^1\underline{Q}^2_nQ^1$

F

$\underline{Q}^3$

C

$\underline{Q}^2_3$

$Q^1\overline{Q^3\underline{Q}^2\underline{Q}}^2$

E

$Q^1\overline{\underline{Q}^3Q^2Q}^2$

The assignment of peaks A, B, D and F was not disputed. However, it was proposed that peak C was due to the cyclic trinuclear species and peak E was assigned to the Q^3 unit in the substituted cyclic trinuclear species. It is believed[16] that these questionable assignments by Harris and Newman have now been verified by additional work. Consequently the assignments suggested by Harris and Newman[11] will be used in this work, and indeed, are given in Fig. 6.2.

6.4 EXPERIMENTAL

Silicon has only one naturally occurring isotope with non-zero spin, thus isotope ^{29}Si, with $I = \frac{1}{2}$ and a natural abundance of 4.70% is the only one suitable for n.m.r. studies. Its low natural abundance and negative magnetogyric ratio make it a relatively difficult nucleus to observe. Its relative sensitivity is approximately half that of ^{13}C.

All ^{29}Si n.m.r. measurements were carried out using a Varian XL-100 spectrometer operating at 19.9 MH_z in the Fourier transform mode (F.T. mode). Spectra were recorded at a probe temperature of approximately 26°C (unless otherwise stated) using a 10 mm outside diameter delrin (polyformaldehyde) n.m.r. tube and insert. This tube and insert were used since glass gives a broad peak corresponding to Q^4 species which affects the signal to noise ratio in that region. Typical conditions involved a 90° tip angle with 0.8S acquisition time. No relaxation delay (see later) was used in the experiments described here. Samples were given sufficient pulses to ensure a reasonable signal to noise ratio, in most cases this required approximately 10,000 pulses. All resonances were measured relative to an external sample of TMS (tetramethylsilane $(CH_3)_4Si$) contained in 5 mm outside diameter n.m.r. tube. All chemical shifts are defined as positive to high frequency (low field) of the standard resonance i.e. anti-cartesian on the XL-100 traces. The chemical shifts reported in this work are given relative to the TMS resonance and not relative to the Q^0 or monomer peak as done by Harris and Newman[11]. This approach was adopted because although the advantage of an internal reference is appreciated, it is believed that the monomer peak may not be the best reference to use since it is known that the position varies with pH. How the position of the monomer and other peaks depend on concentration, counter ion, temperature and viscosity has not been established. Thus the monomer peak position was not used as the only reference in this work. Results were obtained in four periods of approximately five days. At the end of one period the position of the reference line was checked and found to have moved by 5 Hz. This corresponds to an error of approximately 0.25 p.p.m., although the reproducibility of results would seem to be well within this. Most studies of ^{29}Si n.m.r. spectra are hampered by the available resolution being less than the observed line widths. Although the resolution of the spectra obtained here could have been improved by using a longer acquisition time this would have involved runs of much longer duration. However, since the amount of spectrometer time allocated to this project was strictly limited it was not possible to carry out such long runs. Similarly a relaxation delay was not employed in most spectra. This means that the peak heights are almost certainly not proportional to the amount of species to which they correspond. Although it is unlikely that any silicate species are not observed as examples of all types of silicate anions can be identified in the spectra.

The solutions studied were prepared by dissolving the silica in the relevant hydroxide solution at 95°C for 30 minutes. When more than one hydroxide was used e.g. in the 'mixed base' experiments the hydroxide solutions were mixed before the addition of the silica. Once a clear solution had been obtained it was cooled, transferred to a volumetric flask (10 cm^3), and made up to the mark with distilled water. A portion was then transferred to the n.m.r. tube for analysis. Ageing of the silicate solutions was not required since in all experiments the alkali:silica ratio was sufficiently high to be outwith the "instability region" described by Glasser[8]. This instability of silicate solutions occurs when the alkali: silica ratio is sufficiently low to produce colloidal silica. Silicate solutions were prepared using the following species; tetramethylammonium (TMA), tetraethylammonium (TEA), tetrapropylammonium (TPA), tetrabutylammonium (TBA), sodium (Na), potassium (K) and hexamethonium (HEX).

TABLE 6.1 Sources of materials used to prepare the silicate solutions

Material	Source
Tetramethylammonium hydroxide solution (30%)[a]	B.D.H.
Tetraethylammonium hydroxide solution (20%)[a]	Koch-Light
Tetrapropylammonium hydroxide solution (10%)[a]	Eastman-Kodak
Tetrabutylammonium hydroxide solution (40%)[a]	B.D.H.
Hexamethonium hydroxide solution	b
Sodium hydroxide (Aristar)	B.D.H.
Potassium hydroxide (Analar)	B.D.H.
Fumed silica (CAB-O-SIL, M5)	B.D.H.
Hexanediol	Aldrich
Trimethylamine (30% aqueous solution)	B.D.H.
Tripropylamine	Aldrich

[a] solutions were concentrated (when necessary) by heating at 60°C under partial vacuum

[b] hexamethonium hydroxide was prepared by ion-exchange from hexamethonium bromide, supplied by Koch-Light. For ion-exchange technique see Chapter 3.

6.5 RESULTS

6.5.1 EFFECT OF SILICA CONCENTRATION

Comparison of the sodium and potassium silicate spectra in Fig. 6.3 and Fig. 6.4 shows the effect of an increase in silica concentration on the silicate anion distribution. It can be seen that in both the sodium and potassium solutions an increase in silica concentration from 1.0 mol dm^{-3} (Fig. 6.3) to 1.3 mol dm^{-3} (Fig. 6.4) causes the appearance of a peak at approximately -93.1 p.p.m. This peak corresponds to Q^3 units in non-cyclic silicate species. Thus an increase in silica concentration causes greater polymerisation in silicate solutions. These results are in disagreement with those reported by MacGilp[13]. The results for the quaternary ammonium silicate solutions shown in Fig. 6.3 and Fig. 6.4 cannot be compared in a similar fashion since some of the solutions had crystallised and thus their composition is uncertain.

6.5.2 EFFECT OF DIFFERENT CATIONS

^{29}Si n.m.r. spectra for a series of aqueous silicate solutions can be seen in Fig. 6.3 and Fig. 6.4. Both sets of spectra refer to silicate solutions of Na, K, TMA, TEA, TPA, TBA and HEX. For all of these solutions the M_2O/SiO_2 ratio was 1/1. The SiO_2 concentration of the solutions in Fig. 6.3 was 1.0 mol dm^{-3} and for those in Fig. 6.4 it was 1.3 mol dm^{-3}. These spectra can be compared in several ways. Comparison of peaks A, B and C in Fig. 6.3 shows that although the positions are similar for all spectra their relative intensities vary

Fig. 6.3 ^{29}Si n.m.r. spectra of aqueous silicate solutions. ($[SiO_2]$ = 1.0 mol dm^{-3}; M_2O/SiO_2 = 1/1).

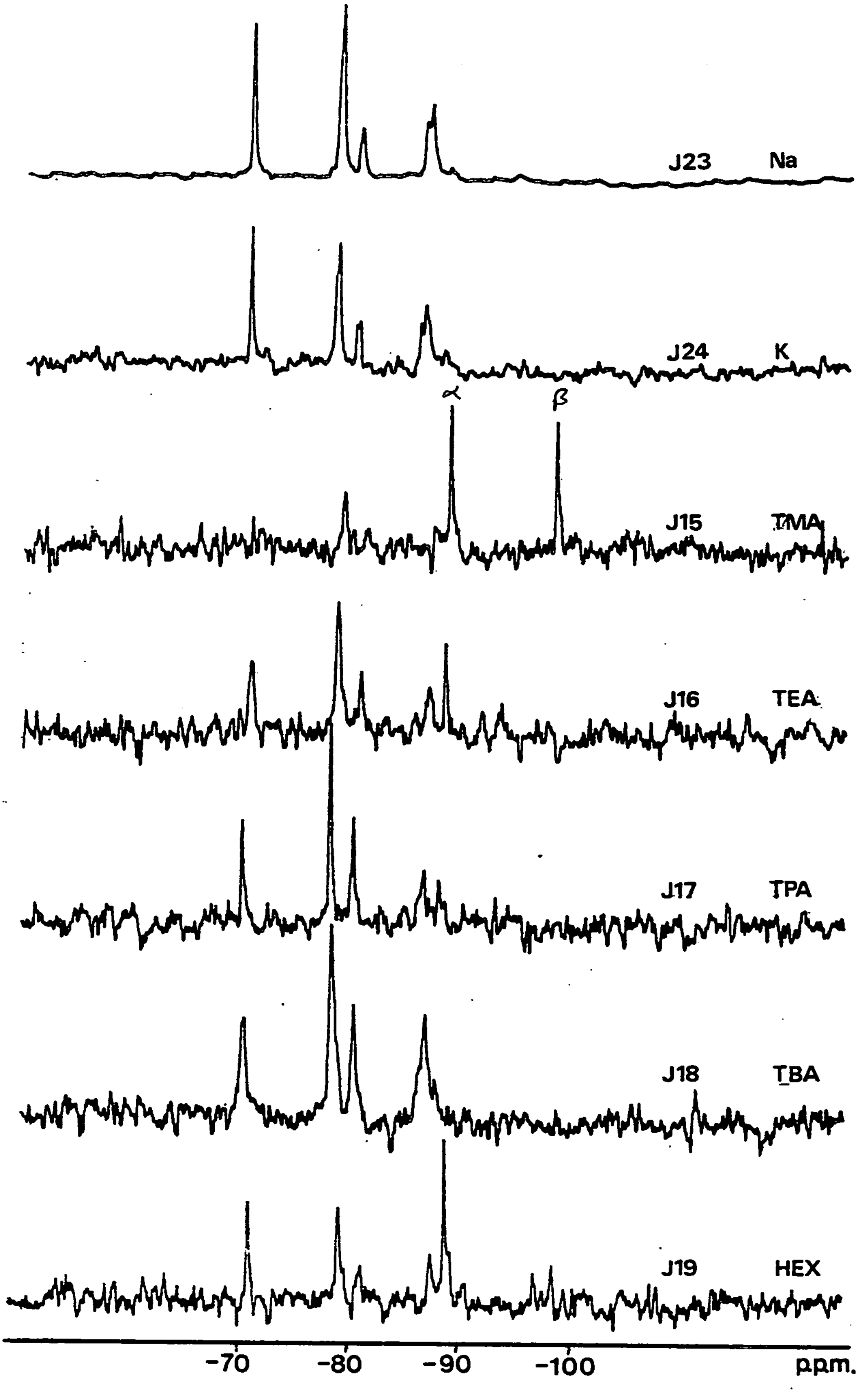
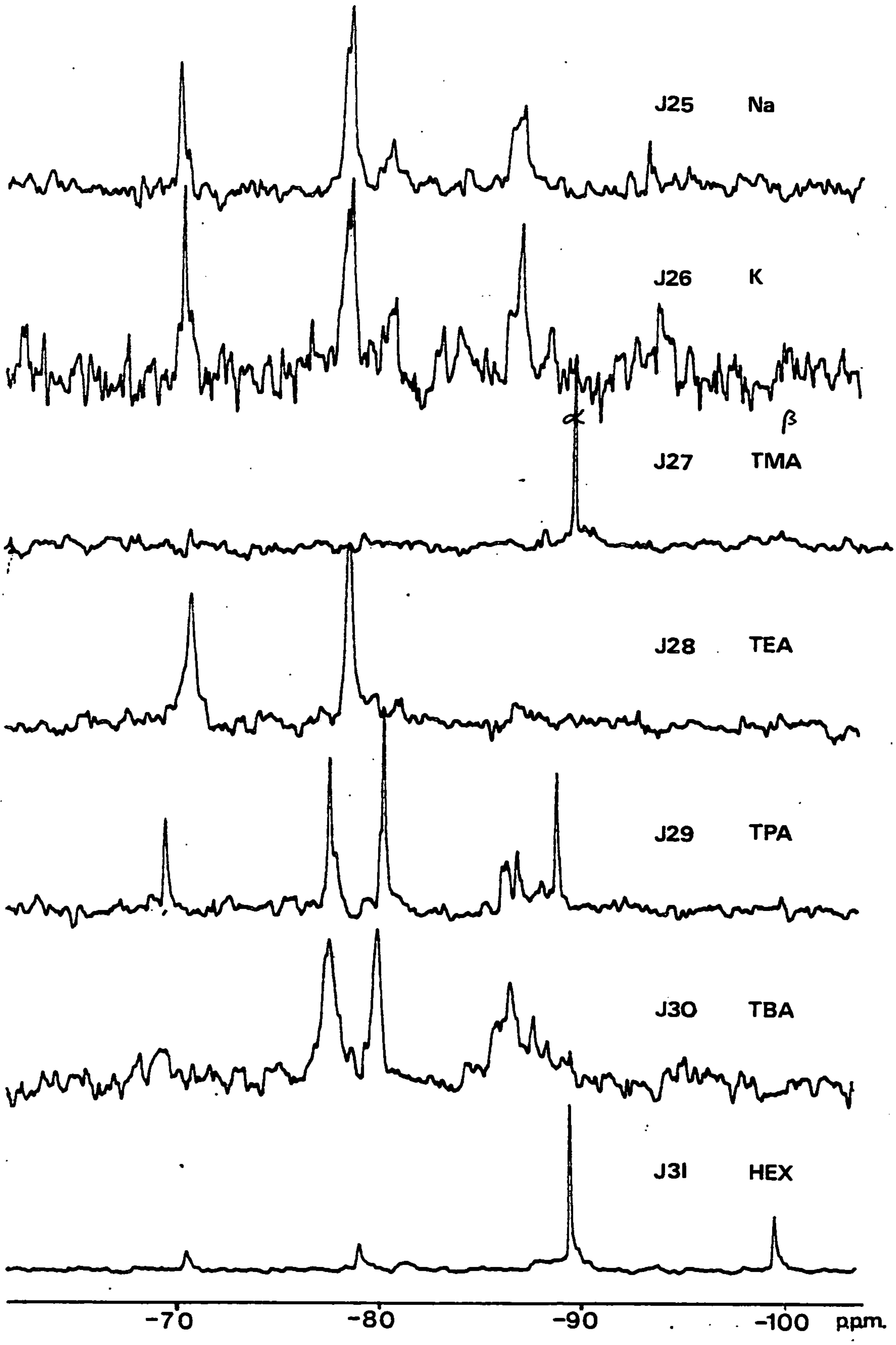


Fig. 6.4 ^{29}Si n.m.r. spectra of aqueous silicate solutions. ($[SiO_2]$ = 1.3 mol dm^{-3}; M_2O/SiO_2 = 1/1).



quite considerably. Comparison of the spectra for the Na and K silicate solutions (J23 and J24) shows that the silicate anion distribution in these solutions is very similar. The spectra for the quaternary ammonium silicate solutions are however quite different to those of the Na and K silicate solutions. This is most noticeable in the spectrum for TMA silicate (J15). The main difference is in the appearance in the organic silicate spectra of two 'new' peaks labelled α and β. That peak β is 'new' can easily be seen in Fig. 6.3. From chemical shift data, Table 6.2 and Table 6.3, it can be seen that peak α also represents a species not present in either the Na or K silicate systems. Although there may also be differences between the Na and K spectra and those of the quaternary ammonium species particularly in the D, E region, problems with peak intensities and resolution make this inconclusive. The major difference is undoubtedly the appearance of peaks α and β with chemical shifts approximately -89.0 p.p.m. and -98.8 p.p.m. respectively. Peak α occurs in the spectra of all the quaternary ammonium silicates while peak β occurs only in the spectra of TMA and HEX silicate solutions. The pH of the Na, K and TEA silicate solutions (J23, J24 and J16 respectively) were measured and all three were found to be very high, above a pH of 13.5 and certainly much too high for accurate measurements by conventional techniques.

Spectra of the TMA and HEX silicate solutions were markedly different from those of the other quaternaries. Both solutions began to crystalline while their n.m.r. spectra were being obtained. For this reason two things

TABLE 6.2 Chemical Shifts for Resonances in Fig. 6.3

Spectra No.	Cation	Chemical shifts relative to TMS/p.p.m.							
		A	B	C	D	E		α	β
J23	Na	-70.83	-78.96		-86.38				
				-80.64		-87.07			
							-87.17		
J24	K	-70.83	-78.85		-86.30				
				-80.83		-86.76			
							-87.03		
J15	TMA	-70.60		-79.63				-89.22	-98.96
J16	TEA	-71.04	-79.07			-87.40			
				-81.23				-88.89	
J17	TPA	-70.47	-78.52			-87.00		-88.43	
				-80.68		-87.12			
J18	TBA	-70.63	-78.70						
				-80.77					
J19	HEX	-71.12	-79.41			-87.81		-89.09	-98.74
				-81.30				-89.59	

TABLE 6.3 Chemical Shifts for Resonances in Fig. 6.4

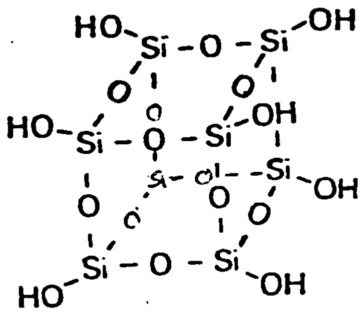
		Chemical shifts relative to TMS/p.p.m.							
Spectra No.	Cation	A	B	C	D	E	α	F	β
J25	Na	-70.99	-78.81	-80.76	-86.65			-93.10	
			-79.03	-81.00	-87.02				
						-87.27			
J26	K	-71.18	-78.86	-81.17	-87.01			-93.25	
			-79.07			-87.12			
J27	TMA	-71.31					-89.64		
J28	TEA	-71.53	-78.95						
J29	TPA	-70.36	-78.10	-80.51	-86.22		-88.78		
			-78.37	-80.68	-86.43				
J30	TBA	-70.22	-77.88						
			-78.05	-80.36	-86.59		-88.12		
						-87.56			
J31	HEX	-71.28	-79.44						
							-89.76		-99.10

should be noted about their spectra. Firstly, identification of the silicate units in the crystalline materials could give information about the nature of the anions corresponding to peaks α and β. Secondly, the silicate anion distribution seen in their ^{29}Si n.m.r. spectra might not be of the silicate solutions themselves but could have been influenced by the presence of the crystalline material.

Crystalline TMA silicate has been reported previously[17]. It has the composition:

$$[(CH_3)_4N]_8^+ \quad [Si_8O_{20}]^{8-} \quad 68\text{-}70\ H_2O$$

Analysis by paper chromatography, trimethylsilylation and mass spectrometry showed that the silicate anion $(Si_8O_{20})^{8-}$ is a 'cage' type species made up of two four-membered rings:



Hoebbel and Wieker[17] also presented results of an X-ray diffraction study of TMA silicate. The cell constants they reported are:

$a = 18.1$ Å $\alpha = 121^\circ$
$b = 16.0$ Å $\beta = 131^\circ$
$c = 16.0$ Å $\gamma = 55^\circ$

What is surprising is that although cell constants have been reported at no stage are the lines in the X-ray diffraction pattern indexed. A comparison of the diffraction patterns for TMA silicate produced in this work and that obtained by Hoebbel and Wieker can be seen in Table 6.4. The diffraction pattern calculated[a] using the cell constants of Hoebbel and Wieker is also given in Table 6.4. Examination of the diffraction patterns in Table 6.4 shows that Hoebbel and Wieker have failed to report diffraction lines for 2θ values less than 9.0. Furthermore the calculated diffraction pattern is not in very close agreement with their experimental values, indeed it is in better agreement with the results of the present work. However there would seem to be sufficient similarities between the two experimental diffraction patterns to suggest that they are of similar if not identical materials. This is supported by the fact that the diffraction pattern of TMA silicate varies quite considerably with water content. Tga of the TMA silicate, produced in this work, gives the approximate composition as:

$$0.98\ \text{TMA} : SiO_2 : 3.22\ H_2O$$

<u>or</u>

$$7.8\ \text{TMA}\quad Si_8O_{20}\quad 25.8\ H_2O$$

[a] The X-ray diffraction pattern was calculated using a computer program supplied by R.O. Gould.

TABLE 6.4 X-RAY DIFFRACTION PATTERNS FOR TMA SILICATES

This work	Hoebbel Wieker[17]		Calculated
d/Å	d/Å	I rel	d/Å
14.57 vs			
			13.87
13.54 vs			
12.87 vs			12.77
			12.72
12.45 vs			12.37
			11.77
11.27 vs			11.31
11.03 s			
9.14 s			
8.96 m			8.98
	8.66	50	
8.17 vw			
7.98 w			
	7.89	20	
7.81 w			7.82
			7.71
	7.62	30	7.66
7.56 w			7.59
	7.49	20	
7.29 vw	7.25	30	7.29
7.03 vw	6.91	5	7.03
6.84 vw	6.70	30	6.85
			6.76
6.61 vw			
	6.51	30	
	6.32	5	6.33
5.95 vw	5.98	5	5.99
5.71 vw	5.68	5	5.65
5.45 vw	5.47	10	5.43
5.30 vw	5.27	10	5.25
5.18 vw	5.15	30	5.18
5.03 vw	5.09	5	5.04
			5.02
	4.98	30	4.99
	4.81	20	4.81
	4.77	5	4.80
4.67 vw	4.67	5	4.67
	4.62	10	4.62
4.56 vw			4.56
4.50 w	4.48	10	4.49
4.37 m	4.39	50	
4.33 w	4.35	50	
4.25 vw	4.23	50	
	4.11	10	
4.05 m	4.07	10	

Thus the water content is very much less than that reported by Hoebbel and Wieker. Therefore, it seems likely that the TMA silicate produced in run J15 is made up of double four-membered ring (DFR) silicate units.

The silicate which crystallised from the HEX silicate solution, J19, had also been previously characterised[18]. Analysis was carried out by trimethylsilylation followed by g.l.c.[19]. The silicate unit in this material is also the DFR.

It seems highly probable that peaks α and β can be assigned to the four-membered ring (SFR) and the DFR respectively. The chemical shifts for the SFR (α) and DFR (β) are in very close agreement with those reported by Lippmaa et al[20]. A comparison of the chemical shifts can be seen in Table 6.5 below.

TABLE 6.5 Chemical shifts of SFR and DFR species

	Lippmaa et al[20]		This Work	
	$K_4H_4Si_4O_{12}$ [1]	$(NMe_4)_8Si_8O_{20}$ [2]	TMA silicate	HEX silicate
SFR	-89.2		-89.22	-89.07 -89.59
DFR		-98.6 (-97.7[1])	-98.96	-98.74

[1] Powdered sample at 20°C

[2] 1.5 mol dm^{-3} aqueous solution.

It should be noted that the results reported by Lippmaa et al are part of a study of ^{29}Si solid-state n.m.r. spectroscopy. The chemical shifts for TMA silicate reported by Lippmaa et al are for DFR in both the solid state and also in solution. However the chemical shift for the SFR (in potassium cyclotetrasilicate) is for the solid state only since they report that the SFR rapidly rearranges in solution.

To check the stability of the DFR when it was not in equilibrium with the crystalline material a sample of TMA silicate solution (which contained some crystalline material) was warmed, in the n.m.r. probe, to 60°C. At this temperature all the TMA silicate crystals dissolved. The spectra of this TMA silicate solution at 60°C can be seen in Fig. 6.5. Comparison with the spectra obtained at ambient temperature shows that while the DFR is indeed stable when not in equilibrium with the crystalline material the four-membered ring has broken down at the higher temperature. This rearrangement of the SFR is consistent with the observations of Lippmaa et al[20].

The stability of these cyclic and 'cage type' species to an increase in pH is illustrated in Fig. 6.6. Some of the TMA silicate crystals were dissolved in water and their pH measured. Concentrated TMA hydroxide (to reduce the effect of dilution) was then added and the pH adjusted from 12.6 to 13.3. The spectra in Fig. 6.6 show that the distribution is apparently unchanged by an increase in pH.

Fig. 6.5 Spectra of TMA silicate at room temperature and 60°C

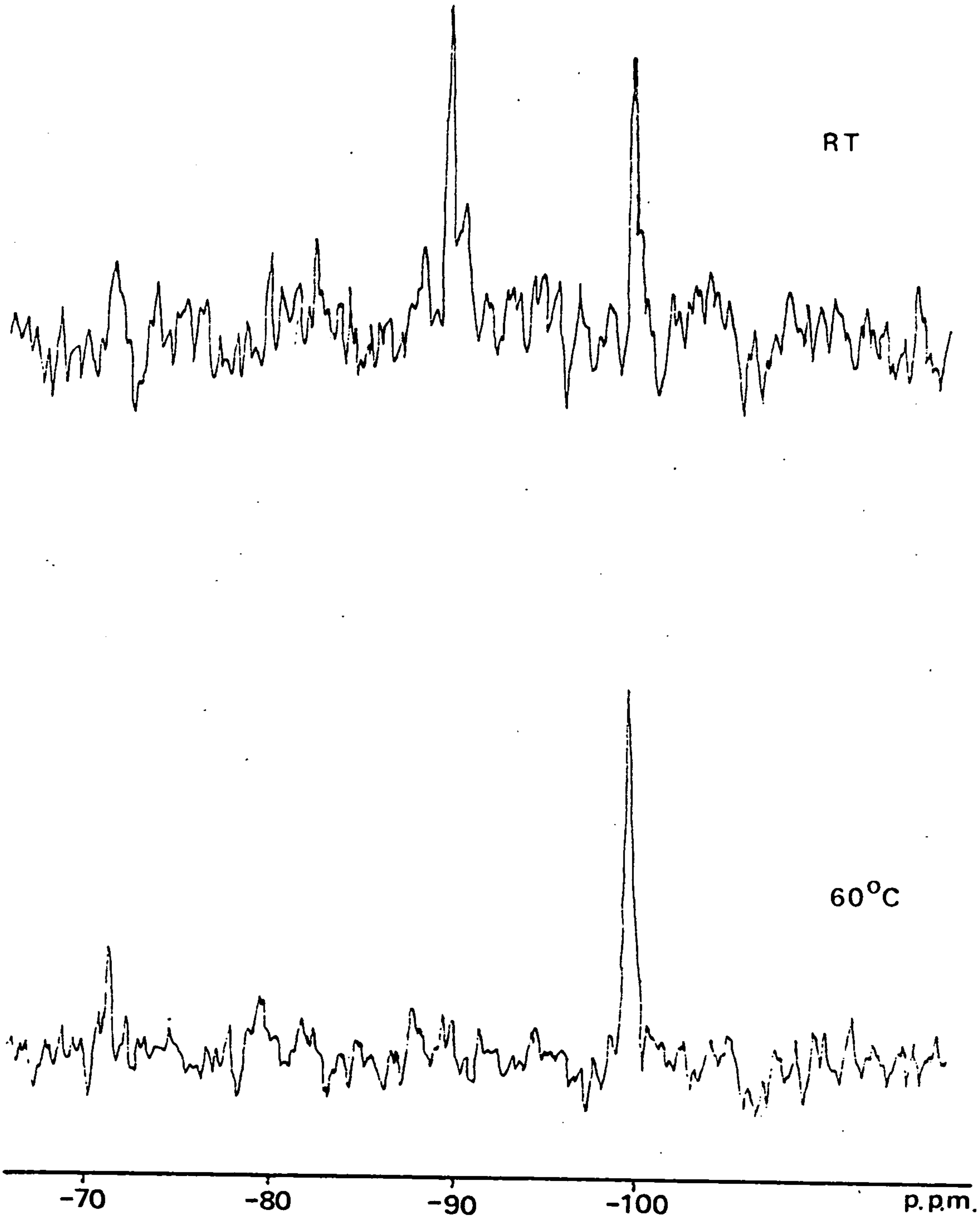
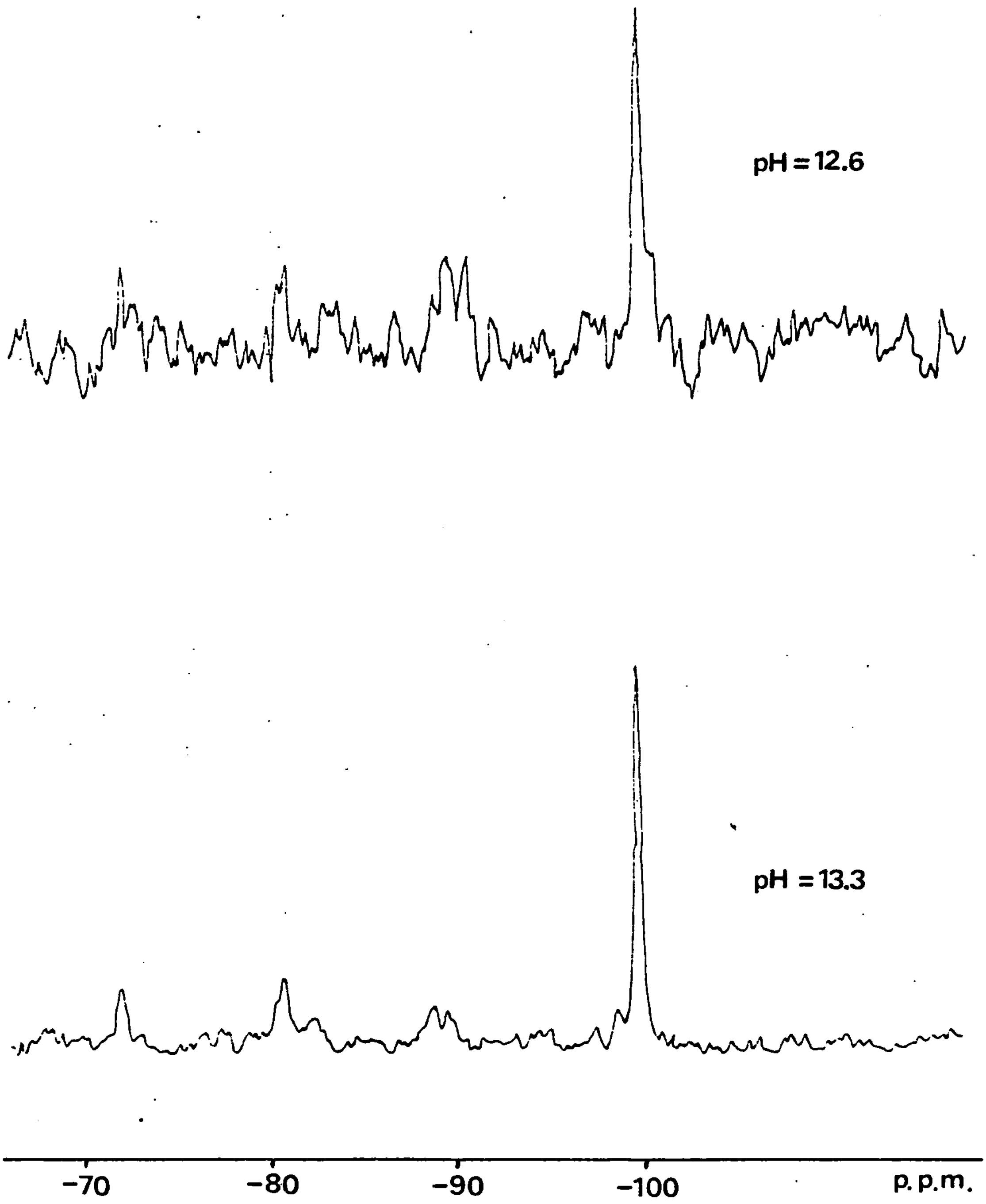


Fig. 6.6 Spectra of TMA silicate at pH = 12.6 and 13.3



6.5.3 MIXED BASE SYSTEM

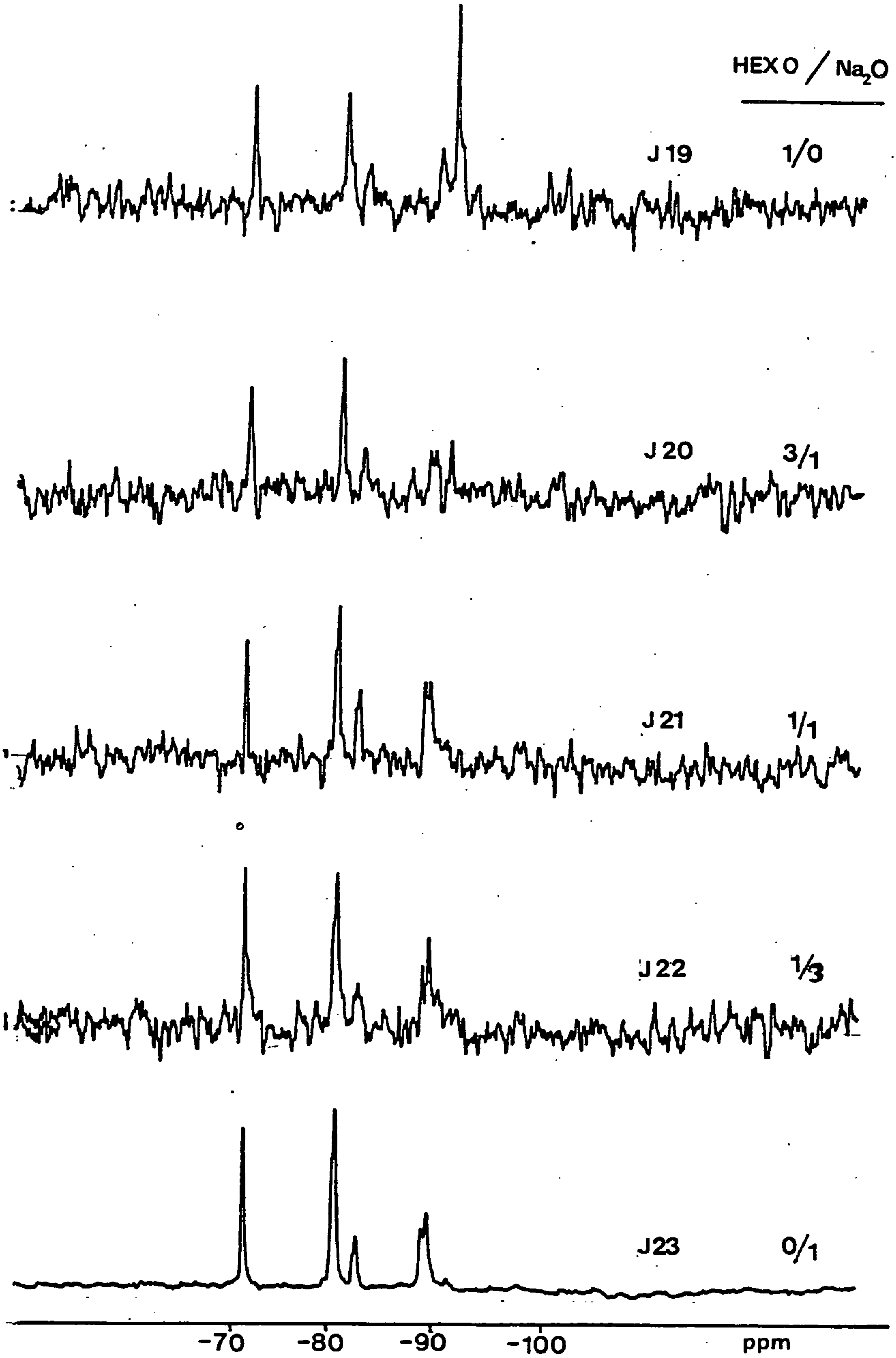
Fig. 6.7 shows a series of spectra for a 1 mol dm^{-3} silicate solution. Two cations were used in these solutions. J19 contained only HEX while J23 only Na. J20, J21 and J22 contained mixtures of both HEX and Na. The composition of these solutions can be seen below in Table 6.4.

TABLE 6.4 Compositions of silicate solutions in Fig. 6.7

Spectrum No.	$HEX(OH)_2$	NaOH
J19	1	0
J20	0.75	0.5
J21	0.5	1
J22	0.25	1.5
J23	0	2

The most notable aspect of the spectra is that the peaks specifically associated with HEX i.e. α and β (SFR and DFR) are quickly lost on the replacement of the HEX by even a small amount of Na. Peak β is lost immediately Na is added and the intensity of peak α is markedly decreased. In solution J21 which contained equi-equivalent amounts of HEX and Na neither α nor β can be seen. Less noticeable but very significant is the rearrangement of peaks in the D, E region. As Na replaces HEX and peak α collapses then two peaks can be seen in the D, E region (J20) instead of only one in the HEX only spectrum (J19). Although lack of good resolution makes this inconclusive it is quite possible

Fig. 6.7 ^{29}Si n.m.r. spectra of a series of aqueous silicate solutions. $[SiO_2]$ = 1.0 mol dm^{-3}



that we are seeing the rearrangement of the four-membered ring to some other Q_4 species e.g.

$$Q_4^2 \rightleftharpoons Q^1 \, \overline{Q^3 \; Q^2 \; Q^2}$$

6.5.4 OTHER RELATED EXPERIMENTS

It has already been mentioned (Chapters 1 and 4) that alcohols and amines have been used with some success in zeolite synthesis. The following experiments were carried out to determine if the addition of organic species other than quaternary ammonium compounds could affect the silicate anion distribution in an aqueous sodium silicate solution. The organic species used were tetramethylammonium chloride (TMA Cl), hexanediol, trimethylamine and tripropylamine. None of the solutions prepared gave detectable ^{29}Si n.m.r. signals, which suggests that little silica is in solution (probably less than 0.2 moles). Since no solid material was present this suggests that the silicate species have polymerised to colloidal silica. However there was no peak corresponding to colloidal silica suggesting that the relaxation time has been affected in some way. Furthermore all of the organic materials when added to the sodium silicate solution produced two phase systems. The formation of two phase systems is a well known consequence of the addition of organic solvents, particularly alcohols and ketones, to silicate solutions[21]. It is thought that this occurs because the organic solvent dehydrates the silicate solution producing the two phase system. In these two phase systems the organic is concentrated in the upper layer and the silica concentrated in the lower layer. It has been reported that the sodium is present in both layers consequently the ratio of silica to sodium in the bottom layer is higher than in the original solution.

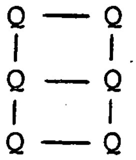
6.6 DISCUSSION

The work described in this chapter has been concerned with several aspects of aqueous silicate solutions. It has been shown that the silicate anion distribution is dependent on the concentration of silica and nature of the counter-ion. As the silica concentration is increased then more highly condensed silicate species are formed, this also suggests that in very dilute solutions the silicate monomer or Q^0 species will predominate. It is believed[16] that this has indeed been verified. The effect of the nature of the cation on the silicate anion distribution had not been previously noted. It has been shown, in this investigation, that quaternary ammonium species direct the distribution of silicate species towards more 'cyclic' and 'cage' type species than either Na or K. Even when Na and K silicate solutions do produce Q^3 (caused by an increase in the concentration of silica) they are branched linear species not the 'cage' type found in the presence of organic cations.

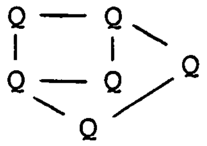
The 'cyclic' and 'cage' type species produced in the quaternary ammonium silicate solutions have been shown to be stable in the absence of the crystalline material. In addition these species have been shown to be unaffected by an increase in pH and the DFR has been shown to be stable to an increase in temperature.

The results of the 'mixed base' experiments are very significant in that they show that replacement of HEX by Na alters the anion distribution. One important point to be noted is that whereas it has been thought that an increase in pH would cause the equilibrium to shift in favour of Q^0 species, it was found that an increase in pH was not, in itself, sufficient to bring this about and that it is essential that the increase in pH is accompanied by an increase in the sodium ion concentration. One further important point about the 'mixed base' system is that the replacement of HEX by sodium causes the SFR (Q_4^2) to rearrange to give the $Q^1\ \overline{Q^3\ Q^2\ Q^2}$ species.

Examination of the spectra of HEX silicate and TMA silicate reveals that there is little evidence for species other than those contained in the Na and K silicate solutions apart from the SFR and DFR. If polynuclear species in silicate solutions are made up by the addition of Q^0 units as suggested by Glasser[8] then one would expect the formation of the DFR to proceed through Q_5, Q_6 and Q_7 species. Alternatively the formation of the DFR could proceed by the condensation of two SFR units. Other condensation reactions could lead to the formation of other species e.g. the hexagonal prism (Q_6^3) and the following species,



and

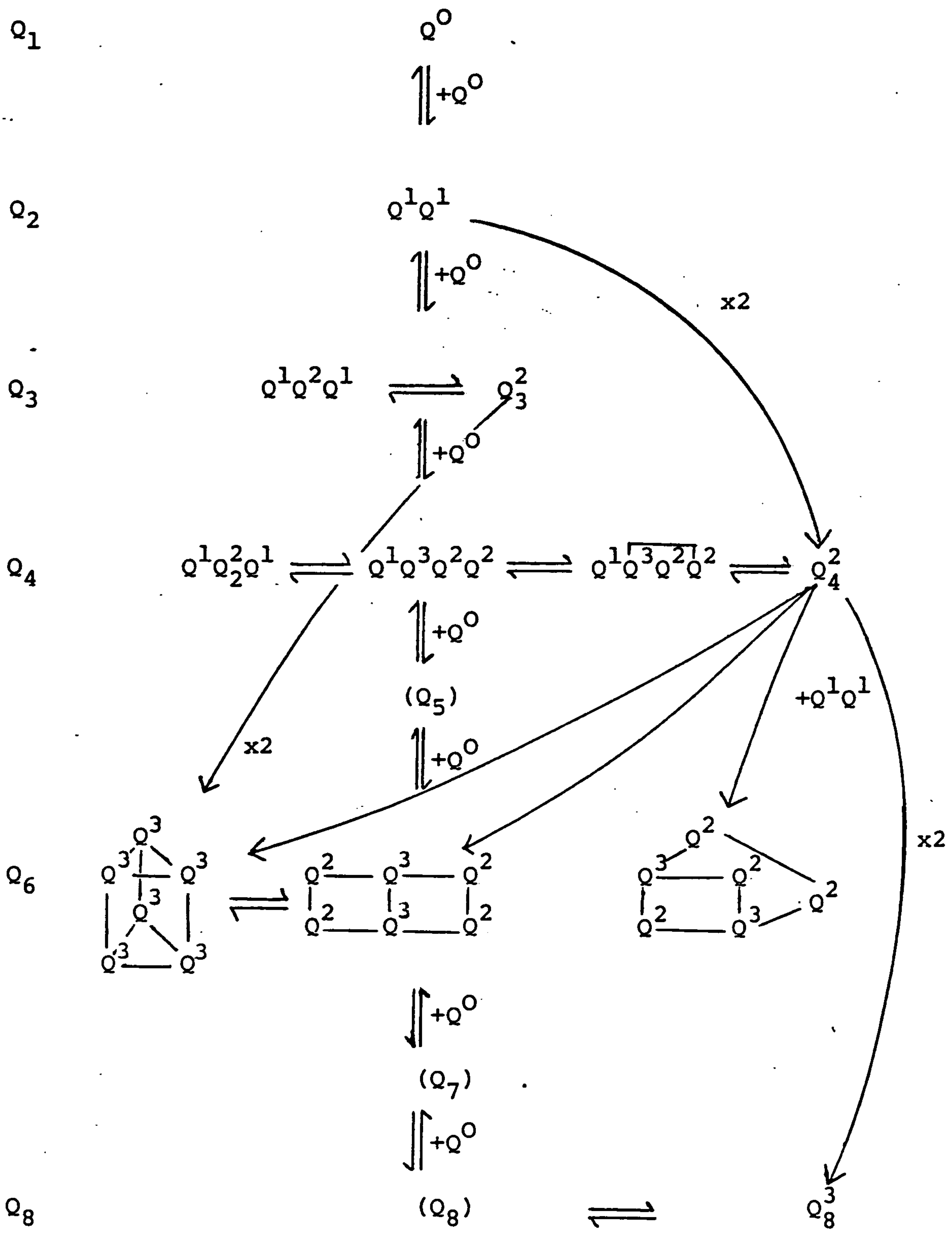


which were proposed by Hoebbel et al[22], as being the most probable Q_6 species. Thus silicate solutions may undergo rearrangements as shown in Fig. 6.8.

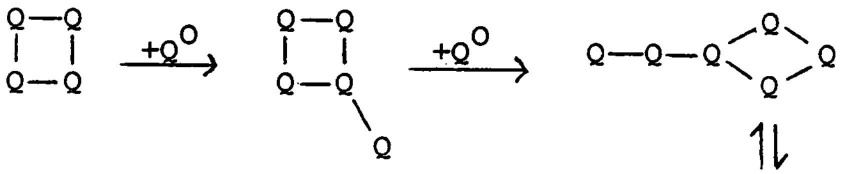
In zeolite synthesis the role of the cation(s) is still not fully understood. This present work however, has shown that quaternary ammonium species have a fundamental effect on silicate solutions. The action of the cations may be based on the removal of some of the water from the system thus forcing the silicate anions into species which require less water of solvation than, for example, the monomer species. Alternatively their effect could be due to ion-pair formation.

The condensation of silicate units to form larger structures is of fundamental importance in the synthesis of zeolites and it may be that the quaternary ammonium species aid this process. However one feature of zeolite synthesis using quaternary ammonium compounds still remains unsolved: the question of the five-membered ring. The five-membered ring is known to occur in several of the medium and high-silica zeolites e.g. ZSM-5 and ZSM-11. However, there is no evidence for its presence in the silicate solutions of the quaternary ammonium ions, in particular in the solutions of TPA. The difference in the value of the chemical shift for peak α in this solution and for those of TMA silicate and HEX silicate was initially thought to

Fig. 6.8 Species present in aqueous silicate solutions and the type of rearrangments they may undergo

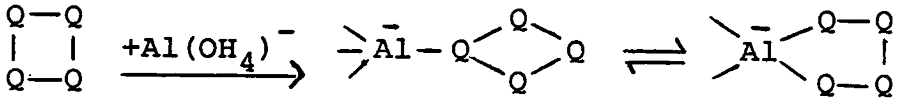


be due to the presence of the five-membered rather than the four-membered ring. However the large differences in the chemical shift of the three-membered and four-membered rings make this unlikely. It should also be noted that the presence of aluminium may have a profound effect on the system. Glasser[8] suggested that reaction of the four-membered ring with further Q^0 units proceeds by the scheme outlined below.



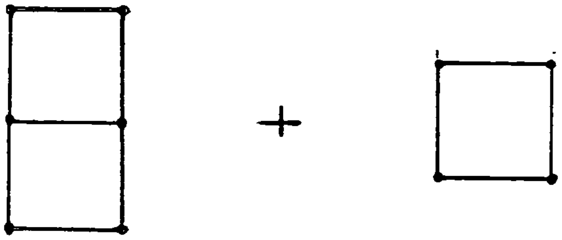
(I) Other Q_6 species

Thus the reaction of (I) with an additional Q^0 unit occurs before rearrangement to the five-membered ring. However, when aluminium is present the following may occur.



(II)

So that (II) rearranges to the five-membered alumino-silicate species before any further Q^0 can add to it. An apparent inconsistency with the above view, that the five-membered silicate ring is 'unstable', was the report[23] that the silicate unit in crystalline TBA silicate was the double-five membered ring. However this double-five membered species need not have been formed by the condensation of two five-membered rings but could have been formed by the condensation of the following 'known' species.



It is obvious, even from a limited study such as this that ^{29}Si n.m.r. spectroscopy has immense potential for the study of silicate solutions and their role in zeolite synthesis. In addition it is believed that ^{27}Al n.m.r. of alumino-silicate solutions may provide an excellent method for determining the action of aluminium in these solutions and hence its role in zeolite crystallisation.

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APPENDIX A

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C      PROGRAM STOD (S TO D) CONVERTS SCALE READINGS S ON
C      GUINIER FILM TO D SPACINGS.
C      PROGRAM ALSO REQUIRES LINE INTENSITIES ESTIMATED
C      VISUALLY ON SCALE 1 TO 5, 1 IS THE MOST INTENSE AND 5
C      IS THE LEAST INTENSE. IF INTENSITIES HAVE NOT BEEN
C      ESTIMATED USE A 6 IN THE DATA.
C      INPUT DATA AS FOLLOWS
C      TITLE
C      ESTIMATED READING ERROR IN S (ES) XXX.XX
C      POSITION OF FOCAL LINE SF XXX.XX
C      INTENSITY IN COL 1 AND S IN COL2-7 X,XXX.XX
C      REPEAT FOR EACH LINE AND FINALLY FINISH WITH 0000.00
C      START AGAIN WITH NEXT TITLE
   98 READ(5,99,END=107)
   99 FORMAT('                                                          ')
      WRITE(6,99)
      READ(5,100)ES
  100 FORMAT(F6.2)
      READ(5,100)SF
      WRITE(6,101)ES
  101 FORMAT('ESTIMATED ERROR IN S=',F6.2)
      WRITE(6,102)SF
  102 FORMAT('POSITION OF FOCAL LINE=',F6.2)
      N=1
      WRITE(6,105)
  105 FORMAT('LINE    SOBS           S     2THETA          D
     1           ED    RI')
  103 READ(5,104,END=98)I,SOBS
      IF(I.EQ.0) GO TO 98
  104 FORMAT(I1,F6.2)
      S=SOBS-SF
      S=ABS(S)
      THETA=0.28600*S
      T2=2.*THETA
      THETAR=THETA*(3.14159/180.00)
      D=0.770281/(SIN(THETAR))
      ED=D/(TAN(THETAR))
      ED=ED*0.28600*3.14159/180.00*ES
      IF(I.EQ.1)J=100
      IF(I.EQ.2)J=75
      IF(I.EQ.3)J=50
      IF(I.EQ.4)J=25
      IF(I.EQ.5)J=5
      IF(I.EQ.6)J=0
      WRITE(6,106)N,SOBS,S,T2,D,ED,J
  106 FORMAT(I2,3F10.2,2F10.3,I5)
      N=N+1
      GO TO 103
  107 STOP
      END
```