

ION EXCHANGE KINETICS IN ZEOLITE A

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TO MY PARENTS

AND TO HELEN

ABSTRACT

Zeolite A crystals were synthesised by the method of Charnell and were characterised for size and chemical composition.

Kinetics of Na - Mg, Na - Ca and Na - Ba binary ion exchange were measured at 25°C for total solution normalities of 3,9mN, 3,4mN and 3,4mN respectively. Samples of the synthesised zeolite A were compared. The kinetics were followed using a Na selective electrode in the solution phase. Diffusion coefficients calculated by the Danes and Wolf method (using the Paterson solution to the diffusion equation) showed that the Na - Ca and Na - Ba exchanges were very similar but the Na - Mg exchange was not only much slower but had a different form to the diffusion coefficient versus degree of exchange relationship shown by the two other ions.

The Na - Ca exchange kinetics were also measured in a series of small incremental uptakes of calcium. The derived diffusion coefficients showed the same overall trend as that seen in the "complete exchange" experiment. Unlike Danes and Wolf no conclusive evidence of composition effects was seen.

Kinetics of exchange of the Na - Ca/Mg ternary system were measured for two Ca:Mg ratios using both Na selective and Ca selective electrodes. The rate of Ca uptake as a fraction of composition was the same as that seen in binary exchange. The Mg exchange however, was slowed down by the presence of Ca.

The kinetics of Na - Li, Na - K and K - Na, Na - Rb, Na - Cs and Cs - Na, and Na - NH₄ exchanges were measured. The exchanges were much faster than the corresponding Na - divalent exchanges. In all of the Na - univalent exchanges two distinct rates were observed due to rapid exchange followed by a slow loss of sodium due to zeolite hydrolysis.

The K - Na and Cs - Na exchanges were faster than the corresponding Na - K and Na - Cs exchanges as predicted by Brooke and Rees due to the higher selectivity of the zeolite for Na.

Lastly a study was made of the hydrolysis of zeolite A. It was found that the degree of hydrolysis was roughly proportional to the initial pH. There was a rapid initial hydrolysis due to degradation of the outer surface followed by slower hydrolysis as more protons were introduced into the zeolite in an auto catalytic process.

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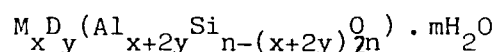
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1. INTRODUCTION

1.1 ZEOLITES

The term zeolite was first used by Cronstedt (1) in 1756 when he discovered the natural zeolite stilbite. When heated a zeolite forms bubbles due to the boiling of zeolitic water and zeolite is the combination of the Greek zeo, "to boil" and litos, "stone". Since Cronstedt discovered stilbite a total of 34 natural zeolites have been found and some 100 synthetic zeolites have been made.

A zeolite is effectively an open tectosilicate framework in which up to half of the silicon atoms have been replaced by aluminium atoms. In tectosilicates each silicon is bonded to four oxygens in a tetrahedron and each oxygen is shared with two silicons giving a neutral framework. Since the valency of aluminium is lower than silicon the framework of a zeolite is negatively charged. This charge is balanced by cations which sit in specific sites within the open framework where they are co-ordinated to the framework oxygen atoms. The open framework normally contains water which helps stabilise the structure and gives rise to the effect first seen by Cronstedt. The general formula of a zeolite is:-



where M is a univalent cation, D a divalent cation, n is the number of tetrahedral units and x+2y is the number of silicon atoms replaced by aluminium atoms.

Smith (2) therefore defined a zeolite as a "crystalline alumino-silicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of

movement to permit cation exchange and reversible dehydration."

The last part of the statement differentiates zeolites from feldspars and feldspathoids whose frameworks are so compact that at normal temperatures the cations are trapped (3). Some feldspathoids have more open frameworks allowing ion exchange but also contain irreversibly occluded salt or other molecules. Synthetic forms can be made without occluded molecules and are then true zeolites.

Zeolites have a large number of applications due to their characteristic structures. Dehydrated zeolites act as desiccants and are used to dry gases e.g. Zeolite A is used in double glazing to remove water vapour in place of silica gel. The open framework of zeolites allows molecules to enter the framework but only if they are below a certain size and are the right shape. This property is referred to as molecular sieving and the critical size is determined by the size of the openings (also called apertures or windows) controlling access to the spaces in the framework (cages or cavities). The aperture size is itself dependent upon the structure of the particular zeolite and upon the charge balancing cations present (the cation form). Large cations tend to decrease the aperture size by blocking the aperture. Because fewer divalent cations are needed than univalent cations to balance the framework charge the apertures are often increased in size in many cases. In dehydrated zeolite A the potassium form sorbs only water, ammonia and other small polar molecules, the sodium sorbs some permanent gases and the calcium form sorbs propane and n-butane (4). A similar effect was seen with Chabazite (5) but the aperture size of calcium zeolite X was found to be smaller than that of sodium zeolite X(6) probably due to distortion of the framework (when dehydrated) and the fact that no cations reside

in the apertures controlling access to the supercages.

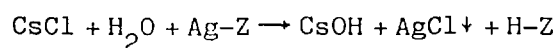
Zeolites with relatively high aluminium content have electric fields and sorb polar molecules strongly. Conversely high silica zeolites where aluminium is present in only trace amounts tend to sorb small polar molecules weakly and large organic molecules such as n-paraffins will displace them.

Zeolites are used extensively as catalysts. They were first used for catalytic cracking of long chain hydrocarbons (Durabead 5) in 1962 (7,8). The catalytic activity of zeolites is due to the Bronsted and Lewis acid sites (9) present in hydrogen and rare earth-hydrogen zeolites. Zeolites possess cracking activity up to four orders of magnitude greater than silica-alumina catalysts (10), give less coke, increase production capacity and improve gasoline yields by up to 25%. Zeolites are highly selective catalysts because of their molecular sieve action which prevents some of the reagents entering the zeolite, prevents the formation of large transition states and also prevents large products leaving the zeolite. The conversion of methanol to gasoline using the high silica zeolite ZSM-5(11) is a complex example of the selective conversions possible with zeolites. In zeolite Ca-A chemical dehydration of n-butanol was observed but not of isobutanol which cannot enter the framework (12). When a mixture of ethylene and propylene is hydrogenated on a Pt-Na-mordenite hydrogenation catalyst only the resultant ethane can escape and so only ethylene can react continuously (13).

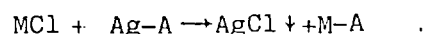
The zeolite property with which this thesis is concerned is that of ion exchange. As has been mentioned the charge balancing cations in a zeolite can be replaced to varying extents by other cations such that charge balance is maintained. Zeolites exhibit differences in ion selectivity. As a result of this property zeolites have been used for

the removal of caesium and strontium in radioactive wastes (14), removal of ammonia from waste water (15), and recently as a builder in detergents (16) to soften the water i.e. to replace Ca^{2+} and Mg^{2+} by Na^+ . Ion exchange is also important commercially because of the previously described effect of cations upon the molecular sieve property of zeolites.

Zeolites can act as ion sieves with large cations being unable to enter the zeolite or sometimes, when there is insufficient space in the zeolite cages to accommodate all of the ions needed for complete exchange, show limited exchange capacity. These effects are clearly seen with alkylammonium ions. For example Clinoptilolite will not admit tetramethyl- and tert-butyl ammonium ions (17), and zeolite A will only admit small amounts of branched mono alkyl ammonium and trimethylammonium ions (18). Ion sieve effects have also been demonstrated for inorganic cations. Caesium cannot exchange with sodium in analcime or sodalite hydrate under mild conditions (19) and it is possible therefore to hydrolyse CsCl by treatment with Ag-analcime or Ag-sodalite:



where Z represents the zeolite. It is similarly possible to remove sodium and potassium from mixtures with caesium:



where A represents analcime and M represents Na or K.

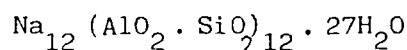
Other more recent novel uses of zeolites are as veterinary drug releasing agents, as pig feed additives to encourage weight gain and as a paper whitener.

1.2 ZEOLITE A

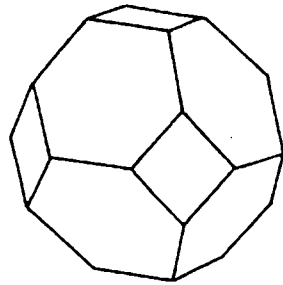
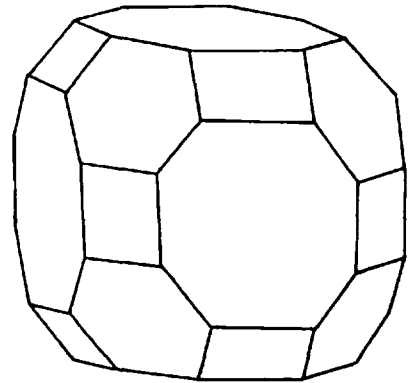
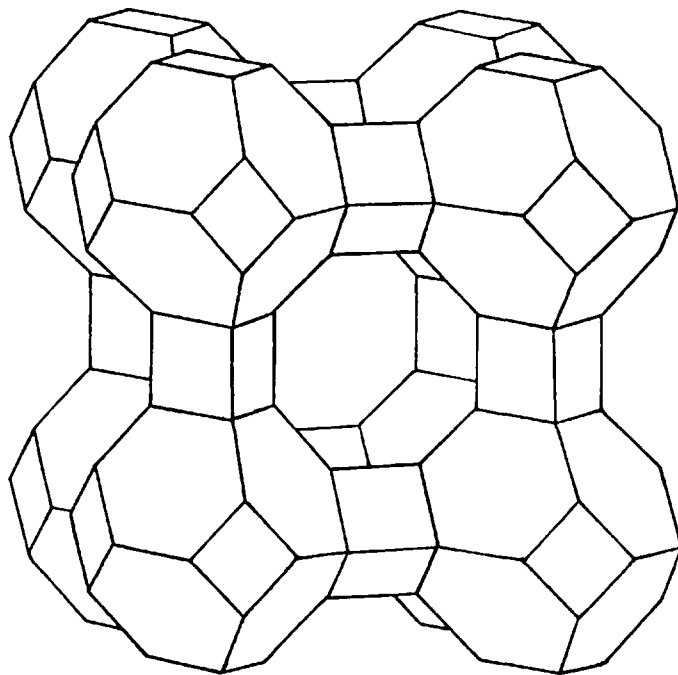
Ion exchange kinetics have been measured using zeolite A (or Linde type A) which is a synthetic zeolite with no naturally occurring equivalent. The zeolite was first prepared and characterised in 1956 (4, 20, 21). Its structure can be considered as consisting of truncated octahedrons (14 hedrons or sodalite cages), Fig. 1, which are connected by square prisms to give a regular open framework, Fig. 2. At each corner in the structure there is a tetrahedrally co-ordinated (T) silicon or aluminium atom with the oxygen atoms situated between the T atoms. Loewenstein (22) stated that two aluminiums cannot share the same oxygen atom and this combined with the silicon to aluminium ratio of one for zeolite A leads to the T atoms being alternately silicon then aluminium. (102)

The arrangement of sodalite cages forms a larger cage which is a truncated cubo octahedron (26 hedron or α cage) Fig. 3 and combined with eight times $\frac{1}{8}$ of a sodalite cage (at each corner of the α cage) plus twelve times $\frac{1}{4}$ of a square prism (at each edge of the α cage) this gives the pseudo unit cell. If the difference between aluminium and silicon atoms is ignored then the structure of the pseudo unit cell is repeated throughout the zeolite but allowing for silicon aluminium alternation gives a true unit cell equal to eight pseudo unit cells.

The pseudo unit cell constant is 1,23nm and contains 24 tetrahedra and the sodium form in which zeolite A is usually synthesised (zeolite 4A) has the average composition:



which is represented by Na_{12}A or just NaA. In some samples of NaA an excess of aluminium has been found which has been interpreted as

Figure 1.Figure 3.Figure 2.

being due to sodium aluminate occluded in the sodalite cage (23). Recent crystallographic studies have tentatively located 0,2 to 0,3 AlO_4 complexes in Ca_6A (24) and Sr_6A (25) but no such complexes were found in univalent forms of zeolite A, although NMR studies (26) implied an unknown amount of occluded aluminium in NaA. The Al complex is believed to be formed during ion exchange with divalent ions or during subsequent dehydration (24, 25) possibly due to some lattice collapse.

Access to the α cage is via the octahedral rings which have a free diameter of 0,42nm and the hexagonal rings have a free diameter of 0,22nm. Cations can be located in the hexagonal rings (6 rings, site I, eight per pseudo unit cell), octahedral rings (8 rings, site II, three per pseudo unit cell) and in the square rings (4 rings, site III, twelve per p.u.c.) Fig. 4. Cations in site I can be in the plane of the ring or can be slightly out of the plane and thus project into the sodalite cage or into the α cage.

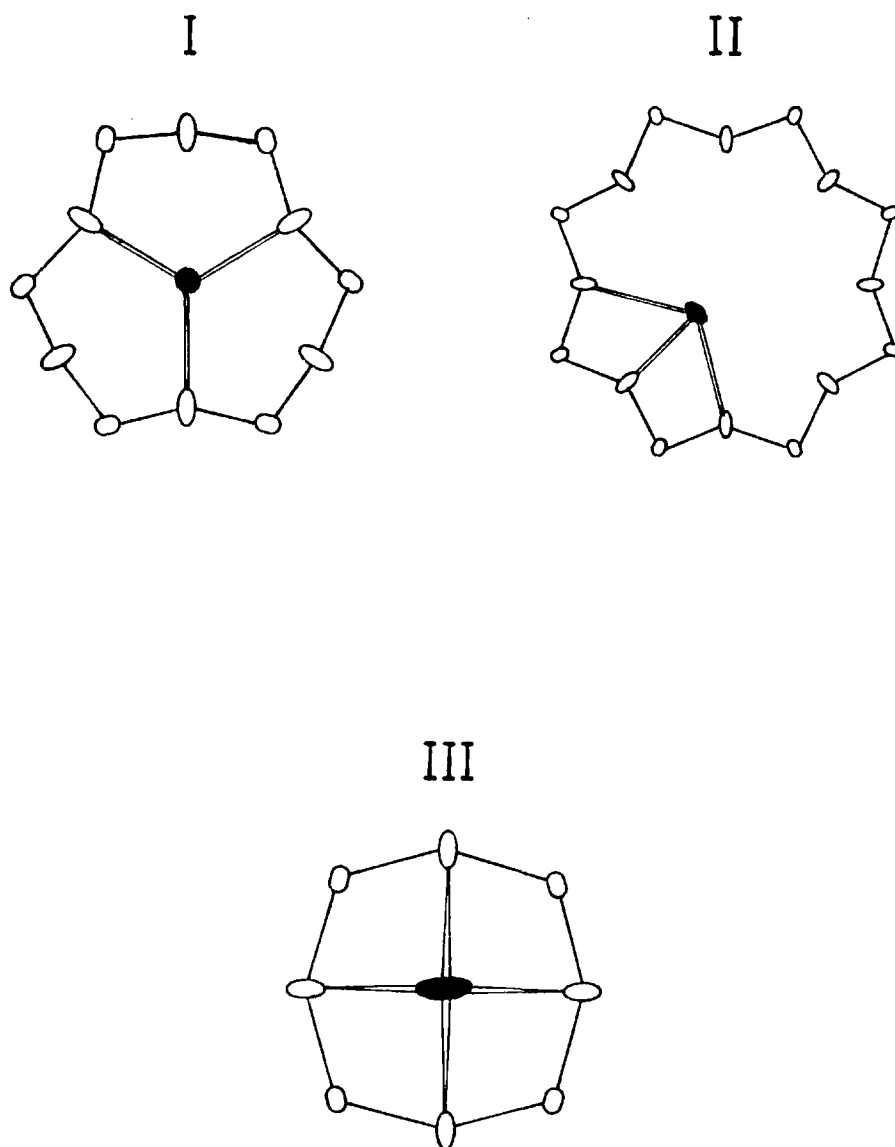
1.3 CATION POSITIONS IN ZEOLITE A

Whilst the structure of the zeolite A framework is well known the positions of the cations are not so clearly defined, Seff and co workers claim to have located near zero co-ordinate cations in dehydrated A, that is cations further from framework oxygens than the combined ionic radii (27-34). This claim is rigorously denied by Smith (24, 25, 35-38) and the debate continues.

In dehydrated sodium-A eight cations are tightly bound in site I (20, 39) and three cations are less tightly bound in site II (40). The last cation is loosely bound opposite site III and its nearest

Figure 4.

Na ions in sites I,II and III (not to scale).



approach to framework oxygens has been measured as 0,23nm (40), or 0,28nm (near zero co-ordinate) (33), or 0,26nm (36). In the last case a Si/Al ratio of 1,03 was reported lending to slight structure disorder, a result discounted by Seff (38) on the basis of symmetry effects on the structure.

In hydrated sodium A as in the dehydrated form eight cations are tightly bound in site I (41) and the other four cations are less tightly bound. Gramlich and Meier tentatively located three cations in site II (42) and the last cation was associated with a water molecule in the centre of the α cage. They also found a cubically distorted pentagonal-dodecahedral arrangement of 20 water molecules in the α cage.

In dehydrated potassium A eight cations are in site I and three are in site II (27, 35). The last cation is in the α cage either 0,345nm from the plane of an already occupied site I (27) or some 0,280 to 0,299nm from site III (35). In $\text{Cs}_7\text{K}_5\text{A}$ a potassium ion was found 0,376nm from the plane of site I (32).

In hydrated potassium A the cation positions were found to be essentially the same as for dehydrated potassium A apart from small shifts from the ring planes into the α cages (27). The twelfth cation was associated with water of hydration.

The exchange of Na by Rb has a limit which has been found to be 8,3 (43), 8,4 (44), 9,6 (45) and 11 (30,31) cations out of twelve per pseudo unit cell (p.u.c.) due to the size of the Rb^+ ions limiting the number which can be accommodated in the α cage. In dehydrated Rb_{11}NaA seven of the Rb^+ ions and the Na^+ ion were located in site I,

three Rb^+ ions were located in site II and the last Rb^+ ion was 0,362nm from the plane of an occupied site I (30, 31) (zero-coordinate) according to Seff et al but Smith et al found no evidence from this (46) and found Ba and K impurities in the crystal. The last cation was in site I.

The limit of exchange by Cs has been found to be 6,1 (43), 7,0 (28) and 7,4 (45) out of twelve due to size restriction. For hydrated and dehydrated $\text{Cs}_7\text{Na}_5\text{A}$ three Cs^+ ions were located in site II, four Cs^+ ions and four Na^+ ions were located in site I and one Na^+ ion was unlocated (28). Calculations of the potential experienced by Cs^+ and Rb^+ ions in dehydrated zeolite A (47) gave the possibility of the ions "floating", that is at greater distance from the framework than expected.

The cation positions in zeolite 5A ($\text{Ca}_4\text{Na}_4\text{A}$), a sieve which adsorbs larger molecules than zeolite 4A, have been determined (41, 48) and all eight cations were located in site I. In calcium A (Ca_6A) five Ca cations are located in site I with the sixth also in site I (25) or weakly located 0,31nm from framework oxygens in site II (34). The Ca ion in site II was tentatively predicted by percolation theory (49) and energy calculations also gave this result (50). Chemical analyses, however, showed a tendency for potassium impurity (25) which may give rise to a site II cation.

In hydrated calcium A the cations were located in site I (51) with three recessed far into the sodalite cage and three relatively far into the α cage.

In dehydrated Sr_6A it was also found that six cations sit in site I (24) or five sit in site I and one in site II (34). It should be noted that by "or" it is meant that different workers have put forward different cation positions.

The selectivities of cations for the described sites have been studied experimentally and theoretically mainly for dehydrated zeolite A. Table 1 gives the preferred sites, that is the site into which the first cation will go during ion exchange (52).

Table 1

Site selectivity of first incoming ion in dehydrated zeolite A.

Cation	Theoretical (52)	Experimental
Li	I	I (20, 53, 54)
Na	I	I (48, 54, 55)
K	II	II (54, 55, 56)
Cs	II	II (28)
Mg	I (50)	I (57)
Ca	I	I (54, 55)
Sr	I	I (58)
Ba	II	-

Similar theoretical calculations predict that the last incoming ion for Mg, Ca, Sr, and Ba exchange is selective for site II (50).

The experimental site selectivities are found by measuring the sorption characteristics of partially exchanged dehydrated zeolite A and this method cannot be applied by hydrated zeolite A. It is however considered that the site selectivities in hydrated zeolite A are relatively random (52) although they are probably not too different

from the selectivities in dehydrated zeolite A as the cation size is a major factor in site selectivity. Large cations (K^+ , Cs^+ , Ba^{2+}) will tend to prefer site II and small cations (Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+}) will tend to prefer site I (59).

1.4. ION EXCHANGE IN ZEOLITE A - EQUILIBRIUM

The process of ion exchange depends on a number of factors which affect the extent to which a particular exchange will occur (equilibrium) and the rate of the exchange (kinetics). These factors are (15):-

- 1) the nature of the cation species, the cation size, both anhydrous and hydrated, and the cation charge;
- 2) the temperature;
- 3) the concentration of the cation species in solution;
- 4) the anion species associated with the cation in solution;
- 5) the solvent (most work carried out in aqueous solutions);
- 6) the structural characteristics of the particular zeolite.

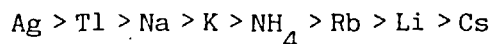
Binary ion exchange equilibria in zeolite A have been studied for sodium exchange with most of the alkali metal and alkaline earth cations.

Early studies (23, 60) determined the extent to which cations, in particular, methylammonium ions, could be exchanged into the zeolite. The limit is determined by the volume of the cation.

From equilibrium studies the selectivity of the zeolite for one cation over another cation is determined and a series formed to

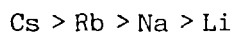
show the relative selectivity of the zeolite for a number of cations.

For univalent cations this series is (4, 44, 60, 61):



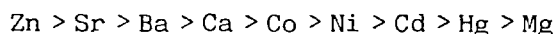
Thus Ag^+ ion is the most favoured ion whilst Cs^+ ion is the least favoured. Other workers have produced similar series but with the selectivity of Na and K reversed ($\text{K} > \text{Na}$) (62, 63) due to the selectivity of zeolite A for Na and K being very similar.

Measurements have also been carried out for trace components in concentrated electrolyte solutions (64, 65) and gave a different selectivity series (64).

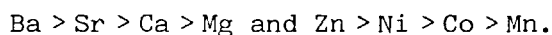


It was also shown that zeolite A may be considered to be a highly "cross-linked" exchanger (65).

Apart from Ag^+ and Tl^+ zeolite A is more selective for divalent ions than univalent ions and the selectivity series has been determined (4, 66, 67):



Wolf et al (62) found slight differences:

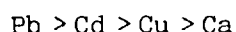


A number of other studies have been made of divalent exchange (59, 65, 68-77) including some for trace components. A study of Sr - Ca exchange (72) showed the selectivity for Sr to be slightly greater than that for Ca and Nikashina et al (71) found the following

selectivity series.



Other workers confirmed this series and found that Cd had a higher selectivity than that of Zn (69, 70). Wiers et al (75) studied divalent - divalent exchange and hence found



A study by Barri & Rees (59, 78, 79) of Na - Ca and Na - Mg exchange confirmed that the relationship between the isotherms and the solution concentration was valid (see later). A study of the Na - Ca/Mg ternary system (59, 78, 79) showed the divalent ions were preferred to Na and that the Ca was preferred to Mg.

1.5 ION EXCHANGE IN ZEOLITE A - KINETICS

A number of workers have investigated the kinetics of isotopic exchange in zeolite A (80-89).

Both Levi et al (82-84) and Sherry et al (85) found a fast initial process followed by a slow second process. Levi et al assumed two separate processes involving mobile ions and firmly bound ions whereas Sherry et al proposed a single, fast, diffusion process of mobile ions and a simultaneous, slow, adsorption-desorption reaction between firmly bound and mobile ions. The measurements of Sherry et al showed the slow stage to be independent of particle size (85) in support of their proposals. These proposals were reviewed by Rees (90) along with work on other zeolites.

Dyer et al measured isotope kinetics and found only one process (45, 80, 81, 88, 89) as these measurements started only after the fast process would have finished. Overall the diffusion rate of univalent cations

was found to be much greater than that of divalent cations. Dyer et al (45, 88) showed that for divalent cations the activation energy decreases with increasing cation radius whereas for univalent cations the energy increases with radius. The activation energy of divalent cations is some two or three times higher than that of the univalent cations.

Very few ion exchange kinetic measurements have been made (59, 87, 91-96, 99-100) with zeolite A. Wolf et al (91) first measured the exchange of Na with Ni and found a two stage process which they ascribed to Ni blocking the openings to the α cage. They later measured the kinetics of exchange of Na with Mg, Ca and Mn (92-94), covering the entire range of compositions in a series of experiments. Using a technique which will be described later they derived diffusion coefficients and explained the variation of the diffusion coefficients in terms of zeolitic composition. Unfortunately they assumed in their explanation that six site IIs are available to six divalent cations whereas there are only three. Their results nevertheless stand and will be discussed later.

Barri (59) measured kinetics of exchange of Na with Mg, Ca and Mg/Ca showing that Mg exchange is much slower than Ca exchange. Also in Mg/Ca exchange the rate is equal to Ca exchange until the ratio of Mg to Ca is greater than one.

Gaus et al (87) measured the kinetics of exchange of Sr with Ca and Ba and the reverse exchanges and compared them with isotopic exchange rates using the equations of Rees and Brooke (97, 98) which will be discussed later.

Hoinkis & Levi (99) measured self diffusion kinetics and Na - Sr, Sr - Na and Na - Cs/Sr exchange kinetics. They found the Na - Sr exchange to be much faster than the reverse exchange and the Na - Cs/Sr exchange showed a maximum in Cs uptake followed by a decrease and preferential Sr uptake.

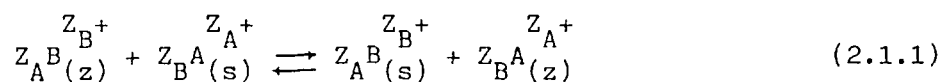
Ames (100) measured Na - Cs and Na - Sr exchange kinetics but used cemented bundles of crystals so that his measurements refer to inter-crystalline diffusion i.e. diffusion between crystals in the bundle. His results cannot therefore be compared with experiments with single crystals where the kinetics depend upon intracrystalline diffusion.

Ikeda et al used a pressure jump method with conductivity detection (101) to measure the relaxation of alkylammonium ions (95, 96) in zeolite A, initially in a suspension. They found a slow and a fast relaxation process which they explained in terms of a two step mechanism in which a sodium vacates its site in the zeolite cage and an alkylammonium ion is adsorbed onto the zeolite surface and then diffuses into the cage. Whilst their results apparently support this mechanism it would require a charge separation and the diffusion of an adsorbed alkylammonium ion through the zeolite would be a most unfavourable process.

2. ION EXCHANGE THEORY

2.1 EXCHANGE EQUILIBRIA

The process of ion exchange may be represented by the following equation:-



where Z_A , Z_B are the charges of the ingoing and outgoing cations and the subscripts z and s refer to the zeolite and solution phase respectively (103).

Defining equivalent fractions of the ions in the solution and zeolite phase respectively by:-

$$A_s = \frac{Z_A m_A}{Z_A m_A + Z_B m_B} \quad (2.1.2)$$

and

$$A_z = \frac{Z_A M_A}{Z_A M_A + Z_B M_B} = \frac{Z_A M_A}{C} \quad (2.1.3)$$

where m_A , m_B represents the molalities of ions A and B in solution and M_A , M_B represents the concentration in moles per gram of ions A and B in the zeolite. C is the ion exchange capacity of the zeolite in equivalents per gram. The exchange capacity of a sample of zeolite A in two different cation forms, A and B, will differ due to the differing atomic weights of the two ions. This does not create difficulties as the sample used in an experiment will have a known capacity in equivalents (weight.C) to which subsequent measurements can be related.

An isotherm is a plot of A_z as a function of A_s at a given total solution normality (TN) and temperature and shows the preference of

the zeolite for one ion over the other involved in the ion exchange reaction. The diagonal from (0,0) to (1,1) represents an ideal isotherm (dashed line in Fig.5) with no preference and the law of mass action is obeyed.

Fig.5 shows the five types into which isotherms can be classified (15). In curve (a) the zeolite is selective for the incoming ion and in curve (c) for the outgoing ion. In most cases the zeolite selectivity varies with the degree of exchange to give a sigmoidal isotherm like curve (b). Curve (d) shows an isotherm where the incoming ion cannot replace all of the outgoing ions and curve (e) shows a hysteresis loop due to two zeolite phases being formed during exchange.

Ion exchange equilibria are described by three equilibrium coefficients. The rational selectivity (mass action) coefficient, K_m , is given by:-

$$K_m = \frac{Z_B^A \cdot B_S^Z}{Z_A^B \cdot A_S^Z} \quad (2.1.4)$$

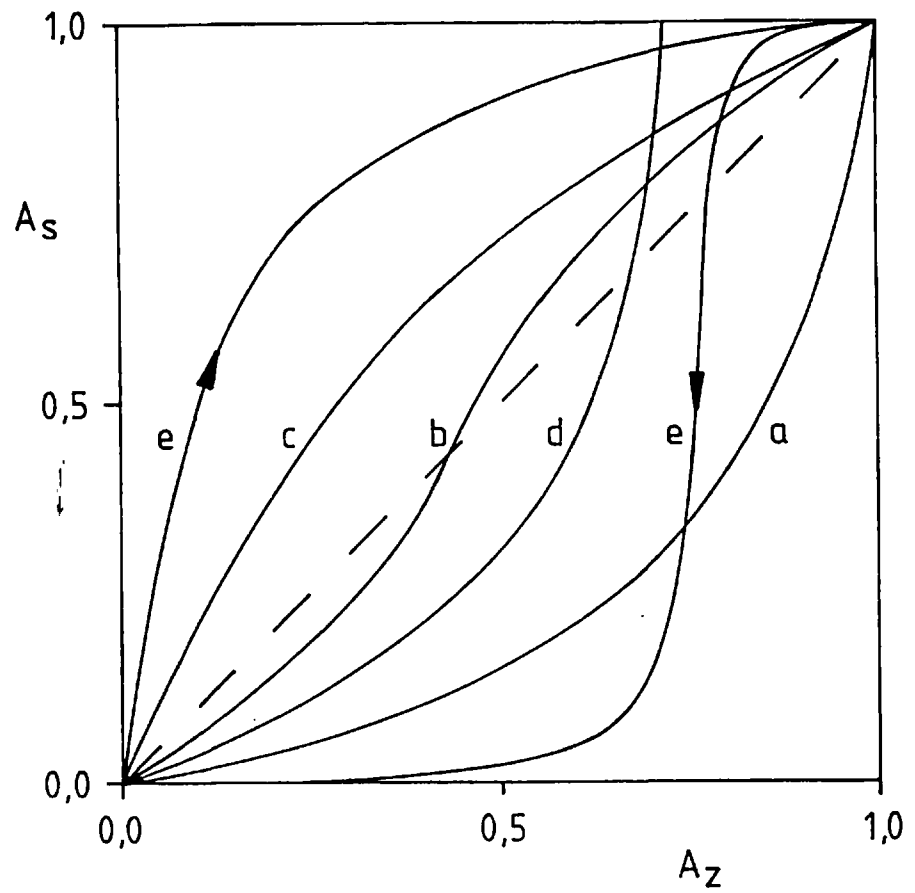
The corrected selectivity (Keilland) coefficient, K_c , includes a correction for the activity coefficients of the ions in solution:-

$$K_c = \frac{Z_B^A \cdot a_{B_S}^Z}{Z_A^B \cdot a_{A_S}^Z} \quad (2.1.5)$$

where a_{A_S} , a_{B_S} represents the activities of ions A and B in solution and eliminates the selectivity generated by the solution phase to give the selectivity of the zeolite phase only.

Figure 5.

Types of ion exchange isotherms for
the reaction $A_{(s)} + B_{(z)} = A_{(z)} + B_{(s)}$



Lastly the thermodynamic equilibrium coefficient, K_a , also includes the activity coefficients of the ions in the zeolite and is a true constant for the system considered.

$$K_a = \frac{a_{A_z}^{Z_B} \cdot a_{B_s}^{Z_A}}{a_{B_z}^{Z_A} \cdot a_{A_s}^{Z_B}} \quad (2.1.6)$$

or alternatively

$$K_a = \frac{\frac{Z_B}{Z_A} \cdot f_A^{Z_B} \cdot \frac{Z_A}{m_B} \cdot \gamma_B^{Z_A}}{\frac{Z_A}{Z_B} \cdot f_B^{Z_A} \cdot \frac{Z_B}{m_A} \cdot \gamma_A^{Z_B}}$$

where $f_{A, B}$ represents the activity coefficients of ions A and B in the zeolite on the equivalent fraction scale and $\gamma_{A, B}$ the same in the solution on the molality scale. It should be noted that there has been some controversy over the use of equivalent fractions rather than molar fractions (104) and the effect on calculated ΔH^θ and ΔG^θ values. In the cases which will be considered in this thesis, the fraction used has no effect provided the same fraction is used throughout the calculations.

For the dilute solutions used in this study molality may be replaced by molarity and hence the total solution normality is given by:

$$TN = (Z_A m_A + Z_B m_B) \quad (2.1.7)$$

and from (2.1.2)

$$m_A = \frac{A_s}{Z_A} \cdot TN \quad \text{and} \quad m_B = \frac{B_s}{Z_B} \cdot TN \quad (2.1.8)$$

hence substituting into (2.1.5) using the form of a_{A_s}, a_{B_s} used in (2.1.6) gives:-

$$K_C = \frac{\frac{Z_B}{A_Z} \cdot \frac{Z_A}{B_S} \cdot \Gamma}{\frac{Z_A}{B_Z} \cdot \frac{Z_B}{A_S} \cdot Q}$$

$$\text{where } \Gamma = \frac{\frac{Z_A}{Y_B}}{\frac{Z_B}{Y_A}} \quad (2.1.9)$$

$$\text{and } Q = \frac{\frac{Z_A}{Z_B} \cdot (TN) (Z_B - Z_A)}{\frac{Z_B}{Z_A}}$$

K_C has been determined experimentally for a number of systems (59, 105) and for sodium-calcium and sodium-magnesium exchange a polynomial fit made (59, 78) of the form:-

$$\log_{10} K_C = b_0 + b_1 A_Z + b_2 A_Z^2 + b_3 A_Z^3 \quad (2.1.10)$$

where $b_0, 1, 2, 3$ are constants (see table 2).

Kielland (106) found an empirical formula for the activity coefficients in the zeolite for uni-univalent exchange:-

$$\log_{10} f_A = k B_Z^2; \quad \log_{10} f_B = k A_Z^2 \quad (2.1.11)$$

where k is the Kielland coefficient and hence derived the following expression by substituting into (2.1.6) with K_C defined as in (2.1.5) and putting $Z_A = Z_B = 1$

$$\log_{10} K_A = \log_{10} K_C + k (1 - 2 A_Z) \quad (2.1.12)$$

A plot of $\log_{10} K_C$ versus A_Z is therefore linear with a slope of $2k$. This equation was found to hold true for Na-Li, -K, -Rb and -Cs exchange in zeolite A (44, 105) (see table 2).

The ratio of activity coefficients, Γ , can in some cases be determined by ion selective electrodes (59) but usually the equations of Glueckauf (107) are used to calculate Γ despite doubts about their accuracy (59, 78) particularly at higher concentrations.

If A is a divalent cation, B a univalent cation and X the common univalent anion then:-

$$\log_{10} \gamma_{AX}^{(BX)} = \log_{10} \gamma_{AX} - \frac{B_s}{4 + 2A_s} \left[\log_{10} \gamma_{AX} - \frac{8}{3} \log_{10} \gamma_{BX} - \frac{\frac{1}{3}}{1 + [TN(1 + \frac{1}{2}A_s)]^{-\frac{1}{2}}} \right] \quad (2.1.13)$$

$$\log_{10} \gamma_{BX}^{(AX)} = \log_{10} \gamma_{BX} - \frac{A_s}{8 + 4A_s} \left[8 \log_{10} \gamma_{BX} - 4.5 \log_{10} \gamma_{AX} - \frac{\frac{1}{2}}{1 + [TN(1 + \frac{1}{2}A_s)]^{-\frac{1}{2}}} \right]$$

where γ_{AX}, γ_{BX} are the mean activity coefficients of pure solution of AX and BX respectively at the same ionic strength as the mixture being considered.

The mean activity coefficients are given from the individual ion activity coefficients by :-

$$\gamma_{AX} = (\gamma_A^{Z_X} \cdot \gamma_X^{Z_A})^{1/(Z_A + Z_X)} \quad (2.1.14)$$

and the γ_{AX}, γ_{BX} values are found in tables (108) or calculated by extended Debye-Huckel equations (109).

$\gamma_{AX}^{(BX)}$, $\gamma_{BX}^{(AX)}$ are the calculated mean activity coefficients of AX and BX in the mixture of AX plus BX and are related to the individual ion activity coefficients in the mixture by eqn (2.1.14). For the case considered Γ is therefore given by:-

$$\Gamma = \frac{(\gamma_{BX}^{(AX)})^4}{3(\gamma_{AX}^{(BX)})} \quad (2.1.15)$$

A linear fit is then taken of Γ as a function of A_s , that is:-

$$\Gamma = a + bA_s \quad (2.1.16)$$

for use in the following calculations (see table 3).

If A and B are both univalent cations then Glueckauf's equations (107) give Γ as a constant,

$$\Gamma = \frac{\gamma_{BX}}{\gamma_{AX}} \quad (2.1.17)$$

given by the mean activity coefficients in the pure solutions of AX and BX at the ionic strength considered.

From these equations it is possible to construct an isotherm for any total normality if K_c and Γ are known. For a given A_z value K_c is calculated and then for A divalent, B and X univalent,

$$f(A_s) = bA_s^3 + (a - 2b)A_s^2 + (b - 2a - Q \cdot AA)A_s + a = 0$$

$$\text{where } AA = \frac{K_c \cdot B_z^2}{A_z} \quad (2.1.18)$$

This is solved by Newton-Raphson iteration to yield the required A_s value.

For A and B univalent,

$$f(A_s) = A_s (AA + \Gamma) - \Gamma = 0 \quad (2.1.19)$$

$$\text{where } AA = \frac{K_c \cdot B_z}{A_z}$$

It should be noted that for uni-univalent exchange the isotherm is independent of total normality apart from a small variation in the value of Γ .

The above equations are used to calculate a value of A_s from a given A_z value. The reverse process is slightly more difficult as K_c has to be calculated from an estimate of A_z .

The following is then solved by Newton-Raphson iteration:

$$f(A_z) = \frac{K_c (1 - A_z)^{Z_A}}{BB} - A_z^{Z_B} = 0 \quad (2.1.20)$$

$$\text{where } BB = \frac{\Gamma \cdot (1 - A_s)^{Z_A}}{Q \cdot A_s^{Z_B}}$$

to yield the value of A_z . It must be noted that at every iteration a better estimate to A_z is found and a better estimate of K_c is then calculated.

TABLE 2Values of K_c used.

$$\text{For } \log_{10} K_c = b_0 + b_1 A_z + b_2 A_z^2 + b_3 A_z^3 \quad (59, 78)$$

System	b_0	b_1	b_2	b_3
Na-Ca, 25°C	2,83	-6,03	11,5	-9.11
Na-Mg, 25°C	1,46	-2,66	-6,34	5,08

$$\text{For } \log_{10} K_c = (\log K_a - k) + 2k A_z \quad (44, 105)$$

System	$\log K_a - k$	$2k$
Na-Li	-0,74	-0,42
Na-K	0,105	-0,41
Na-Rb	0,20	-1,40
Na-Cs	0,85	-4,60

TABLE 3Values of activity coefficient ratio, Γ , used for $\Gamma = a + b A_s$.

System	TN	a	b
Na-Li	$3,4 \cdot 10^{-3}$	0,999	0
Na-K	$3,4 \cdot 10^{-3}$	1,000	0
Na-Rb	$3,4 \cdot 10^{-3}$	1,000	0
Na-Cs	$3,4 \cdot 10^{-3}$	1,001	0
Na-unival	$1,0 \cdot 10^{-2}$	1,000	0
Na-Ca	$3,4 \cdot 10^{-3}$	1,081	0,3913
Na-Mg	$3,9 \cdot 10^{-3}$	1,062	0,208

2.2 KINETICS OF EXCHANGE

The kinetics of ion exchange are not dependent upon the actual exchange in the zeolite cages, which is very fast, but are instead dependent upon the diffusion of the cations. The diffusion of cations occurs within the Nernstian layer around the zeolite and within the zeolite itself. If the rate is dependent upon the former the process is termed film kinetics and if it is dependent upon the latter the process is termed particle kinetics.

Different rate laws apply to the two determining rates with the half time in film kinetics proportional to the particle radius and inversely proportional to solution concentration whereas that of particle kinetics is proportional to the square of the particle radius and independent of solution concentration. Studies of Na-Ca and Na-Mg exchange in Zeolite A (110) have shown that for small particles ($< 5,9 \mu\text{m}$), low solution concentrations and high selectivity for incoming ion, film kinetics are favoured, particularly during initial exchange.

The present studies, however, mainly use larger particles and will be dominated by particle kinetics. The kinetics will therefore be considered in terms of cation diffusion within the zeolite particles as in previous studies (91-94, 99).

Diffusion in any material is described by Fick's first law:-

$$J = - \bar{D} \text{ grad } \bar{C} \quad (2.2.1)$$

where J is the rate of diffusion, $\bar{C}$ the concentration of the diffusing component in the material and $\bar{D}$ the variable or differential diffusion coefficient. This law states that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient normal to the section (111).

Fick further developed this theory to give the diffusion equation:-

$$\frac{\partial \bar{C}}{\partial t} = \text{div} (\bar{D} \text{grad } \bar{C}) \quad (2.2.2)$$

For diffusion in one dimension this equation may be written as:-

$$\frac{\partial \bar{C}}{\partial t} = \frac{\partial}{\partial x} (\bar{D} \frac{\partial \bar{C}}{\partial x}) \quad (2.2.3)$$

and if the diffusion coefficient is constant (or integral, $\bar{D}$) further simplifies to:-

$$\frac{\partial \bar{C}}{\partial t} = \bar{D} \frac{\partial^2 \bar{C}}{\partial x^2} \quad (2.2.4)$$

For radial diffusion in a sphere the diffusion equation simplifies to the above form and for an infinite bath, that is for the case where the concentration of the outer bath remains constant during exchanges, the solution is (112):-

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{\bar{D} n^2 \pi^2 t}{r_0^2} \right) \quad (2.2.5)$$

where M_t/M_∞ (or F) is the degree of exchange and r_0 the particle radius.

For the similar boundary conditions but with cubic particles with sides $2a_0$ (as is the case with zeolite A) the solution is:-

$$\frac{M_t}{M_\infty} = 1 - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{512}{\pi^6} \left\{ \frac{\exp \left[-\frac{\pi^2 \bar{D} t}{4a^2} \cdot S \right]}{T} \right\} \quad (2.2.6)$$

where $S = (2l-1)^2 + (2m-1)^2 + (2n-1)^2$

and $T = (2l-1)^2 \cdot (2m-1)^2 \cdot (2n-1)^2$

These equations have been evaluated by computer and Langerwall and Zemen (113) published tables of $\tau (\equiv \bar{D}t/x^2, x = r_0 \text{ or } a_0)$ versus M_t/M_∞ for various crystal shapes.

It should be noted that a plot of M_t/M_∞ versus $\sqrt{t}$ (plot) is initially linear and that from eqns (2.2.5, .6) it can be shown that this initial slope is given by:-

$$\text{Slope} = \frac{6}{x} \cdot \left(\frac{\bar{D}t}{\pi} \right)^{1/2} \quad (2.2.7)$$

so that an initial average value of the diffusion coefficient may be calculated.

Since $\bar{D}$ is an average value a value of $\bar{D}$ should be calculated which when inserted into eqn. (2.2.5) or (2.2.6) gives M_t/M_∞ , t pairs which match the experimentally determined points as closely as possible. This curve fitting is carried out by determining the area, I , above the experimental M_t/M_∞ versus t curve.

The area above an M_t/M_∞ versus time plot has a finite value such that:-

$$\text{Area, } I = \int_0^\infty \left[1 - \frac{M_t}{M_\infty} \right] dt \quad (2.2.8)$$

For spherical particles it is found that:

$$I = \frac{6r_0^2}{\pi \bar{D}} \sum_{n=1}^{\infty} \frac{1}{n^4}$$

hence:-

$$\frac{\bar{D}}{r_0^2} = \frac{1}{15I} \quad (2.2.9)$$

For a cube:-

$$I = \frac{4a^2}{D\pi^2} \cdot \frac{512}{\pi^6} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{S \cdot T}$$

S and T as above.

A computer program gave:-

$$\sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{S \cdot T} = 0,37377$$

$$\text{hence : } \frac{\bar{D}}{a_0^2} = \frac{1}{12,396I} \quad (2.2.10)$$

A value of $\bar{D}$ can hence be calculated.

These equations were first applied to isotopic exchange and can be applied to ion exchange when no change in total volume occurs in which case the diffusion coefficients of the two ions are equal, (114).

The above equations assume an infinite bath but the experiments carried out in this work used a finite bath. In this case the variation in the outer solution leads to a non-constant concentration gradient at the solution particle interface. This gives the additional boundary condition (115, 116):-

$$\frac{\partial \bar{C}}{\partial t} = - \frac{3w\bar{D}}{r_0} \frac{\partial \bar{C}}{\partial r} \quad (2.2.11)$$

where w is the "dimensionless parameter of the change in the border concentration". , or mathematically (116):

$$w = \frac{M_z}{M_s} \left(\frac{\partial \bar{C}}{\partial C} \right)_{r=r_0} \quad (2.2.12)$$

where M_z , M_s is the capacity in equivalents of the zeolite and solution

respectively and C is the concentration of the diffusing component in the solution. For the purposes of ion exchange the parameters $\bar{C}$ and C are replaced by A_z and A_s and $\partial A_z / \partial A_s$ is the slope of the relevant isotherm at the solution corresponding to the degree of exchange being considered. The solution for this boundary condition is (115):-

$$\frac{M_t}{M_\infty} = 1 - \sum_{j=1}^{\infty} \frac{\exp(-S_j^2 \tau)}{\left\{ 1,5w + \frac{S_j^2}{6(w+1)} \right\}} \quad (A)$$

where the S_j are the successive positive roots of the transcendental equation:-

$$\frac{S}{3w} + \frac{1}{S} - \cot S = 0$$

such that $j\pi < S_j < j\pi + \pi/2$

This equation is not suitable for evaluating diffusion coefficients because of the summations necessary and (117, 118) Wolf et al published a set of approximations together with their range of applicability (119), see Fig.6.

Two of these equations were derived by approximating equation (A):-

$$\frac{M_t}{M_\infty} = \frac{w+1}{w} \left[1 - \frac{\alpha \cdot \phi(\alpha\sqrt{\tau}) - \beta \cdot \phi(\beta\sqrt{\tau})}{\alpha - \beta} \right] \quad (B)$$

where: $\phi(\eta) = \exp(\eta^2) \cdot (1 + \operatorname{erf} \eta)$

and $\operatorname{erf} \eta$ is the error function,

$$\operatorname{erf} \eta = \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-\xi^2} d\xi$$

α and β are the roots of the quadratic equation:-

$$\frac{x^2}{3w} + x - 1 = 0$$

such that: $\alpha < 0 < \beta$

also:

$$F = (a + 3) \sum_{j=1}^{\infty} (-1)^{j+1} \cdot H_j \tau^{j/2} \quad (C)$$

where $a = 3w$ and the first four polynomials H_j are:-

$$H_1 = 2/\sqrt{\pi}$$

$$H_2 = a + 1$$

$$H_3 = \frac{4}{3\sqrt{\pi}} a(a + 2)$$

$$H_4 = \frac{1}{2}a(a^2 + 3a + 1)$$

Wolf et al recommended a special procedure for $w < 0,1$. A correction factor R is used to give the correct value of τ from a value (τ_B) calculated using the solution to the diffusion equation (2.2.5) due to Boyd.

$$\sqrt{Dt}/a_0^2 = \tau = \tau_B/R \quad (D)$$

τ_B can be calculated using simple approximations of equation (2.2.5) (120)

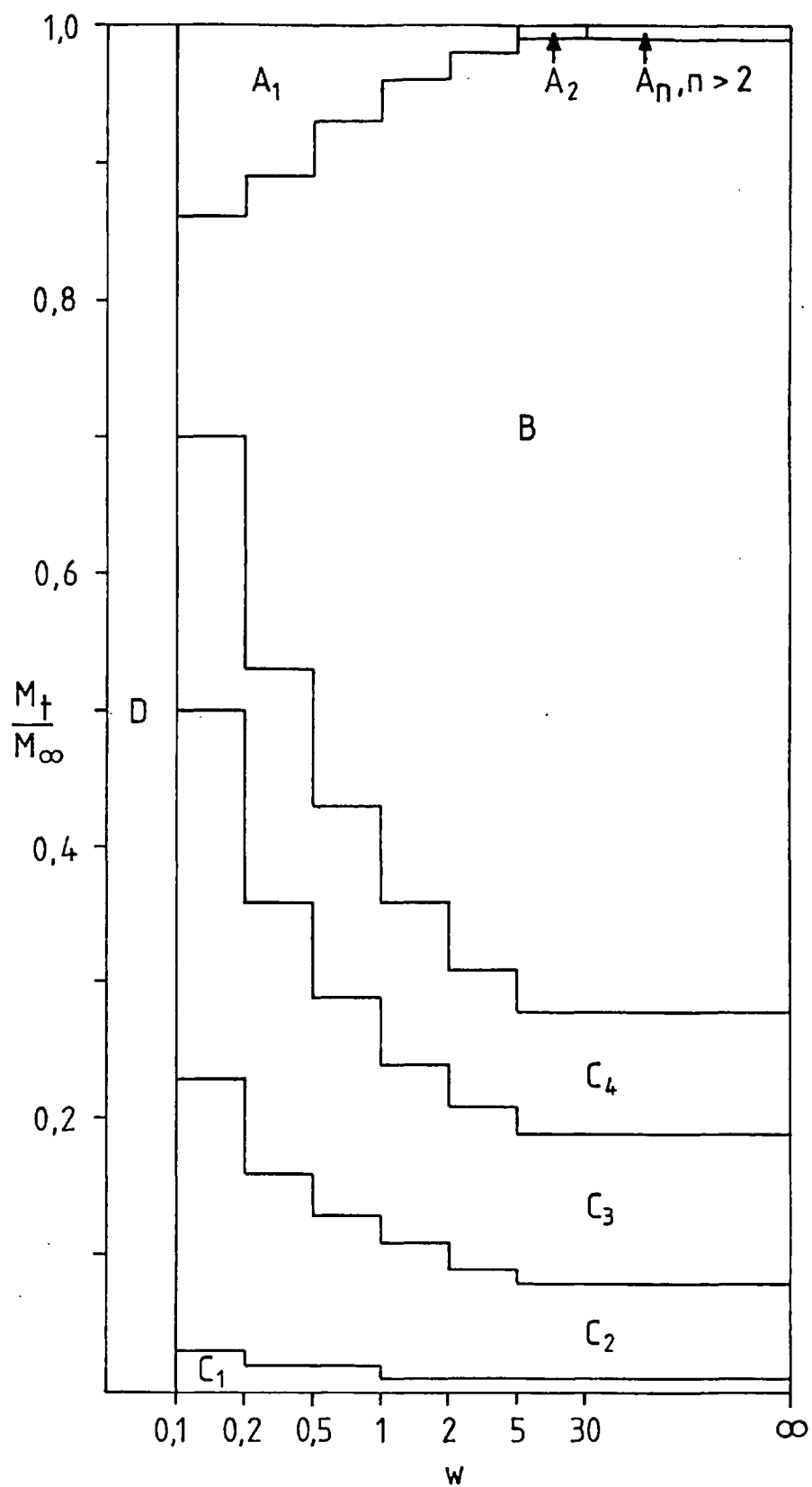
$$\tau_B = \frac{\pi}{36} F^2 \quad 0 \leq F \leq 0,003 \quad (2.2.13a)$$

$$\tau_B = \frac{1}{\pi} \left(1 - \sqrt{1 - \frac{\pi}{3} F}\right)^2 \quad 0,003 \leq F \leq 0,887 \quad (2.2.13b)$$

$$\tau_B = \frac{\ln 10}{\pi^2} \left[\log \frac{6}{\pi^2} - \log (1 - F) \right] \quad 0,887 < F \leq 1,000 \quad (2.2.13c)$$

Figure 6.

Equations used in EXCHANG.



A diagram showing the variation in R with $F(\equiv M_t/M_\infty)$ and w was included (119), see fig.7, as were three equations:-

$$R = (1 + w)^2 - 1,2wF [w + 0,79 + F(0,5w + 0,2)] \quad 0 < F < 0,80 \quad (R1)$$

$$R = 1 + w(1 - 0,4w) \cdot (2,93 - 1,6F) \quad 0,80 < F \leq 0,95 \quad (R2)$$

$$R = 1 + (1 - 0,46w) \cdot \left[0,608 - \frac{0,226}{\log(1 - F) + 0,216} \right] \quad (R3)$$

$$0,95 < F < 1,00$$

Wolf et al stated that if the change in the differential diffusion coefficient $\bar{D}$ was not too large then the diffusion coefficient calculated, $\tilde{D}$, is then approximately the average for all $\bar{D}$ values found between $F = 0$ and $F = F_t$ where F_t is the F value at time t.

Mathematically:-

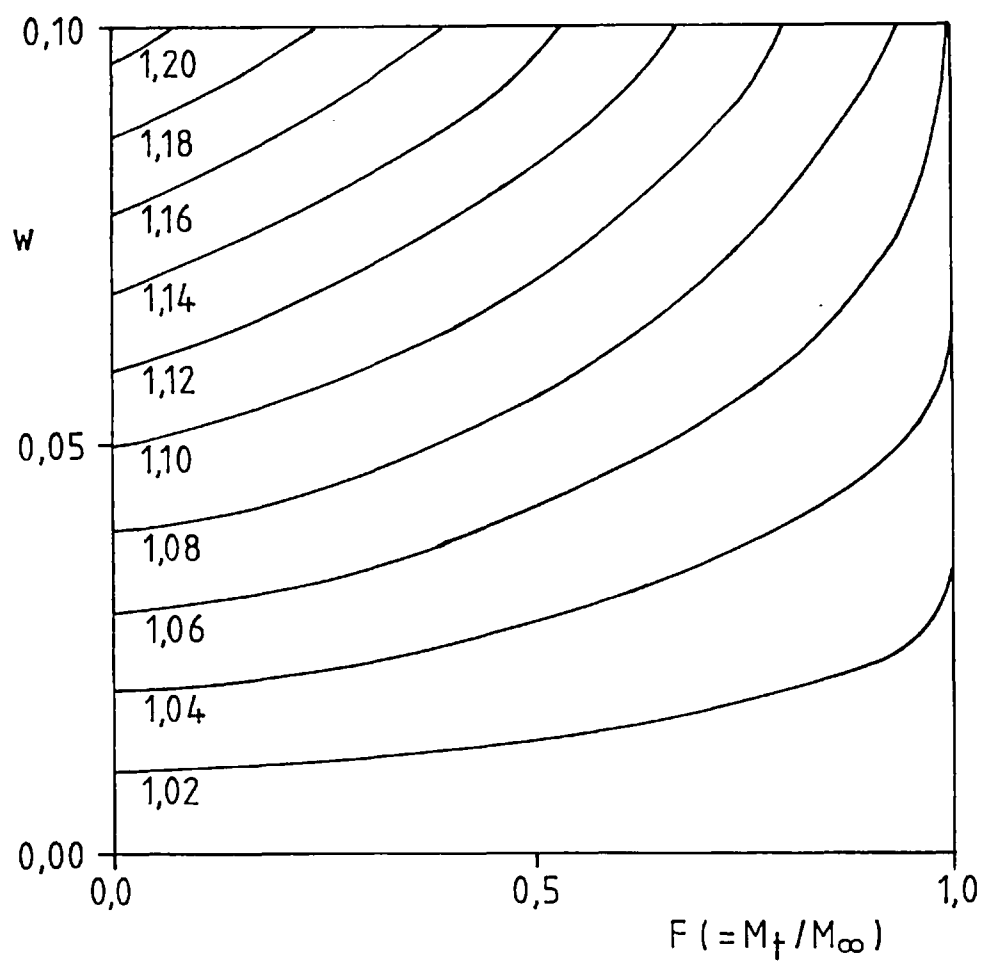
$$\log \tilde{D} = \frac{1}{F_t} \int_0^{F_t} \log \bar{D} dF \quad (2.2.14)$$

The $\tilde{D}$ values calculated therefore vary with F and show the variation of exchange rate corrected for the concentration gradient at the particle-solution interface (w factor). If the values of $\tilde{D}$ are extrapolated to $F = 0$ then $\tilde{D}_0 = \bar{D}_0$ and hence values of $\bar{D}$ may be calculated. It has been found, however, that such an extrapolation has a large uncertainty because of the time response of the ion selective electrodes used to measure the rate of exchange. $\bar{D}$ values were not therefore calculated.

A program, EXCHANG, was written to calculate diffusion coefficients using the above equations and a modification of the method of Wolf et al (121).

Figure 7.

Values of correction factor R for
calculation of τ using equation D



2.3 PROGRAM EXCHANG

The program is written in the version of FORTRAN 77 used at the University of London (FTN5) and is run on the CDC Cyber 174 and CDC 6500 at Imperial College. The computation of diffusion coefficients for fifty M_t/M_∞ , t pairs requires approximately one second of central processor time.

The binary version of the program and the data file to be used are obtained and the National Algorithms Library is called up (see page 53). The program is then executed and asks the user to select one of five options.:-

1. To use M_t/M_∞ , t pairs from the datafile and calculate diffusion coefficients for an ideal isotherm (w constant) and for the actual isotherm.
2. To read M_t/M_∞ , t and w from the datafile in cases where w can only be determined graphically from the isotherm.
3. To read M_t/M_∞ , t and w from the terminal allowing the user to test the effects of the three variables on the diffusion coefficients.

Options 2 and 3 have the further option of using a constant w for cases where the isotherm is unknown.

4. To read M_t/M_∞ , t pairs from the terminal and calculate diffusion coefficients for two w values as in option 1.
5. Calculates values of equivalent fraction of ingoing cation in the solution of (A_s) from fraction in zeolite (A_z); that is calculates isotherm for A_s values read from the terminal.

For example for option 1 the reply to the prompt would be "YNNNN". On the basis of the option selected the computer then prompts

for further data:-

RATIO OF EQUIVS IN ZEOLITE TO THOSE IN SOLUTION:

$$\left(= \frac{M_z}{M_s} \right)$$

CHARGES OF IN- AND OUT- GOING IONS - ie cation charges.

TOTAL NORM., A AND B (FROM GAMMA = A + B * AS)

ie TN, a and b - see eqns (2.1.7, 16)

BØ, B1, B2, B3? FROM

LOG KC = BØ + B1. AZ + B2. AZ **2 + B3. AZ **3

- see eqn (2.1.10)

INITIAL AND FINAL AZ, INITIAL AS (PERCENT)

- self explanatory, initial A_s is usually 100%,

ie solution contains only ingoing cation.

HALF CUBE LENGTH = a₀

The computer then prints headings for the results tables and for option 5 calculates A_s from A_z (2.1.18, 19) (subroutine CALCAS) then recalculates A_z from A_s (2.1.20) (subroutine CALCAZ) as a double check.

For the other options the computer proceeds to the main part of the program and for options 1 and 4 calculates the value of w corresponding to the solution composition using subroutine CALCAZ to calculate A_z values for A_s and A_s + 10⁻⁴ and hence find a good approximation to $\partial A_z / \partial A_s$.

The program then selects the w value to be used (the value calculated above or w constant) and then selects the equation

(A, B, C, D) needed to calculate τ from the F and w value using Fig. 6. Eqn - C1 is equation C with one term, eqn - C2 is with two terms etc.

For $w < 0,1$, that is eqn D the value of τ can be calculated directly but for the other equations an iterative method is used to arrive at the correct value of τ .

First an approximate τ is calculated using an extension of eqn. D. The extension is based on a table of R values (DATA RR) which cover the range $F = 0,01$ to $0,99$ and $w = 0,1$ to 10^6 . The correct R value is found by interpolating linearly for F and interpolating w^2 . For $w > 10^6$ and $F > 0,99$ the value of R is roughly extrapolated.

From the first τ value a value of F is calculated using the selected equation and a second τ value calculated from the slope, ρ , of the F versus τ plot, Fig. 8, for the correct w value (subroutine SLOPE).

$$\rho = \frac{dF}{d \log \tau} \quad (2.3.1)$$

Subroutine SLOPE uses eqn D as above to give an approximation to ρ .

The second τ value is then given by (120):-

$$\sqrt{\tau_2} = \sqrt{\tau_1} \cdot 10^{\frac{\rho}{2} (F - F_1)c} \quad (2.3.2)$$

where F is the actual F value, F_1 the value calculated from τ_1 and $c = 1, 2$.

A new F value, F_2 , is then calculated from τ_2 then the program calculates new τ values from (121):

$$\sqrt{\tau}_n = 0,9 \left[\frac{(F - F_{n-1})\sqrt{\tau}_{n-2} + (F_{n-2} - F)\sqrt{\tau}_{n-1}}{F_{n-2} - F_{n-1}} \right] + 0,1\sqrt{\tau}_{n-1} \quad (2.3.3)$$

and calculates an estimated F value which is compared with the actual F value. The process stops when the two agree to within 10^{-4} . The diffusion coefficient is then calculated and corrected by a factor K_1 which is tabulated in a DATA statement at the beginning of the program (122). The equation assume a spherical particle form and K_1 corrects to a cubical form using the effect of particle form on τ values calculated for an infinite bath (2.2.5,.6).

SPECIAL FEATURES

In the main routine $F > 0,99$ and $w > 30$ the data is rejected as unsuitable for calculation. During the calculations if the first or second estimate of F (F_1 or F_2) is $> 1,0$ the program terminates. If the difference between any two subsequent estimates is $< 10^{-100}$ the program goes on to the next F, T values to prevent division by zero. In subroutine EQNA the values of $S_j(SN)$ calculated are checked to ensure that they are in the correct range (see Equation A). These precautions are taken to ensure that the iteration converges and that the program does not run away.

For the calculation of τ using equation B the value of $\phi(x) = \exp(x^2) \cdot (1 + \operatorname{erf} x)$ is required. For $x > -10$ the NAG function S15ADF is used to give $\operatorname{erfc}(-x)$ ($= 1 - \operatorname{erf}(-x)$) and $\phi(x)$ is then given by:-

$$\phi(x) = \exp(x^2) \cdot \operatorname{erfc}(-x) \quad (2.3.4)$$

For $x < -10$ $\phi(x)$ is given by an asymptotic series where $X = |x|$:-

$$\phi(x) = \frac{1}{X\sqrt{\pi}} \left(1 + \sum_{n=1}^{n=x^2-0,5} \frac{(-1)^n 1.3 \dots (2n-1)}{2^n x^{2n}} \right) \quad (2.3.5)$$

This procedure was used because the error function tends to +1 for $x > 4$ and tends to -1 for $x < -4$.

Format of Datafile

1st Row

Number of data points, NPTS, presented in columns 11 to 13 as an integer.

2nd Row

Half cube length of particles, RM, presented in columns 11 to 18 with the format E8,2, e.g. $6\mu\text{m}$ 0,60E-05.

3rd and 4th Row

The third row is blank and the fourth row has the headings for the data i.e. F in column 3, T/S in columns 13 to 15 and W in column 25 if w values included in file.

5th to (4+NPTS) Row

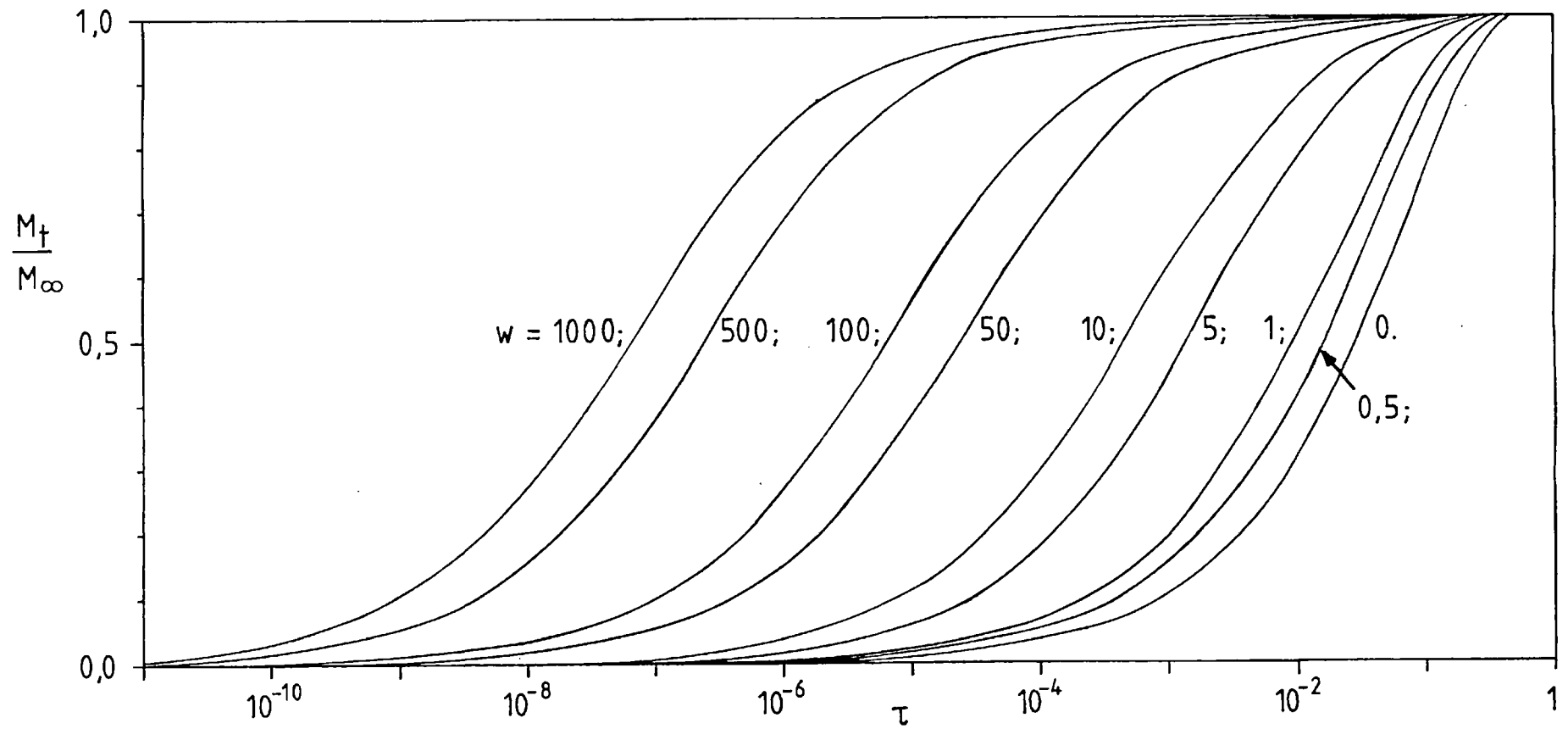
The data is presented with F in columns 1 to 6, format F6,4, T (in seconds) in columns 9 to 18, format F10,1, and when required w in columns 21 to 28, format E8,2 (see above example).

After the data particulars of the data may be entered e.g. date, system, without interfering with the data file operation.

Figure 8.

Variation of M_t/M_∞ with τ for various values of w .

See S. Paterson, Figure 1 (115).



** PROCEDURE FILE (PEXCHAN) USES BINARY FILE (BEXCHAN), **
 ** INITIATE WITH COMMAND -PEXCHAN(DATA=DSYSTEM). **

GET,BEXCHAN
 GET,DATA
 PRESENT(NAG8F)
 LIBRARY(NAG8F)
 BEXCHAN(DATA,INPUT,OUTPUT)

** TYPICAL DATA FILE - DSYSTEM. **

019
 0.63E-05

F	T/S	W
0.2430	15.0	0.10E+01
0.3430	30.0	0.92E+00
0.4190	45.0	0.86E+00
0.4850	60.0	0.82E+00
0.5400	75.0	0.79E+00
0.5960	90.0	0.76E+00
0.6360	105.0	0.74E+00
0.6700	120.0	0.73E+00
0.7210	150.0	0.71E+00
0.7580	180.0	0.70E+00
0.7940	240.0	0.69E+00
0.8230	300.0	0.68E+00
0.8450	360.0	0.68E+00
0.8550	420.0	0.67E+00
0.8770	600.0	0.67E+00
0.9130	1200.0	0.66E+00
0.9300	1800.0	0.66E+00
0.9470	3600.0	0.65E+00
0.9600	7200.0	0.65E+00

NA-K EXCHANGE,TN=3.4E-3,ISOTHERM END
 POINT(0.53),MZ/MS=0.771.

```
1      PROGRAM EXCHANG(DEXCHAN,INPUT,OUTPUT,TAPE4=DEXCHAN,  
2      +      TAPE5=INPUT,TAPE6=OUTPUT)  
3      C      *****  
4      C      THIS PROGRAM EVALUATES THE DIFFUSION COEFFICIENT FOR A      *  
5      C      SYSTEM OF UNIFORM CUBICAL ION EXCHANGER PARTICLES GIVEN      *  
6      C      THE DEGREE OF EXCHANGE F AT TIME T(S).THE METHOD IS      *  
7      C      GIVEN IN:      *  
8      C      F.DANES AND F.WOLF,Z. PHYS.CHEMIE (LEIPZIG),252,      *  
9      C      1/2,15-32 (1973).      *  
10     C      *****  
11     REAL AZ1,AZA,AZB,AS1,ASA,ASB,ASINIT,AZINIT,AZEND,DIFF,  
12     +     DCCORR,DP,F,F1,F2,F3,K1(101),K1C,RF,RM,ROOTTAU,T,  
13     +     TAU1,TAU2,TAU3,TAU,W  
14     INTEGER I,IF,N,NPTS  
15     CHARACTER SELECT*6,CHOICE1*1,CHOICE2*1,CHOICE3*1,CHOICE4*1,  
16     +     CHOICE5*1,CHOICE6*1  
17     C      *****  
18     C      VALUES OF K1 FOR F = 0 TO 1.      *  
19     C      *****  
20     DATA(K1(I),I=1,101)/1.0000,1.0014,1.0029,1.0043,  
21     +1.0058,1.0073,1.0088,1.0103,1.0119,1.0134,  
22     +1.0150,1.0166,1.0182,1.020,1.021,1.023,1.025,  
23     +1.026,1.028,1.030,1.032,1.033,1.035,1.037,1.039,  
24     +1.040,1.042,1.044,1.046,1.048,1.050,1.051,1.053,  
25     +1.055,1.058,1.060,1.062,1.064,1.066,1.068,1.071,  
26     +1.072,1.075,1.078,1.080,1.082,1.085,1.087,1.089,  
27     +1.091,1.094,1.097,1.099,1.102,1.104,1.107,1.110,  
28     +1.113,1.116,1.119,1.122,1.125,1.128,1.131,1.134,  
29     +1.137,1.140,1.144,1.147,1.151,1.154,1.158,1.162,  
30     +1.165,1.169,1.173,1.177,1.180,1.185,1.189,1.193,  
31     +1.197,1.201,1.205,1.210,1.214,1.219,1.224,1.228,  
32     +1.232,1.238,1.243,1.248,1.252,1.257,1.263,1.269,  
33     +1.275,1.281,1.291,1.333/  
34     PRINT *, 'F,T FROM DATAFILE. 2 DIFFERENT W FROM SUBROUTINE ?'  
35     PRINT *, 'OR W FROM DATAFILE ?'  
36     PRINT *, 'OR F,T AND W FROM TERMINAL ?'  
37     PRINT *, 'OR 2 DIFFERENT W FROM SUBROUTINE ?'  
38     PRINT *, 'OR AS FROM AZ ? ( 5*Y/N )'  
39     READ(5,25)CHOICE1,CHOICE2,CHOICE3,CHOICE4,CHOICE5  
40     IF(CHOICE1.EQ.'Y'.OR.CHOICE4.EQ.'Y'.OR.CHOICE5.EQ.'Y')THEN  
41     PRINT *, 'RATIO OF EQUIVS IN ZEOLITE TO THOSE IN SOLUTION ?'
```

```
42      READ(5,*)RAZAS
43      WCONST=RAZAS
44      PRINT *, 'CHARGES OF IN- AND OUT-GOING IONS?'
45      READ(5,*)ZA,ZB
46      PRINT *, 'TOTAL NORM., A AND B (FROM GAMMA=A+B*AS)?'
47      READ(5,*)TN,A,B
48      PRINT *, 'B0,B1,B2,B3? FROM'
49      PRINT *, 'LOGKC=B0+B1.AZ+B2.AZ**2+B3.AZ**3'
50      READ(5,*)B0,B1,B2,B3
51      Q=((ZB**ZA)*(TN**(ZB-ZA)))/(ZA**ZB)
52      ENDIF
53      IF(CHOICE1.EQ.'Y'.OR.CHOICE2.EQ.'Y')THEN
54          READ(4,100)NPTS
55          READ(4,200)RM
56      ENDIF
57      IF(CHOICE2.EQ.'Y'.OR.CHOICE3.EQ.'Y')THEN
58          PRINT *, 'CONSTANT W ? (Y/N) '
59          READ(5,325)CHOICE6
60          IF(CHOICE6.EQ.'Y')THEN
61              PRINT *, 'W VALUE ?'
62              READ(5,*)WCONST
63          ENDIF
64      ENDIF
65      PRINT *, 'INITIAL AND FINAL AZ , INITIAL AS (PERCENT) ?'
66      READ(5,*)AZINIT,AZEND,ASINIT
67      IF(CHOICE3.EQ.'Y'.OR.CHOICE4.EQ.'Y')THEN
68          PRINT *, 'HALF CUBE LENGTH ?'
69          READ(5,*)RM
70          PRINT *, 'VALUES OF F,T ( AND W ) ?'
71      ENDIF
72      IF(CHOICE5.EQ.'N')THEN
73          IF(CHOICE2.EQ.'Y'.OR.CHOICE3.EQ.'Y')THEN
74              WRITE(6,300)
75          ELSE
76              WRITE(6,310)
77          ENDIF
78      ENDIF
79      I=1
80      350 CONTINUE
81      IF(CHOICE1.EQ.'Y')THEN
82          READ(4,400)F,T
```

```

83      ELSEIF(CHOICE2.EQ.'Y')THEN
84          READ(4,450)F,T,WVAL
85      ELSEIF(CHOICE3.EQ.'Y')THEN
86          READ(5,*)F,T,WVAL
87      ELSEIF(CHOICE4.EQ.'Y')THEN
88          READ(5,*)F,T
89      ELSE
90          PRINT *, 'VALUES OF F ?'
91          WRITE(6,460)
92      ENDIF
93      IF(CHOICE5.EQ.'Y')THEN
94          C *****
95          C THIS ROUTINE CALCULATES POINTS ON THE ISOTHERM
96          C CORRESPONDING TO THE ZEOLITE COMPOSITION WHEN CHOICE5 IS
97          C SELECTED.
98          C *****
99          C 470
100         CONTINUE
101         READ(5,*)F
102         AZ1=(AZINIT+F*(AZEND-AZINIT))*0.01
103         CALL CALCAS(AZ1,Q,ZA,ZB,A,B,Q,B0,B1,B2,B3,AS1)
104         CALL CALCAZ(AS1,ZA,ZB,A,B,Q,B0,B1,B2,B3,AZCALC)
105         WRITE(6,480)AZ1,AS1,AZCALC
106         GO TO 470
107     ELSE
108         AZ1=(AZINIT+F*(AZEND-AZINIT))*0.01
109     ENDIF
110     IF(CHOICE2.NE.'Y'.AND.CHOICE3.NE.'Y')THEN
111         C *****
112         C IF CHOICE1 OR CHOICE4 IS SELECTED THE FOLLOWING ROUTINE
113         C CALCULATES POINTS ON THE ISOTHERM CORRESPONDING TO THE
114         C SOLUTION COMPOSITION AND HENCE FINDS THE DIMENSIONLESS
115         C BORDER CONCENTRATION PARAMETER W WHICH IS GIVEN BY;
116         C
117         C W=AZ/AS * D(M(Z))/D(M(S))
118         C ACCORDING TO PILCHOWSKI ET AL.
119         C *****
120         ASA=0.01*(ASINIT-(RAZAS*F*(AZEND-AZINIT)))
121         IF(ASA.LE.0.0)THEN
122             PRINT *, 'AS= ',ASA,' JOB ABORTED'
123             STOP
124         ENDIF
125         CALL CALCAZ(ASA,ZA,ZB,A,B,Q,B0,B1,B2,B3,AZA)

```

```

124      ASB=ASA+1.0E-4
125      CALL CALCAZ(ASB,ZA,ZB,A,B,Q,B0,B1,B2,B3,AZB)
126      WAS=RAZAS*(AZB-AZA)*1.0E4
127      ENDIF
128      C *****
129      C VALUE OF W TO BE USED IS SELECTED.
130      C *****
131      K=1
132      IF(CHOICE1.EQ.'Y'.OR.CHOICE4.EQ.'Y')K=2
133      DO 10,I2=1,K
134          IF(I2.EQ.1)THEN
135              W=WCONST
136              IF(CHOICE3.EQ.'Y'.AND.CHOICE6.NE.'Y')W=WVAL
137              IF(CHOICE2.EQ.'Y'.AND.CHOICE6.NE.'Y')W=WVAL
138          ELSE
139              W=WAS
140          ENDIF
141      C *****
142      C FROM VALUES OF F AND W DECIDE ON EQUATION (AN,B,CN,D)
143      C TO BE USED TO FIND TAU AND HENCE THE DIFFUSION COEFF..
144      C *****
145      IF(W.LT.0.1)THEN
146          SELECT='EQN-D'
147      ELSEIF(F.LE.0.01.OR.(F.LE.0.02.AND.W.LE.1.)).
148      + OR.(F.LE.0.03.AND.W.LE.0.2))THEN
149          SELECT='EQN-C1'
150      ELSEIF(F.LE.0.08.OR.(F.LE.0.09.AND.W.LE.5.)).
151      + OR.(F.LE.0.11.AND.W.LE.2.)).
152      + OR.(F.LE.0.13.AND.W.LE.1.)).
153      + OR.(F.LE.0.16.AND.W.LE.0.5)).
154      + OR.(F.LE.0.23.AND.W.LE.0.2))THEN
155          SELECT='EQN-C2'
156      ELSEIF(F.LE.0.19.OR.(F.LE.0.21.AND.W.LE.5.)).
157      + OR.(F.LE.0.24.AND.W.LE.2.)).
158      + OR.(F.LE.0.29.AND.W.LE.1.)).
159      + OR.(F.LE.0.36.AND.W.LE.0.5)).
160      + OR.(F.LE.0.50.AND.W.LE.0.2))THEN
161          SELECT='EQN-C3'
162      ELSEIF(F.LE.0.28.OR.(F.LE.0.3.AND.W.LE.5.)).
163      + OR.(F.LE.0.36.AND.W.LE.2.)).
164      + OR.(F.LE.0.43.AND.W.LE.1.)).

```

```

165      + DR.(F.LE.0.53.AND.W.LE.0.5).
166      + DR.(F.LE.0.70.AND.W.LE.0.2))THEN
167      SELECT='EQN-C4'
168      ELSEIF(F.LE.0.86.DR.(F.LE.0.89.AND.W.GT.0.2).
169      + DR.(F.LE.0.93.AND.W.GT.0.5).
170      + DR.(F.LE.0.96.AND.W.GT.1.)).
171      + DR.(F.LE.0.98.AND.W.GT.2.)).
172      + DR.(F.LE.0.99.AND.W.GT.5.))THEN
173      SELECT='EQN-B'
174      ELSEIF(F.LE.0.99.DR.(F.LT.0.999.AND.W.LE.30.))THEN
175      SELECT='EQN-A'
176      ELSE
177      PRINT *, 'F AND W OUTSIDE RANGE'
178      ENDIF
179      C *****
180      C IF W IS LESS THAN 0.1 THEN BOYD'S SOLUTION OF THE DIFFN *
181      C EQUATION WITH A CORRECTION FACTOR(R) IS USED(EQND), *
182      C OTHERWISE TRIAL AND ERROR(TAE) IS USED WITH ONE OF THE *
183      C EQUATIONS A TO C. *
184      C *****
185      IF(SELECT.EQ.'EQN-D')THEN
186      CALL EQND(F,W,TAU)
187      ELSE
188      C *****
189      C THE FIRST ESTIMATE FOR TAU IS FOUND DIRECTLY BY USING *
190      C EQND AND THE SECOND ESTIMATE IS FOUND FROM THE GRADIENT, *
191      C D(F)/D(LOGTAU), USING SLOPE WHICH USES EQND TO FIND *
192      C DELTA(F)/DELTA(LOGTAU) AS AN APPROXIMATION TO THE GRADIENT.*
193      C *****
194      CALL EQND(F,W,TAU1)
195      CALL FCALCN(W,TAU1,SELECT,F1)
196      IF(F1.GE.1.0)THEN
197      PRINT *, 'F1 =', F1, ' NO GOOD'
198      STOP
199      ENDIF
200      CALL SLOPE(F,W,P)
201      TAU2=(SQRT(TAU1)*10.0**((P*1.2*(F-F1))/2.0))**2
202      CALL FCALCN(W,TAU2,SELECT,F2)
203      IF(F2.GE.1.0)THEN
204      PRINT *, 'F2 =', F2, ' NO GOOD'
205      STOP

```

```

206          ENDIF
207          DIFF=100.0
208 20 CONTINUE
209          TAU3=(F-F2)*SQRT(TAU1)+(F1-F)*SQRT(TAU2)
210          ERROR=ABS(F1-F2)
211          IF(ERROR.LT.1.0E-100)THEN
212              PRINT *, 'F1-F2=', F1-F2, 'F1 =', F1, 'F =', F
213              PRINT *, 'TAU 1=', TAU1, 'TAU 2=', TAU2
214              I=I+1
215              IF(I.LE.NPTS)GO TO 350
216              STOP
217          ENDIF
218          TAU3=((0.9*TAU3)/(F1-F2)+0.1*SQRT(TAU1))**2
219          CALL FCALCN(W,TAU3,SELECT,F3)
220          TAU1=TAU2
221          TAU2=TAU3
222          F1=F2
223          F2=F3
224          DIFF=ABS((TAU1-TAU2)/TAU2)
225          IF(DIFF.GT.1.0E-4)GO TO 20
226          ROOTTAU=(F-F1)*SQRT(TAU1)+(F2-F)*SQRT(TAU2)
227          TAU=(ROOTTAU/(F2-F1))**2
228          ENDIF
229 C *****
230 C D FOR SPHERES(DP) IS CALCULATED THEN CORRECTED(K1C) TO *
231 C GIVE A VALUE OF D FOR CUBES(DCORR). *
232 C *****
233          DP=RM**2*TAU/T
234          IF=INT(100.0*F)
235          RF=100.0*F-FLOAT(IF)
236          K1C=(K1(IF+2)-K1(IF+1))*RF+K1(IF+1)
237          DCORR=K1C*DP
238          IF(CHOICE2.EQ.'Y'.OR.CHOICE3.EQ.'Y')THEN
239              WRITE(6,500)AZ1,F,W,DCORR,TAU
240              IF(CHOICE3.EQ.'Y')GO TO 350
241              I=I+1
242              IF(CHOICE2.EQ.'Y'.AND.I.LE.NPTS)GO TO 350
243              STOP
244          ENDIF
245          IF(I2.EQ.1)THEN
246              DCNST=DCORR

```

```
247         ELSE
248             DAS=DCORR
249         ENDIF
250     10 CONTINUE
251     WRITE(6,600)AZ1,F,WCONST,DCONST,WAS,DAS
252     IF(CHOICE4.EQ.'Y')GO TO 350
253     I=I+1
254     IF(I.LE.NPTS)GO TO 350
255     STOP
256     25 FORMAT(5A)
257     100 FORMAT(10X,I3)
258     200 FORMAT(10X,E8.2//)
259     300 FORMAT(/12X,'AZ',7X,'EXP. F',11X,'W',10X,'DIFFN. COEFF',9X,
260         + 'TAU')
261     310 FORMAT(/1X,'AZ',7X,'F',8X,'WCONST',4X,'DCONST',
262         + 7X,'WAS',7X,'DAS')
263     325 FORMAT(A)
264     400 FORMAT(F6.4,2X,F10.1)
265     450 FORMAT(F6.4,2X,F10.1,2X,E8.2)
266     460 FORMAT(3X,'AZ',6X,'ASCALC',6X,'AZCALC')
267     480 FORMAT(F7.5,3X,F7.5,5X,F7.5)
268     500 FORMAT(/10X,F5.3,6X,F5.3,7X,E10.3,6X,E10.3,6X,E10.3)
269     600 FORMAT(/F5.3,3X,F5.3,3X,4E10.3)
270     END
```

```

1      SUBROUTINE CALCAS(AZ,Q,ZA,ZB,A,B,BO,B1,B2,B3,AS)
2      *****
3      C      THIS SUBROUTINE CALCULATES AS FOR A GIVEN AZ USING
4      C      NEWTON-RAPHSON ITERATION TO SOLVE A POLYNOMIAL:
5      C      AO+A1AS+A2AS**2+A3AS**3=0.
6      C      *****
7      REAL LOGKC,AS,AZ
8      LOGKC=BO+AZ*(B1+AZ*(B2+B3*AZ))
9      RKC=10.0**LOGKC
10     AA=RKC*((1.0-AZ)**ZA)/(AZ**ZB)
11     AS=AZ
12     DIFF=10.0
13     110 CONTINUE
14         TEMP=A+B*AS
15         FAS=TEMP*((1.-AS)**ZA)-AA*Q*(AS**ZB)
16         FAS1=B*((1.-AS)**ZA)-AA*Q*ZB*(AS**(ZB-1.))
17         FAS1=FAS1-TEMP*ZA*((1.-AS)**(ZA-1.))
18         DIFF=ABS(FAS/FAS1)
19         AS=AS-FAS/FAS1
20     IF(DIFF.GT.1.0E-8)GO TO 110
21     RETURN
22     END

```

```

1      SUBROUTINE CALCAZ(AS,ZA,ZB,A,B,Q,BO,B1,B2,B3,AZ)
2      *****
3      C      THIS SUBROUTINE CALCULATES AZ FOR A GIVEN AS USING
4      C      NEWTON-RAPHSON ITERATION.
5      C      *****
6      REAL AS,AZ,KC
7      BB=((A+B*AS)*(1.-AS)**ZA)/(Q*AS**ZB)
8      AZ=AS
9      DIFFAZ=1.
10     210 CONTINUE
11         KC=10.**(BO+AZ*(B1+AZ*(B2+B3*AZ)))
12         DIFFKC=KC*ALOG(10.)*(B1+AZ*(2.*B2+3.*B3*AZ))
13         FAZ=KC*((1.-AZ)**ZA)/BB-AZ**ZB
14         FAZ1=DIFFKC*((1.-AZ)**ZA)/BB-KC*ZA*((1.-AZ)**(ZA-1.))/BB
15         FAZ1=FAZ1-ZB*(AZ**(ZB-1.))
16         DIFFAZ=ABS(FAZ/FAZ1)
17         AZ=AZ-FAZ/FAZ1
18     IF(DIFFAZ.GT.1.0E-8)GO TO 210
19     RETURN
20     END

```

```

SUBROUTINE EQND(F,W,TAU)

```

```

*****
THIS SUBROUTINE EVALUATES TAU FOR W LESS THAN 0.1, USING
BOYD'S SOLUTION OF THE DIFFUSION EQUATION TOGETHER WITH
A CORRECTION FACTOR, R; AND IS ALSO USED TO FIND THE 1ST
APPROXIMATION FOR THE TAE PROCESS.
*****

```

```

REAL RR(8,12), LGW, LGW1, LGW2

```

```

DATA((RR(IW,IF),IW=1,8),IF=1,12)/1.22,4.02,122.,1.03E4,1.01E6,

```

```

+ 1.00E8,1.00E10,1.00E12,
+1.20,3.77,109.5,9150.,8.97E5,8.95E7,8.95E9,8.95E11,
+1.18,3.58,97.7,8070.,7.90E5,7.88E7,7.88E9,7.88E11,
+1.17,3.35,85.9,6980.,6.83E5,6.81E7,6.81E9,6.81E11,
+1.16,3.13,73.9,5890.,5.75E5,5.74E7,5.73E9,5.73E11,
+1.15,2.90,61.8,4790.,4.66E5,4.65E7,4.65E9,4.65E11,
+1.13,2.66,49.6,3690.,3.57E5,3.56E7,3.56E9,3.56E11,
+1.12,2.41,37.4,2600.,2.50E5,2.49E7,2.49E9,2.49E11,
+1.11,2.15,25.3,1550.,1.46E5,1.45E7,1.45E9,1.45E11,
+1.09,1.88,13.6,611.,5.78E4,5.64E6,5.86E8,5.44E10,
+1.08,1.74,8.25,230.,1.85E4,1.81E6,1.80E8,1.80E10,
+1.07,1.59,4.15,30.7,1.46E3,1.50E5,1.50E7,1.50E9/
PI=3.141592654
IF(F.LE.0.003)THEN
  TAUBOYD=PI*F**2/36.0
ELSEIF(F.LE.0.877)THEN
  TAUBOYD=(1-SQRT(1.0-PI*F/3.0))**2/PI
ELSE
  TAUBOYD=(2.302585093/(PI**2))*(ALOG10(6.0/(PI**2))
+ -ALOG10(1.0-F))
ENDIF
IF(W.EQ.0.0)THEN
  R=1.0
ELSEIF(W.LT.0.1.DR.F.LT.0.01)THEN
  IF(F.LE.0.80)THEN
    R=(1.0+W)**2-1.2*W*F*(W+0.79+F*(0.5*W+0.2))
  ELSEIF(F.LE.0.95)THEN
    R=1.0+W*(1.0-0.4*W)*(2.93-1.6*F)
  ELSE
    R=1.0+(1.0-0.46*W)*(0.608-(0.226/(ALOG10(1.0-F)+0.216)))
ENDIF
ELSE

```

```

42 LGW=ALOG10(W)
43 IF(F.LE.0.99)THEN
44   IF(F.LT.0.95)THEN
45     IF1=INT(F*10.0+1.0)
46     F1=FLOAT(IF1-1)/10.0
47     IF(F1.EQ.0.0)F1=0.01
48     F2=FLOAT(IF1)/10.0
49     IF(F2.EQ.1.0)F2=0.95
50   ELSE
51     IF1=11
52     F1=0.95
53     F2=0.99
54   ENDIF
55   IF2=IF1+1
56 ENDIF
57 IF(LGW.LE.6.0)THEN
58   IW1=INT(LGW+2.0)
59   LGW1=IW1-2.0
60   W1=10.0**LGW1
61   IW2=IW1+1
62   LGW2=LGW1+1
63   W2=10.0**LGW2
64 ENDIF
65 IF(LGW.LE.6.0.AND.F.LE.0.99)THEN
66   RLOWW=(RR(IW1,IF2)-RR(IW1,IF1))*(F-F1)/(F2-F1)+RR(IW1,IF1)
67   RHIGHW=(RR(IW2,IF2)-RR(IW2,IF1))*(F-F1)/(F2-F1)+RR(IW2,IF1)
68   R=(RHIGHW-RLOWW)*((W**2.0)-(W1**2.0))/((W2**2.0)-(W1**2.0))
69   + RLOWW
70 ENDIF
71 IF(LGW.GT.6.0)THEN
72   RF=(RR(8,IF2)-RR(8,IF1))*(F-F1)/(F2-F1)+RR(8,IF1)
73   R=RF*10.0**((2*(LGW-6.0))
74 ENDIF
75 IF(F.GT.0.99)THEN
76   RW=(RR(IW2,12)-RR(IW1,12))*((W**2.0)-(W1**2.0))/((W2**2.0)
77   -(W1**2.0))+RR(IW1,12)
78   + R*RW*10.0**((F-0.99)*50.0*LGW)
79 ENDIF
80 ENDIF
81 TAU=TAUBOYD/R
82 RETURN
83 END

```

SUBROUTINE SLOPE

73/174 OPT=1

FTN 5.1+552

PAGE 1

```
1      SUBROUTINE SLOPE(F,W,P)
2      C *****
3      C THIS SUBROUTINE FINDS DELTA(F)/DELTA(LOGTAU) AS AN APPROX. *
4      C TO FIND D(F)/D(LOGTAU) IN ORDER TO FIND A SECOND APPROX. *
5      C TO TAU IN THE TAE PROCESS. *
6      C *****
7      CALL EQND(F,W,TAUA)
8      RLGTUA=ALOG10(TAUA)
9      G=F+1.0E-3
10     CALL EQND(G,W,TAUB)
11     RLGTAUB=ALOG10(TAUB)
12     P=(1.0E-3)/(RLGTAUB-RLGTUA)
13     RETURN
14     END
```

SUBROUTINE FCALCN

73/174 OPT=1

FTN 5.1+552

PAGE 1

```
1      SUBROUTINE FCALCN(W,TAU,SELECT,FN)
2      C *****
3      C THIS SUBROUTINE ENSURES THAT THE CORRECT EQUATION IS USED *
4      C TO DETERMINE FN IN THE TAE PROCESS. *
5      C *****
6      CHARACTER SELECT*6
7      IF(SELECT.EQ.'EQN-A ')THEN
8          CALL EQNA(W,TAU,FN)
9      ELSEIF(SELECT.EQ.'EQN-B ')THEN
10         CALL EQNB(W,TAU,FN)
11      ELSE
12         CALL EQNC(W,TAU,SELECT,FN)
13      ENDIF
14      RETURN
15      END
```

```

1      SUBROUTINE EQNA(W,TAU,FN)
2      *****
3      C THIS SUBROUTINE USES EQUATION AN TO EVALUATE FN. *
4      C *****
5      PI=3.141592654
6      FN=1.0
7      N=0
8      TN=1.0
9      310 CONTINUE
10         N=N+1
11         RN=FLOAT(N)
12         RP=RN*PI
13         IF(W.EQ.0.0)THEN
14             SN=RP
15         ELSE
16             IF(RN/W.GE.1.5)THEN
17                 SN=RP+(3.0*W)/RP-(9.0*W**2)*(W+2.0)/(RP**3)
18                 + (27.0*W**3*(W+2.0)**2)/(RP**5)
19             ELSE
20                 SN=(0.5*W/(2.5+W)+RN)*PI
21             ENDIF
22             320 CONTINUE
23             A=1.0
24             330 CONTINUE
25                 H1=SN/(3.0*W)+1.0/SN-(COS(SN)/SIN(SN))
26                 H2=1.0/(3.0*W)-1.0/(SN**2)+1.0/(SIN(SN)**2)
27                 SN=SN-H1/H2
28                 A=ABS(H1/(SN*H2))
29                 IF(A.GT.1.0E-4)GO TO 330
30                 RU=RP+PI/2.0
31                 IF(SN.LT.RP)THEN
32                     SN=SN+0.5
33                     GO TO 320
34                 ELSEIF(SN.GT.RU)THEN
35                     SN=SN-0.5
36                     GO TO 320
37                 ENDIF
38             ENDIF
39             TN=(EXP(-TAU*SN**2))/(1.5*W+SN**2/(6*(W+1.0)))
40             FN=FN-TN
41             TN=TN/FN
42             IF(TN.GT.1.0E-2)GO TO 310
43             RETURN
44             END

```

```
1      SUBROUTINE EQNB(W,TAU,FN)
2      REAL ALPHA,BETA,FN,PHIA,PHIB,RALPHA,RBETA,S15ADF,U,W
3      C *****
4      C THIS SUBROUTINE USES EQUATION B TO EVALUATE FN. *
5      C *****
6      ALPHA=1.5*W*(-1.0+SQRT(1.0+4.0/(3.0*W)))
7      BETA=1.5*W*(-1.0-SQRT(1.0+4.0/(3.0*W)))
8      RALPHA=ALPHA*SQRT(TAU)
9      RBETA=BETA*SQRT(TAU)
10     CALL PHI(RALPHA,PHIA)
11     CALL PHI(RBETA,PHIB)
12     U=(ALPHA*PHIA-BETA*PHIB)/(ALPHA-BETA)
13     FN=(1.0-U)*(W+1.0)/W
14     RETURN
15     END
```

```
1      SUBROUTINE PHI(X,PHIX)
2      C *****
3      C THIS SUBROUTINE EVALUATES THE FUNCTION PHI WHICH IS *
4      C EXP(X**2)*(1+ERF(X)) FOR USE IN SUBROUTINE EQNB. *
5      C NAG FUNCTION S15ADF IS USED TO GIVE ERF(X) (=1-ERF(X)) *
6      C FOR X>-10 AND AN ASYMPTOTIC SERIES IS USED TO GIVE PHI(X) *
7      C DIRECTLY FOR X<-10. *
8      C *****
9      IF(X.LT.-10.0)THEN
10         X=ABS(X)
11         PHIX=1.0
12         RMULT=1.0
13         NUMBER=INT(X**2-0.5)
14         DO 410,I=1,NUMBER
15             TERM=((1.0/(2.0*X**2))**I)*RMULT
16             PHIX=PHIX+TERM
17             RMULT=RMULT*FLOAT(2*(I+1)-1)
18             TERM=ABS(TERM/PHIX)
19             IF(TERM.LT.1.0E-10)GO TO 420
20         410 CONTINUE
21         420 CONTINUE
22         PHIX=PHIX/(X*1.772453851)
23     ELSE
24         X1=-X
25         ERF(X)=S15ADF(X1,1)
26         PHIX=EXP(X**2+ALOG(ERF(X)))
27     ENDIF
28     RETURN
29     END
```

```

1      SUBROUTINE EQNC(W,TAU,SELECT,FN)
2      *****
3      C THIS SUBROUTINE USES EQUATION CN TO EVALUATE FN.
4      C *****
5      CHARACTER SELECT*6
6      PI=3.141592654
7      SQPI=SQRT(PI)
8      T=0.0
9      A=3*W
10     T=(2.0*SQRT(TAU))/SQPI
11     IF(SELECT.EQ.'EQN-C2'.OR.SELECT.EQ.'EQN-C3'.OR.
12 +    SELECT.EQ.'EQN-C4') THEN
13         T=T-TAU*(A+1.0)
14     ENDIF
15     IF(SELECT.EQ.'EQN-C3'.OR.SELECT.EQ.'EQN-C4') THEN
16         T=T+(4.0*A*(A+2.0)*TAU**1.5)/(3*SQPI)
17     ENDIF
18     IF(SELECT.EQ.'EQN-C4') THEN
19         T=T-0.5*A*(A**2+3.0*A+1.0)*TAU**2
20     ENDIF
21     FN=(A+3.0)*T
22     RETURN
23     *****
24     C FOR MORE DETAILED DERIVATIONS OF EQUATIONS SEE:
25     C K.PILCHOWSKI,F.DANES AND F.WOLF,
26     C KOLLOID Z.,Z. POLYM,225,6-15 (1968).
27     C K.PILCHOWSKI,F.DANES AND F.WOLF,
28     C KOLLOID Z.,Z. POLYM,230,328-36 (1969).
29     C F.DANES,K.PILCHOWSKI AND F.WOLF,
30     C BER. BUNSENGES. PHYS. CHEM.,73,99-106 (1969).
31     C F.DANES,K.PILCHOWSKI AND F.WOLF,
32     C BER. BUNSENGES. PHYS. CHEM.,74,250-6 (1970).
33     C *****
34     END

```


2.4 THEORY OF BROOKE AND REES (97,98)

The theory of Brooke and Rees is a modification of the theory of Helfferich and Plesset (123, 124) which describes ion exchange kinetics in terms of the self diffusion of the exchanging cations. The self diffusion of a cation is measured by adding a sample of zeolite, containing a radioactive isotope of the cation, to a solution containing cation and measuring the rate of increase of the solution radioactivity. If the $\sqrt{t}$ plot is linear then for small times (98):

$$\frac{Q_t}{Q_\infty} = \frac{Q_0}{Q_0 - Q_\infty} 2a\rho \sqrt{\frac{D^* t}{\pi}} \quad (2.4.1)$$

where Q_0 is the amount of radioactive tracer cation in the solution at time, $t=0$, Q_t and Q_∞ are the same at time t and at equilibrium. ρ is the density of the zeolite and A is its surface area. D^* is the self diffusion coefficient of the cation which is needed for calculations using Brooke and Rees's theory.

Self diffusion coefficients for a number of cations in zeolite A have been determined by Dyer et al (45,80,81, 88, 89) and for non-linear $\sqrt{t}$ plots they have used (80) for small values of τ (125):

$$\frac{M_t}{M_\infty} = (1 + \lambda) \left[(6\sqrt{\tau/\lambda\sqrt{\pi}}) - (1 + \lambda/3) \cdot 9\tau/\lambda^2 + (1 + 2\lambda/3) \cdot 36\tau^{3/2}/\lambda^3\sqrt{\pi} + \dots \right] \quad (2.4.2)$$

where $\tau = D^* t/r^2$, r being the equivalent particle radius which is given by finding the surface area of the particle form used and calculating the radius of a spherical particle with the same surface area.

$\lambda = VM/vm$ where V and v are the volumes of the solution and zeolite respectively and M and m are the respective molarities of non active cations.

Dyer et al have also used (81) the equation from which the above expansion was derived (for larger τ values):

$$\frac{M_t}{M_\infty} = (1 + \lambda) \left[\frac{\gamma_1}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left(\frac{3\gamma_1}{\lambda} \sqrt{\tau} \right) + \frac{\gamma_2}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left(-\frac{3\gamma_2}{\lambda} \sqrt{\tau} \right) \right] - \lambda \quad (2.4.3)$$

where $\gamma_1 = \frac{1}{2}(\sqrt{(1 + 4\lambda/3)} + 1)$ and $\gamma_2 = \gamma_1 - 1$

and $e \operatorname{erfc}(x) = \exp(x^2) \cdot \operatorname{erfc}(x)$

Self diffusion coefficients measured at different temperatures are related by the Arrhenius equation.

$$D^* = D_0 \exp(-E_a/RT) \quad (2.4.4)$$

From these self diffusion coefficients (Table 4) an inter-diffusion coefficient can be calculated (97) from:-

$$D_{AB} = \frac{D_A^* D_B^*}{(D_A^* - D_B^*) C_A + D_B^*} \cdot \frac{\partial \ln a_A}{\partial \ln C_A} \quad (2.4.5)$$

provided that $Z_A = Z_B$, that is the exchanging cations have the same valency. C_A is the mole fraction of ion A in the zeolite and a_A is its activity in the zeolite. D_A^* and D_B^* are the self diffusion coefficients of A and B respectively. Ion A is initially in the zeolite.

In some cases the activity term ($\partial \ln a_A / \partial \ln C_A = g$) gives a discontinuity in D_{AB} which is unfavourable for use in the unmodified diffusion equation and this was overcome by using a transform due to Crank (126) such that a parameter S is defined.

$$S = \int_0^{C_A} D_{AB} dC_A / \int_0^1 D_{AB} dC_A \quad (2.4.6)$$

That is S is the average D_{AB} up to the point considered divided by the overall average D_{AB} . The diffusion equation for a sphere is then transformed to:

$$\frac{\partial C_A}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \int_0^1 D_{AB} dC_A \frac{\partial S}{\partial r} \right)$$

which simplifies to:

$$\frac{\partial C_A}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial S}{\partial \rho} \right) \quad (2.4.7)$$

where $\tau = \left(\int_0^1 D_{AB} dC_A \right) \cdot t / r_0^2$ and $\rho = r / r_0$

where r is the distance from the centre of a spherical zeolite particle with radius r_0 . This can be solved using the finite difference scheme:-

$$C_A(\rho, \tau + \Delta\tau) = C_A(\rho, \tau) + [\Delta\tau / (\Delta\rho)^2] \cdot [R_{++} S_{++} - R_{--} S_{--}] \quad (2.4.8)$$

where:

$$R_{++} = (\rho + \frac{1}{2}\Delta\rho)^2 / \rho^2; S_{++} = S(\rho + \Delta\rho, \tau) - S(\rho, \tau)$$

and

$$R_{--} = (\rho - \frac{1}{2}\Delta\rho)^2 / \rho^2; S_{--} = S(\rho, \tau) - S(\rho - \Delta\rho, \tau)$$

A program which uses this scheme to give C_A values for increasing τ (and hence t) was written by Brooke (97, 98) and was used to compare with experimental values.

The values of g were calculated using the Kielland coefficient, k (eqn 2.1.11), Table 2). It can be shown that (106):

$$g = 2k C_A (C_A - 1) + 1 \quad (2.4.9)$$

since:-

$$\frac{\partial \ln a_A}{\partial \ln C_A} = 1 + C_A \frac{\partial \ln f_A}{\partial C_A}$$

Table 4

Self diffusion parameters from Dyer et al (45, 80, 81, 88, 89).

Self diffusion coefficients hence calculated using eqn. (2.4.4).

Ionic Species	$D_0/\text{m}^2\text{s}^{-1}$	$E_a/\text{KJ mol}^{-1}$
K	$1 \cdot 10^{-10}$	26,5
Na	$4 \cdot 10^{-11}$	22,4
Rb	$6 \cdot 10^{-10}$	27,9
Cs	$5 \cdot 10^{-9}$	36,3
Mg	$7,00 \cdot 10^{-7}$	77
Ca	$4,75 \cdot 10^{-8}$	67,4
Sr	$7,40 \cdot 10^{-8}$	82,0
Ba	$1,59 \cdot 10^{-5}$	90,4

The univalent self exchange was measured in the temperature range 243 to 273K using a 1:1 ethanol/water mixture.

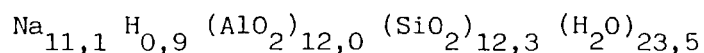
3. EXPERIMENTAL PROCEDURE

3.1 ZEOLITE A

Zeolite A was synthesised using the method of Charnell (127). A silicate solution consisting of precipitated silica (21g), sodium hydroxide (28g), triethanolamine (112g) and water (700cm³) and an aluminate solution consisting of sodium aluminate (80g), triethanolamine (112g) and water (700cm³) were left to "age" for 12 hours, filtered and then the aluminate solution was added to the silicate solution and the resulting gel was thoroughly mixed by stirring mechanically at room temperature for 12 hours. The gel was inserted into a plastic bottle and placed in an oven at 80°C. The crystallisation was complete after three weeks and yielded well formed zeolite A crystals. The crystals were washed with 10⁻³ M NMe₄OH (pH 10) to remove excess sodium. The high pH was used to limit hydrolysis. The crystals were dried, ground and equilibrated over saturated NaCl.

An X-ray diffraction pattern was taken and gave lines all of which could be designated to zeolite A. Scanning electron micrographs of the crystals (Fig.9) showed them to be mainly well formed cubes with some intergrown crystals and a small amount of gel. The micrographs were used to give the size distribution shown in Fig.10 which yielded a weighted half cube length of 6,3 µm.

The crystals were analysed chemically and gave an average pseudo unit cell formula of:-



The hydrogen probably entered the zeolite during washing and no attempt was made to remove it by treatment with sodium as it was considered that further hydrolysis could occur.

Figure 9

Electron micrographs of Charnell synthesised zeolite A.
Magnification of prints x1000.

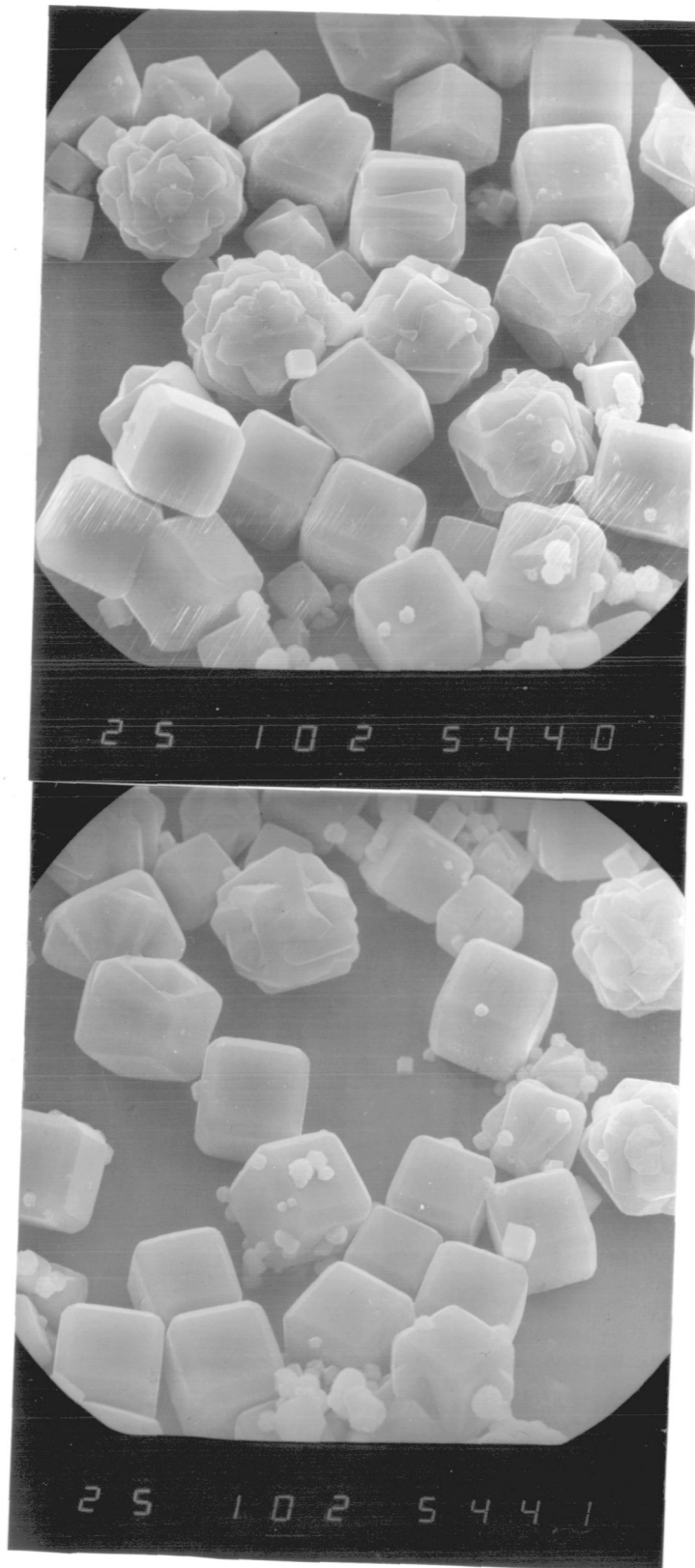
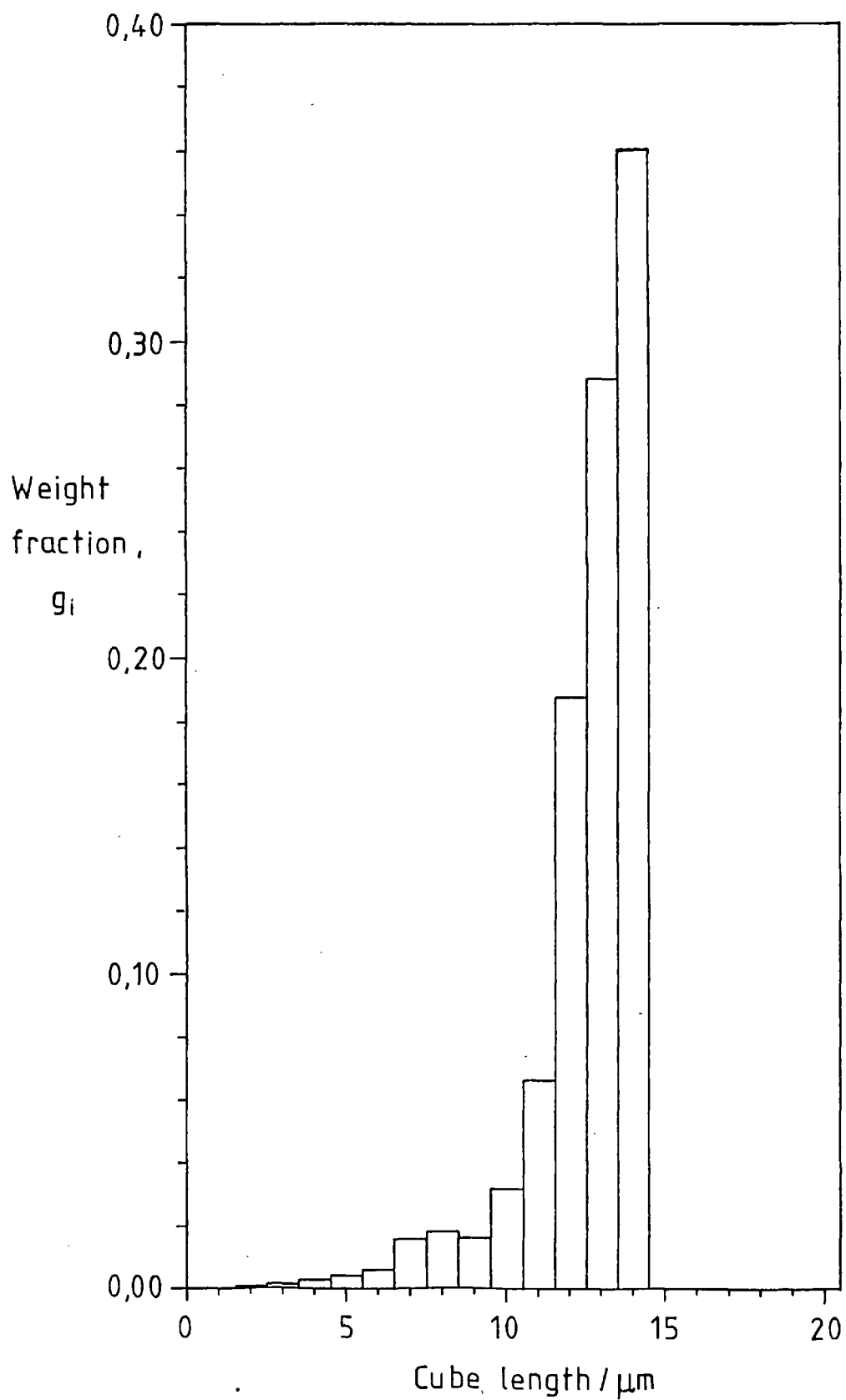
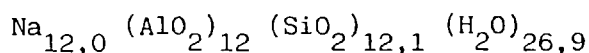


Figure 10.

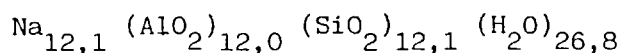
Size distribution of Charnell 4A;
weight fraction.



Other zeolite A samples used were a sample prepared by S.A.I. Barri using the Charnell method with an average half cube length of 9 μm and formula of:-



and a commercial sample made by Laporte, batch number RD6/78, average half cube length of 2,6 μm and formula of:-



The water content was determined using a Stanton Redcroft 760 thermo-gravimetric balance. The sample of $\sim 10\text{mg}$ was heated to 700°C at $10^\circ\text{C}/\text{min}$ and held at 700°C until constant weight was achieved.

Further analyses was carried out as described below on 0,2g samples dissolved in 2N HCl (50cm^3) and diluted to 250cm^3 . In cases where little zeolite was available 60mg was dissolved in 2N HCl (20cm^3) and diluted to 100cm^3 .

Analysis for sodium was carried out by flame emission using a Perkin Elmer 280 or 290 Atomic Absorption Spectrometer at 589,0 nm using an air-acetylene flame. Aluminium was determined by a back titration method (128). To 100cm^3 dissolved zeolite 10% sulphosalicylic acid ($1-2\text{cm}^3$) and 0,05N EDTA (10cm^3) were added. The solution was heated to boiling then 5% ammonia was added until a pH electrode gave pH 4,5 to 5. Acetate buffer (pH 4,8, $10-20\text{cm}^3$) was then added and the solution allowed to cool. The solution was backtitrated with 0,05N Iron (III) (Ammonium ferric sulphate) to determine the amount of uncomplexed EDTA and hence the amount complexed by the aluminium taking one cm^3 0,05N EDTA to be equivalent to 2,949mg AlO_2 .

The silica content by difference was found to be only 2% higher than ideality and this was the case with most samples. Due to its difficulty and comparative inaccuracy, silica analyses were carried out only in cases where the Si:Al ratio was anomalous and a large sample was available. An attempt was made to measure silicon by plasma spectroscopy but the results were low due to incomplete silica solubilisation in 2N HCl. The method was however, successful for analysing the silica lost from a zeolite in the course of an equilibrium or kinetic experiment. The plasma spectrometer had a silica burner, which would have dissolved if a strong acid had been used to dissolve the silica in the zeolite.

In a few cases silica was analysed gravimetrically (59). A sample of zeolite (0,5g) was dissolved in 1:1 HCl (100cm³) and evaporated to dryness over a period of some hours. 10cm³ 1:1 HCl was added and also evaporated to dryness. This latter step was repeated and the residue was then dried in an oven at 100°C (90 mins). 1:1 HCl (20cm³) was then added and the solution heated for 20 minutes, with stirring to ensure solubilization. Distilled water (100cm³) was added and heating continued for 30 minutes. The silica was then filtered off through ashless paper. The silica was washed with 1:10 HCl then distilled water until no Cl⁻ was detected to silver nitrate additions. The filter paper was folded and put in a weighed platinum crucible. The filtrate was evaporated and the process repeated to give a second filter paper which was added to the first. The whole was combusted at red heat to give a white residue of constant weight. The silica was dissolved in a few drops of 1:4 H₂SO₄ and HF (10cm³) was heated until no more H₂SO₄ fumes were evolved. This process was repeated twice with less HF (5cm³) and then the crucible was heated to red heat. The crucible was weighed and the difference in weight before and after HF treatment gave the silica content.

During the subsequent kinetic measurements some of the end solutions and zeolite samples were analysed to detect any hydrolysis. In these cases, caesium was analysed by flame emission at its secondary line (455,5 nm) with 1000ppm K background for the samples and standards; potassium was analysed by flame emission (766,5 nm) with 1000ppm Li background, calcium by atomic absorption (422,7 nm) with 1% v/v 1N Sr Cl_2 background and magnesium by atomic absorption (285,2 nm) with 1% v/v 1N La Cl_3 background. All analyses used air-acetylene flames and the conditions were summarised in table 5.

Table 5

Analysis conditions using atomic absorption and flame emission.

Air-acetylene flame throughout:-

Element	Method	Wavelength/nm	Conc./ppm	Background
K	E	766,5	0 - 10	1000ppm Li
Na	E	589,0	0 - 5	-
Cs	E	455,5	0 - 120	1000ppm K
Mg	A	285,2	0 - 5	1% v/v 1N La Cl_3
Ca	A	422,7	0 - 10	1% v/v 1N Sr Cl_2

E = flame emission, A = atomic absorption.

Conc. = concentration range of samples (achieved by dilution as necessary).

3.2 KINETICS

The kinetics were determined by ion-selective electrode - reference electrode (EIL 1370) pairs connected to a pH meter (EIL 7030 and/or Orion 901). The EMF generated was recorded on a x,t chart recorder. Usually a sodium selective electrode (EIL 1048-400 or Orion 94-11) was used to monitor the increase in sodium concentration during exchange with the exchanging ion (counterion) initially in the solution

phase. The electrode EMF is strictly proportional to sodium activity which is affected by the counterion and thus the electrode response is to some extent dependent on the counterion concentration.

Calibrations were therefore made in mixed solutions corresponding to those encountered during ion exchange in order to relate the EMFs to the actual solution concentration.

The electrodes were first calibrated using $10^{-4}N$ NaCl plus $10^{-3}N$ NH_3 (for pH control) and adding NaCl to give five or six concentrations up to $10^{-2}N$ NaCl. EMFs were then measured in mixtures of sodium and counterion of the required total normality plus $10^{-3}M$ NMe_4OH (for pH, NMe_4^+ non exchangeable cation) going from 0 to 50% Na then 100 to 50% Na. The electrodes were then recalibrated in NaCl plus $10^{-3}N$ NH_3 .

If the initial calibration gave:-

$$E = E_O^i + S^i \log_{10} N_{Na^+} \quad (3.2.1)$$

and the final calibration t_f seconds later gave:-

$$E = E_O^f + S^f \log_{10} N_{Na^+} \quad (3.2.2)$$

then the EMF of a mixture measured at a time t after the initial calibration was taken as relating to the calibration:

$$E = E_O^i + (E_O^f - E_O^i) \cdot \frac{t}{t_f} + [S^i + (S^f - S^i) \frac{t}{t_f}] \log_{10} N_{Na^+} \quad (3.2.3)$$

where N_{Na^+} is the concentration of sodium in the initial and final calibrations and the "equivalent" concentration in the mixture.

The above equation assumes that any drift in slope and intercept of the calibration (S and E_O) occurs linearly with time. A value of

N_{Na^+} was hence calculated for each mixture and the initial calibration was then used to calculate EMFs corrected for drift, and hence give a calibration of the form:

$$E_{corr} = E_0^{mix} + S^{mix} \log N_{Na^+}^{mix} \quad (3.2.4)$$

where $N_{Na^+}^{mix}$ is the actual sodium concentration in the mixture.

This calibration could then be compared with the initial calibration to give:

$$\begin{aligned} S^{mix} &= S^i - \Delta S \\ E_0^{mix} &= E_0^i - \Delta E_0 \end{aligned} \quad (3.2.5)$$

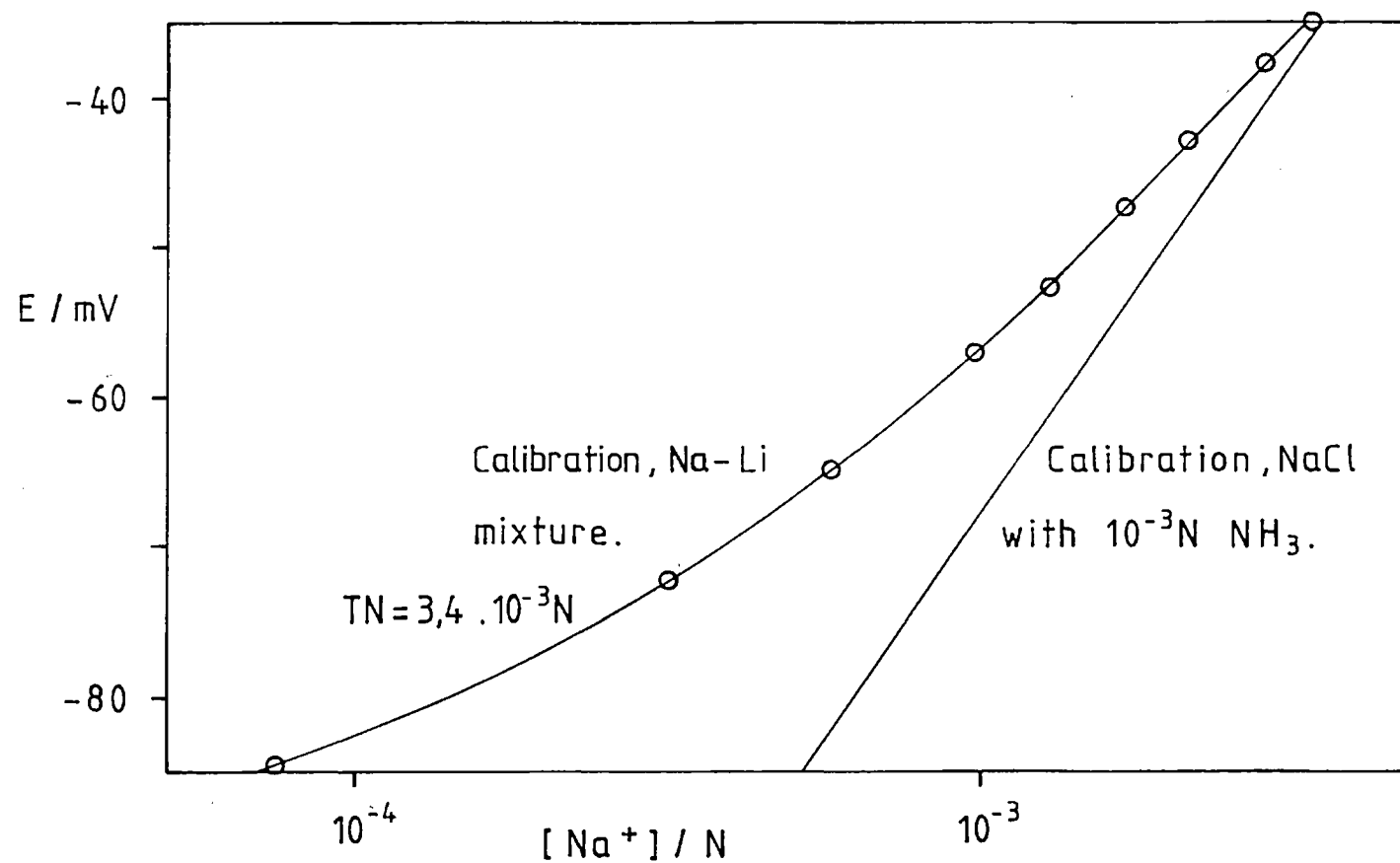
For each kinetic experiment a calibration with NaCl plus $10^{-3}N$ NH_3 was carried out before and after the experiment.

The EMFs were corrected for drift as described for the calibration in the mixture and the initial calibration relates to the calibration in the mixture by the previous relationship (3.2.5). Knowing the exchange capacity of the zeolite used, and assuming the amount of sodium released equals the counterion taken up, it is therefore possible to calculate the variation with time of the zeolite composition and of the fractional attainment of equilibrium (M_t/M_∞).

The calibration in the mixture was also used to derive the activity coefficient of the sodium ion in the mixture although the results in some cases suffered from the electrode displaying some selectivity for the counterion. Figure 11 shows a calibration in a sodium/lithium mixture and the curvature at lower concentrations is due to the sodium electrode responding to lithium.

Figure 11.

Electrode calibrations.



During some experiments involving calcium the Ca concentration was monitored using a calcium selective electrode (Radiometer F2112 Ca or Orion 93-20) and techniques similar to those described for sodium were used. During experiments to measure the hydrolysis of zeolite A the pH was monitored by pH electrode (Russell CTW).

In some cases sodium chloride ($10^{-5}N$) was added to the initial solution to bring the electrodes EMF onto the chart recorder's span, to give a stable baseline and to increase the response as the electrode takes some time to respond to a change of concentration from $10^{-6}N$ to $10^{-5}N$ which is a negligible part of the exchange kinetics.

Values of the sodium ion activity coefficient were calculated using the method of Kielland (129) whereby:-

$$\log_{10} \gamma_i = \frac{-0,5056 z_i^2 I^{1/2}}{1 + 10^8 r_i \cdot 0,3283 I^{1/2}} \quad (3.2.6)$$

where r_i is the effective diameter of the ion, z_i its charge, and I the ionic strength given by:-

$$I = \frac{1}{2} \sum 1,003 N_i |z_i|$$

where N_i is the solution normality. Table 6 gives the values of z_i and r_i and table 7 the ionic strength.

Table 6

Values of z_i and r_i used in equation 3.2.6

Ion	z_i	$10^8 r_i$
Na^+	1	4,2
Cl^-	-1	3,0
Mg^{2+}	2	7,4
Ca^{2+}	2	6,0

Table 7

Calculation of ionic strength.

System	I
NaCl	$1,003 \cdot N_{\text{Na}^+}$
CaCl_2	$1,504 \cdot N_{\text{Ca}^{2+}}$
$\text{NaCl} + \text{CaCl}_2$	$1,003 (N_{\text{Na}^+} + 1,5N_{\text{Ca}^{2+}})$
$\text{NaCl} + \text{MgCl}_2$	$1,003 (N_{\text{Na}^+} + 1,5N_{\text{Mg}^{2+}})$

N_i = Normality of ion

Values of γ_{Na^+} and γ_{Cl^-} were used to calculate mean activity coefficients (see Theory, eqn 2.1.14) and compared well with tabulated values (109).

For calcium and magnes-ium it was also possible to measure the activity coefficients and thus for systems involving Na, Ca and/or Mg an experimental relationship for Γ (see Theory, eqn 2.1.9) was used.

3.3 ELECTRODE USE AND MAINTENANCE

Sodium Selective Electrodes

The Orion 94-11 solid state electrode is a solid state electrode with a glass membrane. It requires a hydrogen concentration at least 1000 times lower than the sodium concentration, i.e. for 10^{-4} N NaCl the pH must be > 7 . The electrode gives 99% response in less than 1 minute for a concentration change from 10^{-4} N to 10^{-3} N although the response is slower at lower concentrations. After a period of use the response time increases and the electrode slope drops. To restore the electrode to its starting characteristics it is dipped in 0,1M $\text{NH}_4\text{F} \cdot \text{HF}$ for 1 minute then washed.

In some cases this treatment is insufficient and the membrane is polished by rotating the electrode against a wet abrasive strip provided by Orion. It should be noted that the electrode has a lifetime of only 6-12 months which is aggravated by abrasion due to the zeolite crystals. At the end of its lifetime the electrode becomes sluggish and loses its selectivity and cannot be restored by the previously mentioned methods.

The EIL 1048-400 electrode is a glass electrode and as such is considerably cheaper than the Orion 94-11. It requires similar operating conditions and responds slightly faster than the Orion (95% response in 10s). It is however more fragile and care must be taken not to damage the membrane. The electrode is restored to full use by dipping the electrode in 1M NaCl + 10^{-3} M NH_3 for 1 to 3 days followed by 1ppm NaCl + 10^{-3} M NH_3 for 7-21 days. At the end of its lifetime the electrode becomes sluggish and its electrode slope lowers although prolonged soaking in 1M NaCl may restore the electrode characteristics.

Calcium Selective Electrodes

The Radiometer F2112 Ca selective electrode is based on a replaceable plastic membrane with refillable inner solutions giving a degree of flexibility. It requires $\text{pH} > 7$ and gives 90% response to a change in concentration for 10^{-3}N to 10^{-4}N in about 1 minute. When the electrode becomes sluggish response is restored by soaking in 10^{-3}M CaCl_2 although in severe cases the electrode was dismantled, thoroughly cleaned and reassembled. Towards the end of its life the electrode slope dropped below 27mV and a new membrane was used.

The Orion 93-20 calcium selective electrode uses a replaceable sensing module and will work at lower pH with faster response than the Radiometer electrode. Response is restored by soaking the electrode in distilled water for 10 minutes then in 10^{-2}M CaCl_2 for more than 10 minutes. Once the electrode response dropped the module was replaced.

Reference Electrodes

The EIL 1370 reference electrode is a calomel reference with a 3.8M KCl salt bridge. The electrode is quite stable for ionic strengths greater than $\sim 5 \times 10^{-3}\text{M}$ but for lower concentrations there is a tendency for the electrode to be noisy due to blocking of the ceramic junction of the reference electrode. This can be unblocked by putting the electrode in boiling water for some hours, washing the electrode and replacing the salt bridge. This procedure will be successful in most cases although the performance varies between different reference electrodes. For best performance the salt bridge should not be allowed to become saturated and the ceramic plug should be kept wet. Eventually the calomel element degrades (the calomel and mercury layers interpenetrate) and the electrode will drift excessively and require replacement.

3.4 UNCERTAINTY IN RESULTS

The uncertainty in the results of a kinetics experiment is mainly dependent upon the accuracy with which the electrode EMF can be read during the experiment and the linearity of the calibration curves made before and after the experiment. Factors such as the accuracy of the weight of zeolite and volume and concentration and time are negligible compared with these electrode factors.

For a linear fit of the form:-

$$y = \alpha + \beta(x - \bar{x}) \quad (3.4.1)$$

where $\bar{x}$ = mean x value, the uncertainty of β for 100(1 - θ)% confidence is (130):

$$\Delta\beta = \pm [t_{(n-2)}(\theta/2)] \cdot \frac{S}{\sqrt{CS(x,x)}} \quad (3.4.2)$$

where $t_{(n-2)}(\theta/2)$ is the value of the t distribution for $n-2$ degrees of freedom (n data points) and the given confidence level, e.g. for 7 data points and 95% confidence, $t_{(n-2)}(\theta/2) = t_5(0,025) = 2,57$.

S^2 is an estimate of the standard deviation given by:-

$$S^2 = \frac{1}{n-2} \cdot \left\{ \sum_{i=1}^n (y_i - \bar{y})^2 - \frac{\left[\sum_{i=1}^n y_i (x_i - \bar{x}) \right]^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right\} \quad (3.4.3)$$

and $CS(x,x)$ is defined by:

$$CS(x,x) = \sum_{i=1}^n (x_i - \bar{x})^2 = \sum_{i=1}^n x_i^2 - \left(\sum_{i=1}^n x_i \right)^2 / n \quad (3.4.4)$$

The uncertainty of α for 100 (1 - θ)% confidence is:-

$$\Delta\alpha = \pm [t_{(n-2)} (\theta/2)] \cdot \frac{S}{\sqrt{n}} \quad (3.4.5)$$

From these equations it is possible to calculate the uncertainty in the slope (ΔS) and intercept (ΔE_0) of the electrode calibration.

The uncertainty in concentration is then given by:-

$$(\Delta N)^2 = \left(\frac{N}{S} \ln 10 \right)^2 \left\{ \Delta E^2 + \Delta E_0^2 + (\log_{10} N)^2 \Delta S^2 \right\} \quad (3.4.6)$$

where ΔE is the uncertainty in the measured EMF. The uncertainty in the M_t/M_∞ values is proportional to the uncertainty in N (ie ΔN).

Example

Calibration of EIL sodium selective plus reference electrode.

$[Na^+]/N$	$1,00 \cdot 10^{-4}$	$2,94 \cdot 10^{-4}$	$6,60 \cdot 10^{-4}$	$1,00 \cdot 10^{-3}$	$2,77 \cdot 10^{-3}$
EMF/mV	- 125,4	- 98,6	- 78,3	- 67,6	- 41,8

Regression factor, $R^2 = 0,99997$ and regression fit (HP41C programmable calculator) gives:-

$$E = 106,32 + 57,98 \log N_{Na^+}$$

For one standard deviation (= 68,3% confidence) uncertainties in E_0 and S are:-

$$\Delta E_0 = \pm 1,1 \text{ mV}$$

$$\Delta S = \pm 0,32 \text{ mV}$$

Taking the uncertainty in reading the electrode EMF during the run as $\pm 0,5 \text{ mV}$ then gives the following uncertainties:-

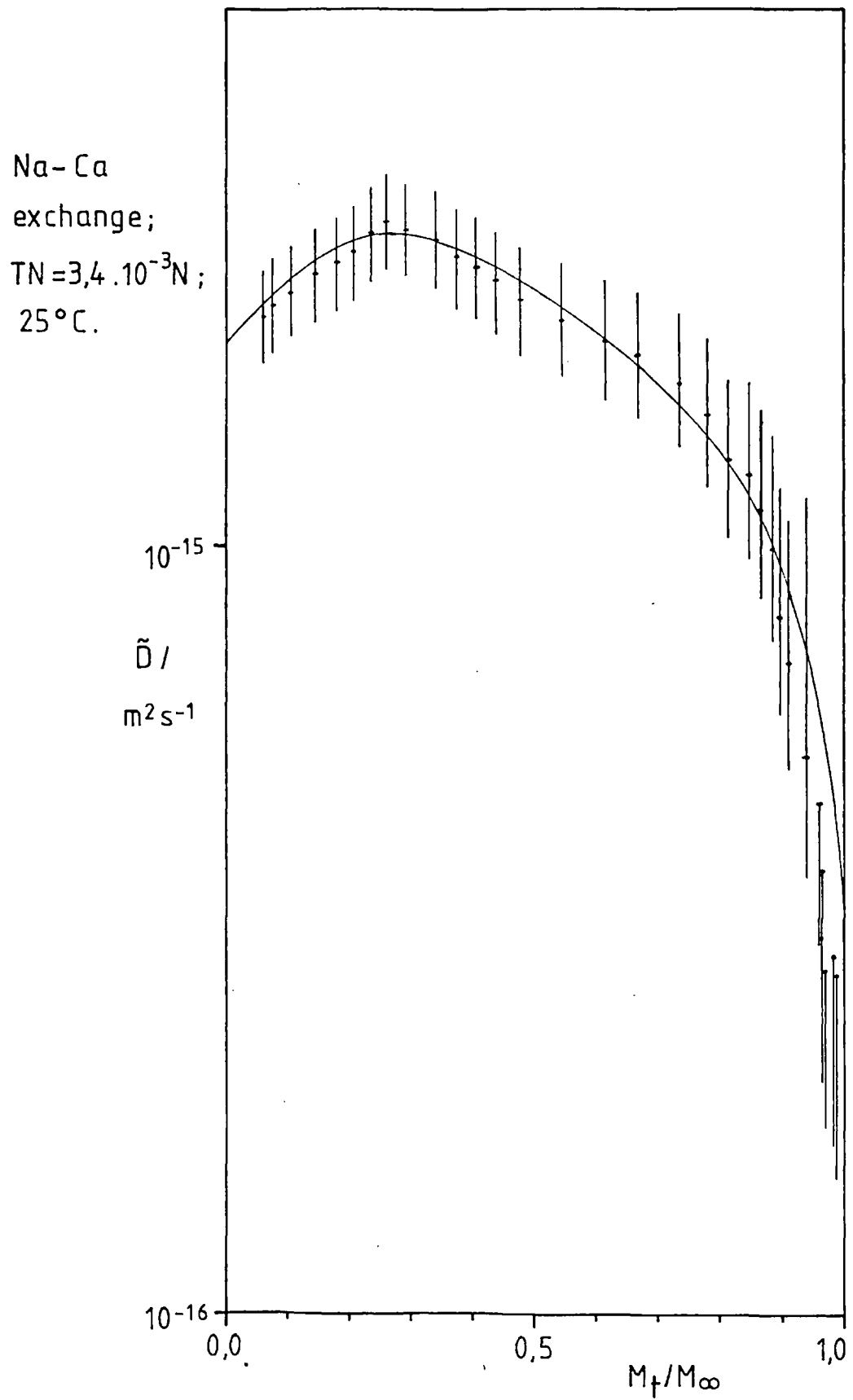
N_{Na^+}/N	$\Delta N_{Na^+} (%)$
$1 \cdot 10^{-5}$	8,1
$1 \cdot 10^{-4}$	7,1
$2 \cdot 10^{-4}$	6,8
$1 \cdot 10^{-3}$	6,2
$2 \cdot 10^{-3}$	5,9

For a typical run $N_{Na^+} = 2 \cdot 10^{-4}$ to $2 \cdot 10^{-3} N$ and therefore:-

$$\Delta M_t/M_\infty = 5,9 \text{ to } 6,8\% \text{ for } M_t/M_\infty = 1 \text{ to } 0.$$

Putting values of $M_t/M_\infty - \Delta M_t/M_\infty$ and $M_t/M_\infty + \Delta M_t/M_\infty$ into program EXCHANG gave uncertainties in the diffusion coefficient, $\tilde{D}$, as shown in Fig.12.

Figure 12.



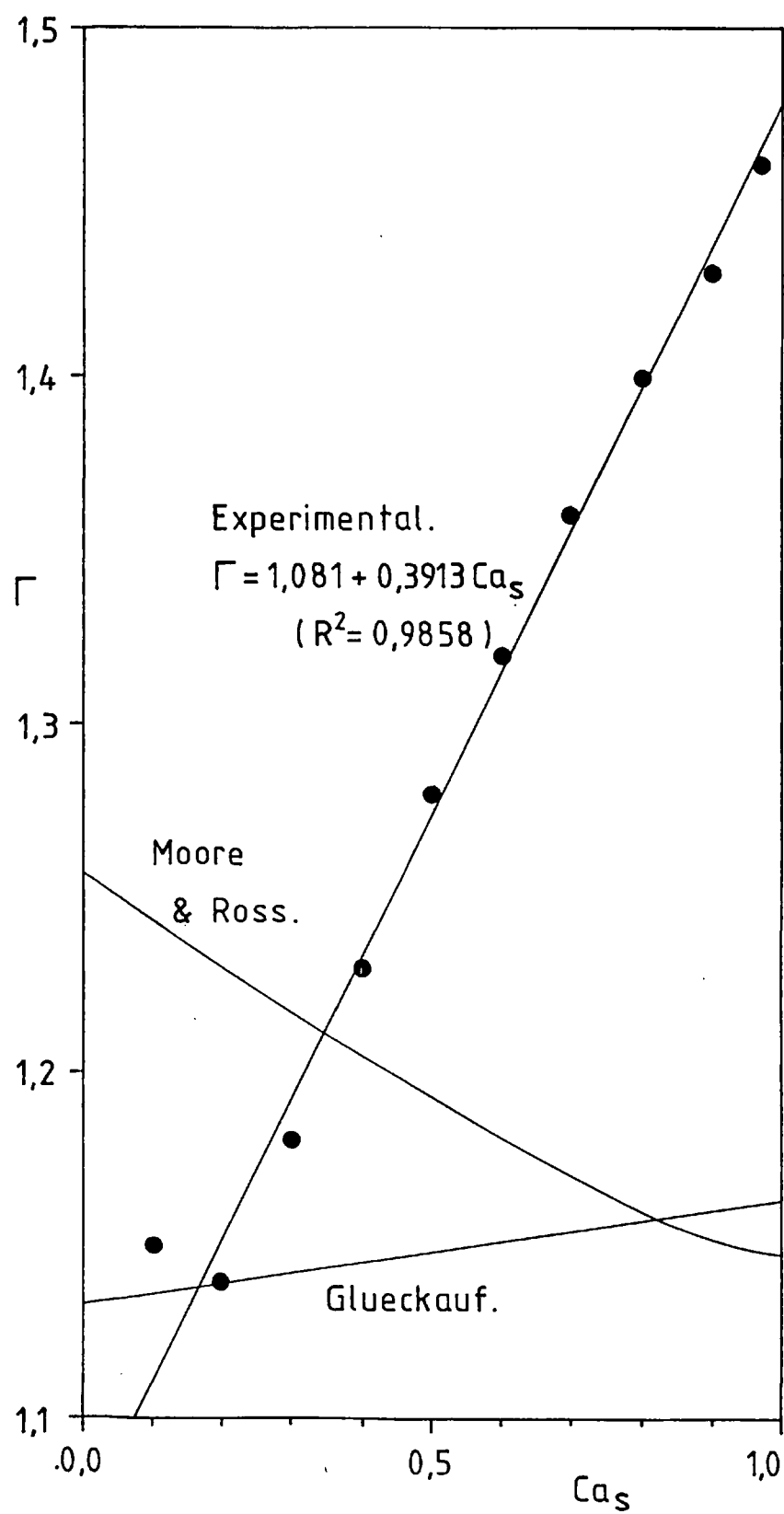
4. SOLUTION ACTIVITY COEFFICIENTS

Solution activity coefficients were determined in a number of sodium chloride-divalent ion chloride mixtures using the method described previously on page 80 . In the case of $\text{NaCl} - \text{CaCl}_2$ and $\text{NaCl} - \text{MgCl}_2$ mixtures the activity coefficients of both cations were determined and hence r , as defined in eqn 2.1.15, was calculated. For the determination of the activity coefficients of Mg^{2+} a divalent electrode (Orion 93-32), which was selective for both Mg^{2+} and Ca^{2+} , was used.

Figure 13 shows the variation of r with Ca_s for a $\text{NaCl} - \text{CaCl}_2$ mixture with total solution normality (TN) of $3.4 \cdot 10^{-3} \text{N}$ (10^{-4}M NaOH gave pH8). In subsequent measurements, including kinetic determinations, 10^{-3}M NMe_4OH was used to give a suitable pH (~ 10). The NMe_4^+ cation is non exchangeable due to size exclusion and is not included in the TN. This is because the equilibrium equations (2.1.7, .9) include only exchangeable cations. The only effect of the NMe_4OH on the equilibria is to increase the ionic strength and hence decrease exchangeable cation activity coefficients. Similarly when calculating the ratio of equivalents in the zeolite to those in the solution (M_z/M_s), only exchangeable cations are considered.

Moore and Ross (131) carried out some sodium activity measurements in $\text{NaCl} - \text{CaCl}_2$ mixtures of ionic strength greater than 0.05M and derived the following expressions based on Harned's rule (109):-

$$\begin{aligned} \log_{10} \gamma_{\text{NaCl}}^{(\text{CaCl}_2)} &= \log_{10} \gamma_{\text{NaCl}} - \alpha_{12} \cdot 1.5 N_{\text{Ca}^{2+}} \\ &\quad (4.1) \\ \log_{10} \gamma_{\text{CaCl}_2}^{(\text{NaCl})} &= \log_{10} \gamma_{\text{CaCl}_2} - \alpha_{21} \cdot N_{\text{Na}^+} \end{aligned}$$

Figure 13.Average Γ in Na-Ca mixture ; $TN = 3,4 \cdot 10^{-3} N$.

where $N_{\text{Ca}^{2+}}$ and N_{Na^+} are the normalities of the respective cations in the mixture and γ_{NaCl} and γ_{CaCl_2} are the mean activity coefficients of the respective salts in pure solutions of the salts with the same ionic strength as that of the mixture. The ionic strength of the mixture is given by:-

$$I_T = TN(1 + \text{Ca}_s/2) \quad (4.2)$$

α_{12} and α_{21} are constants for a given ionic strength. α_{12} was determined by Moore and Ross from the sodium activity measurements and they hence calculated α_{21} . The r variation shown in figure 13 used extrapolated values of α_{12} and α_{21} . As a result of the extrapolation the values of α_{21} had an uncertainty of $\pm 60\%$ leading to an uncertainty in $\gamma_{\text{CaCl}_2}^{(\text{NaCl})}$ of $\pm 0,01$ and in r of $\pm 0,05$. The uncertainty in α_{12} had little effect on r . The variation of r was also calculated using the theory of Glueckauf (107) (see equation 2.1.13).

It can be seen in figure 13 that the experimental values determined in this study differ markedly from those of Moore and Ross, and Glueckauf. The predicted values of Glueckauf appear to follow the experimental values more closely than those of Moore and Ross. Barri's measurements of a TN of $0,1N$ (59) gave the reverse, probably because the theory of Moore and Ross uses experimental values measured in this concentration range. At the much lower concentrations used in the present study the values of $\gamma_{\text{CaCl}_2}^{(\text{NaCl})}$ calculated from Moore and Ross are highly uncertain and differ markedly from the experimental values. The experimental values have an uncertainty of some 10% due to electrode errors inherent in calibrations without pH control (calibrations for kinetics experiments, $10^{-3}M$ NH_4OH or $10^{-3}M$ NMe_4OH was used). pH control could not be used in the calibrations for activity coefficients due to the effect of pH control on them.

For a Na - Mg mixture with a TN (exchangeable cations) of $3,9 \cdot 10^{-3}N$ plus a $10^{-3}M$ N Me₄OH background the prediction of γ variation by Glueckauf's theory is closer to the experimentally determined variation (see figure 14). The NMe₄OH increases the ionic strength and a more general version of Glueckauf's theory than that given in equation 2.1.13 was used. For A a divalent cation, B a univalent cation (both exchangeable), and X their common univalent anion:-

$$\log_{10} \gamma_{AX}^{(BX)} = \log_{10} \gamma_{AX} - \frac{TN \cdot B}{4I_T} S \left[\log_{10} \gamma_{AX} - \frac{8}{3} \log_{10} \gamma_{BX} - \frac{\frac{1}{3}}{1 + I_T^{-\frac{1}{2}}} \right] \quad (4.3)$$

$$\log_{10} \gamma_{BX}^{(AX)} = \log_{10} \gamma_{BX} - \frac{TN \cdot A}{8I_T} S \left[8 \log_{10} \gamma_{BX} - 4,5 \log_{10} \gamma_{AX} - \frac{\frac{1}{2}}{1 + I_T^{-\frac{1}{2}}} \right]$$

where $TN = N_{AX} + N_{BX}$

Ionic strength, $I_T = N_{NMe_4OH} + TN(1 + \frac{1}{2}A_S)$

N_{AX} , N_{BX} , N_{NMe_4OH} are the normalities of the solutions components. γ_{AX} , γ_{BX} are the mean activity coefficients of pure solutions of AX and BX respectively at the same ionic strength as the mixture being considered. Values of γ_{MgCl_2} were taken from a recent paper (132). The paper also gave calculated activity coefficients for NaCl - CaCl₂ and NaCl - MgCl₂ mixtures but only for $[Na^+] \geq 0,05$ molal.

Figure 15 shows the activity coefficients of calcium in NaCl - CaCl₂ mixtures with the concentration of NaCl constant (0,05M),

Figure 14.

Average Γ in Na - Mg mixture ;

$$TN = 3,9 \cdot 10^{-3} N.$$

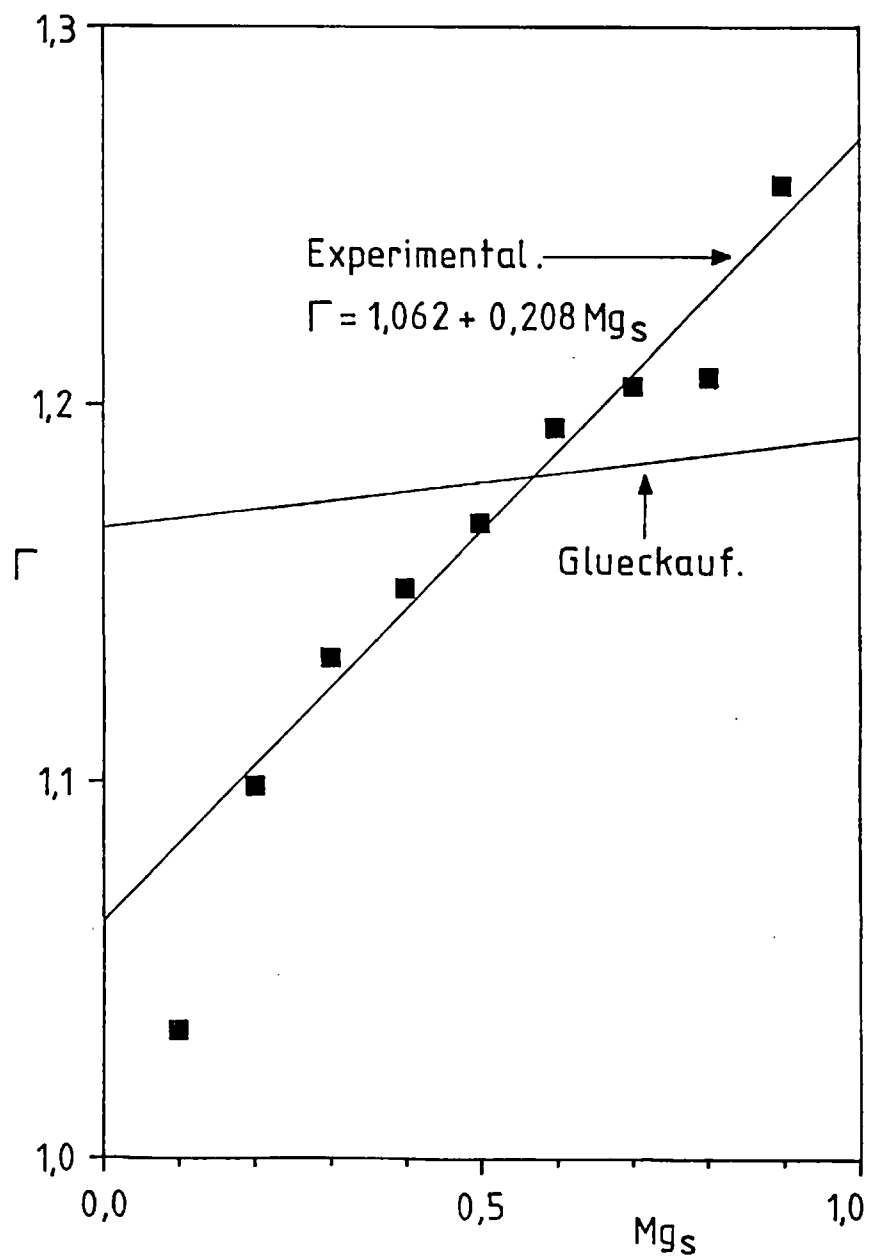
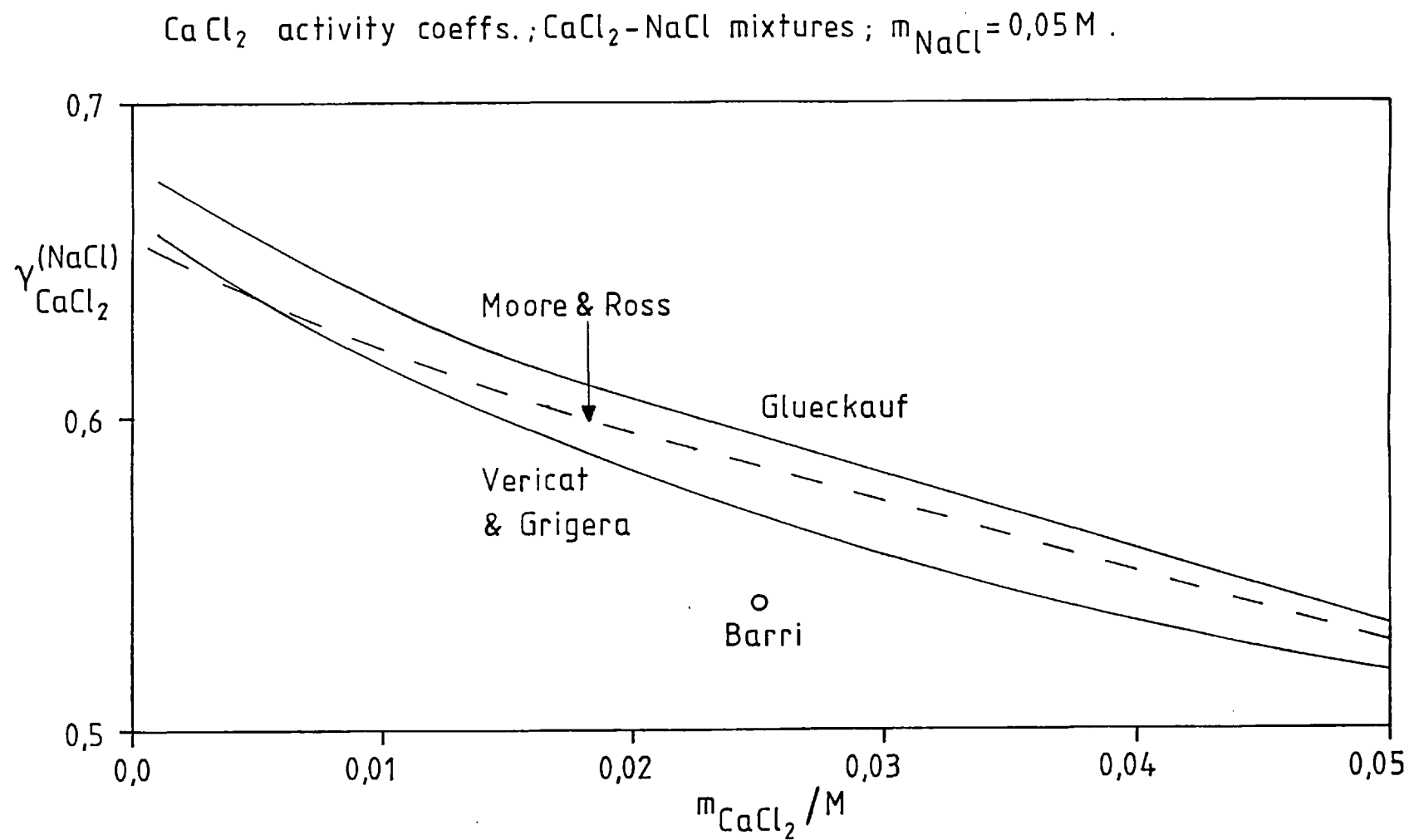


Figure 15.



calculated by the theories of Glueckauf (107), Moore and Ross (131), and Vericat and Grigera (mean spherical approximation) (132). Compared with the experimental value of Barri (59), the theory of Vericat and Grigera gives the closest agreement, although the calculations involved are quite laborious.

In the present study Glueckauf's theory gives a better fit for the $\text{NaCl} - \text{MgCl}_2$ system than for the $\text{NaCl} - \text{CaCl}_2$ system and it would therefore seem that the assumptions made in Glueckauf's theory are more closely followed by the $\text{Na} - \text{Mg}$ system. Glueckauf's theory is derived from that of Guggenheim (133, eqn. 52), who makes the following assumptions:-

- (1) "..... the specific effects of ions on one another negligible except at short distances."
- (2) "..... the interaction corresponding to divergence from the standard electrolyte contribute additively to the thermodynamic potential"
- (3) "..... consider specific interaction of ion pairs only..."
- (4) "..... assumption of Bronsted that need to take account of specific interaction only between ions of opposite sign".

On the basis of the present data it cannot be stated which of these assumptions is less closely followed by CaCl_2 than MgCl_2 .

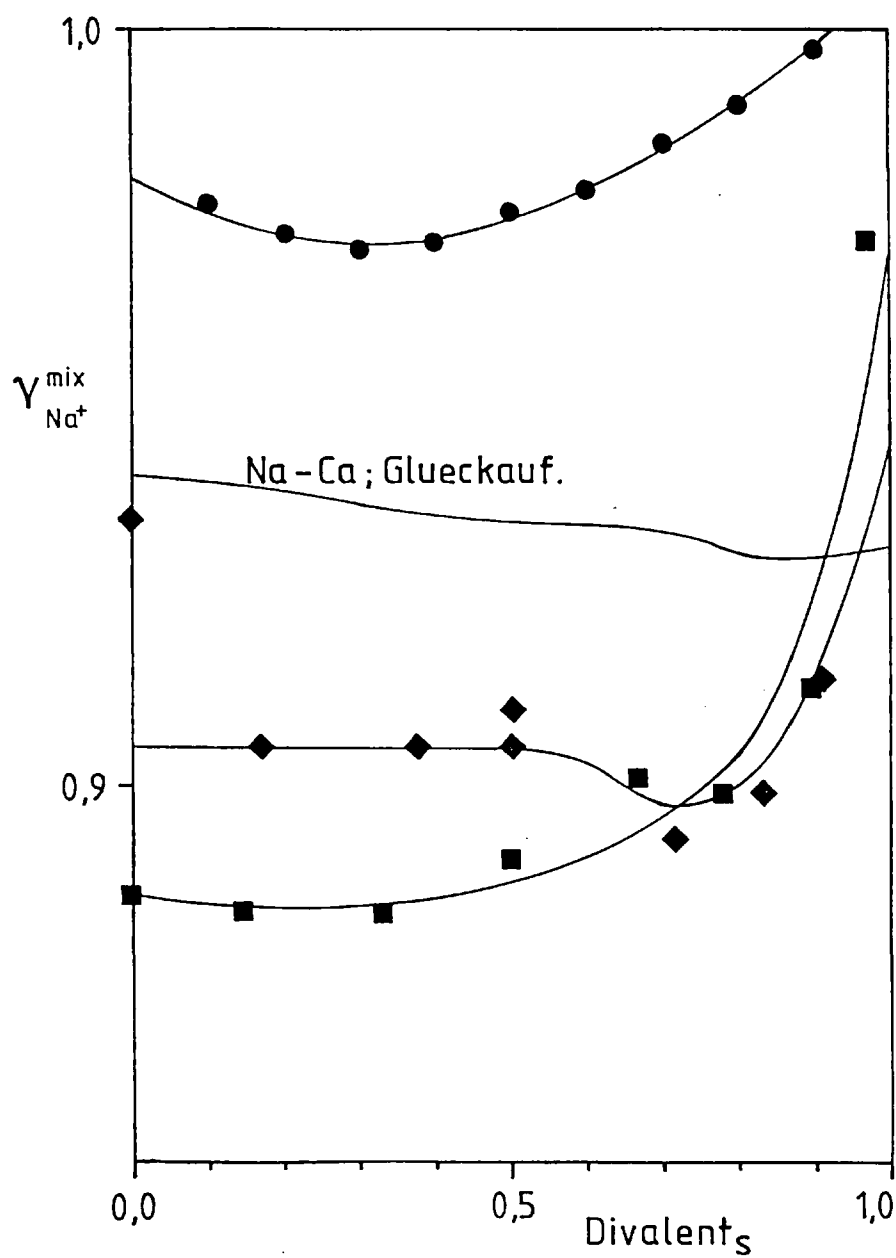
Lastly the activity coefficient variation of sodium in a $\text{NaCl} - \text{BaCl}_2$ mixture with a TN of $3,4 \cdot 10^{-3} \text{N}$ plus a 10^{-3}M NMe_4OH background, was measured. It is shown in figure 16 together with the values of $\text{NaCl} - \text{MgCl}_2$ and $\text{NaCl} - \text{CaCl}_2$ mixtures and the prediction of Glueckauf

for the $\text{NaCl} - \text{CaCl}_2$ mixture. Glueckauf's theory predicts a decrease in activity coefficient as the equivalent fraction of divalent cation in solution increases. The experimental values tend to one as the sodium concentration tends to zero. The activity coefficients for the $\text{NaCl} - \text{MgCl}_2$ and $\text{NaCl} - \text{BaCl}_2$ systems agree within experimental error and for a divalent fraction of less than 0,8 roughly agree with Glueckauf's prediction. For the three systems considered the $\text{NaCl} - \text{CaCl}_2$ system would appear to be the exception, being quite different from Glueckauf's prediction.

Whilst measuring activity coefficients by ion selective electrodes gives results of sufficient accuracy for isotherm prediction, the values are not of sufficient accuracy to test theoretical predictions of activity coefficients. Activity coefficients vary only by $\sim 10\%$ over the complete range of mixtures and this is close to the uncertainty of electrode derived results. Many precise measurements would be necessary to closely define the activity coefficient variation.

Figure 16.

Sodium activity coeffs. in mixtures:

■ Na-Mg ; $TN = 3,9 \cdot 10^{-3} \text{ N}$;● Na-Ca ; $TN = 3,4 \cdot 10^{-3} \text{ N}$;◆ Na-Ba ; $TN = 3,4 \cdot 10^{-3} \text{ N}$.

5. HYDROLYSIS

In order to speed up the initial mixing of zeolite and counter-ion solution phases in an ion exchange kinetics experiment the sodium zeolite was slurried with water at $\text{pH} > 8$ and then the solution of the counterion was added. It was, however, found that the ion selective electrode indicated an abnormally high sodium content in the slurry and the EMF rose quite rapidly before any counterion was introduced. These high implied sodium concentration were confirmed by atomic absorption spectroscopy and a study of this phenomena, which is caused by zeolite A hydrolysis, was therefore carried out.

It was found that the same degree of hydrolysis occurred in commercial and Charnell synthesised (127) zeolite A samples. It was also found that the X-ray diffraction pattern of a sample of Union Carbide Zeolite A after loss of some 40% of its total sodium content showed no loss of crystallinity as long as the samples had not been heated.

For the subsequent measurements tetramethylammonium hydroxide was used to give the desired pH as the NMe_4^+ ion is too large to enter the zeolite A lattice. An experiment was conducted in which a sample of Charnell synthesised zeolite A (Charnell 4A) was hydrolysed for one hour, separated, then introduced to a second solution where further hydrolysis occurred (Fig. 17). It can be seen that a sudden loss of sodium from the zeolite occurred each time it was put into a fresh solution implying that the loss of sodium is not due to release of imbibed sodium salt from the zeolite.

Further experiments were carried out in which the loss of sodium and variation of pH were simultaneously monitored. The experiments with Charnell 4A shows an increase in the degree of hydrolysis with decreasing pH (Fig. 18). In particular the initial "jump" in solution

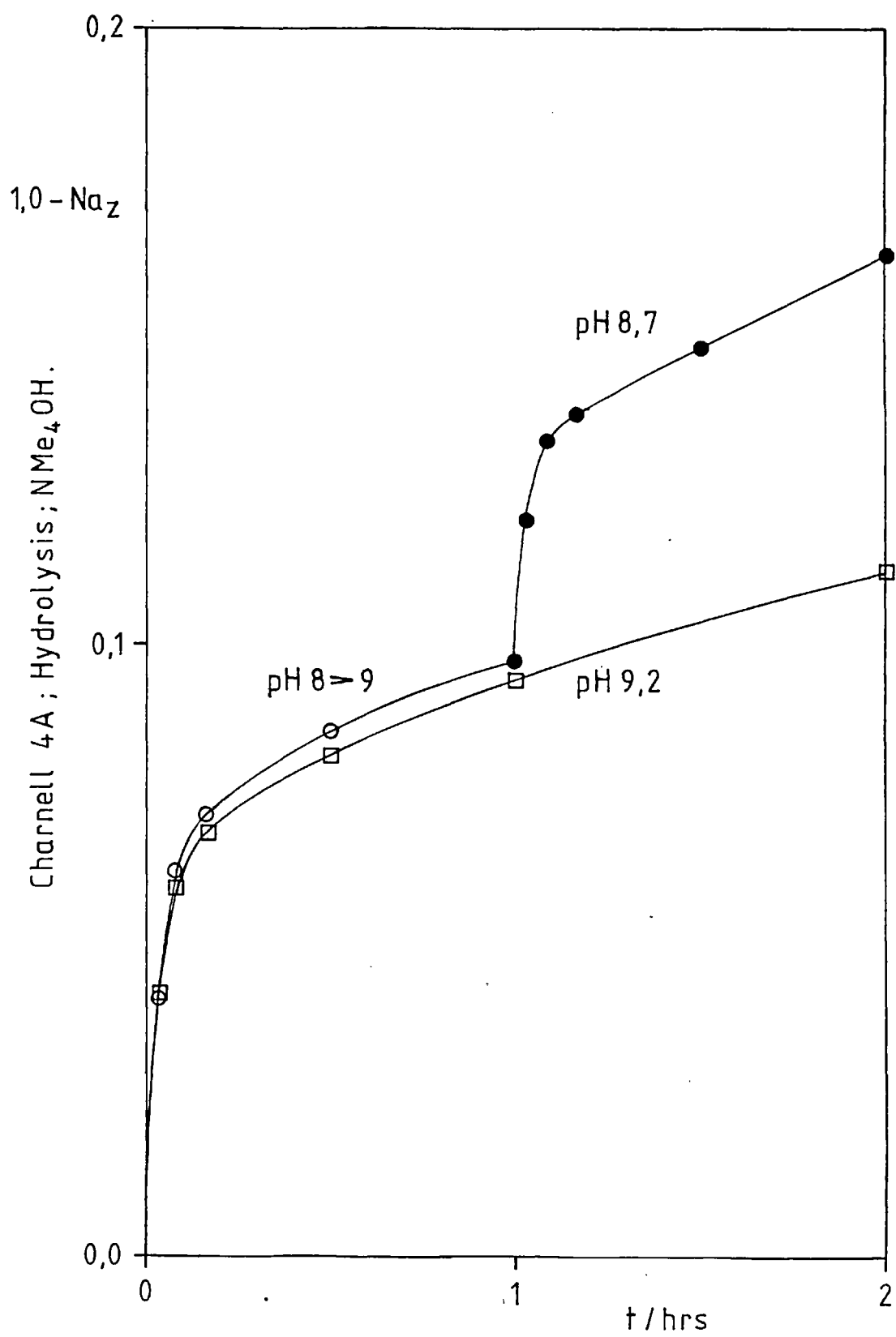
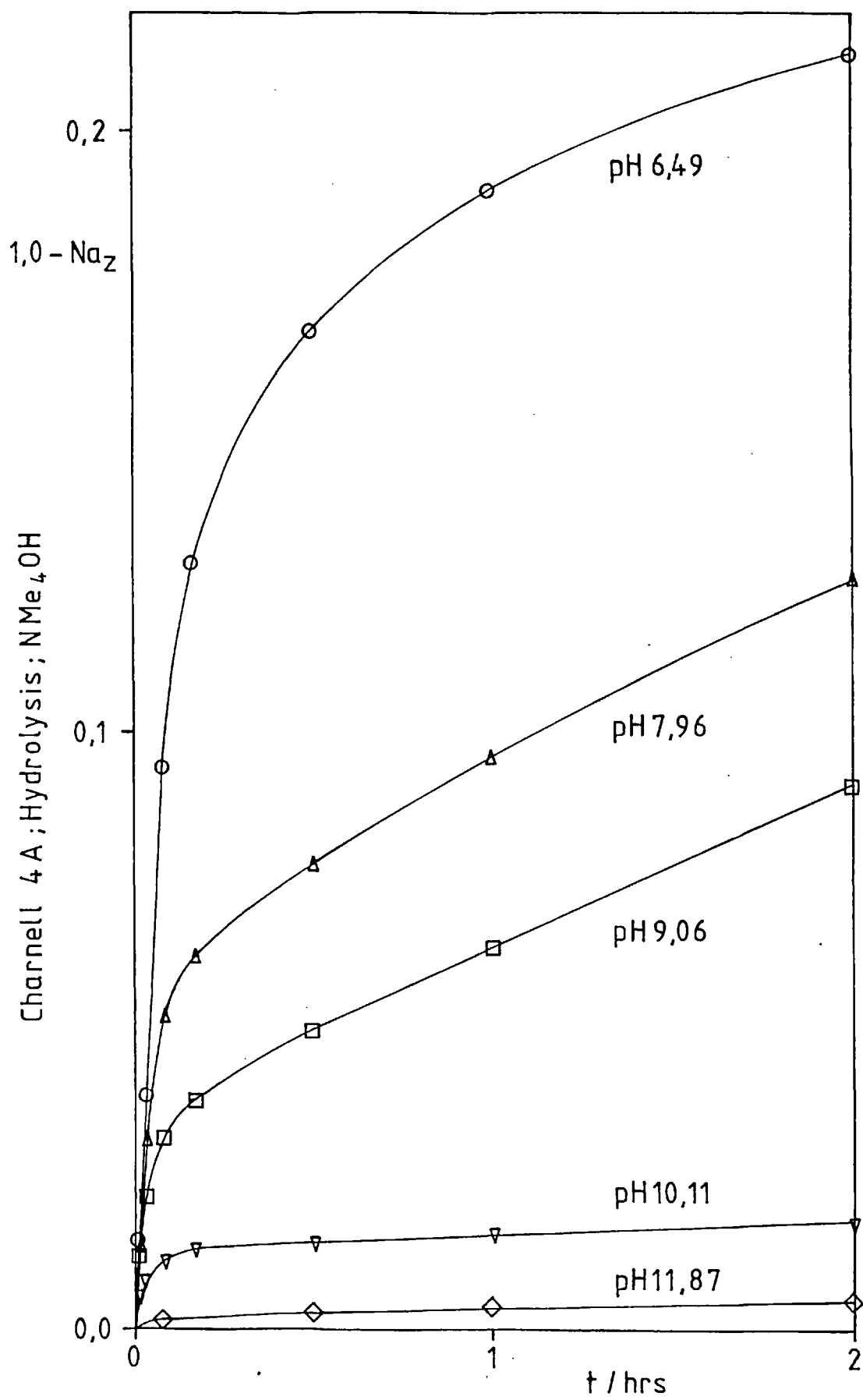
Figure 17.

Figure 18.



sodium concentration increases dramatically as the initial pH is decreased. After some thirty minutes the rate of hydrolysis reaches a constant value which shows no obvious dependence on initial pH. The very low degree of hydrolysis at pH 11,87 confirms that the loss of sodium is not due to occluded salt nor due to some spurious electrode effect.

The pH variation of these experiments (Fig 19) shows a positive initial "jump" in pH followed by a leveling off and slow decrease in pH. The pH "jump" is probably due to $\text{Na}^+ - \text{H}^+$ exchange and the size of the "jump" decreases with increasing initial pH.

In Fig. 20 the results of these experiments are combined to demonstrate the degree of hydrolysis after various lengths of contact time plotted against the initial pH. There seems to be a roughly linear relationship between the degree of hydrolysis and the initial pH in the first hour of contact for initial pHs less than nine.

Similar experiments were carried out using a commercial sample of zeolite A (Laporte 4A) with sodium hydroxide for pH control in the case of three experiments and with NMe_4OH for the other two (Fig 21). Whilst the hydrolysis rates are very similar to those seen with Charnell 4A there is no readily apparent relationship between the degree of hydrolysis and initial pH.

The pH variation (Fig. 22) is very similar to that for Charnell 4A although the experiment starting at pH 7,54 undergoes quite a large increase in pH which is no doubt related to the comparatively low degree of hydrolysis in this case.

A series of Na - Ca exchange experiments were carried out by monitoring sodium and calcium concentration as a sample of sodium

Figure 19.

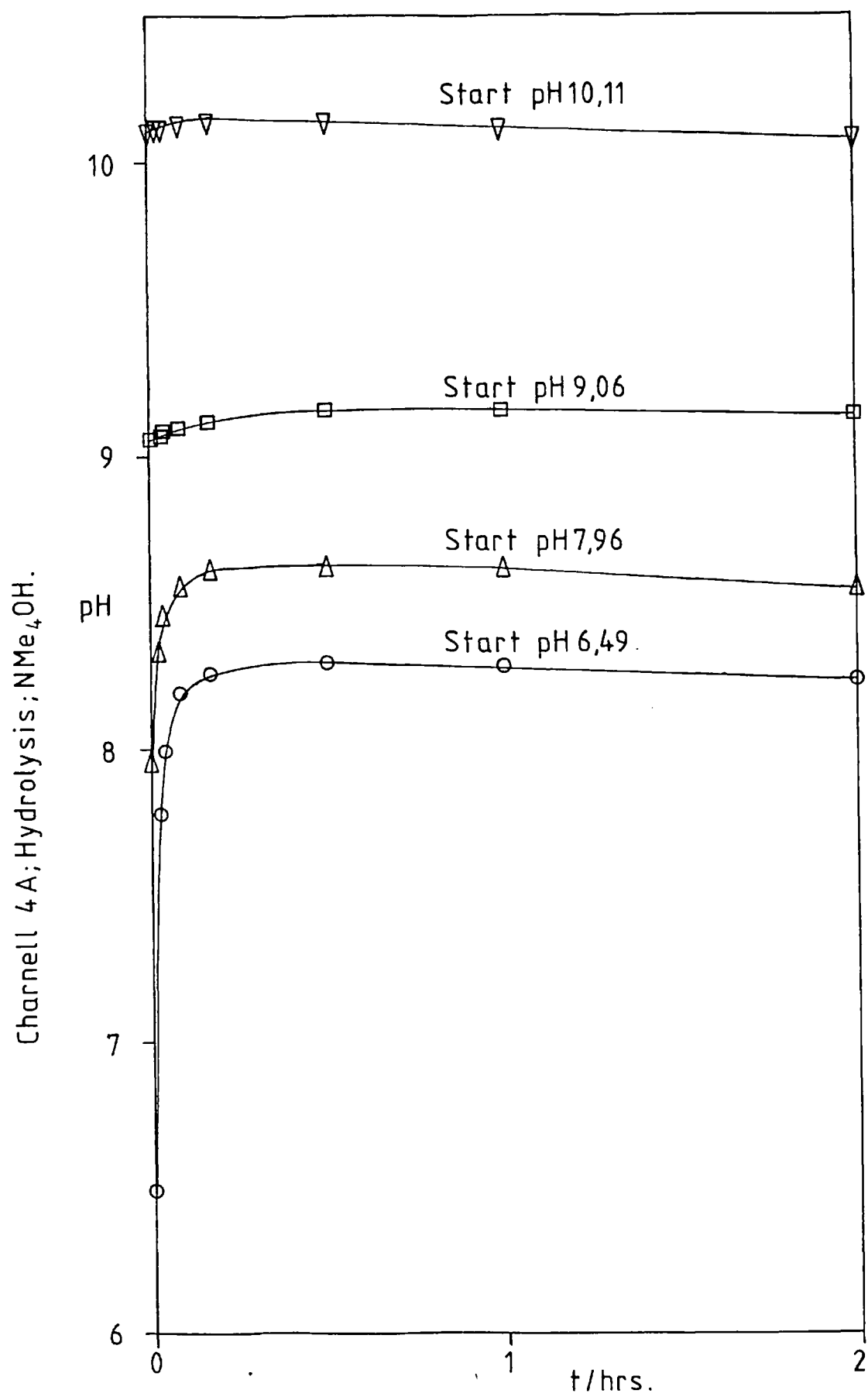


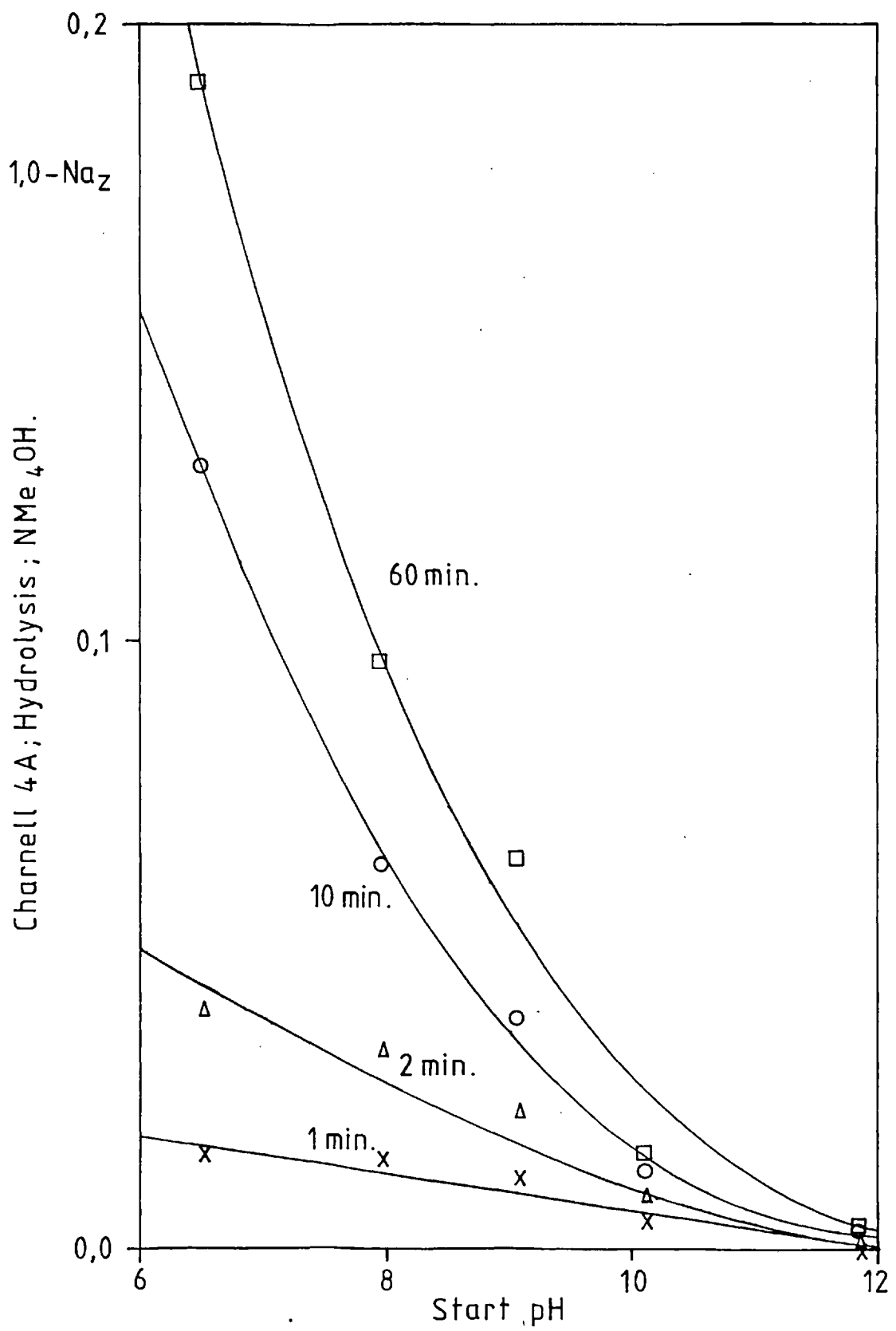
Figure 20.

Figure 21.

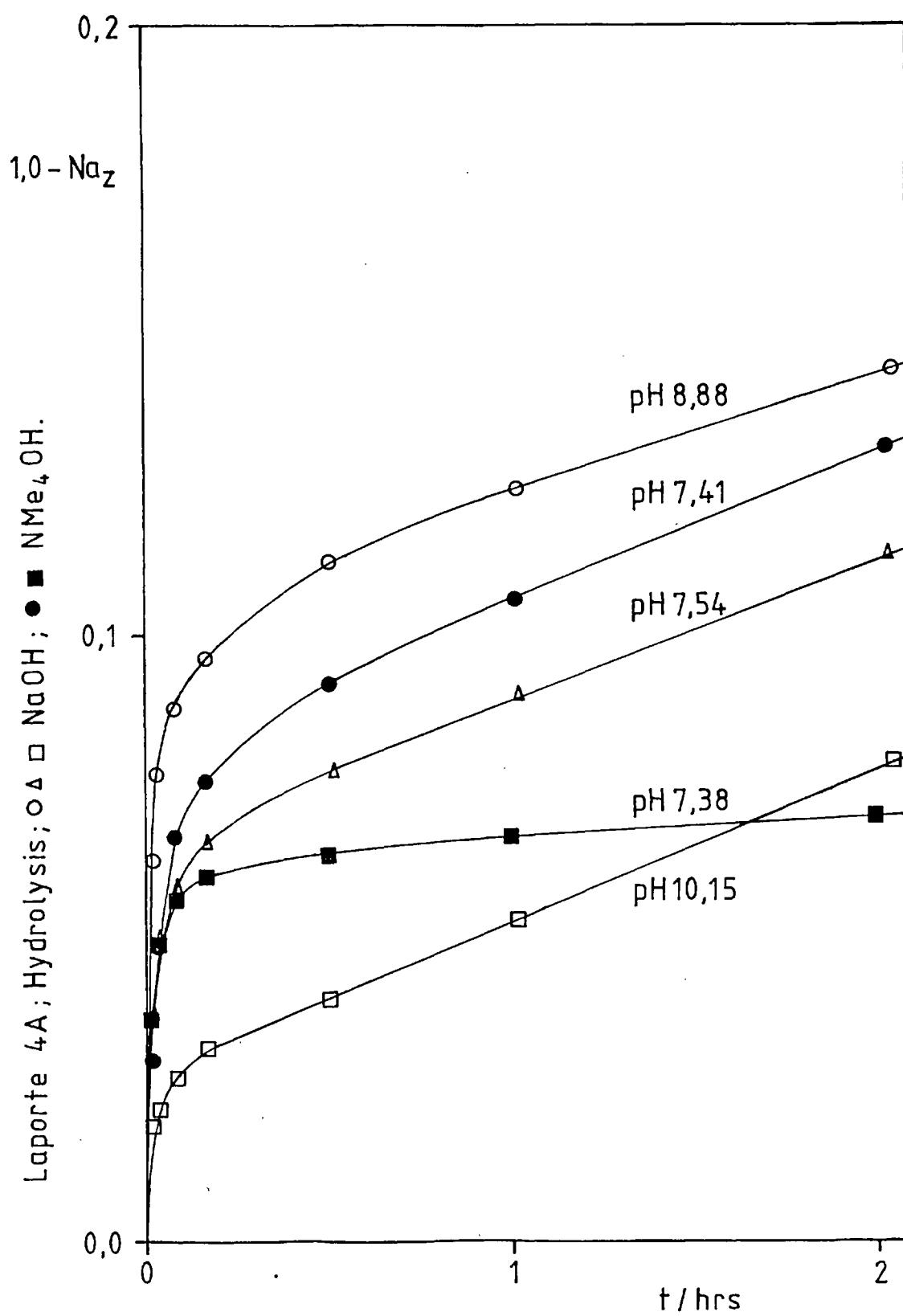
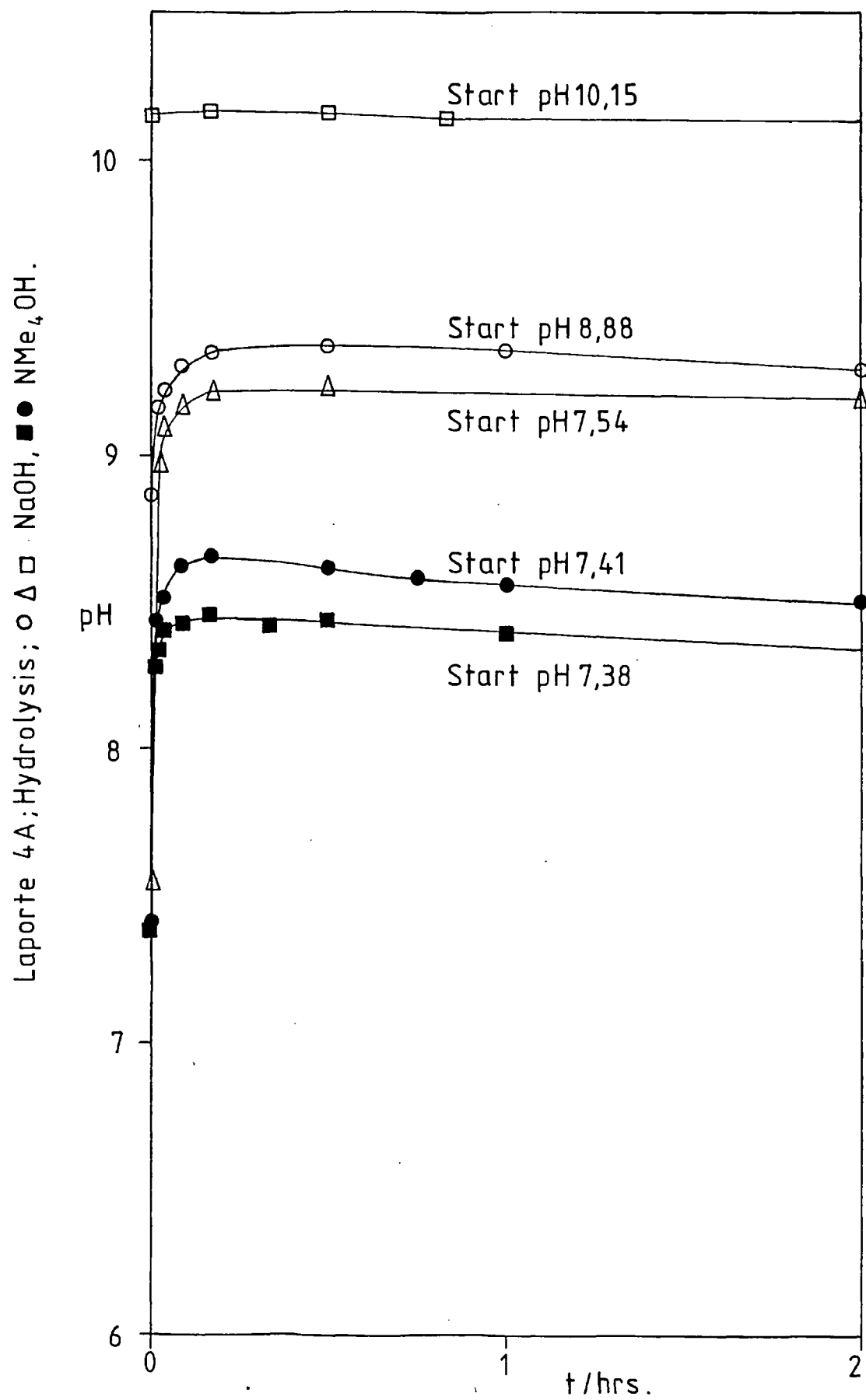


Figure 22.



zeolite A was added to a $3,4 \cdot 10^{-3}$ N CaCl_2 solution of known pH. If any hydrolysis occurred during the exchange the increase in solution sodium concentration would be greater than the decrease in solution calcium concentration. The results for Charnell 4A and Laporte 4A are shown in Figures 23 and 24 respectively. The ordinate represents the sodium removed from the zeolite minus the calcium gained and a positive value indicates hydrolysis.

The results are inconclusive although for Charnell 4A with an initial pH of 6,81 there seems to have been some hydrolysis (Fig. 23). The initial negative values are probably due to differences in the response times of the sodium and calcium selective electrodes. This effect probably causes the positive swing seen with Laporte 4A at initial pH of 10,11 (Fig. 24) as the exchange with Laporte 4A is considerably faster than that with Charnell 4A. The error in the ordinate values is approximately $\pm 0,06$. Considering the initial pH values it can be seen that the calcium ion seems to have a strong stabilising effect upon the zeolite.

Whilst it has been known for sometime that excessive washing of zeolite A could cause hydrolysis (15) but apart from a recent study (134) very little work has been carried out in this area. Cook et al measured acid consumption and solubilization of silicon and aluminium (134). They also proposed a mechanism which has been modified in the light of the present studies and is presented in Figure 25 (135). The actual form which the aluminium and silicon oxides/hydroxides take is not known. Simple calculations show that the initial $\text{Na}^+ - \text{H}^+$ exchange can only account for a small fraction of the observed Na^+ ion release and it therefore seems probable that the hydrolysis process is autocatalytic with the release of H^+ continuing the reaction. The rate of

hydrolysis decreases due to the albeit limited stability of H-A and the diffusion of H^+ to the outer solution which gives rise to the observed pH drop after 1 hour.

Figure 23.

Charnell 4 A ; Na - Ca exchange.

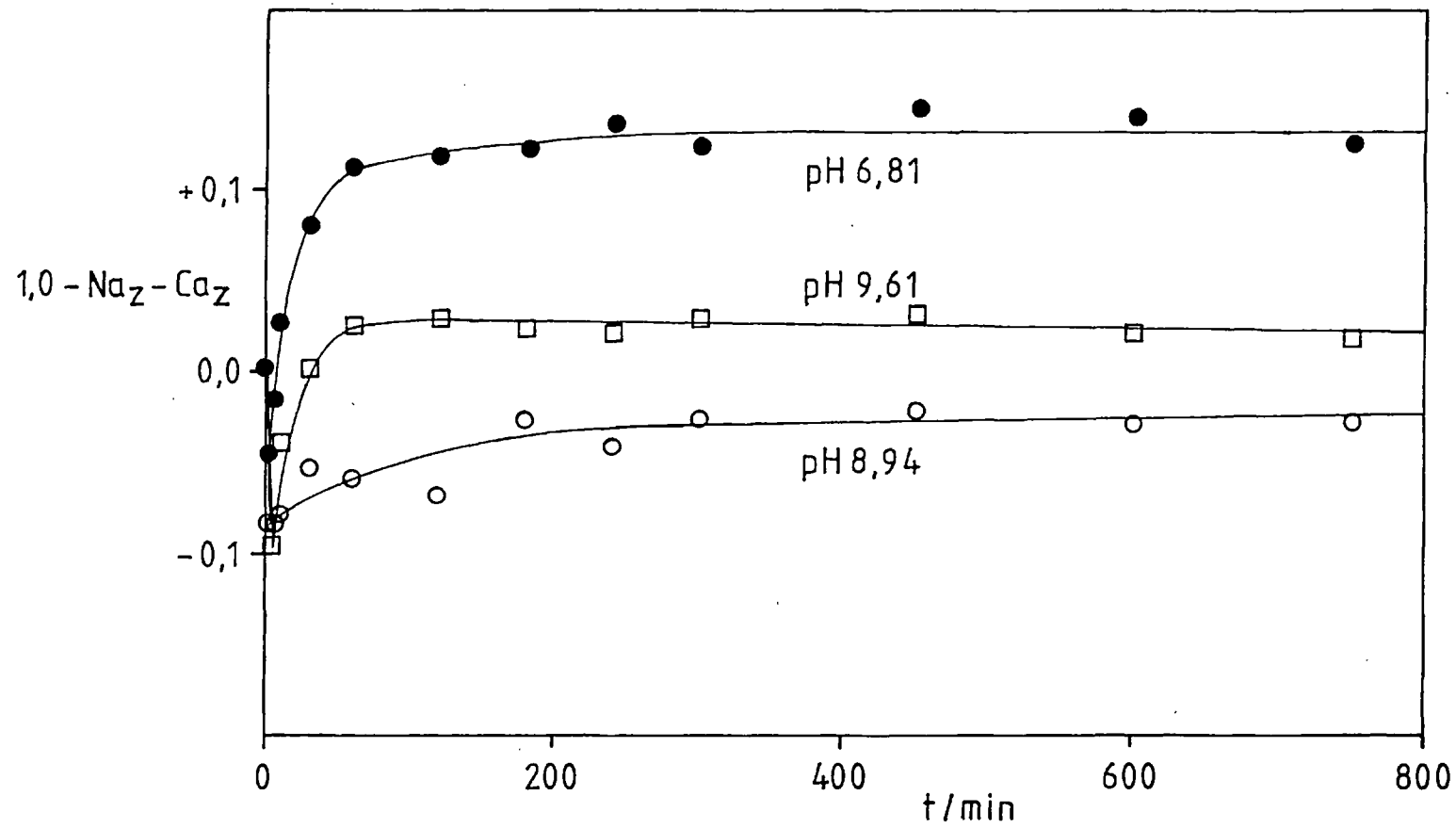


Figure 24.

Laporte 4A; Na - Ca exchange.

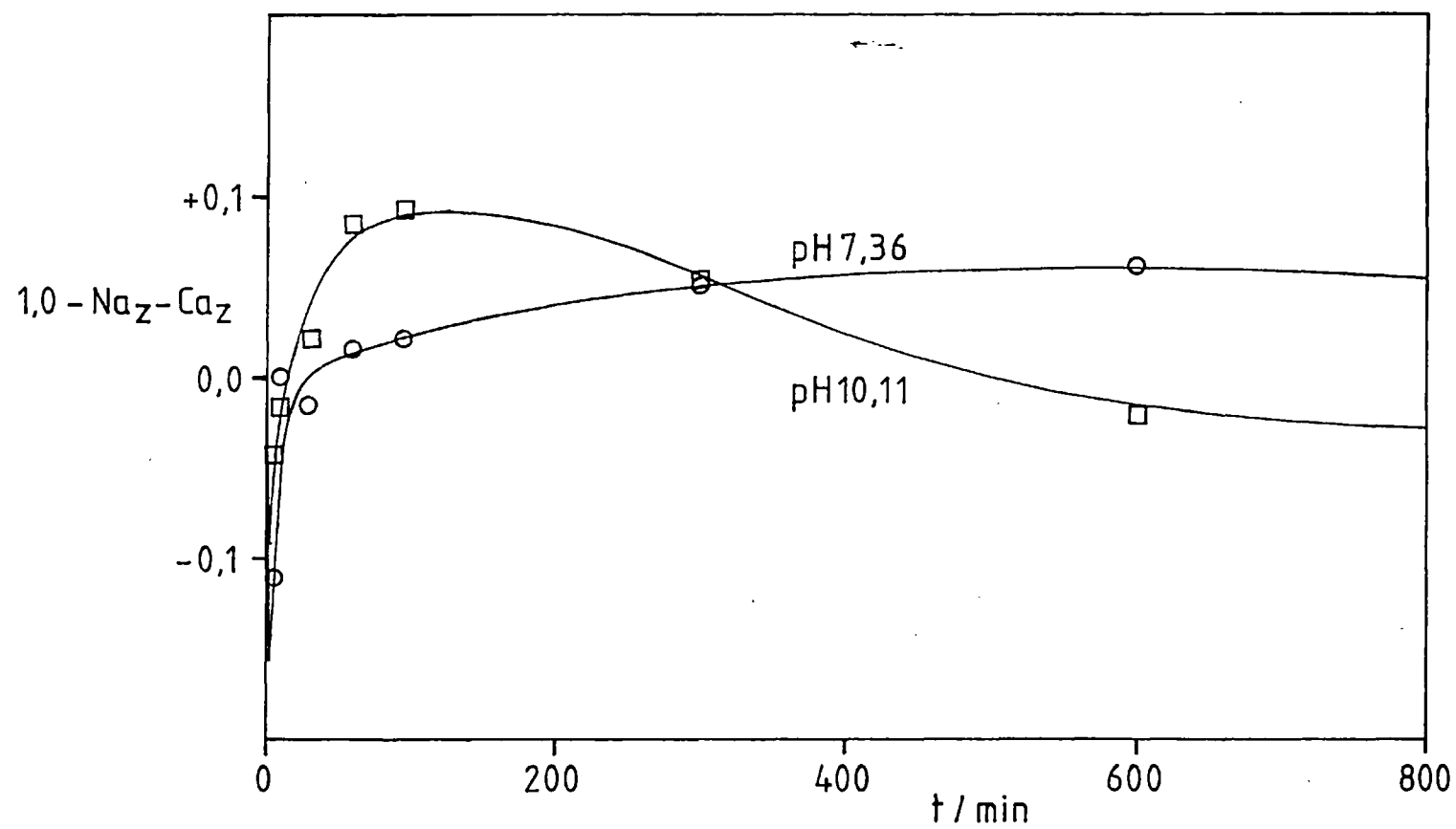
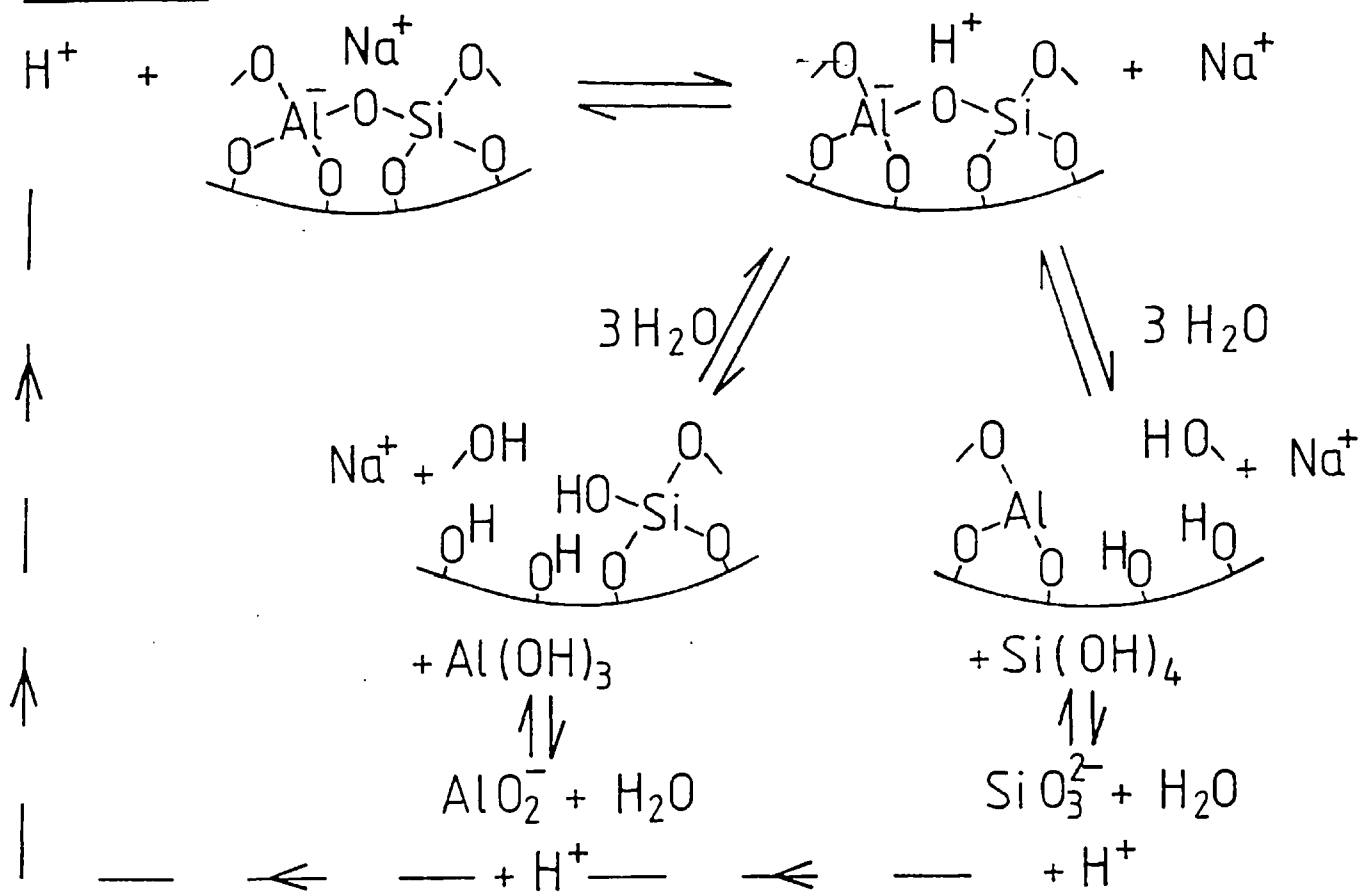


Figure 25.



6. ION EXCHANGE KINETICS

6.1 SODIUM-DIVALENT EXCHANGE

The exchange of sodium by calcium and magnesium is of particular interest because of the previously mentioned use of zeolite A as a builder in detergents. The kinetics of sodium-calcium exchange was determined for a total solution normality (TN) of $3,4 \cdot 10^{-3} \text{N}$ so that there were slightly fewer ions in the zeolite than in the solution ($M_z/M_s = 0,8$) $\cdot 10^{-4} \text{M}$ NaOH (pH8) was used to limit hydrolysis. This along with all other kinetic determinations was made at $25 \pm 0,1^\circ \text{C}$. The resulting $\sqrt{t}$ plot is shown in figure 26 as are the results of S.A.I. Barri (59) and A. De Jonge (135) for a TN of 0,1N ($M_z/M_s = 0,05$) and 0,2N ($M_z/M_s = 0,01$) respectively. The kinetics for $3,4 \cdot 10^{-3} \text{N}$ and 0,1N used the same zeolite sample (half cube length, $a_o = 9,3 \mu\text{m}$) whereas for 0,2N slightly smaller crystals were used ($a_o = 7,2 \mu\text{m}$).

It can be seen that the curves agree within experimental error and that the large difference in TN and the small difference in crystal size has no effect. The isotherms for these systems are shown in figure 27 and the equilibrium fractions of calcium in the zeolite (degree of exchange) were 0,9, 1,0 and 1,0 for TNs of $3,4 \cdot 10^{-3} \text{N}$, 0,1N and 0,2N respectively. From the isotherm for a TN of $3,4 \cdot 10^{-3} \text{N}$ the value of Ca_z at the ingoing surface of the zeolite must always be $> 0,90$ during the time of the exchange as $\text{Ca}_s > 0,20$. Similarly for 0,1N, $\text{Ca}_z > 0,97$ and for 0,2N, $\text{Ca}_z > 0,99$ at the surface of the zeolite. Figure 28 shows the variation with Ca_z of the dimensionless border concentration factor, w , needed for the calculation of diffusion coefficients (see eqn 2.2.12). From the above limitations in the surface calcium concentration it can be seen that for a TN of $3,4 \cdot 10^{-3} \text{N}$, w is around 0,15, for a TN of 0,1N, w is $\sim 0,04$ and for a TN of 0,2N, w is $\sim 0,015$.

Figure 26.

Na - Ca exchange.

$TN = 3,4 \cdot 10^{-3} N$ ○ ; 0,1 N ● ; 0,2 N □ .

$a_o = 9,3 \mu m$ ○ ; 9,3 μm ● ; 7,2 μm □ .

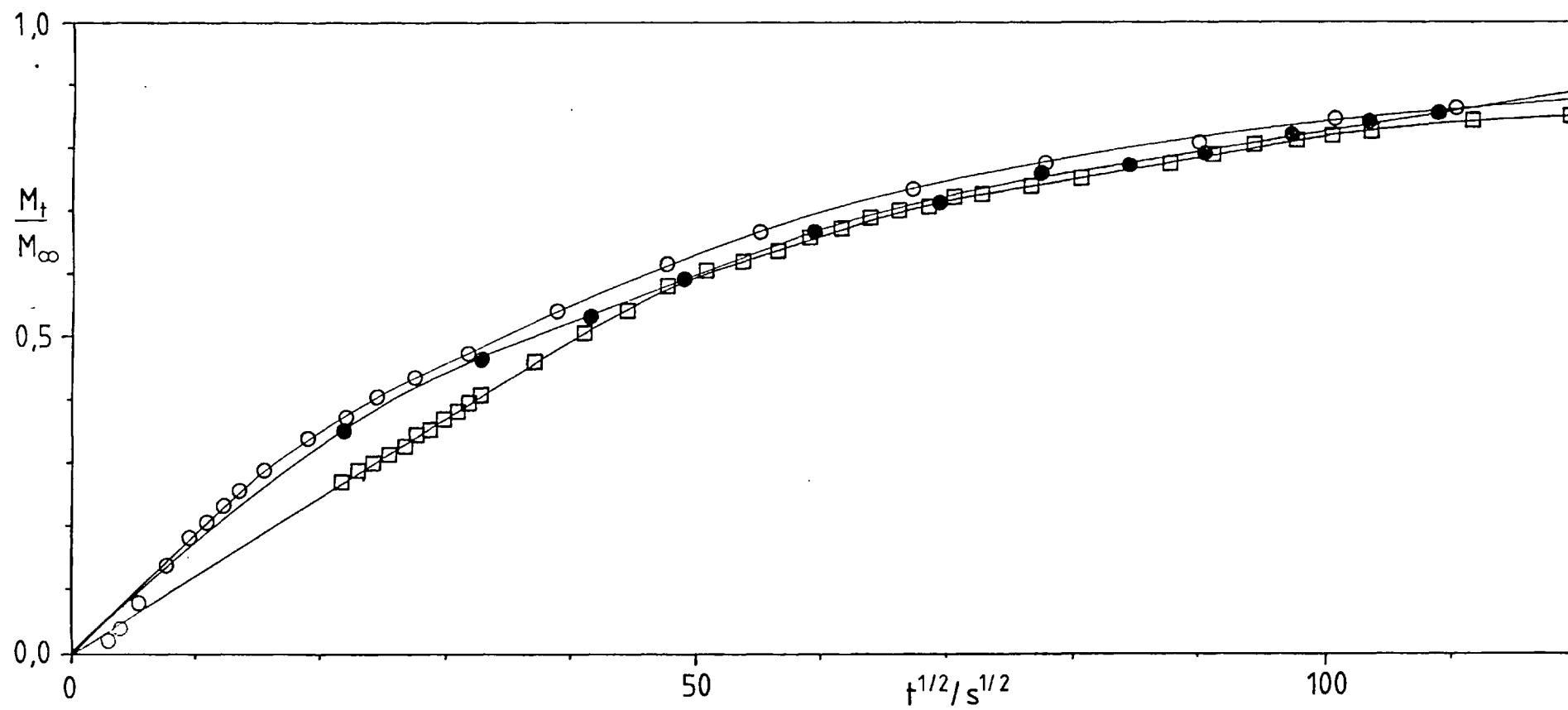


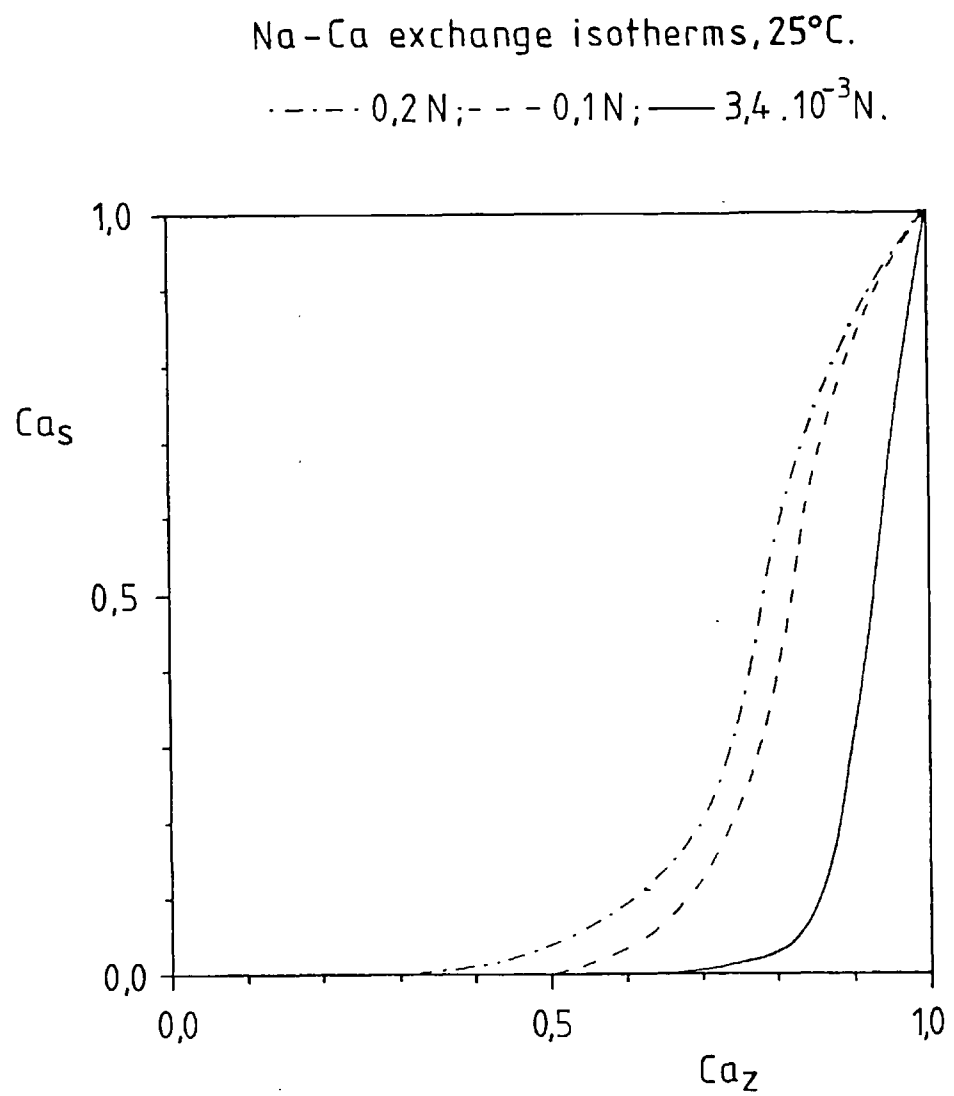
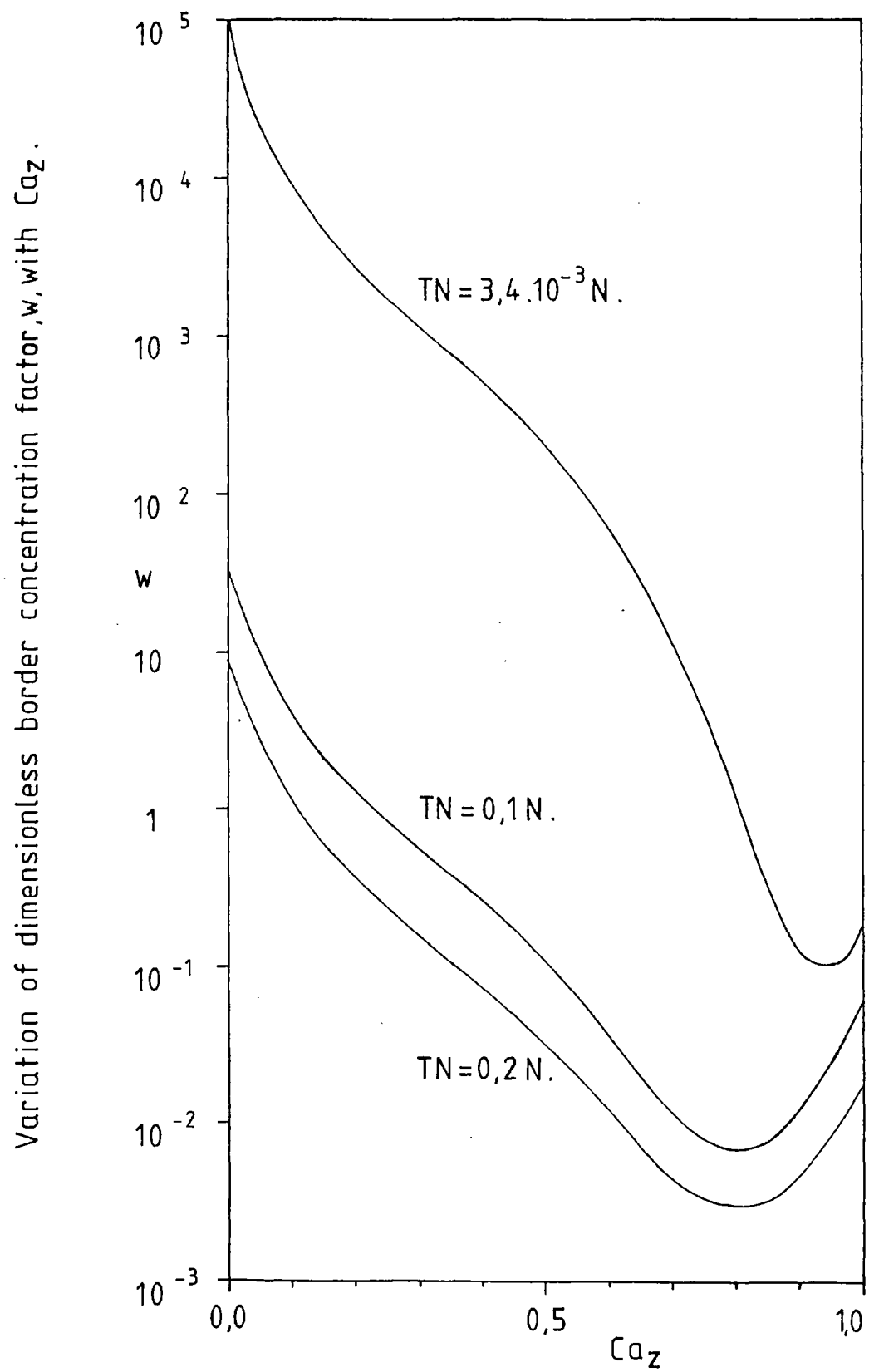
Figure 27.

Figure 28.

The resulting diffusion coefficients ($\bar{D}$) for these systems are shown in figure 29. For $M_t/M_\infty > 0,5$ the curves are very similar. The difference for lower M_t/M_∞ values is not too significant as initially the electrodes lag slightly behind the actual concentration changes and there is also a short time for mixing to occur. For a TN of $3,4 \cdot 10^{-3}N$ the sharp drop in $\bar{D}$ for $M_t/M_\infty < 0,2$ is probably due to this electrode response effect and the extrapolation is probably a better description of the variation of $\bar{D}$ in this region. For a TN of $0,1N$ no data was obtained for $M_t/M_\infty < 0,35$ and the values shown in figure 29 are calculated from an extrapolation of the $\sqrt{t}$ plot (figure 26) to zero.

When M_t/M_∞ is close to one the solution sodium concentration changes only slightly leading to quite a large uncertainty in this area. The large drop in $\bar{D}$ as M_t/M_∞ approaches one (figure 29) is probably due to this uncertainty as equilibrium is reached and diffusion ceases.

It appears, particularly for the $3,4 \cdot 10^{-3}N$ and $0,1N$ exchanges, that $\bar{D}$ and hence the differential diffusion coefficient, $\bar{D}$, both decrease as M_t/M_∞ increases. De Jonge also measured the reverse (Ca - Na) exchange kinetics for a TN of $0,2N$ (135) and found that the rate was slower than the forward (Na - Ca) kinetics in agreement with the theory of Helfferich and Plesset (123, 124). This is based upon the self diffusion coefficient of sodium being higher than that of calcium (see table 4) and the zeolite being more selective for calcium than for sodium (see figure 27). Diffusion coefficients were calculated (figure 30), and it was found that $\bar{D}$ (and therefore $\bar{D}$) decreases with increasing Ca_z for both the forward and the reverse kinetics (for forward kinetics $M_t/M_\infty = Ca_z$, for reverse $M_t/M_\infty = 1 - Ca_z$). The $\bar{D}$ values for the forward kinetics are higher than those for the reverse kinetics

Figure 29.

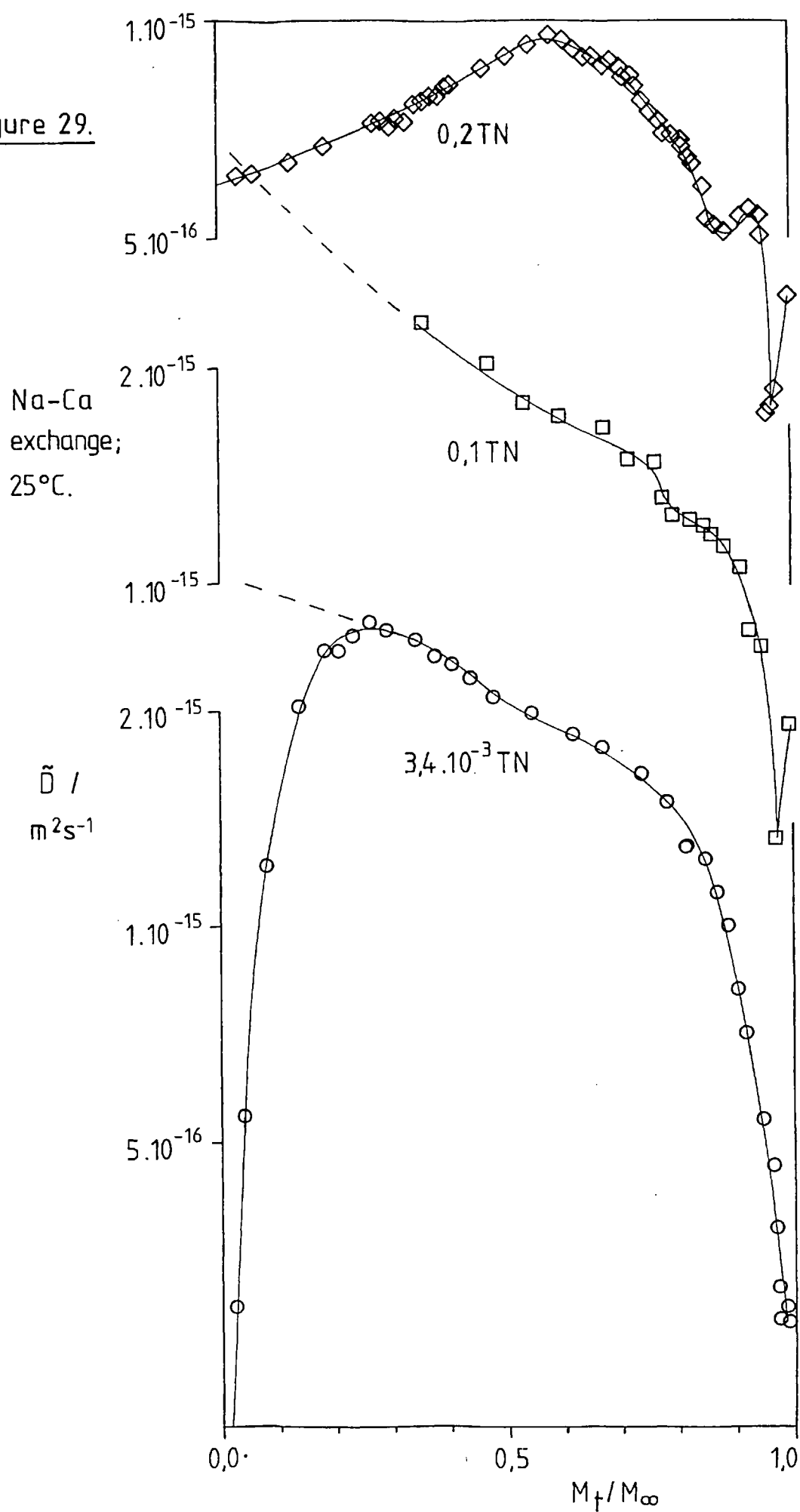
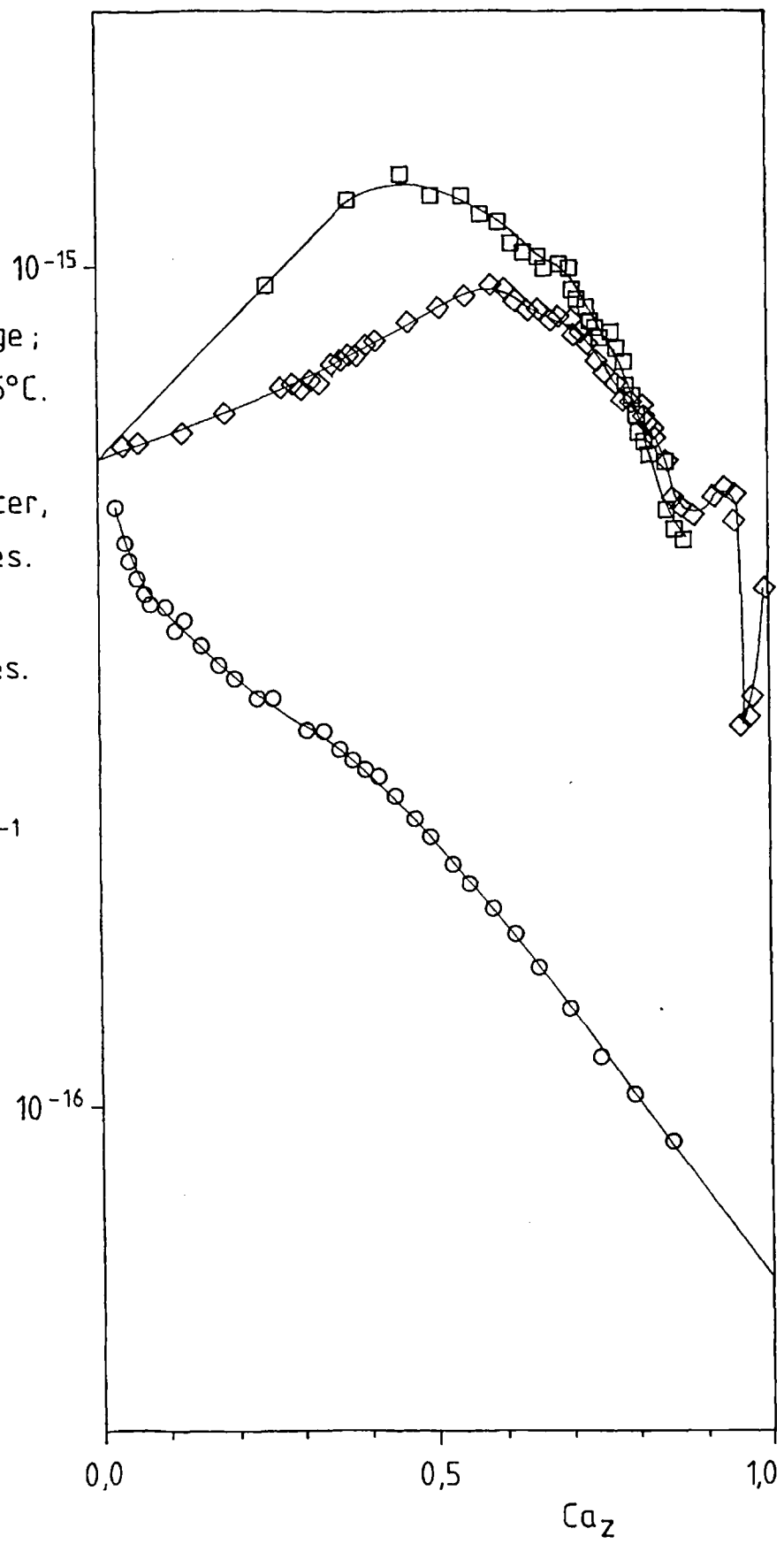


Figure 30.

Ion exchange ;
 TN=0,2 N; 25°C.
 Na-Ca :
 □ Radiotracer,
 ◇ Electrodes.
 Ca-Na :
 ○ Electrodes.

$\tilde{D} /$
 m^2s^{-1}



because of the way in which the average $\bar{D}$ is derived. For the forward kinetics $\bar{D}$ starts at a high value and decreases to the overall average $\bar{D}$ whereas for the reverse kinetics $\bar{D}$ starts low and increases to the same overall average.

The kinetics of Na - Ca exchange were also measured with other zeolite A samples. Figure 31 shows the results for a commercially made zeolite A sample (Laporte 4A RD 6/78) with a TN (exchangeable cations) of $3,4 \cdot 10^{-3}N$ and $0,1N$. A background of $10^{-3}M$ NMe_4OH (pH10) was used to limit hydrolysis. The $0,1N$ kinetics were faster than the $3,4 \cdot 10^{-3}N$ kinetics by an amount that is just outside normal experimental error. The difference in rates was, however, nowhere near the 29 times difference that would imply film diffusion control. The difference could be due to differences at the ingoing surface of the zeolite or simply due to larger than normal errors. Alternatively the difference could be related to the variation of diffusion coefficient with composition which is not strictly allowed for in the theory of Paterson (see equation 2.2.14 and preceding section) and this will be termed non-ideality. Na - Ca kinetics were also measured for a sample of zeolite A synthesised as described earlier (see Chapter 3.1). Figure 32 shows the $\sqrt{t}$ plots for the three crystal sizes. The rate increases with decreasing crystal size although the effect of size is not quite as large as would be expected for particle controlled kinetics (see Chapter 2.2). This is most probably due to agglomeration of the smaller crystals giving a larger effective crystal size than indicated. Electron micrographs of the samples showed that the commercial sample ($a_0 = 2,6\mu m$) tended to form clumps of crystals making the crystal size difficult to estimate. This agglomeration was also noticed at the beginning of kinetics experiments. The non-ideality mentioned above could also be partly responsible for the observed crystal size effect.

Figure 31.

Na - Ca exchange ; $a_o = 2,6 \mu m$.

$TN = 3,4 \cdot 10^{-3} N$ ● ; $0,1 N$ ■ .

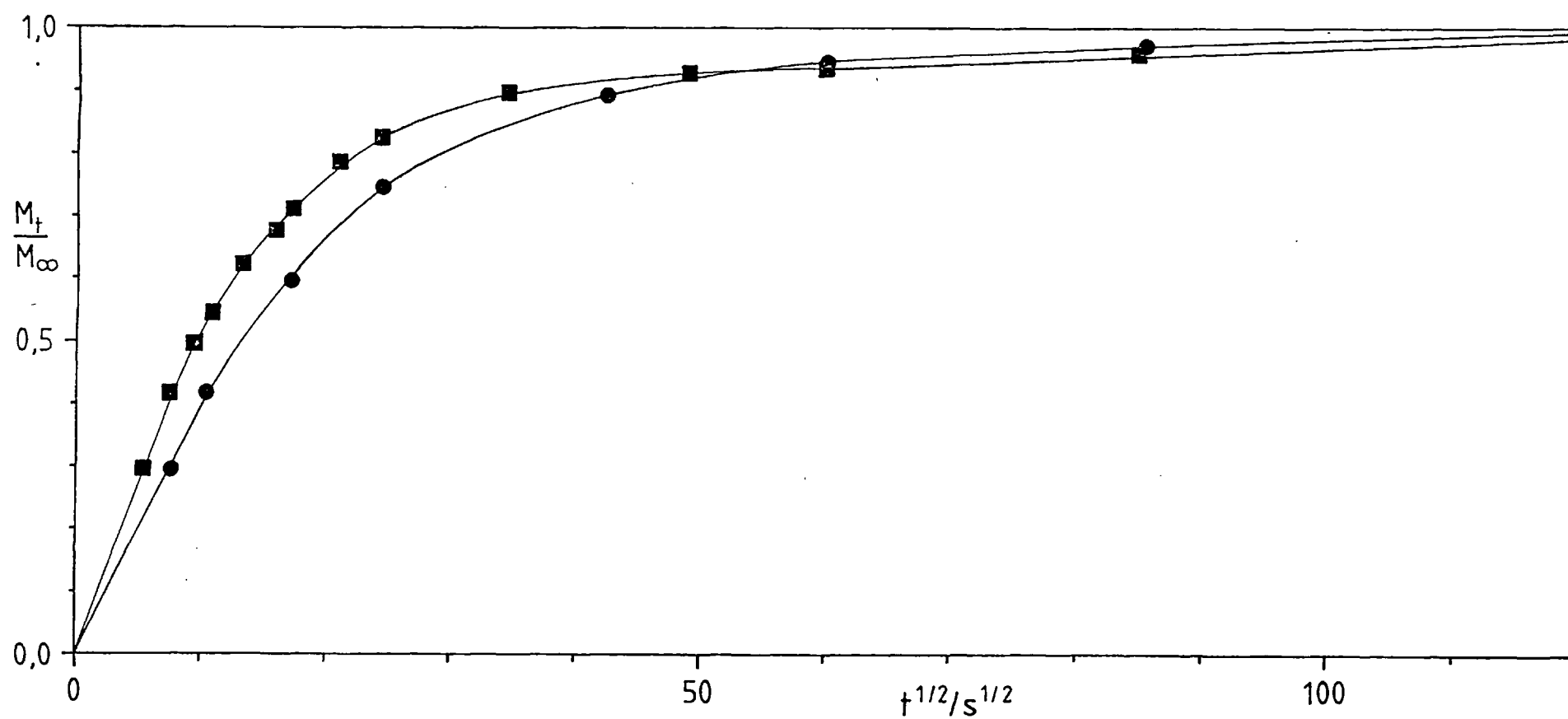
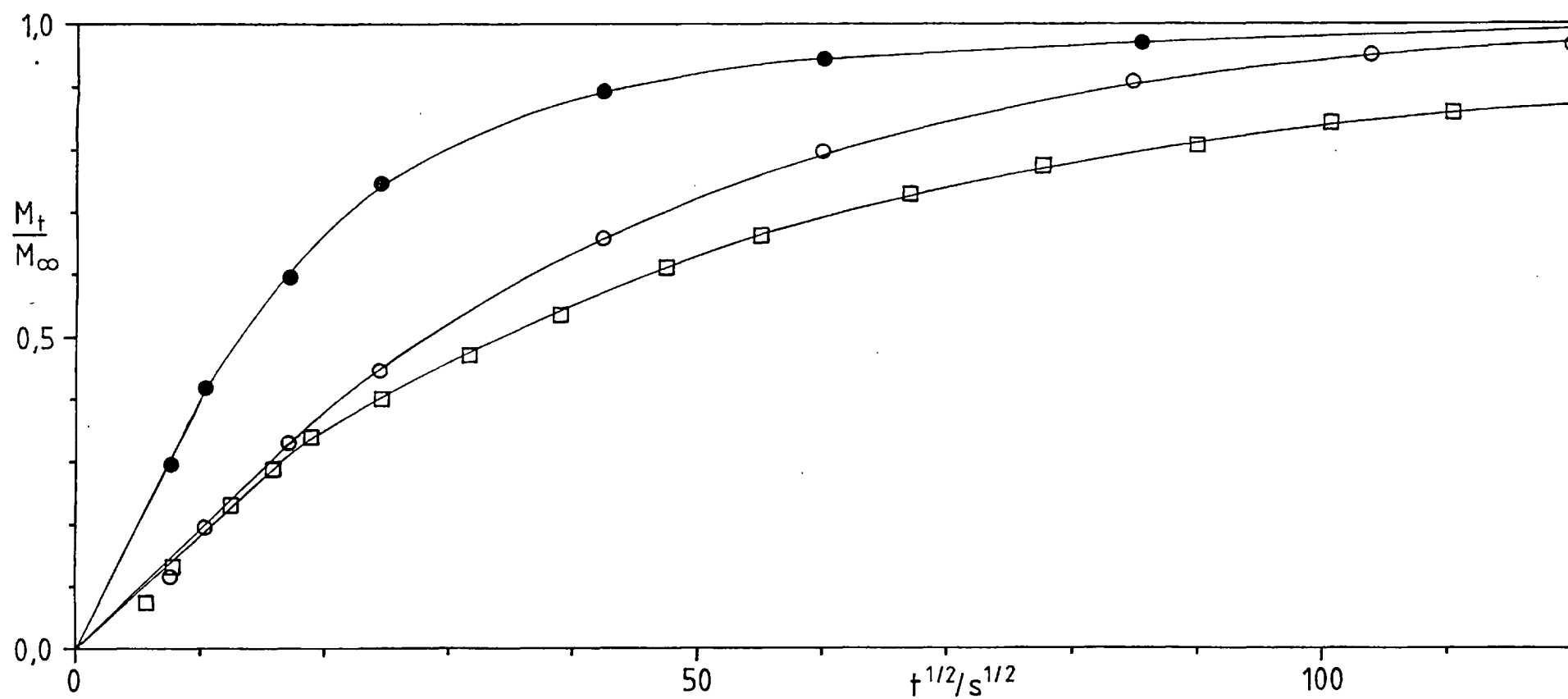


Figure 32.

Na-Ca exchange ; $TN = 3,4 \cdot 10^{-3} N$.

$a_o = 2,6 \mu m$ ● ; $6,3 \mu m$ ○ ; $9,3 \mu m$ □ .



Helffferich (136) gave the following factor to determine whether film or particle diffusion dominates in an ion exchange reaction:-

$$\text{Factor} = \frac{X}{C} \cdot \frac{\bar{D}}{D} \cdot \frac{\delta}{r_0} \cdot (5 + 2\alpha_B^A) \quad (6.1.1)$$

If this factor is less than one then particle diffusion dominates (particle kinetics). X and C are the concentration (in equivs) of ions in the zeolite and solution respectively, $\bar{D}$ and D are the diffusion coefficients in the zeolite and solution, δ is the Nernstian layer thickness, r_0 the effective particle radius and α_B^A the separation factor.

$$\alpha_B^A = \frac{\bar{C}_A C_B}{\bar{C}_B C_A}$$

where $\bar{C}$ and C are the molar concentration of the ions in the zeolite and the solution respectively.

For the cases considered, $\bar{D}/D = 10^{-9}$ to 10^{-6} , $X/C \leq 3000$, and $\alpha_B^A \leq 1$. Therefore

$$\text{factor} \leq 0,02 \cdot \frac{\delta}{r_0}$$

The Nernst-ian layer would therefore have to be some fifty times larger than the actual crystals for film kinetics. This is clearly impossible and agglomeration plus non ideality must be responsible for the exchange rates showing a lower than expected dependence on crystal size.

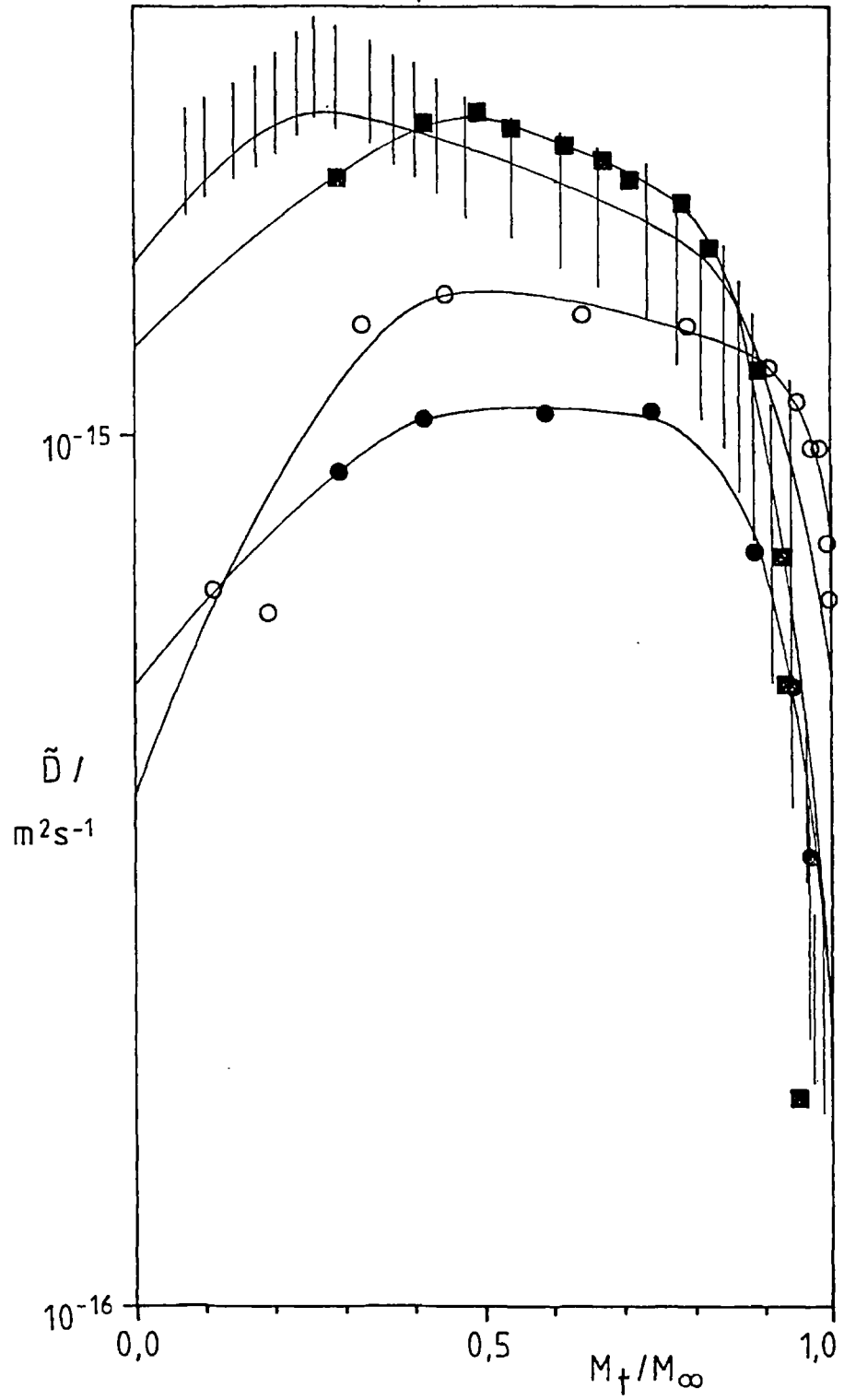
Figure 33 shows the diffusion coefficients for Na - Ca exchange. The form of the diffusion coefficient is the same in each case with small differences in magnitude due to the low crystal size dependence. As was stated earlier the sharp initial rise in $\bar{D}$ was due to experimental effects and the rapid drop towards the completion of exchange was due to the

Figure 33.

Na-Ca exchange.

 $TN = 3,4 \cdot 10^{-3} N$; $a_o = 2,6 \mu m$ ● ; $6,3 \mu m$ ○ ;

 $9,3 \mu m$ | .

 $TN = 0,1 N$; $a_o = 2,6 \mu m$ ■ .


approach of equilibrium. For the major part of the exchange $\bar{D}$ is either almost constant or dropping slowly.

The kinetics of Na - Ca exchange were also measured in a series of experiments in which the calcium content of the zeolite was increased by approximately 6% during each incremental step. The sodium zeolite A was introduced into $3,4 \cdot 10^{-3}$ N NaCl at approximately pH8 and an aliquot (50cm^3) of $3,4 \cdot 10^{-3}$ N CaCl_2 added. The resulting exchange was followed to completion using a calcium selective electrode. For subsequent steps further aliquots of CaCl_2 were added until the total amount of calcium added was equal to that added in the corresponding "straight through" experiment ($3,4 \cdot 10^{-3}$ N). Within experimental error the degree of exchange at final equilibrium (0,88) was equal to that seen in the "straight through" exchange (0,90). For each incremental step $\bar{D}$ values were calculated and are shown against M_t/M_∞ for each step in figures 34 to 38. Table 8 gives the Ca_z , M_z/M_s , and w values for each step. A few of the steps suffered from slow electrode response and were not used for subsequent calculations. For the initial steps the calcium fraction in the solution, Ca_s , varied between 0,05 and ~ 0 , so that the calcium concentration at the zeolite surface varied between 0,85 and 10^{-3} (figure 27) and hence w increased from 0,8 to 100 as M_t/M_∞ increased (figure 28).

$\bar{D}$ dropped rapidly at the end of each step, particularly for the initial steps, $\text{Ca}_z < 0,43$ (figures 34, 35). This was due to the approach of equilibrium and exhaustion of calcium in solution. With all of the steps, apart from the one for $\text{Ca}_z = 0,78$ to 0,81, there is a tendency for $\bar{D}$ to decrease as M_t/M_∞ increases, once past the initial electrode lag period (i.e. for $M_t/M_\infty > 0,4$), in a similar way to the "straight through" exchange (figure 29). If the $\bar{D}$ values of each step are plotted against the corresponding Ca_z values (figure 39), the overall trend is for $\bar{D}$ to

Figure 34.

Na-Ca stepwise
exchange;
 $TN = 3,4 \cdot 10^{-3}N$;
 $25^{\circ}C$.

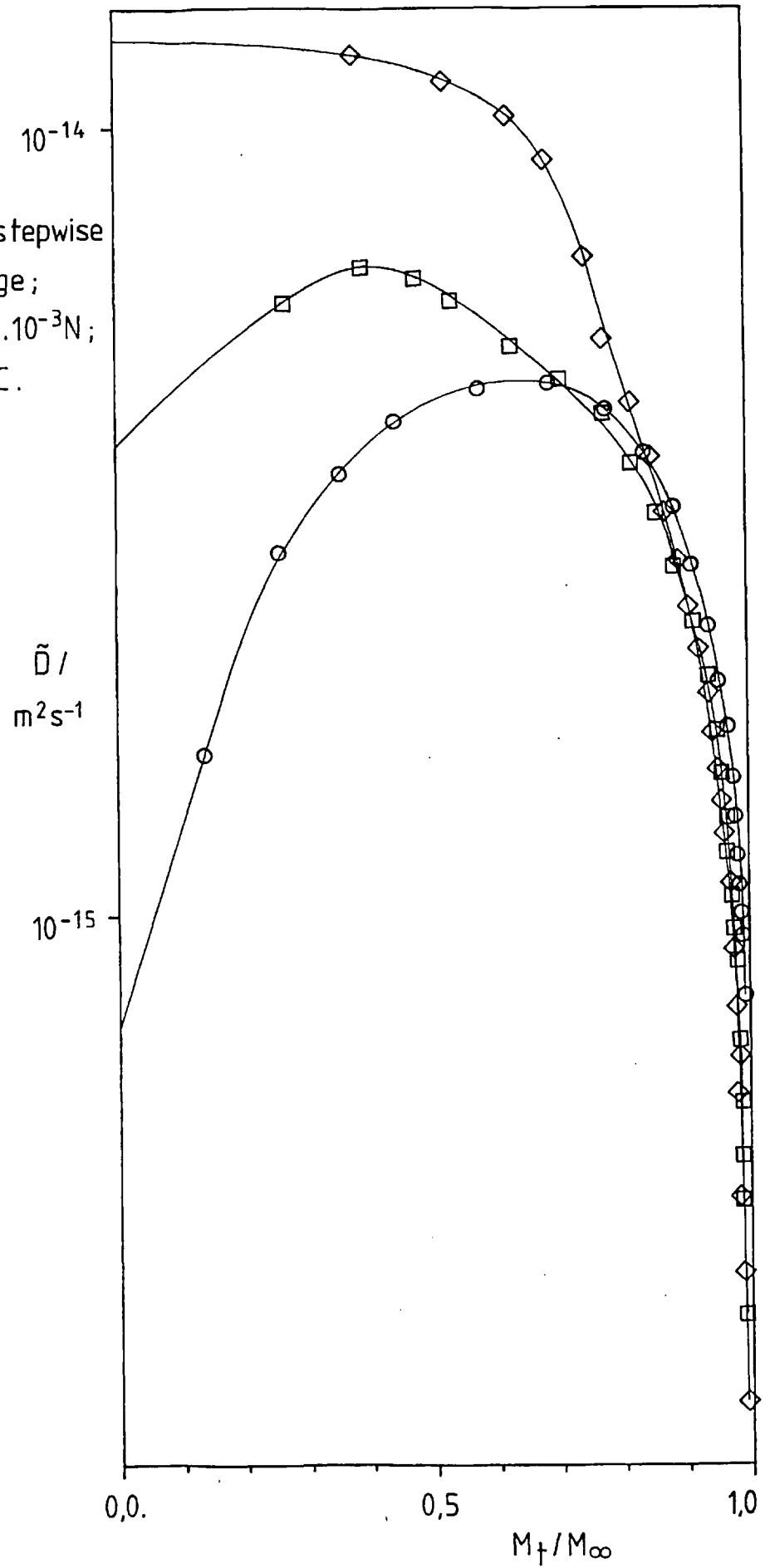


Figure 35.

Na-Ca stepwise
exchange;
 $TN = 3,4 \cdot 10^{-3} N$;
 $25^\circ C$.

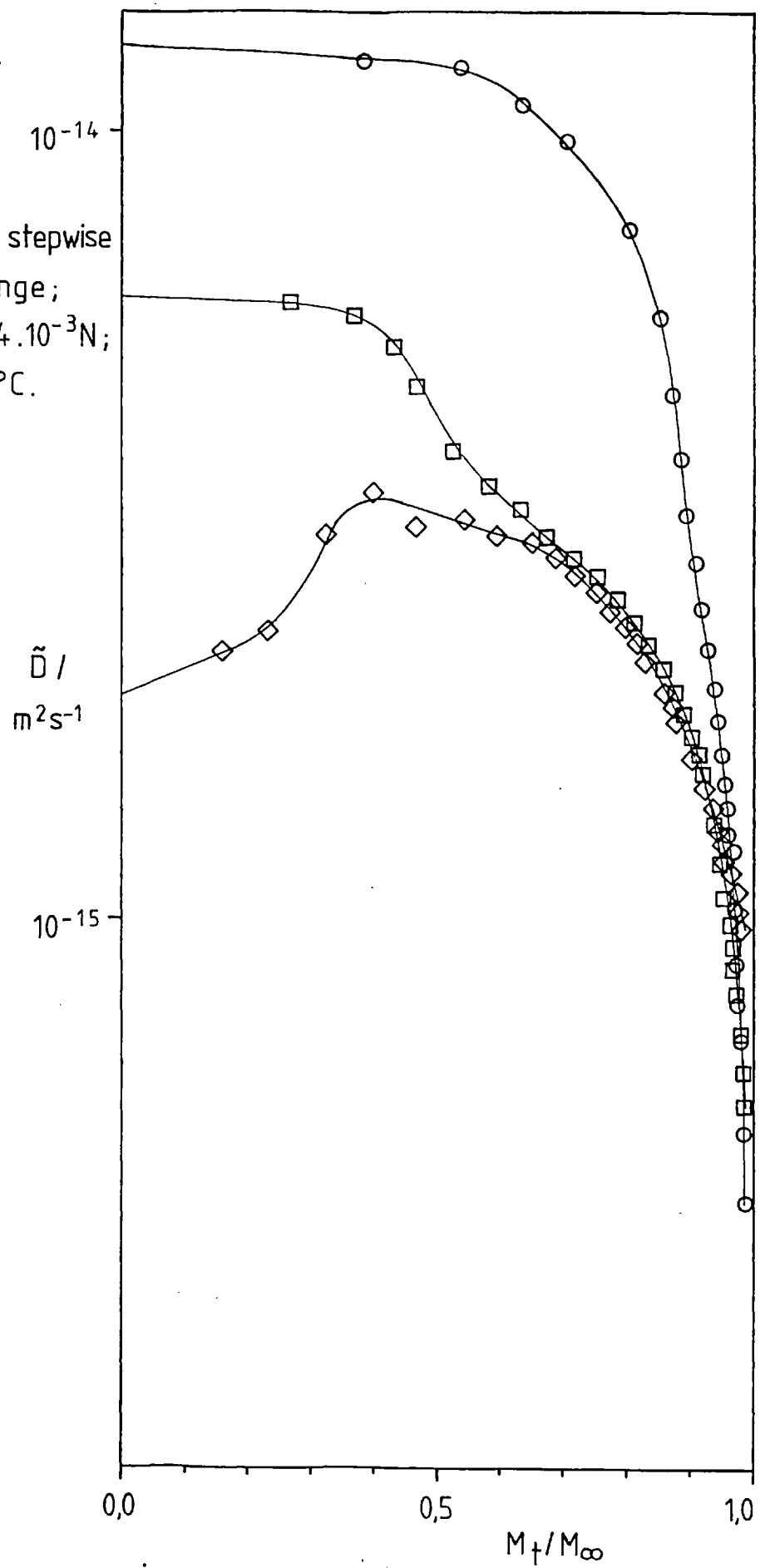


Figure 36.

Na-Ca stepwise
exchange ;
 $TN = 3,4 \cdot 10^{-3} N$;
 $25^{\circ}C$.

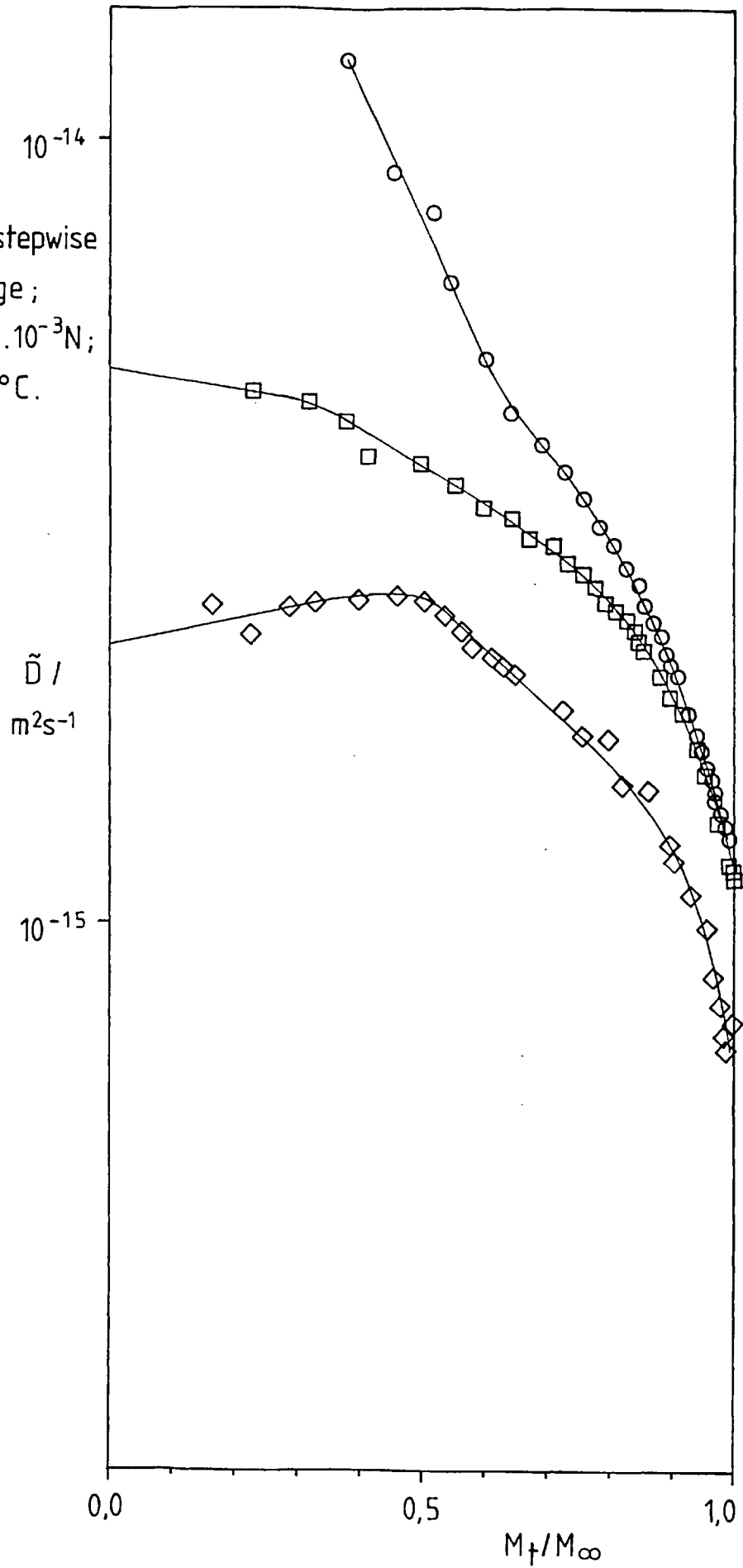


Figure 37.

Na-Ca stepwise
exchange ;
 $TN = 3,4 \cdot 10^{-3} N$;
25°C.

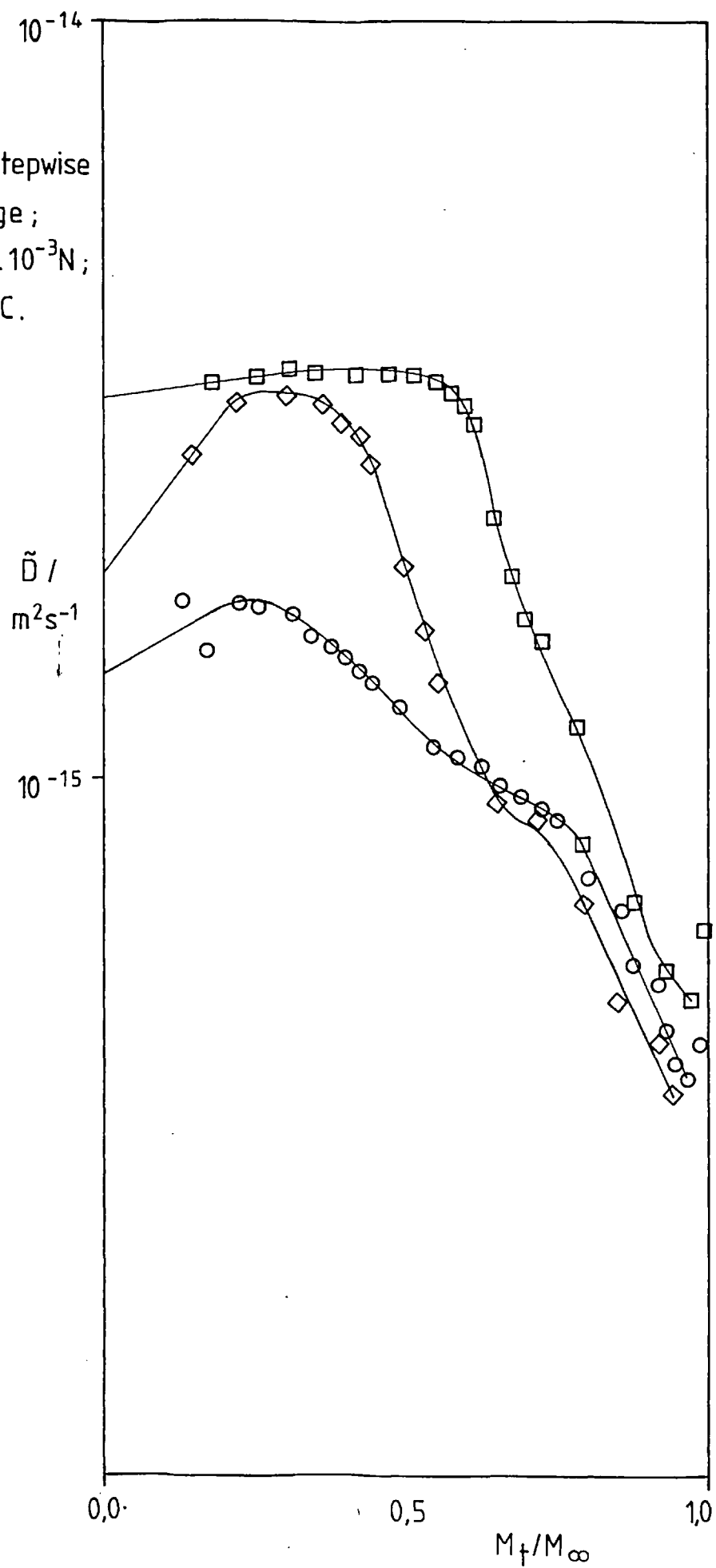


Figure 38.

Na-Ca stepwise
exchange;
 $TN = 3,4 \cdot 10^{-3} N$;
 $25^{\circ}C$.

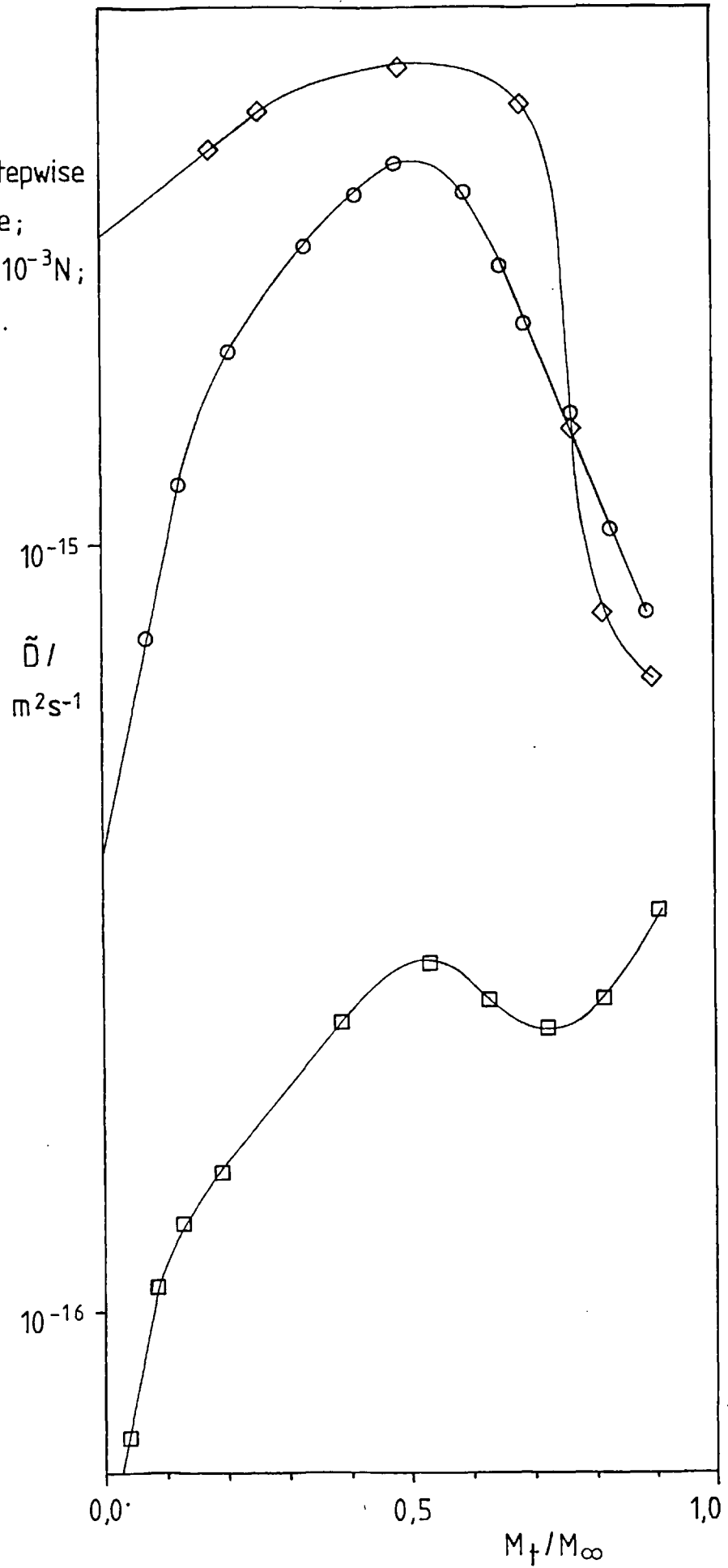


Figure 39.

Na-Ca stepwise
exchange ;

$TN = 34 \cdot 10^{-3} N$;

$25^{\circ}C$.

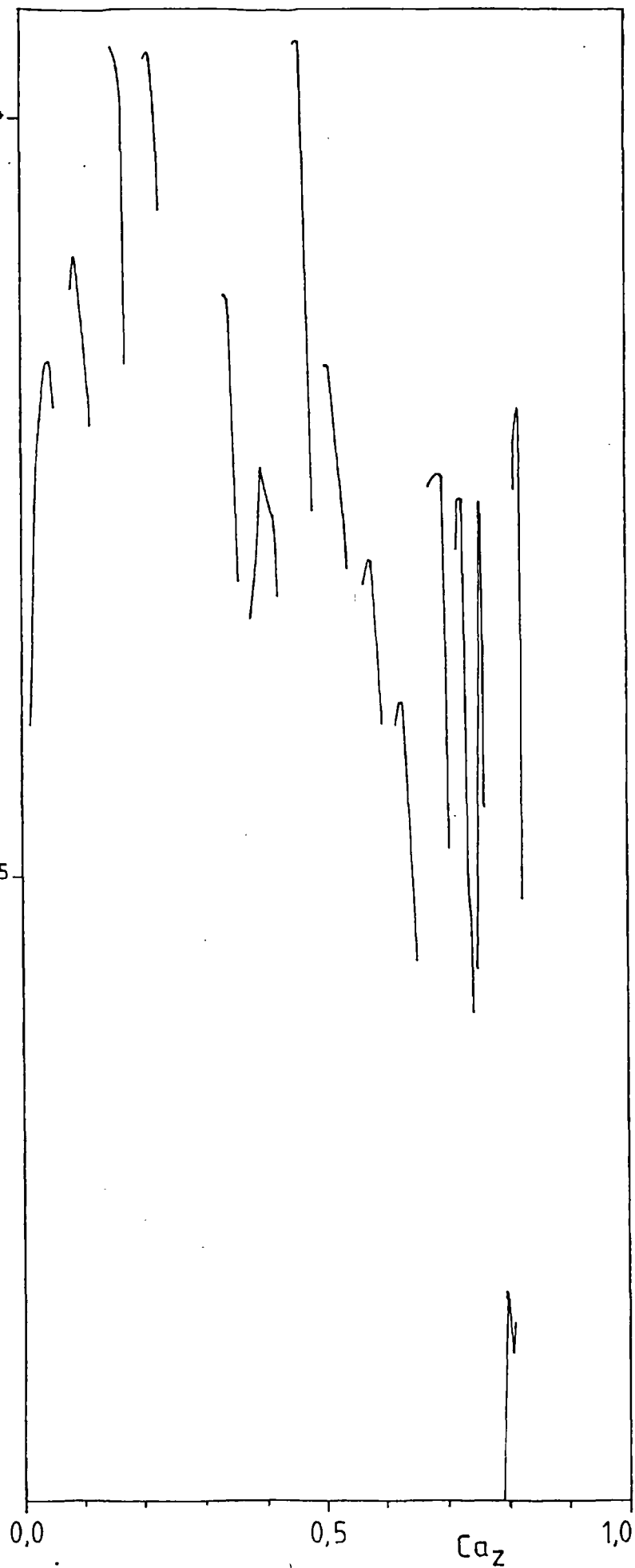
Each step
plotted over
 Ca_z range of
that step.

$a_o = 9,3 \mu m$.

$\tilde{D} /$
 $m^2 s^{-1}$

10^{-15}

10^{-14}



decrease as Ca_2 increases and the variation of $\tilde{D}$ is similar to that of the "straight through" exchange (figure 29). Overall the $\tilde{D}$ values for the stepwise exchange (figure 39) were higher than those from the "straight through" exchange, possibly due to the w factor under-correcting for the variation in zeolite surface concentration. The $\tilde{D}$ curves from each step do not connect with the next step, i.e. $\tilde{D} (M_t/M_\infty=1)$ for step one does not equal $\tilde{D} (M_t/M_\infty=0)$ of step two as the zeolite surface concentration changes dramatically when the CaCl_2 is added to start the next step.

Wolf et al (93, 94) carried out a similar series of experiments for Na - Ca, Na - Mg and Na - Mn exchange. Each step was carried out 20 to 25 times to yield 20 to 25 M_t/M_∞ , t pairs from which $\tilde{D}$ values were calculated. The data pairs were determined by taking one sample at a known time and analysing for the divalent cation. Zeolite A samples with different calcium contents were prepared separately for each step such that the calcium content at equilibrium in one step was equal to the content of the sample used for the next step. Wolf et al used an isotherm to deduce the calcium contents and it should be noted that they found hysteresis (93) unlike more recent determinations (78, 79). For Na - Ca exchange the complete range of calcium content from 0,0 to 0,925 was covered in a similar way to the experiment described herein.

From their $\tilde{D}$ values they proceeded to calculate $\bar{D}$ values using the approximation (122).

$$\log \bar{D} = \frac{2 \log \tilde{D} - (1 - F) \log \tilde{D}_0}{1 + F} \quad (6.1.2)$$

where $F \equiv M_t/M_\infty$ and $\tilde{D}_0$ is the extrapolated value of $\tilde{D}$ at $F=0$.

Table 8

Values for points plotted in figures 34 to 38.

Figure	Symbol	Ca _z range (%)	M _z /M _s	w range
34	○	0,28 + 6,44	0,772	0,809 + 122
	□	6,44 + 12,62	0,737	0,974 + 148
	◇	12,62 + 18,78	0,705	1,19 + 126
35	○	18,78 + 24,94	0,676	1,19 + 89,1
	□	31,10 + 37,23	0,624	0,99 + 51,4
	◇	37,23 + 43,28	0,601	0,84 + 24,5
36	○	43,28 + 49,32	0,579	1,16 + 22,0
	□	49,32 + 55,27	0,559	0,897 + 14,0
	◇	55,27 + 61,03	0,541	0,787 + 6,8
37	○	61,03 + 66,51	0,523	0,699 + 3,29
	□	66,51 + 71,53	0,507	0,703 + 2,34
	◇	71,53 + 74,86	0,492	0,527 + 0,816
38	○	74,86 + 76,32	0,477	0,378 + 0,429
	□	78,33 + 81,18	0,451	0,202 + 0,233
	◇	81,18 + 82,78	0,438	0,174 + 0,184

This equation assumes that:

$$0,6 < \bar{D}_{0,5} / \sqrt{\bar{D}_0 \bar{D}_1} < 1,7$$

The value of $\bar{D}_0$ is subject to quite large errors as the initial period of exchange is effected by the rate of mixing and in the case of Wolf et al by the time to sample the solution phase. This uncertainty

would be increased by their use of small crystals ($a_0 = 2,2\mu\text{m}$) giving appreciably faster exchange than the present study ($a_0 = 6,3\mu\text{m}$). $\bar{D}$ values were therefore recalculated from the results of Wolf et al (fig. 40) rather than calculating $\bar{D}$ values for the present study.

Comparing figures 39 and 40 the diffusion coefficients are of the same magnitude but the trends seen by Wolf et al are not seen in the present study although in both cases there is a maximum at $\text{Ca}_z \approx 0,5$ and a minimum of $\text{Ca}_z = 0,65 \pm 0,03$. The differences between the present results and those of Wolf et al are undoubtedly related to the difference in solution concentration, in particular the tendency in the present study for the solution calcium concentration to approach zero at the end of each step. As was mentioned earlier, Wolf et al explained their results in terms of a composition dependent mechanism (94) but erroneously assumed six site IIs per unit cell.

From the area above the $\sqrt{t}$ plots of the present study an average diffusion coefficient was calculated for each step using equation 2.2.10 and they were plotted against the average Ca_z for that step (figure 41) to show the overall trend. The initial diffusion coefficients are quite high as no allowance has been made for the zeolite surface concentration (i.e. $w = 0$). The diffusion coefficients variation bears some resemblance to that seen by Wolf et al and also to the "straight through" exchange (figure 29) with the diffusion coefficient decreasing as Ca_z increases.

The kinetics of Na-Mg exchange were determined for a TN of $3,92 \cdot 10^{-3} \text{N}$ (plus 10^{-3}M NMe_4OH background) giving a slightly greater excess of ions in the solution than was the case for Na-Ca exchange. The resulting $\sqrt{t}$ plots for Charnell synthesised ($a_0 = 6,3\mu\text{m}$) and commercial (Laporte, $a_0 = 2,6 \mu\text{m}$) zeolite A are shown in figures 42 and 43. Figure 42 is to the same scale as figure 26 and clearly shows that Na-Mg exchange

Figure 40.

Na-Ca stepwise
exchange;
TN = 0,1 N ; 25°C.
Derived from
results of
Wolf et al.
 $a_o = 2,2 \mu\text{m}$.

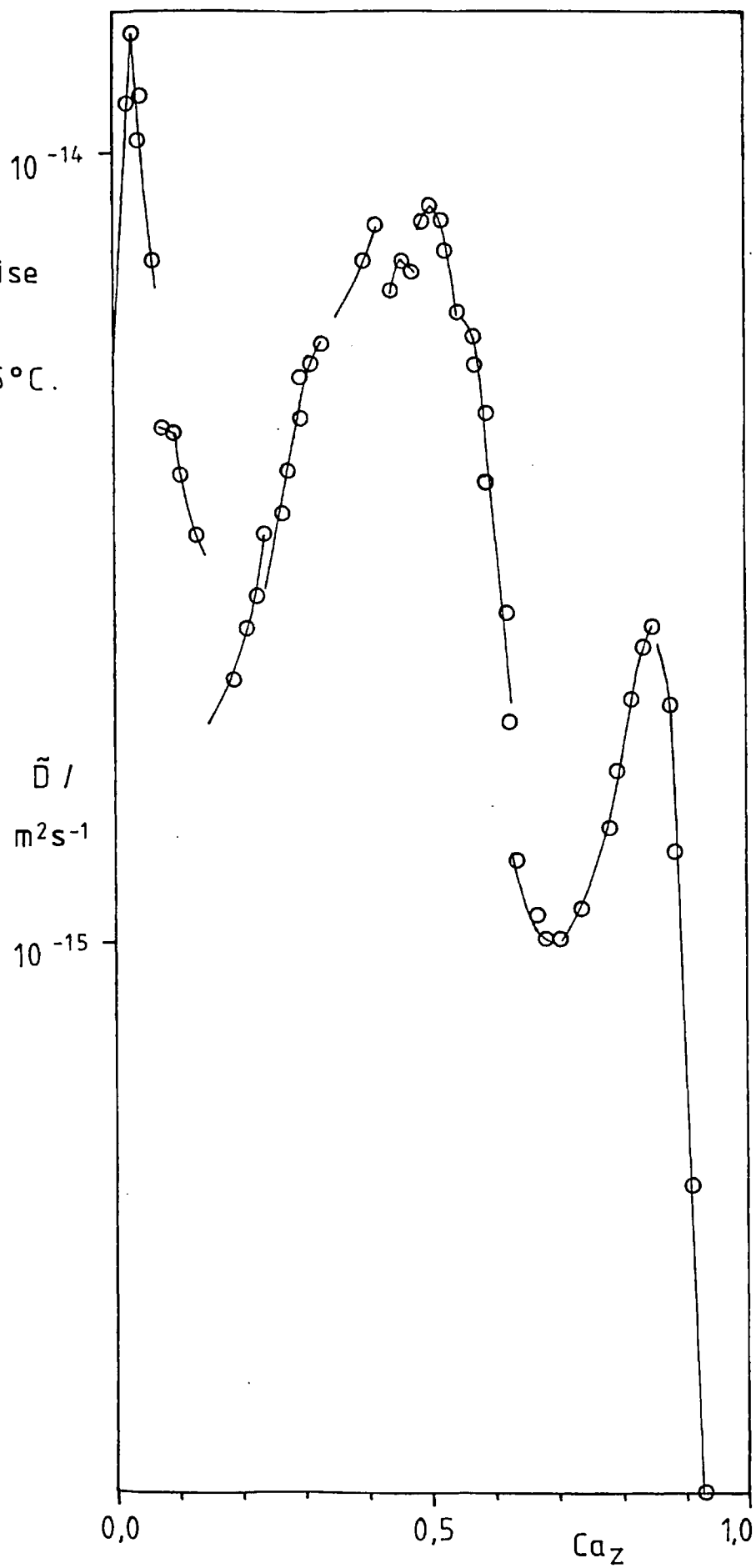


Figure 41.

Na-Ca stepwise
exchange ;
 $TN = 3,4 \cdot 10^{-3} N$;
 $25^{\circ}C$.

Average D vs.
average Ca_z
for each step.

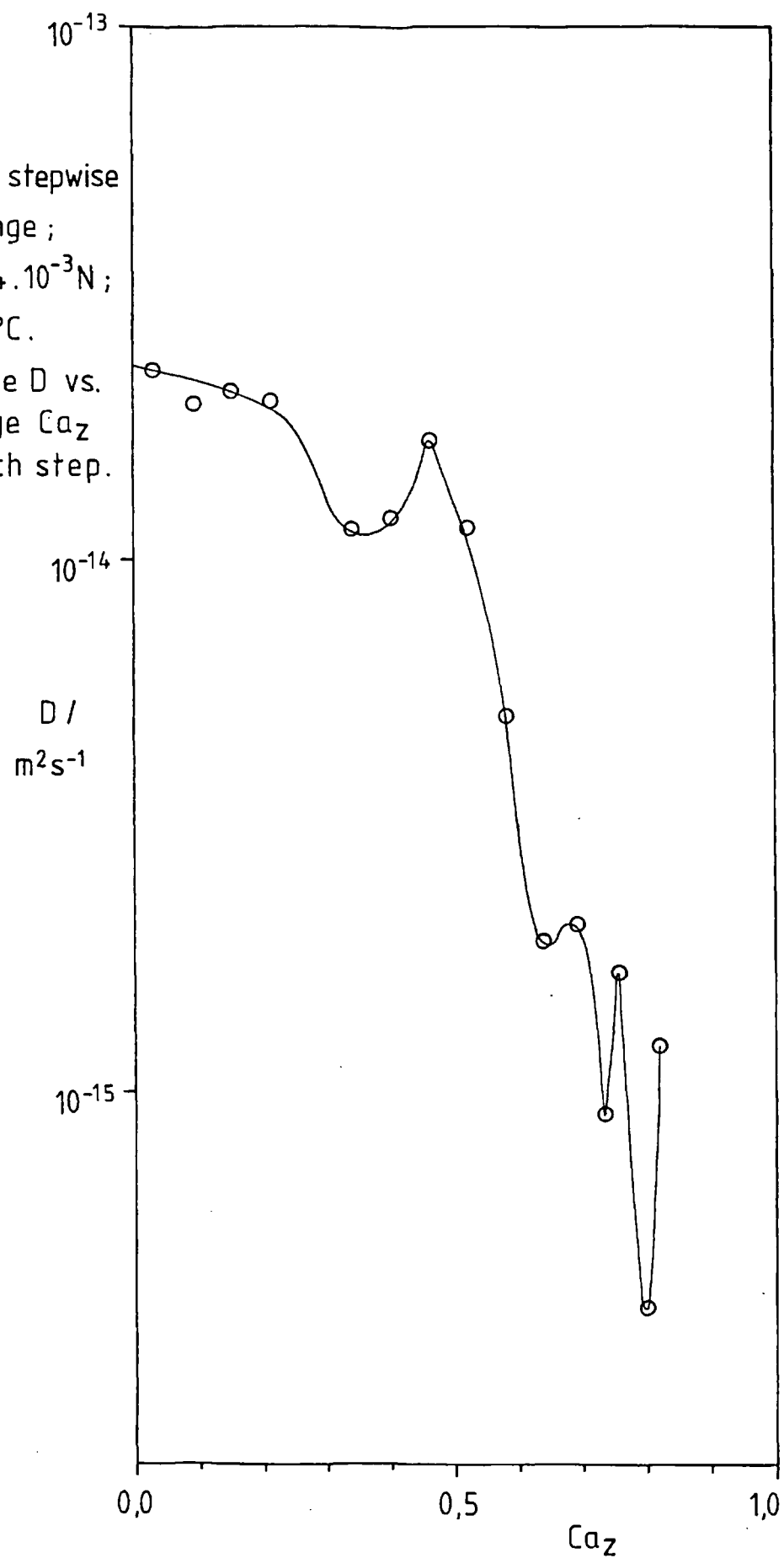


Figure 42.

Na-Mg exchange ; $TN = 3,92 \cdot 10^{-3} N$.

$a_o = 2,6 \mu m$ $\blacklozenge$ $\blacksquare$ $\bullet$ $\blacktriangle$;

$a_o = 6,3 \mu m$ $\diamond$ $\square$ $\circ$.

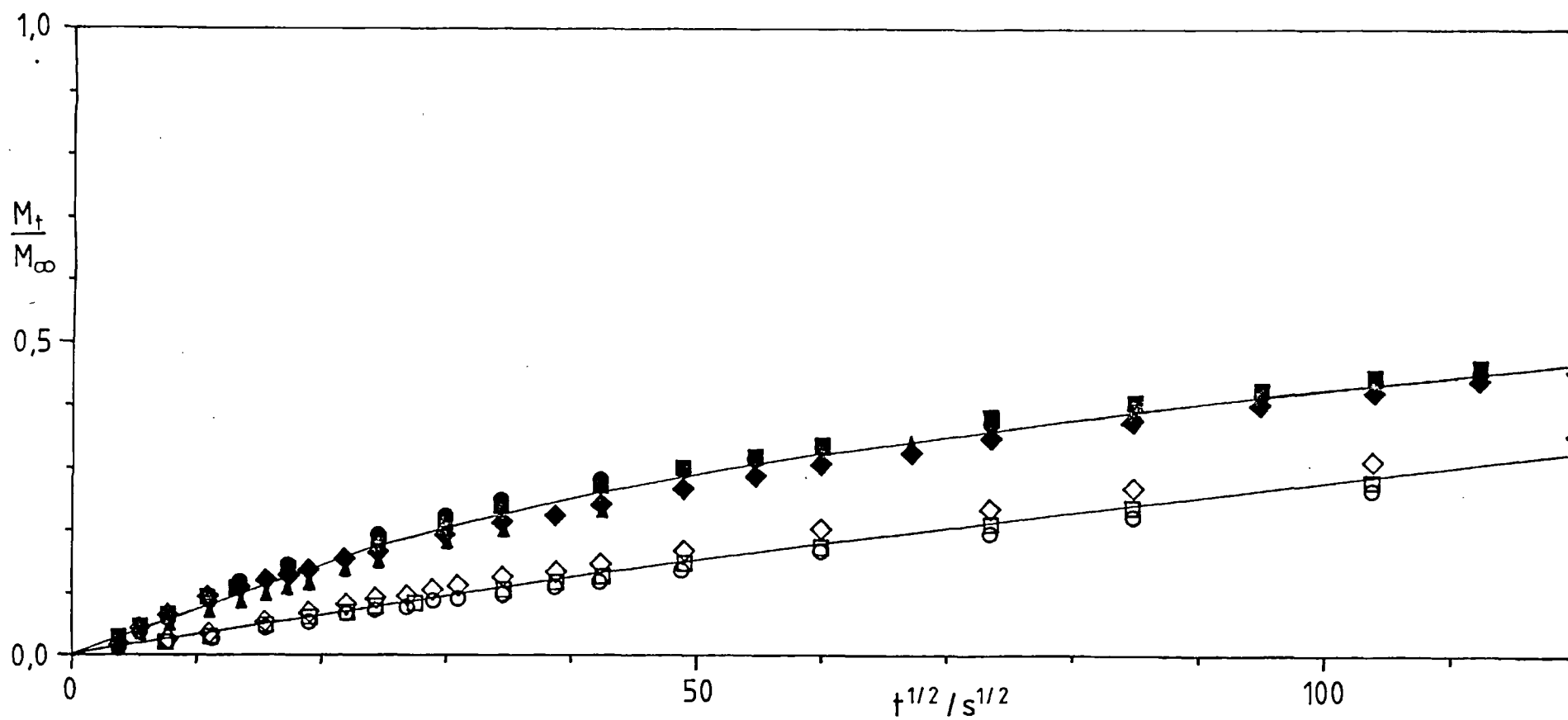
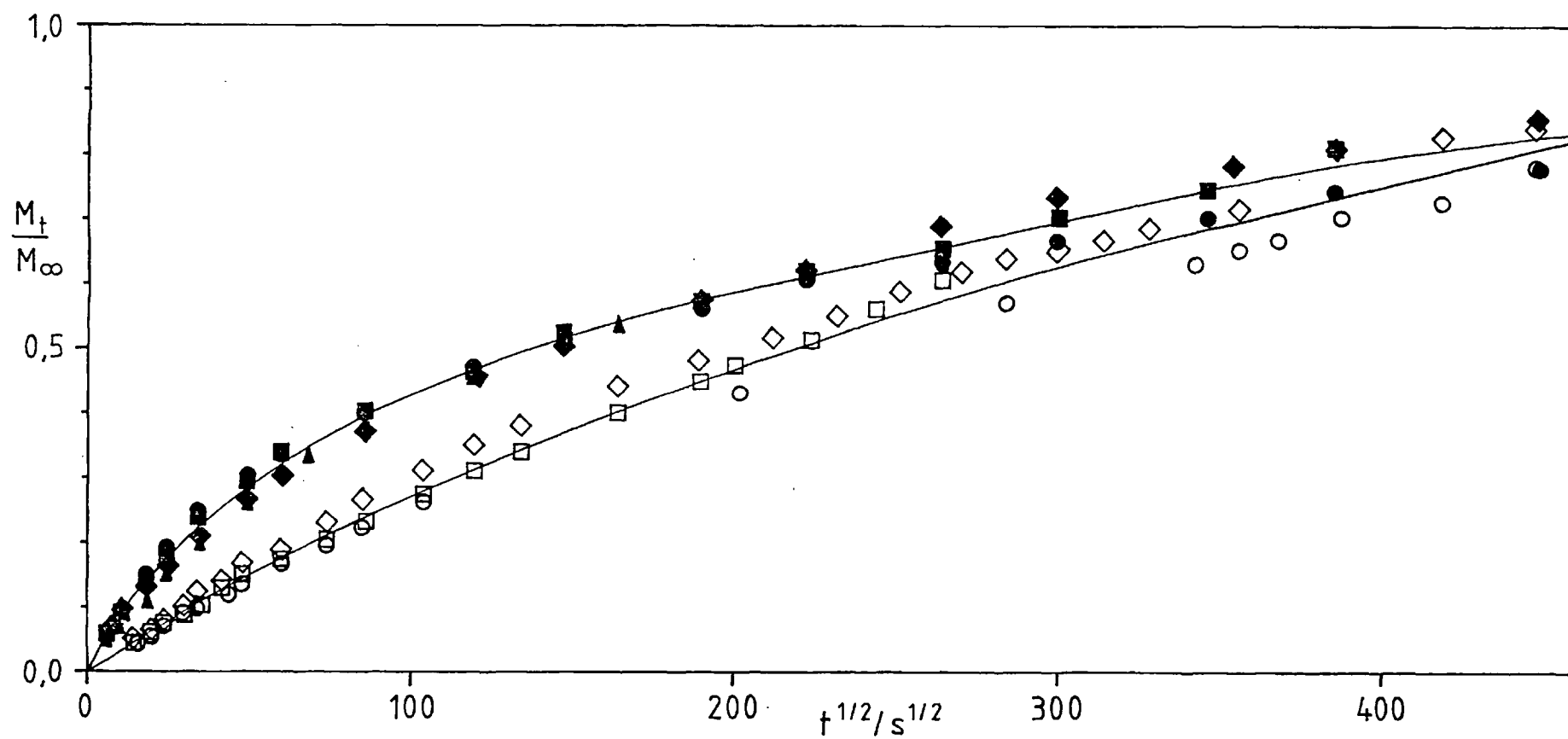


Figure 43.

Na - Mg exchange ; $TN = 3,92 \cdot 10^{-3} N$.

$a_o = 2,6 \mu m$ $\blacklozenge$ $\blacksquare$ $\bullet$ $\blacktriangle$;

$a_o = 6,3 \mu m$ $\diamond$ $\square$ $\circ$.



is much slower than Na - Ca exchange. Dyer et al found that the self diffusion coefficient of magnesium was approximately one-third of that of calcium (at 25°C) and combining this with a slightly less favourable activity term (78) could lead to the observed difference in rates, when considering the theory of Brooke and Rees (eqn. 2.4.5). The large difference between the sodium and calcium/magnesium self diffusion coefficients makes these systems unsuitable for calculation using Brooke's program (97, 98).

Figure 43 shows that the kinetics were initially much faster for the small crystals but after some four hours the curves start to converge. The exact cause of this is not known although the slowness of these kinetics (five days to equilibrium) gave rise to approximately 10% uncertainty in values and an added uncertainty due to hydrolysis. Atomic absorption measurements indicated 5-10% hydrolysis and the kinetics measurements gave high sodium elution (in two cases giving 90% exchange compared with the isotherm value of 70%). This hydrolysis would occur throughout the exchange with unpredictable results as hydrolysis of the zeolites outer layers could alter the rate of cation diffusion. Over the period of the exchange carbon dioxide absorption could alter the pH, and hence the rate of hydrolysis. The exchange could not be carried out for pH >10 due to magnesium hydroxide precipitation. Hydrolysis was not a problem during Na - Ca exchange due to the faster rate of exchange (see chapter 5, figure 23). Measuring Na - Mg kinetics by monitoring the solution magnesium concentration was not possible due to long term instability of the divalent electrode.

Figure 44 shows the results of A. De Jonge (measured radio chemically) and S.A.I. Barri compared with the present work. These exchanges used a TN of 0,2N and 0,1N respectively and S.A.I. Barri used 10^{-4} M NaOH

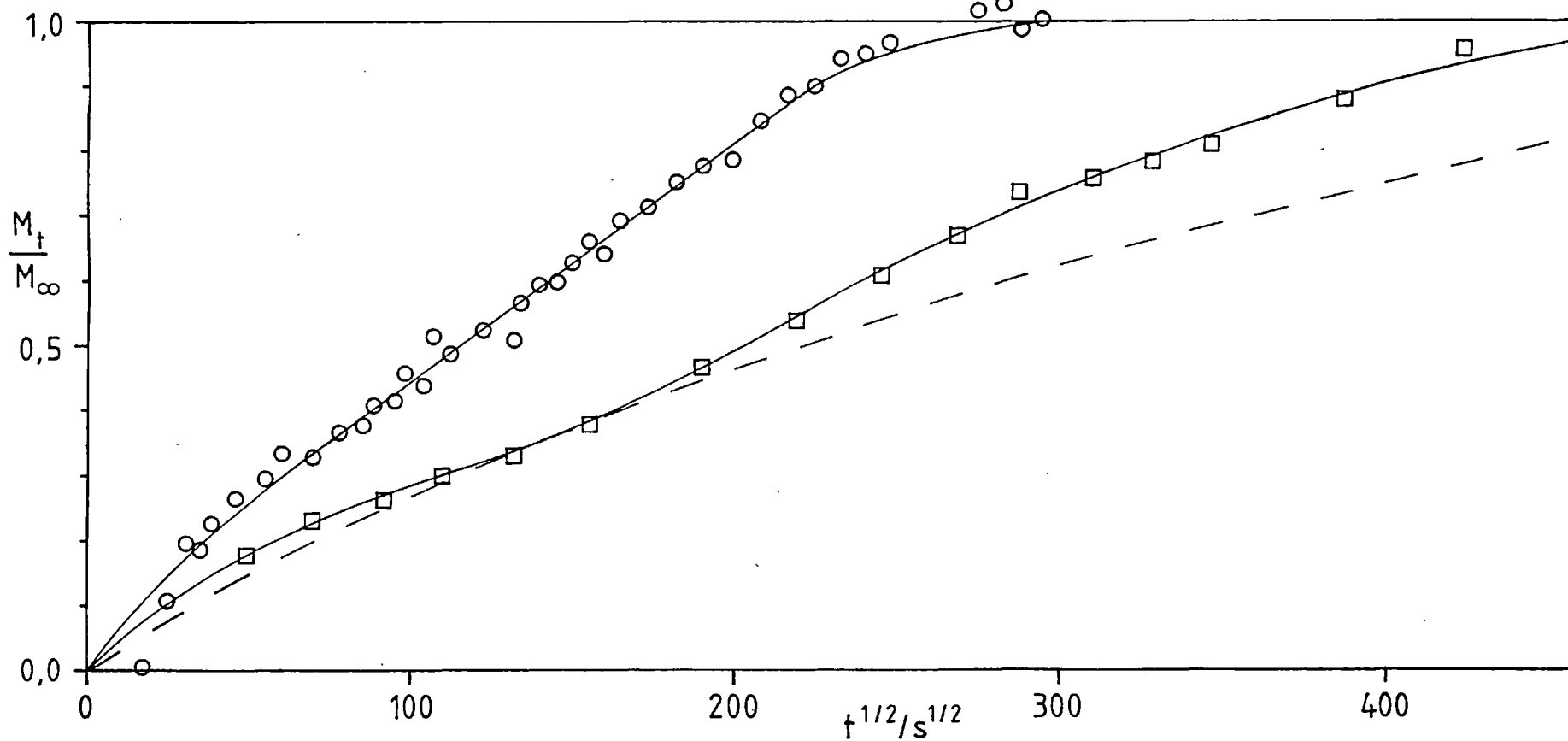
Figure 44.

Na - Mg exchange.

○ $TN = 0,2 \text{ N}$; $a_o = 7,2 \mu\text{m}$ - from A.De Jonge.

□ $TN = 0,1 \text{ N}$; $a_o = 9,3 \mu\text{m}$ - from S.A.I. Barri.

— $TN = 3,92 \cdot 10^{-3} \text{ N}$; $a_o = 6,3 \mu\text{m}$ - this work.



for pH control (8,5). A. De Jonge found a large scatter in values, particularly at equilibrium and analysis of the resulting zeolite A gave 5-10% less sodium than indicated by isotherm (see figure 45). This result obviously implies hydrolysis. The rate measured by S.A.I. Barri bears some resemblance to that found in the present study although the curve is of unusual form and the rate is generally faster despite the larger crystals. The rate found by A. De Jonge is appreciably faster than the other experiments including that using small crystals ($a_0 = 2,6\mu\text{m}$).

The resulting diffusion coefficients from these experiments are shown in figure 46. The diffusion coefficients obtained by A. De Jonge (0,2 TN) and S.A.I. Barri (0,1 TN) were calculated using a constant w value ($= M_z/M_s$) due to lack of activity coefficient data and also because the value of Mg_z at the ingoing surface of the zeolite would be practically constant for such high solution concentrations (see figure 45). The diffusion coefficients for the present experiments are some one hundred times lower than those for Na - Ca exchange. It can be seen that the present experiments with two crystal sizes agree closely for the first 20% of exchange which confirms particle kinetics. The diffusion coefficients then diverge as the $\sqrt{t}$ plots converge, possibly due to hydrolysis although why this should have a different effect on the two crystal sizes is not clear. An alternative explanation would be that the rate determining step changes at 20% exchange and that one exchange continues with the same rate determining step whilst the other changes. Helfferich points out (136) that "the tendency toward particle diffusion control increases as the exchange progresses", so that rate determining step cannot change from particle to film diffusion. One possibility is that the first magnesium ion goes into site II thus blocking the windows into the α cage but this would effect

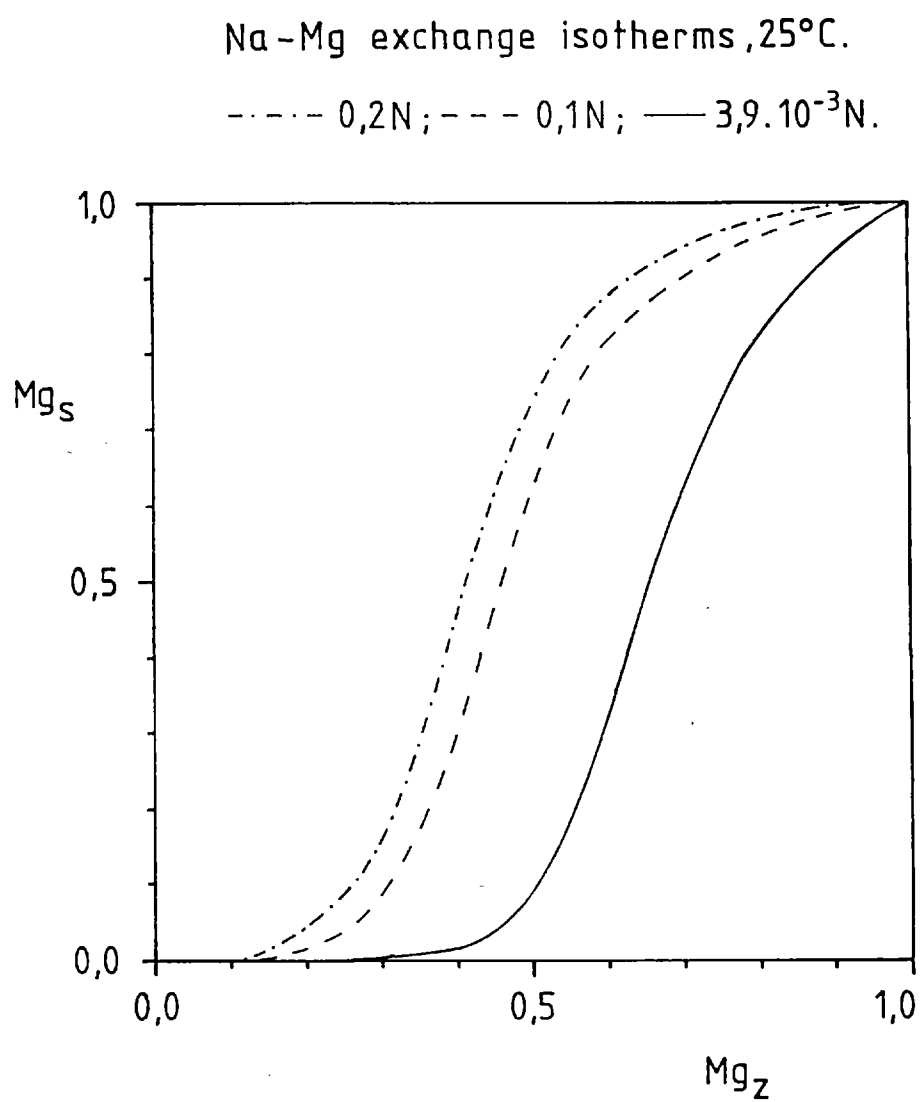
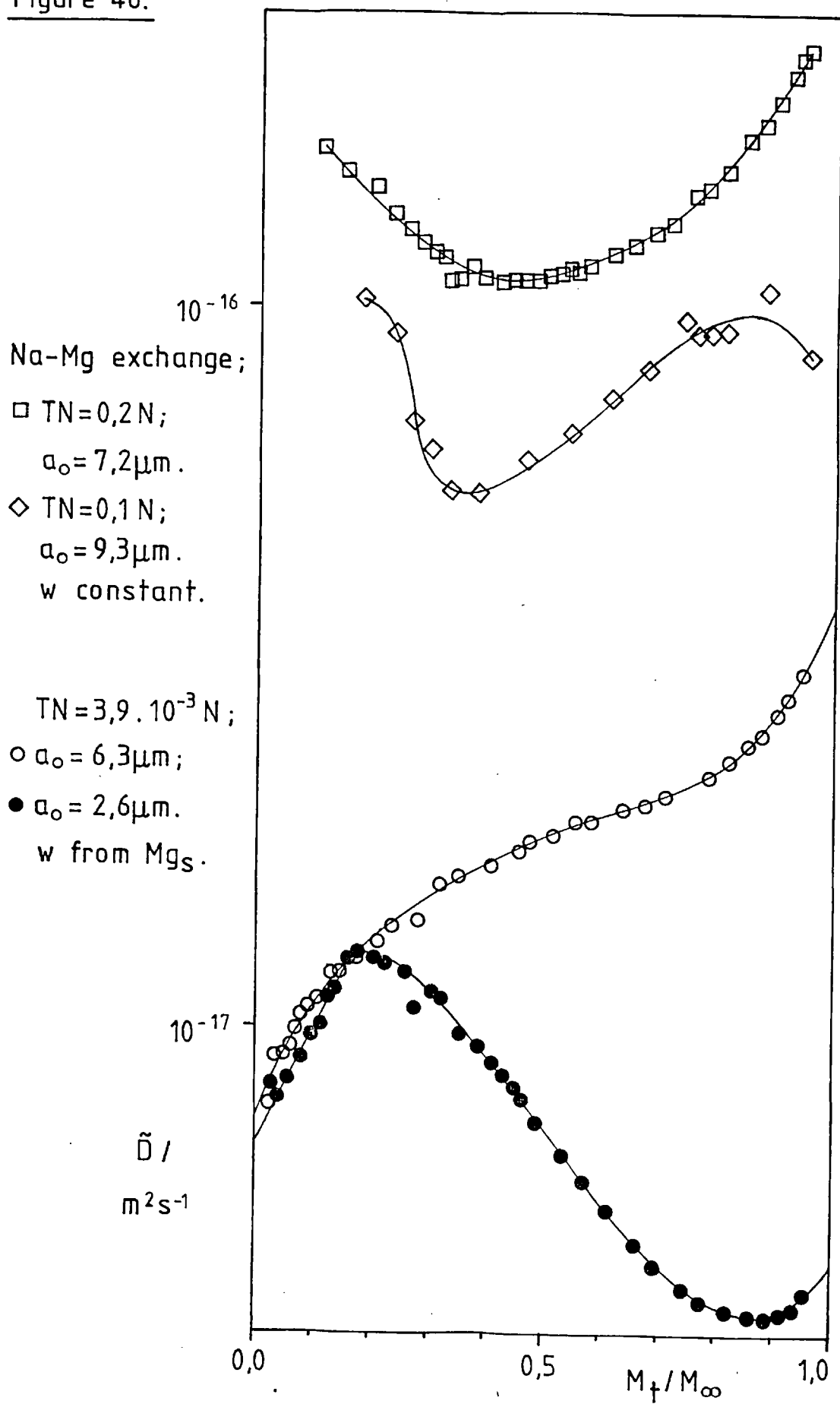
Figure 45.

Figure 46.



the exchange with both crystal sizes. Considering the results of A. De Jonge and S.A.I. Barri both of these experiments gave higher diffusion coefficients which rise for M_t/M_∞ greater than 40%, in a similar way to the present results for $a_0 = 6,3\mu\text{m}$. The higher $\bar{D}$ s would seem to be related to solution concentration although a higher solution concentration favours particle kinetics. The difference could be related to the effect of solution concentration on the composition of the incoming surface of the zeolite, and to variation of self diffusion coefficients with composition (non-ideality).

The kinetics of Na-Ba exchange were also determined for a TN of $3,4 \cdot 10^{-3} \text{N}$ with 10^{-3}M NMe_4OH background. The resulting $\sqrt{t}$ plot is shown in figure 47 where it can be compared with the corresponding Na-Ca exchange. The two curves are identical within experimental error for the first 75% of exchange although the self diffusion coefficients determined by Dyer et al (80, 81) differed by a factor of 30. The activity term in the theory of Brooke and Rees would have to be sufficient to give a D_{AB} variation similar to that for Na-Ca exchange or alternatively the self diffusion coefficients would have to be closer to one another. The calculated diffusion coefficients (figure 48) are in close agreement as were the $\sqrt{t}$ plots.

6.2 SODIUM-CALCIUM/MAGNESIUM TERNARY EXCHANGE

The kinetics of exchange in the Na-Ca/Mg ternary system were studied for Ca:Mg solution phase ratios of 0,87:1 and 1,74:1 with TNs of $3,7 \cdot 10^{-3} \text{N}$ and $3,6 \cdot 10^{-3} \text{N}$ respectively. A background of 10^{-3}M NMe_4OH was used for pH control. Both sodium and calcium solution concentrations were monitored to give a complete picture of the exchange process. Figure 49 shows the total fractional loss of sodium for the

Figure 47.

○ □ Na-Ba exchange, $TN = 3,4 \cdot 10^{-3} N$, $a_o = 6,3 \mu m$.

..... Na-Ca exchange, II , II .

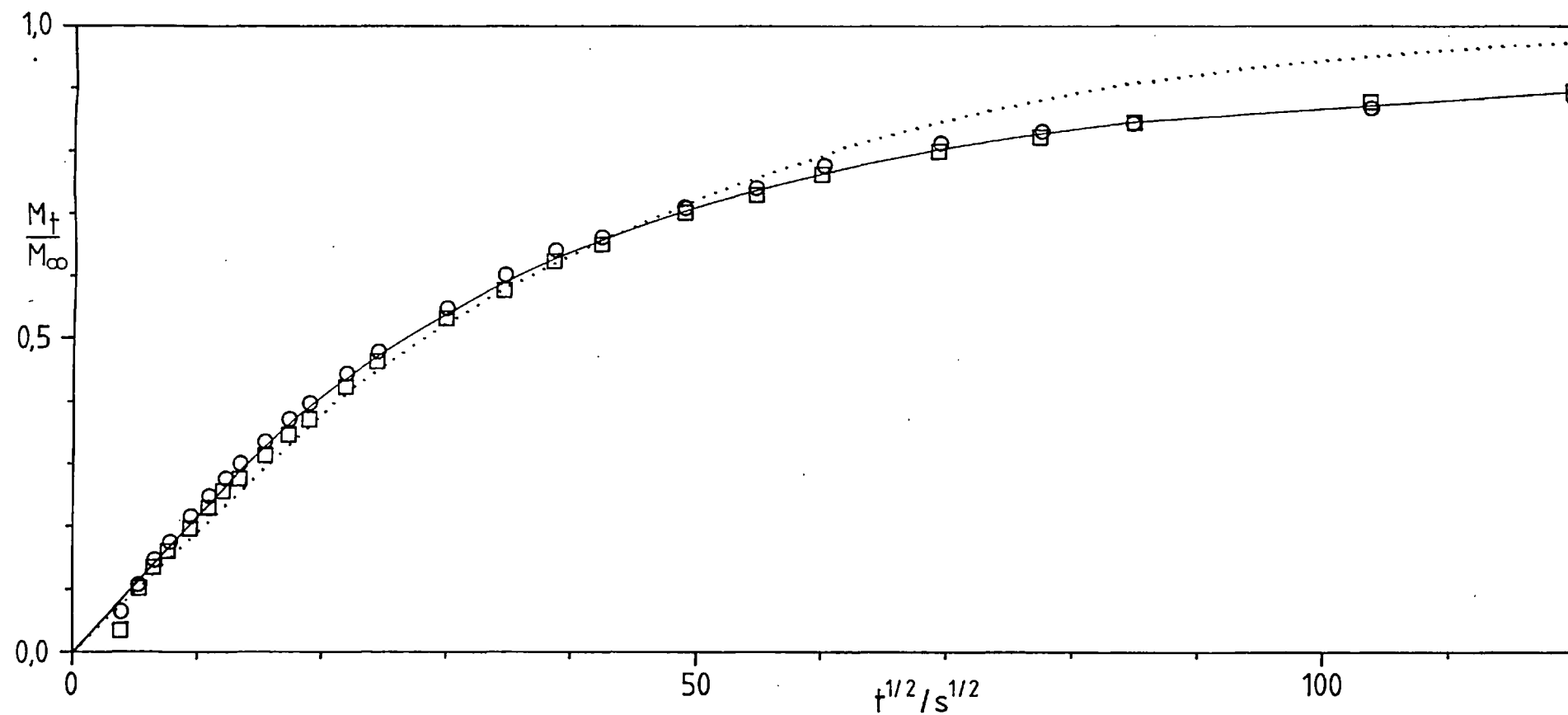
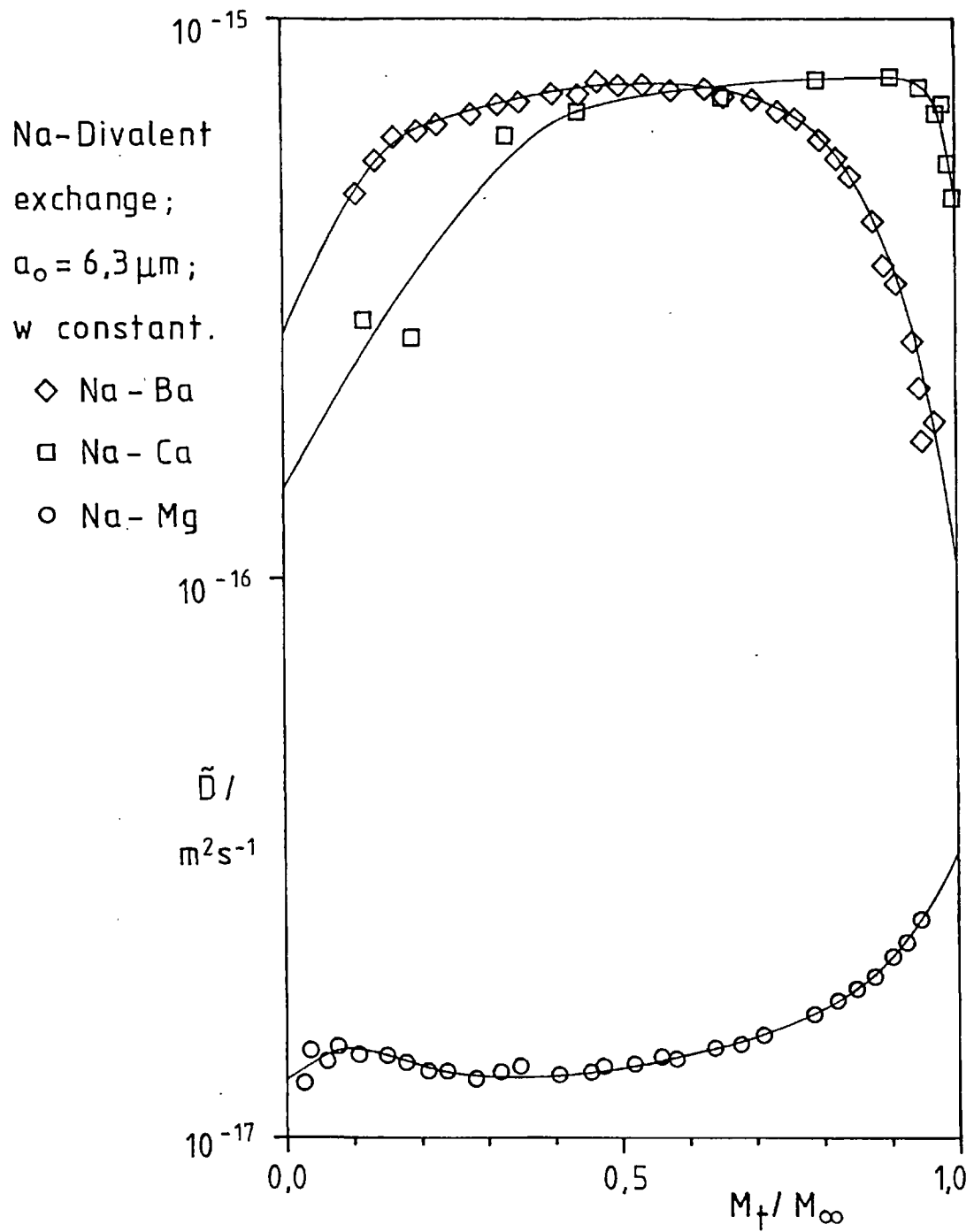


Figure 48.



two Ca:Mg ratios. The AAS error bars were determined in a separate experiment in which samples were taken at known times and analysed by atomic absorption spectrometer. The only effect of the change in ratios was that the exchange with lower solution calcium level gave a lower overall degree of exchange. In fact the calcium was almost completely exchanged into the zeolite. The initial exchange rates were identical and were very close to the Na - Ca rate of exchange.

Figure 50 shows the uptake of calcium and magnesium for the two ratios compared with the rates for Na - Ca and Na - Mg binary exchange. The rates of calcium uptake were identical within experimental error and only differ as equilibrium was approached. The equilibrium uptake of Ca was directly related to the initial solution Ca concentration. The rates of magnesium uptake were initially identical but the rates for ternary exchange then levelled off and no further Mg uptake occurred until the Ca uptake was practically complete. It appears that the Ca uptake either blocks out the Mg or exchanges with any Mg that has itself exchanged with Na. Once this phase was completed the uptake of Mg continued at roughly the same rate as that for the binary Na - Mg exchange. The uptake of Mg was also directly related to the initial solution Mg concentration.

An effect which is not clearly shown in figure 50 was that the solution Ca concentration actually went through a minimum and started to rise very slowly. This corresponds to the prediction of Helfferich (136) that for a particle diffusion controlled exchange in a ternary system with A initially in the ion exchanger and B and C in the solution:

"If B is much more mobile than C..... now B will rapidly replace A and the uptake of C will lag far behind. Later, C will follow, partly replacing the B ions that were taken up in the earlier stages.

Figure 49.

Ternary ion exchange ; Na - Ca / Mg.

○ Ca : Mg = 0,87 : 1 ; ● Ca : Mg = 1,74 : 1.

┘ A.A.S., 5% error bars, Ca : Mg = 0,87 : 1.

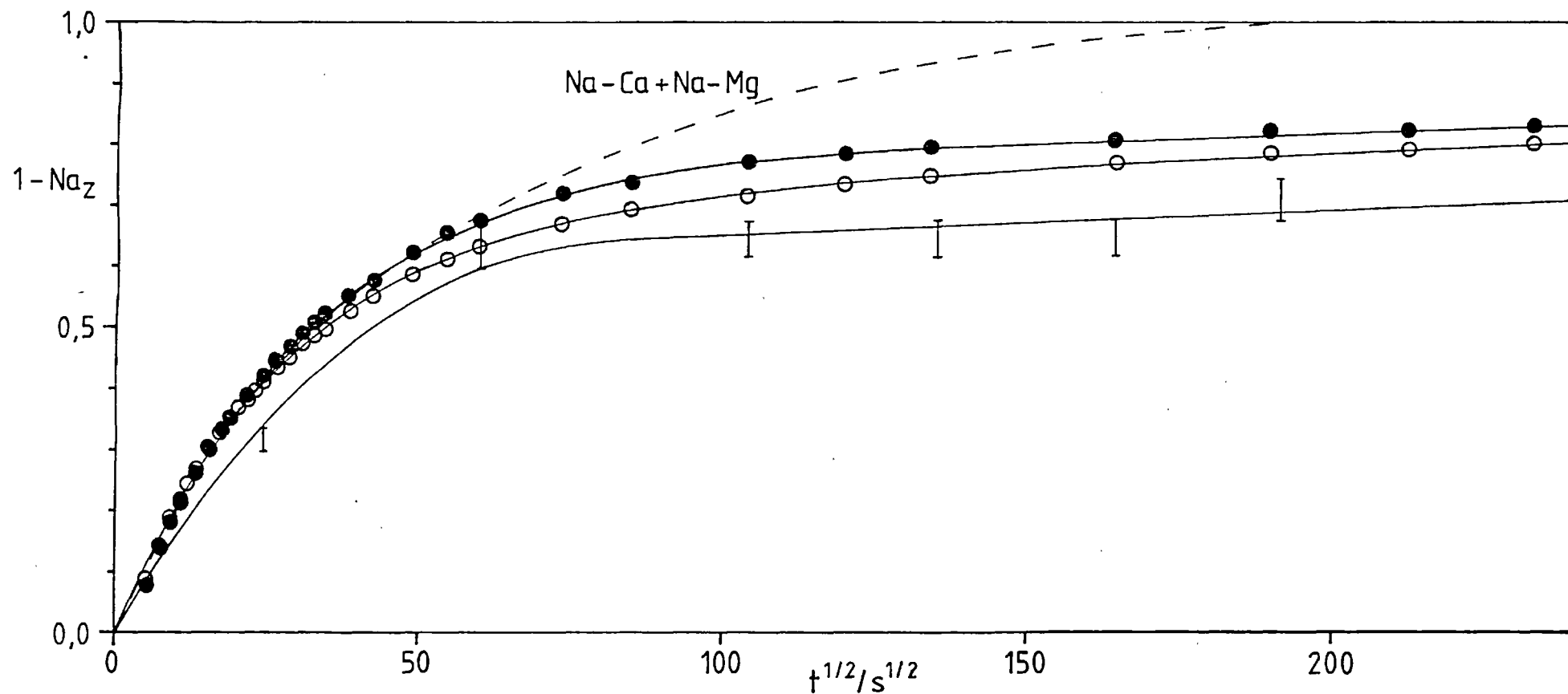
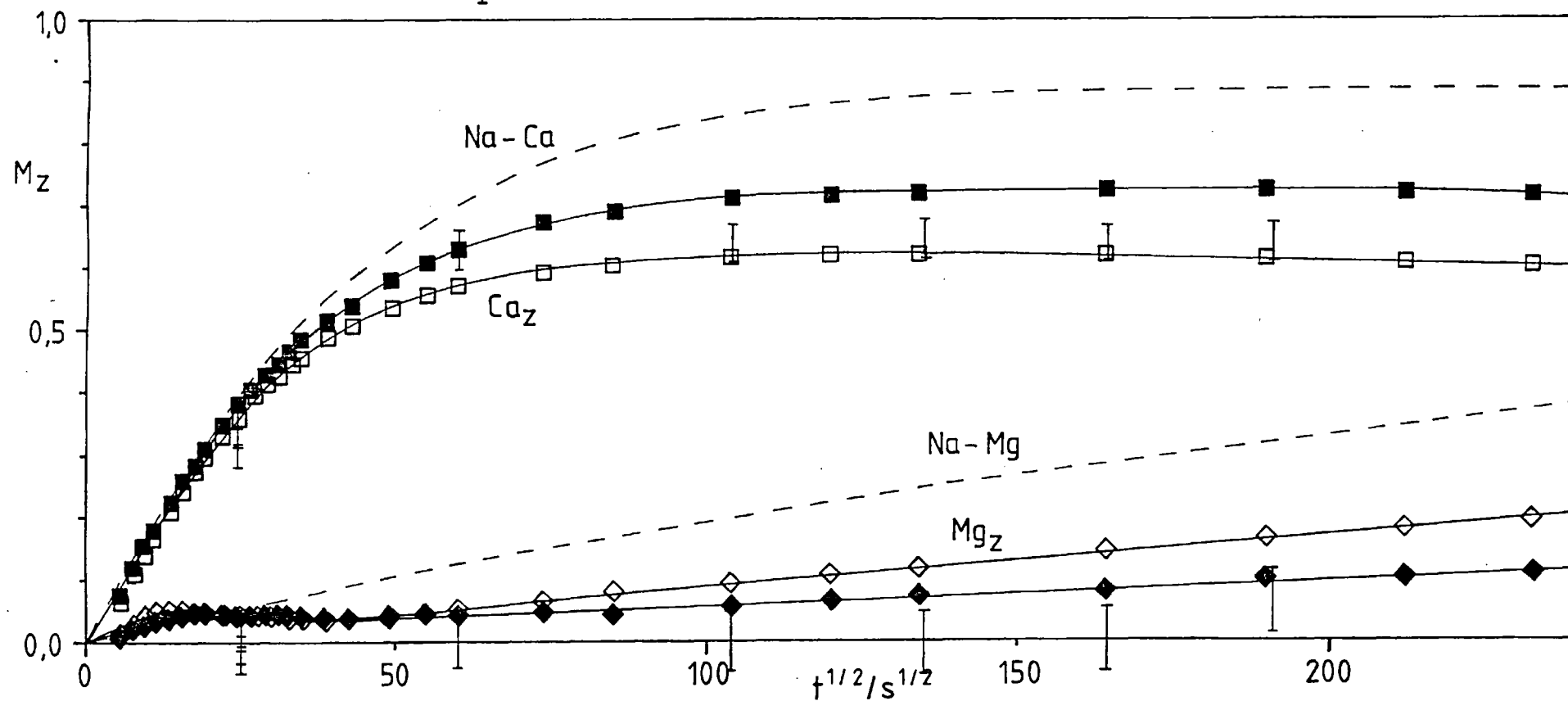


Figure 50.

Ternary ion exchange ; Na - Ca / Mg.

◇ □ Ca:Mg=0,87:1 ; ◆ ■ Ca:Mg=1,74:1.

┃ A.A.S., 5% error bars , Ca:Mg=0,87:1.



Thus, the concentration of B in the exchanger goes through a maximum".

In this case A is sodium, B is calcium and C is magnesium.

6.3 SODIUM-UNIVALENT EXCHANGE

The kinetics of exchange of sodium cations with other univalent cations have also been measured. Initial experiments used a TN of $3,4 \cdot 10^{-3} \text{ N}$ of ingoing ion with $10^{-3} \text{ M NMe}_4\text{OH}$ to give a pH ~ 10 . The Charnell synthesised zeolite A was used ($a_0 = 6,3 \mu\text{m}$) in all of these experiments. The composition changes for the systems Na-Li, Na-K, Na-Rb, Na-Cs, and Na-NH₄ are shown in figures 52 to 56. Most of the exchanges had a fast initial exchange followed by a much slower exchange. The much slower later stage was particularly noticeable for Na-Li and Na-NH₄ exchange (figures 52, 56). The exchanges were measured using a sodium selective electrode and it is believed that the slow rise in solution sodium concentration was caused by hydrolysis of the zeolite rather than by further exchange (see figures 52 to 56). These figures show the loss of sodium from the zeolite ($1 - \text{Na}_z$) which in the absence of hydrolysis is equal to the gain of counterion (see chapter 5, figure 23). The fast initial loss of sodium from the zeolite takes the zeolite to the isotherm predicted end point (figure 51) and the slow loss goes beyond this point.

For the Na-Li system an experiment with $10^{-2} \text{ M NMe}_4\text{OH}$ giving pH 11,7 gave a more regular system with a negligible hydrolysis stage (see figure 52). The effect of increasing pH confirms that the slow loss of sodium was due to hydrolysis. Considering the hydrolysis seen with NaA (see chapter 5, figure 18), it seems that NaLiA and NaNH₄A are more unstable than pure NaA. Even for the Na-Li exchange with pH 11,7 the composition levels off with more Li (and/or less Na) than predicted by isotherms (0,35 versus 0,30) (44) (see figure 51).

Figure 51.

Na- Univalent exchange isotherms, 25°C.

$TN = 3,4 \cdot 10^{-3} N$.

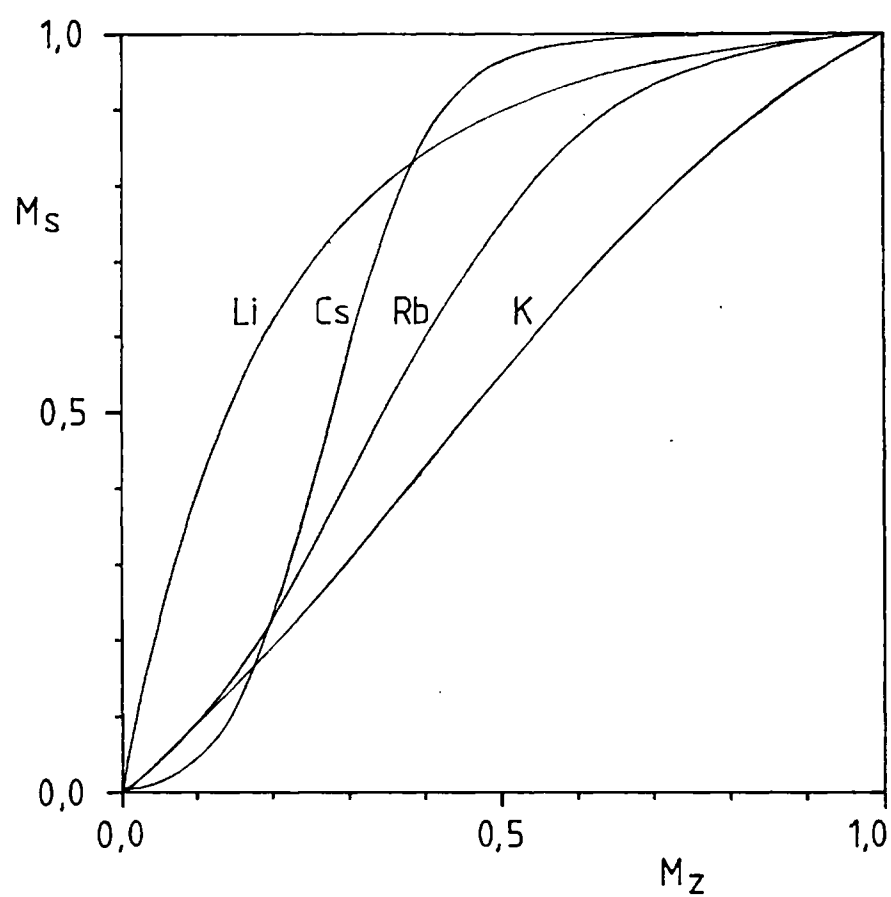


Figure 52.

Na-Li exchange ; $TN = 3,4 \cdot 10^{-3} N$; $a_o = 6,3 \mu m$.

○ pH 11,7

□ pH 10

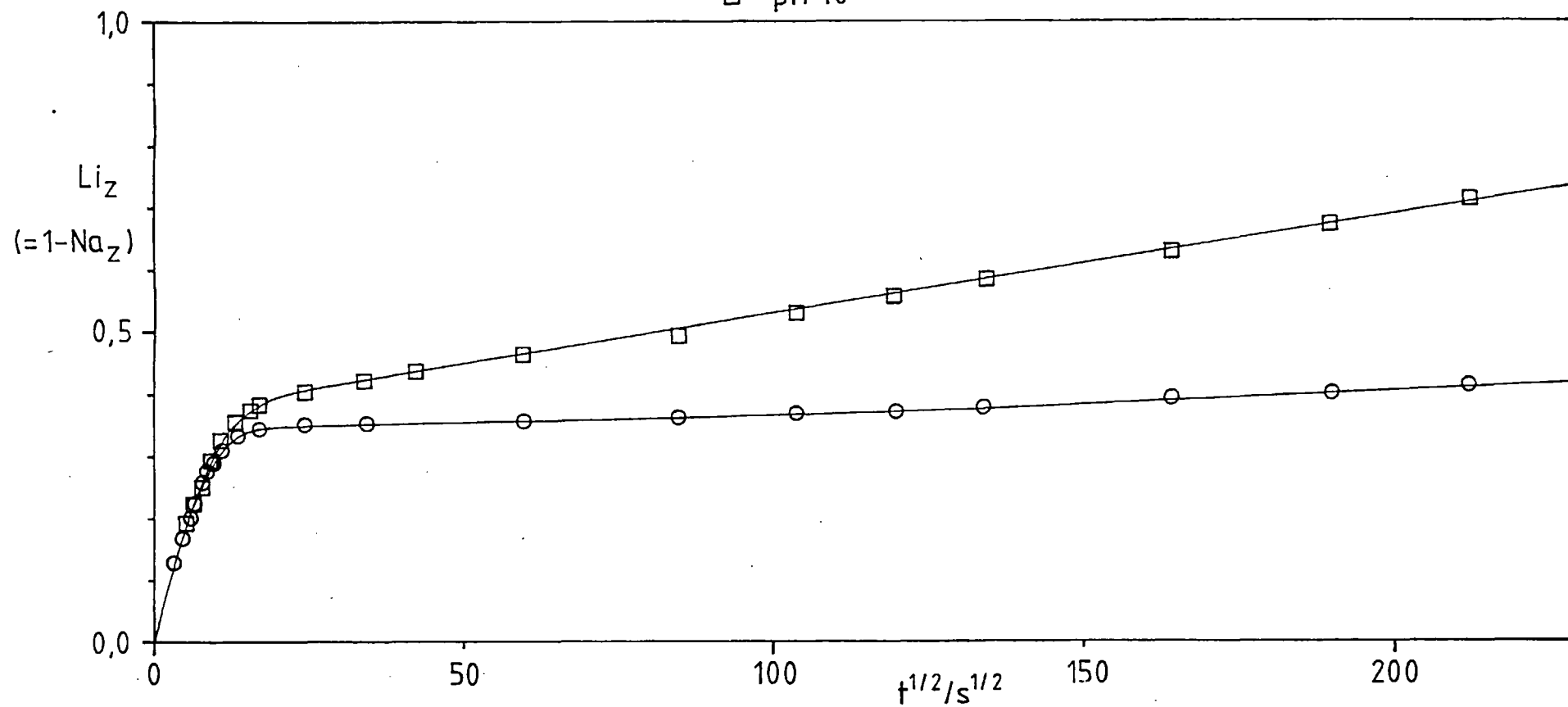


Figure 53.

Na-K exchange ; pH10 ; $a_o = 6,3 \mu\text{m}$.

□ $TN = 3,4 \cdot 10^{-3} \text{N}$

○ $TN = 0,01 \text{N}$

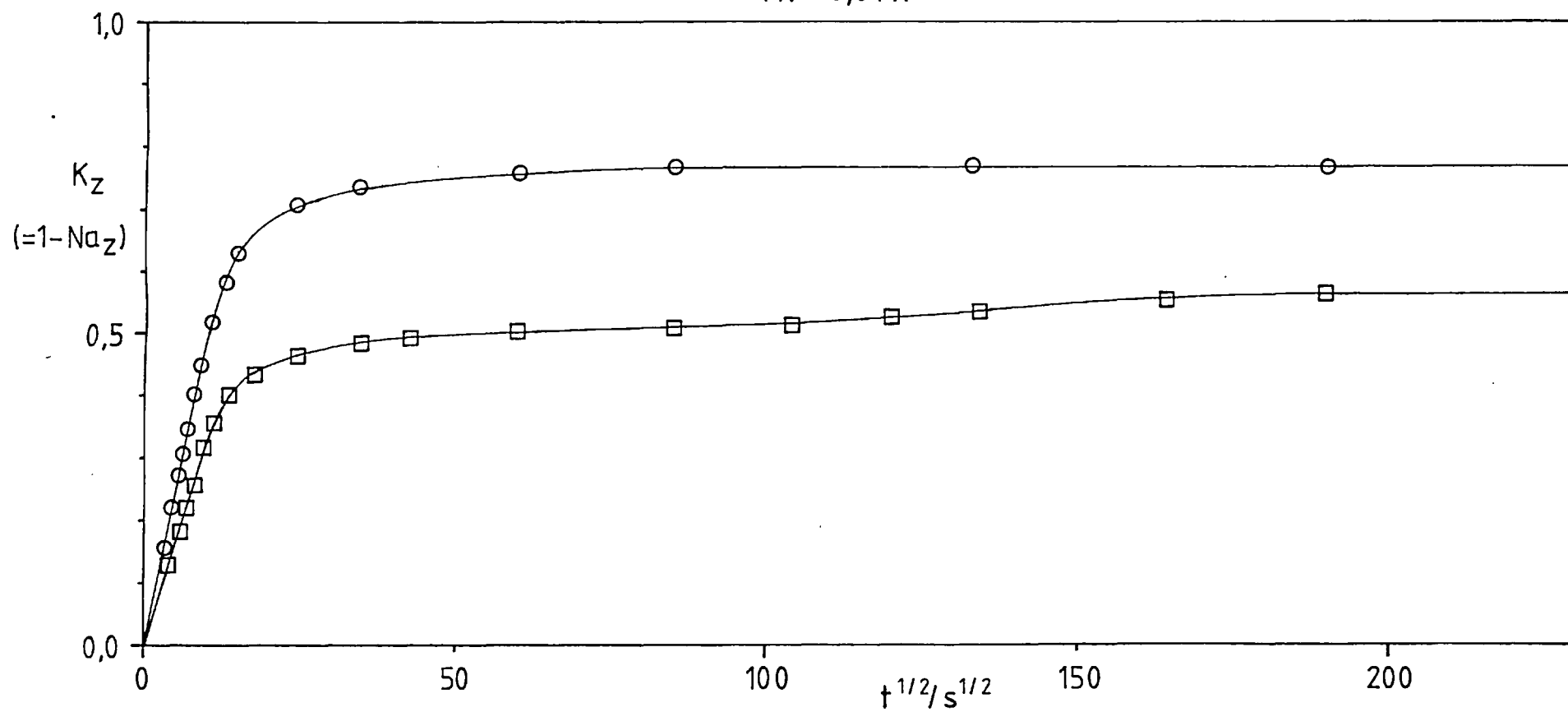


Figure 54.

Na-Rb exchange ; pH 10 ; $a_o = 6,3 \mu m$.

□ $TN = 3,4 \cdot 10^{-3} N$

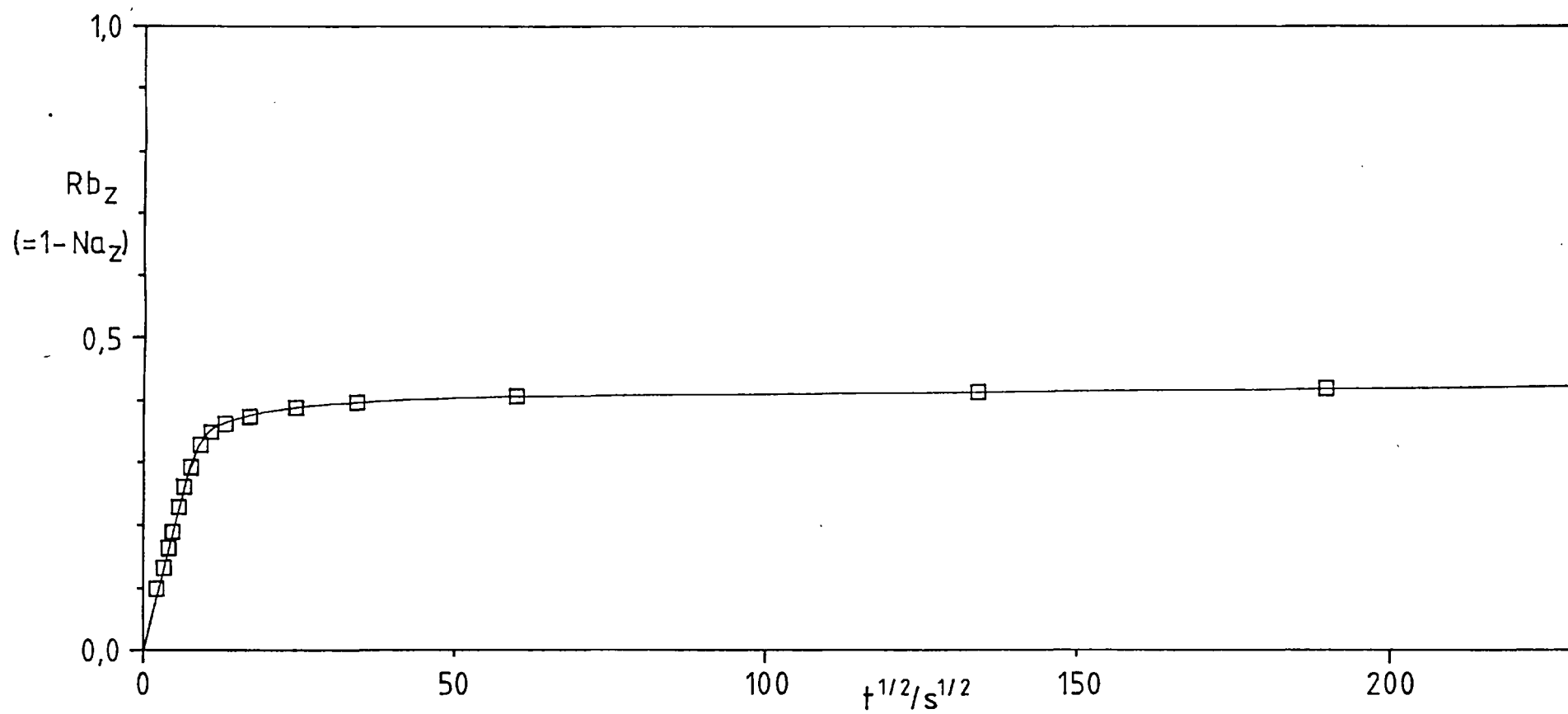


Figure 55.

Na-Cs exchange ; pH 10 ; $a_o = 6,3 \mu\text{m}$.

□ $TN = 3,4 \cdot 10^{-3} \text{N}$

○ $TN = 0,01 \text{N}$

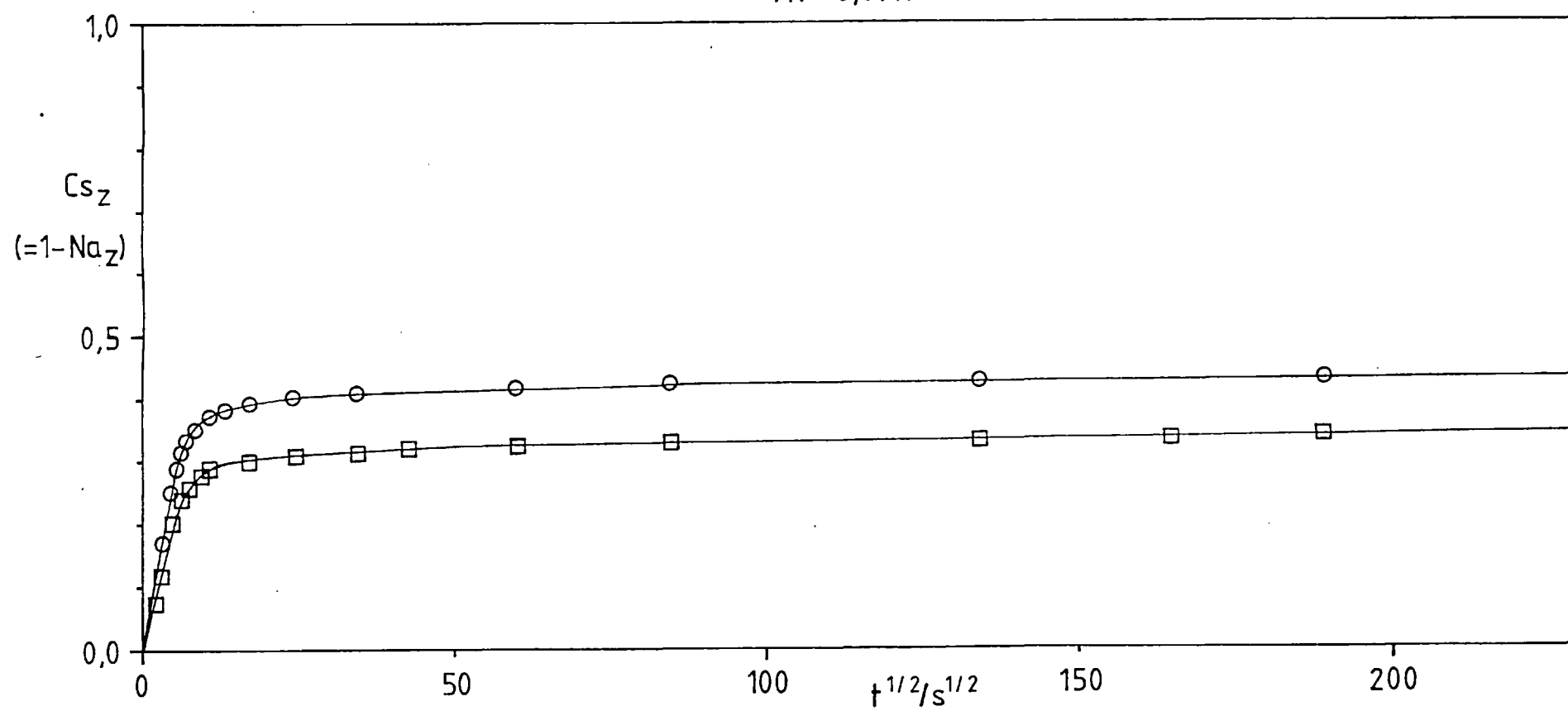


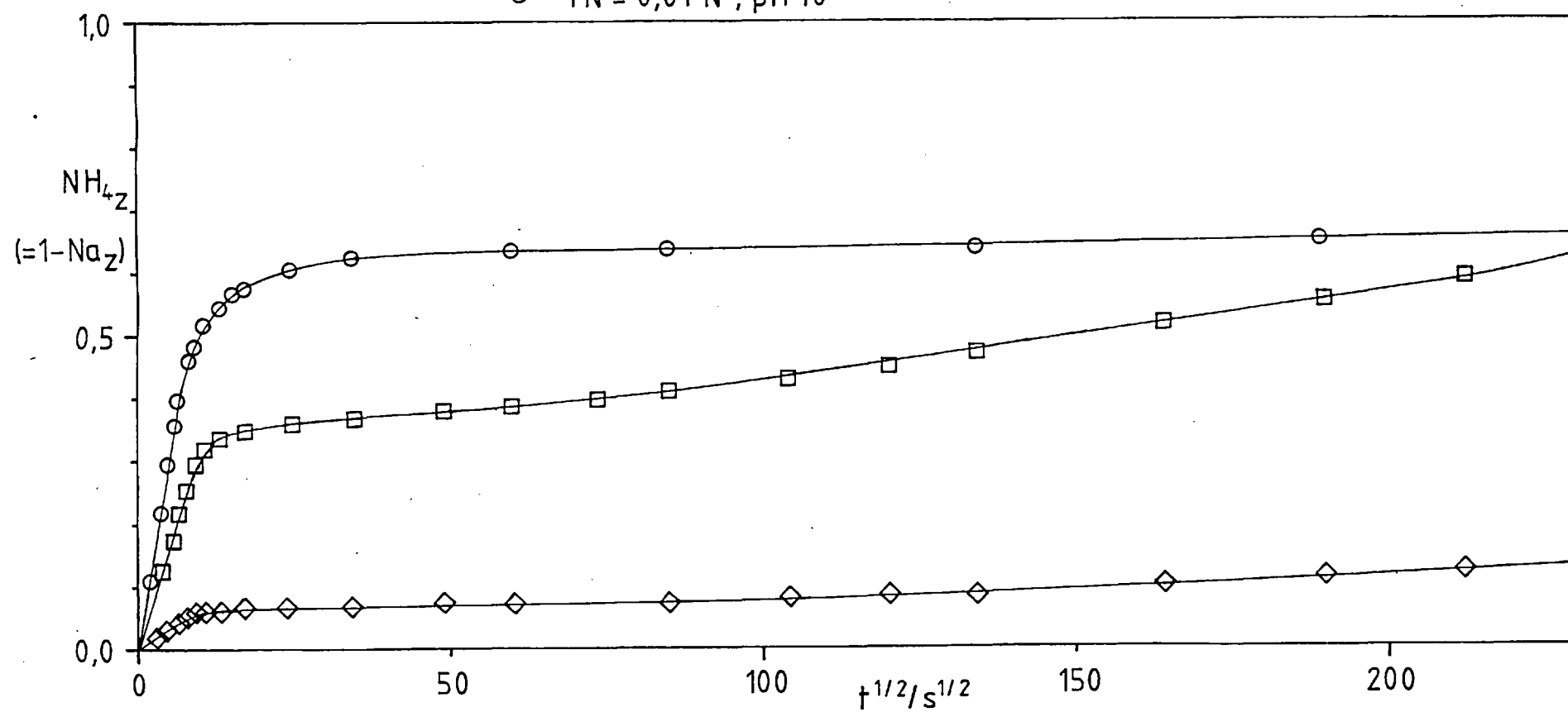
Figure 56.

Na - NH₄ exchange ; $a_0 = 6,3 \mu\text{m}$.

□ TN = $3,4 \cdot 10^{-3} \text{ N}$; pH 10

◇ TN = $3,4 \cdot 10^{-3} \text{ N}$; pH 11,5

○ TN = 0,01 N ; pH 10



For the other systems experiments were carried out using a TN of 0,01N as the higher solution concentration tends to increase zeolite stability. The increase in TN proved effective in this connection with practically no hydrolysis detected (figures 53, 55, 56). The amount of hydrolysis in the Na-Rb system with a TN of $3,4 \cdot 10^{-3}$ N was already very low (figure 54). An attempt to measure Na-NH₄ exchange with a TN of $3,4 \cdot 10^{-3}$ N and pH 11,5 gave an unexpected result (figure 56). Due to the $\text{NH}_3 \rightleftharpoons \text{NH}_4^+$ equilibrium the effective NH₄⁺ concentration was very low and the degree of exchange was therefore very low. Experiments with the commercial zeolite A ($a_0 = 2,6 \mu\text{m}$) gave similar results to those described above.

For all of the experiments, except the Na-Li exchange, which underwent hydrolysis (TN of $3,4 \cdot 10^{-3}$ N and pH10) the isotherm end point was used to calculate M_t/M_∞ values for short time values. For Na-Li exchange the end value was taken as the point at which the composition change levelled off (figure 52, $t \approx 600\text{s}$), as the isotherm value of 0,30 was passed very rapidly.

Figure 57 shows the resulting average $\sqrt{t}$ plots for Na-Li exchange, $a_0 = 6,3 \mu\text{m}$, with a TN of $3,4 \cdot 10^{-3}$ N and pHs of 10 and 11,7. The two curves agree within experimental error even though the end point of the pH10 exchange could only roughly be estimated. The end point of the pH11,7 exchange was more accurately estimated and the resulting curve is a better representation of this system. The rate of this exchange is much faster than the rates of sodium-divalent ion exchange.

The resultant diffusion coefficients are shown in figure 58. The values for the two TNs agree within experimental error and are some ten times higher than those for Na-Ca and Na-Ba exchange. The diffusion

Figure 57.

Na-Li exchange ; $TN = 3,4 \cdot 10^{-3} N$; $a_o = 6,3 \mu m$.

○ pH 11,7 ; $Li_z \text{ end} = 0,355$

□ pH 10 ; $Li_z \text{ end} = 0,40$

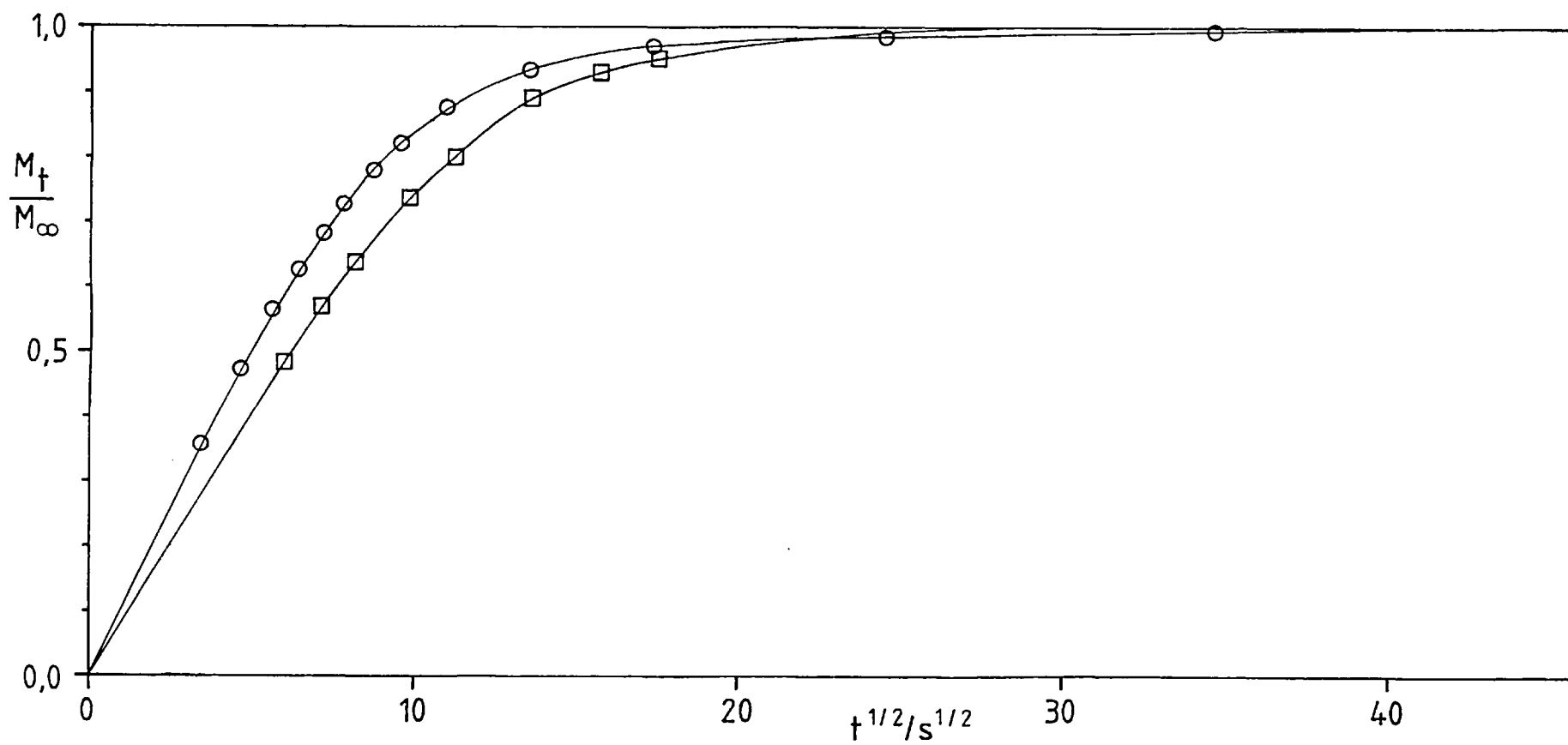
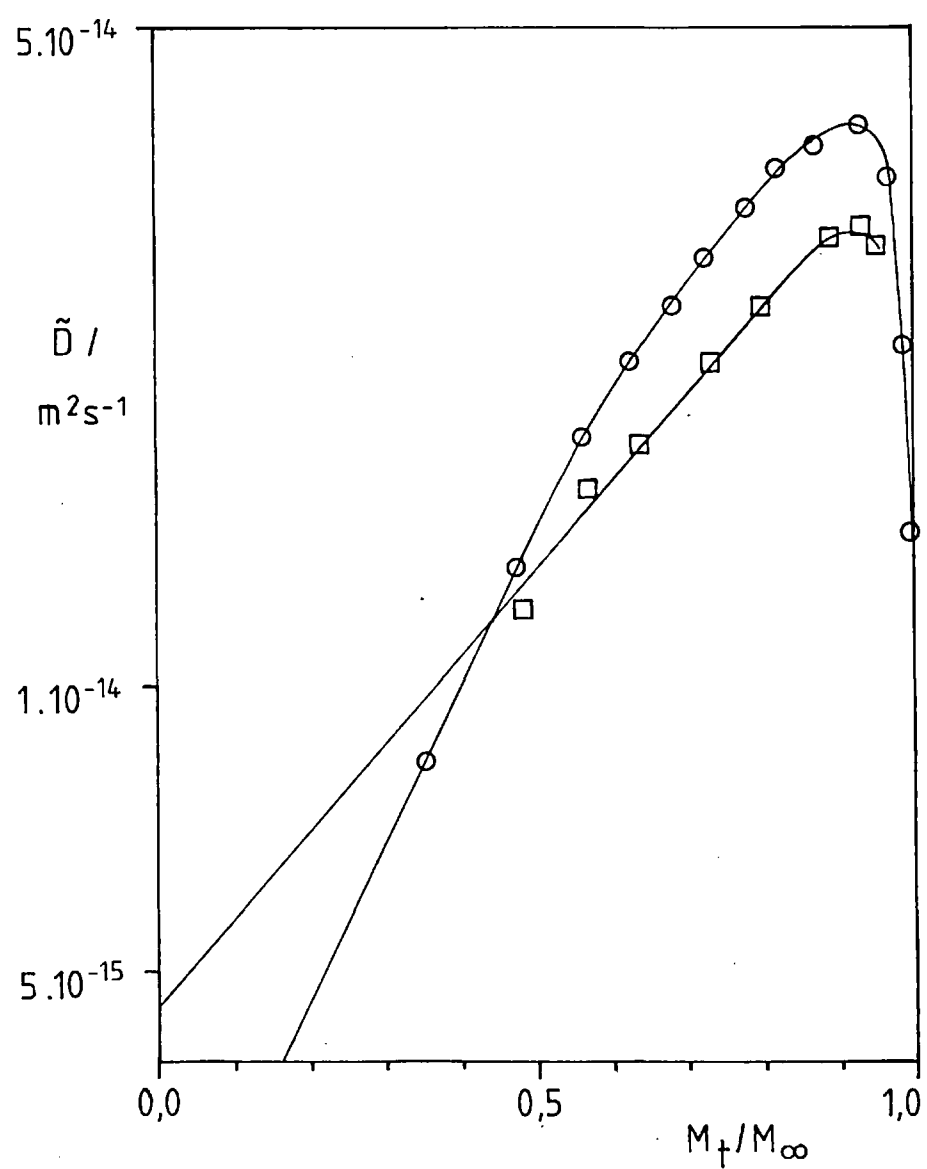


Figure 58.

Na-Li exchange ; $TN = 3,4 \cdot 10^{-3} N$; $a_o = 6,3 \mu m$.

○ pH 11,7

□ pH 10



coefficient rises throughout the exchange and only drops as equilibrium is approached whereas for Na - Ca and Na - Ba exchange (figures 33, 48) the diffusion coefficient is constant or drops slowly for most of the exchange. The values for Na - Mg exchange, $a_0 = 6,3\mu\text{m}$, (figure 46) bear some resemblance to the Na - Li exchange but are 1000 times smaller.

Figure 59 shows average $\sqrt{t}$ plots for Na - K exchange with TNs of $3,4 \cdot 10^{-3}\text{N}$ and $0,01\text{N}$ and also for K - Na exchange with a TN of $1,0 \cdot 10^{-3}\text{N}$ ($a_0 = 6,3\mu\text{m}$). For the Na - K exchange with a TN of $3,4 \cdot 10^{-3}\text{N}$ the end point predicted by the isotherm was used and the resulting plot agrees very closely with that for a TN of $0,01\text{N}$ where the experimental end point was used. Clearly the rate is independent of TN which confirms that particle diffusion is rate determining. The K - Na exchange was measured with a low TN in order to maximise the change in solution concentration and hence increase the accuracy of the measurements. The reverse exchange is somewhat faster than the forward exchange which agrees with the prediction of Brooke and Rees's theory shown in figure 59 when $D_{\text{Na}}^* > D_{\text{K}}^*$ (97, 98, see eqns 2.4.5, .9 and tables 2,4). The theoretical rates are, however, considerably slower than the actual rates and this will be discussed later. For the K - Na exchange the sodium solution concentration actually went through a minimum due to simultaneous exchange (decreasing sodium) and hydrolysis (increasing sodium in solution). The actual exchange rate could therefore be faster than indicated.

Figure 60 shows the average $\sqrt{t}$ plots for the commercial zeolite A ($a_0 = 2,6\mu\text{m}$) for Na - K exchange with TNs of $3,4 \cdot 10^{-3}\text{N}$ and $0,01\text{N}$ (plus $10^{-3}\text{M NMe}_4\text{OH}$). Again the plots agree within experimental error and demonstrate that the rate is independent of TN. The plots show that the exchange was faster than for the larger crystals although not by as large a factor as predicted for particle kinetics (see section 2.2).

Figure 59.

Na-K & K-Na exchange ; pH 10 ; $a_o = 6,3 \mu\text{m}$.

○ Na-K ; $TN = 3,4 \cdot 10^{-3} N$; $K_{Z\text{end}} = 0,53$

□ Na-K ; $TN = 1,0 \cdot 10^{-2} N$; $K_{Z\text{end}} = 0,78$

● K-Na ; $TN = 1,0 \cdot 10^{-3} N$; $K_{Z\text{end}} = 0,73$

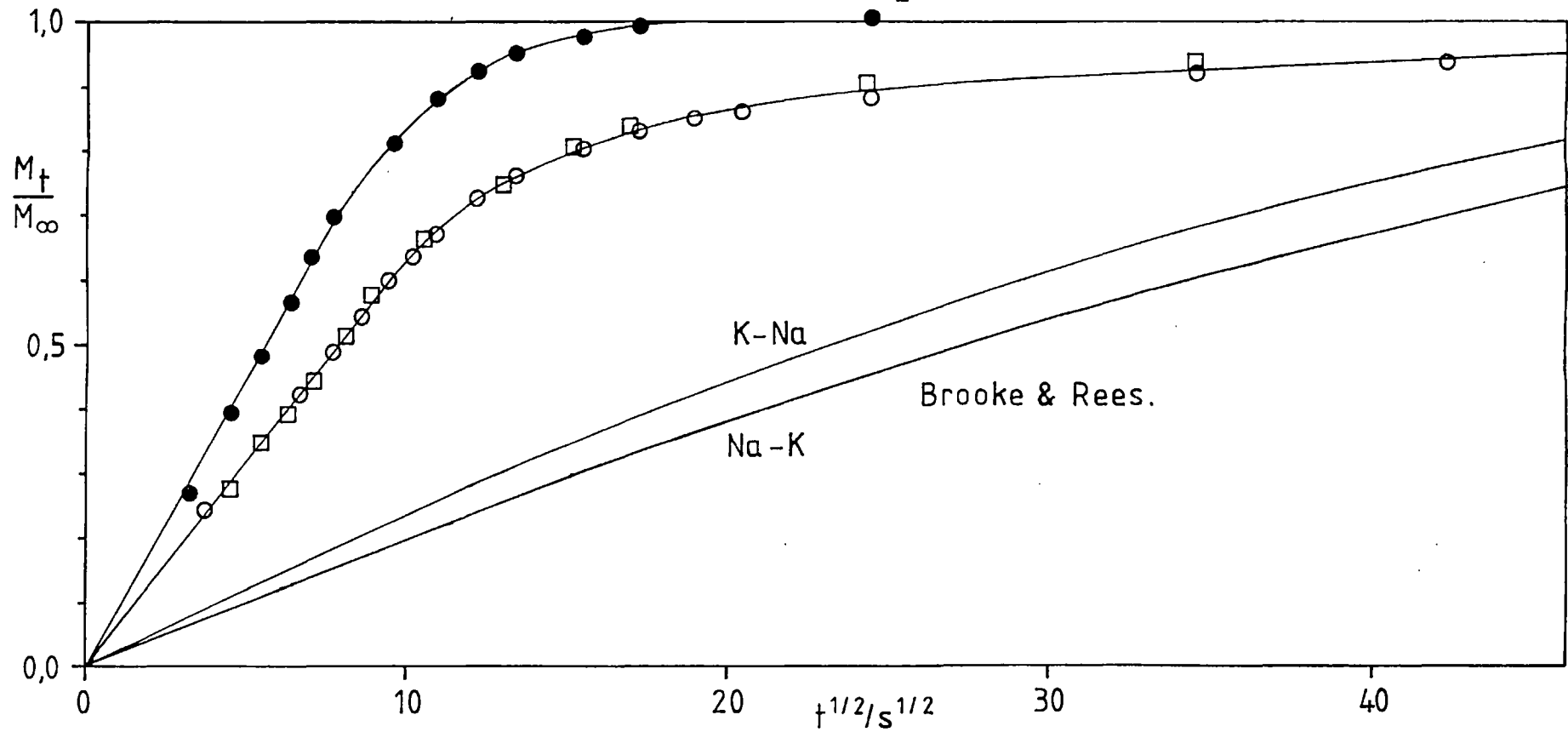


Figure 60.

Na-K exchange ; pH 10 ; $a_o = 2,6 \mu\text{m}$.

○ $TN = 3,4 \cdot 10^{-3} \text{N}$; $K_{Z\text{end}} = 0,53$

□ $TN = 1,0 \cdot 10^{-2} \text{N}$; $K_{Z\text{end}} = 0,79$

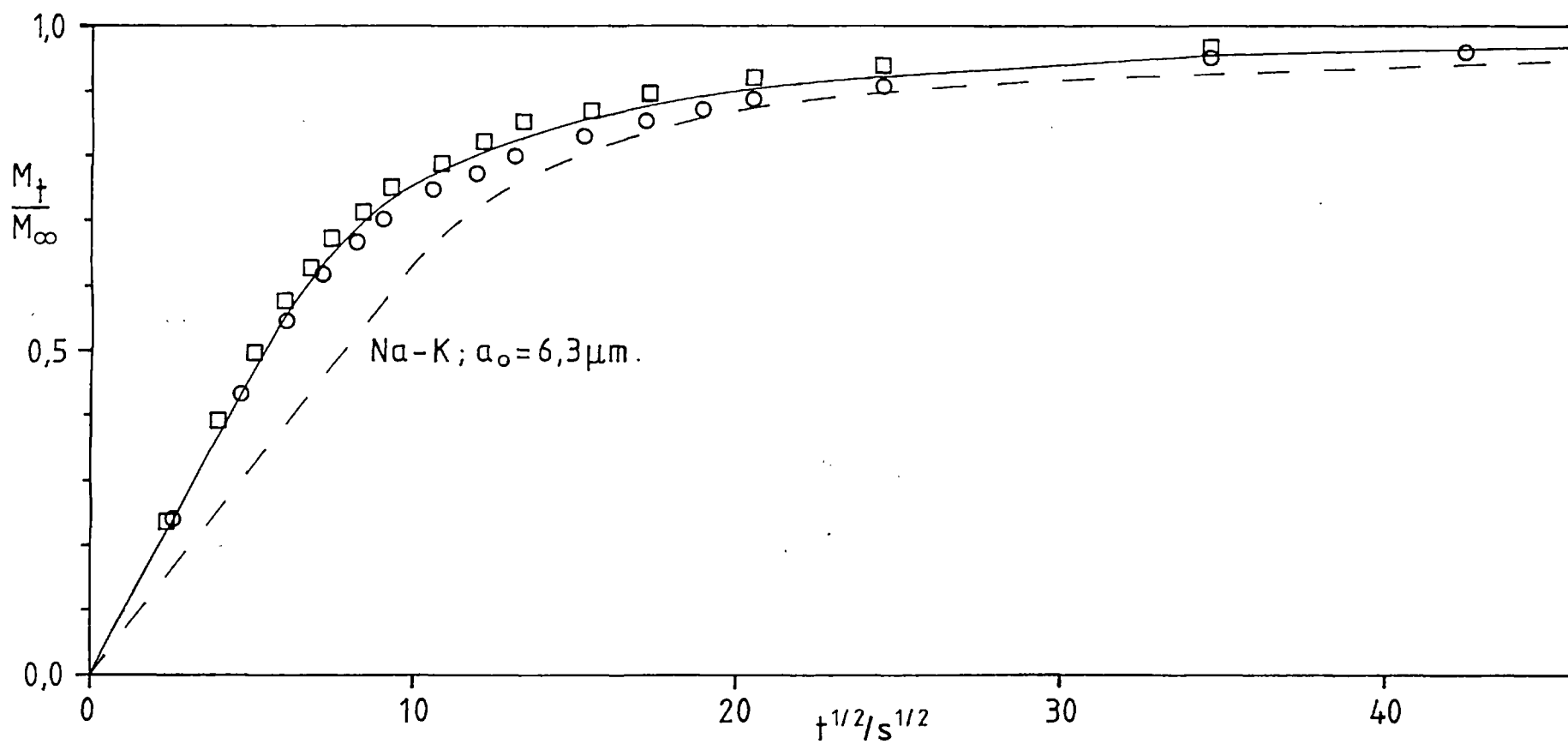


Figure 61 shows the diffusion coefficients for the Na - K exchange. The curves are all of the same form and are similar to those for the Na - Li exchange (figure 58). The diffusion coefficients for Na - Li exchange continue to rise when those for Na - K exchange level off and start to drop. As a result the coefficients for Na - Li exchange reach a higher value than those for Na - K exchange. The diffusion coefficients for the smaller crystals are low due to agglomeration of crystals and non-ideality as discussed earlier for Na - Ca exchange. The diffusion coefficients for the higher concentration are slightly higher, possibly due to differences in the concentration at the zeolite surface, although the difference is within experimental error.

The diffusion coefficients for K - Na exchange also rise throughout the exchange (figure 62) but with no drop as equilibrium is approached and a higher value than that for Na - K exchange is therefore reached. Figure 63 shows the values for Na - K and K - Na exchange plotted against composition. For K - Na exchange the initial value of K_z was 1,00 and the final value was 0,73. At the end of the Na - K exchange $\bar{D}$ decreases with increasing K_z and this trend is seen throughout the K - Na exchange. It is therefore possible that a curve with a maximum could fit both curves, if the Na - K exchange gives the same variation for an exchange going to pure K A and the K - Na exchange reaches a maximum then drops for an exchange going to pure NaA.

Also shown in figure 63 are the averages of the diffusion coefficients that were used in the theory of Brooke and Rees (97, 98) to calculate the curves shown in figure 59. These values are appreciably lower than the experimental ones just as the $\sqrt{t}$ plots were slower. The theory of Brooke and Rees requires D_{AB} values for the complete range of compositions. It was assumed that experiments giving 100% exchange would give the same diffusion coefficient variation as shown in figures 61,

Figure 61.

Na-K exchange ; pH 10.

$\alpha_o = 6,3 \mu\text{m}$; $\square$ $TN = 3,4 \cdot 10^{-3} \text{N}$; $\circ$ $TN = 1,0 \cdot 10^{-2} \text{N}$.

$\alpha_o = 2,6 \mu\text{m}$; $\blacksquare$ $TN = 3,4 \cdot 10^{-3} \text{N}$; $\bullet$ $TN = 1,0 \cdot 10^{-2} \text{N}$.

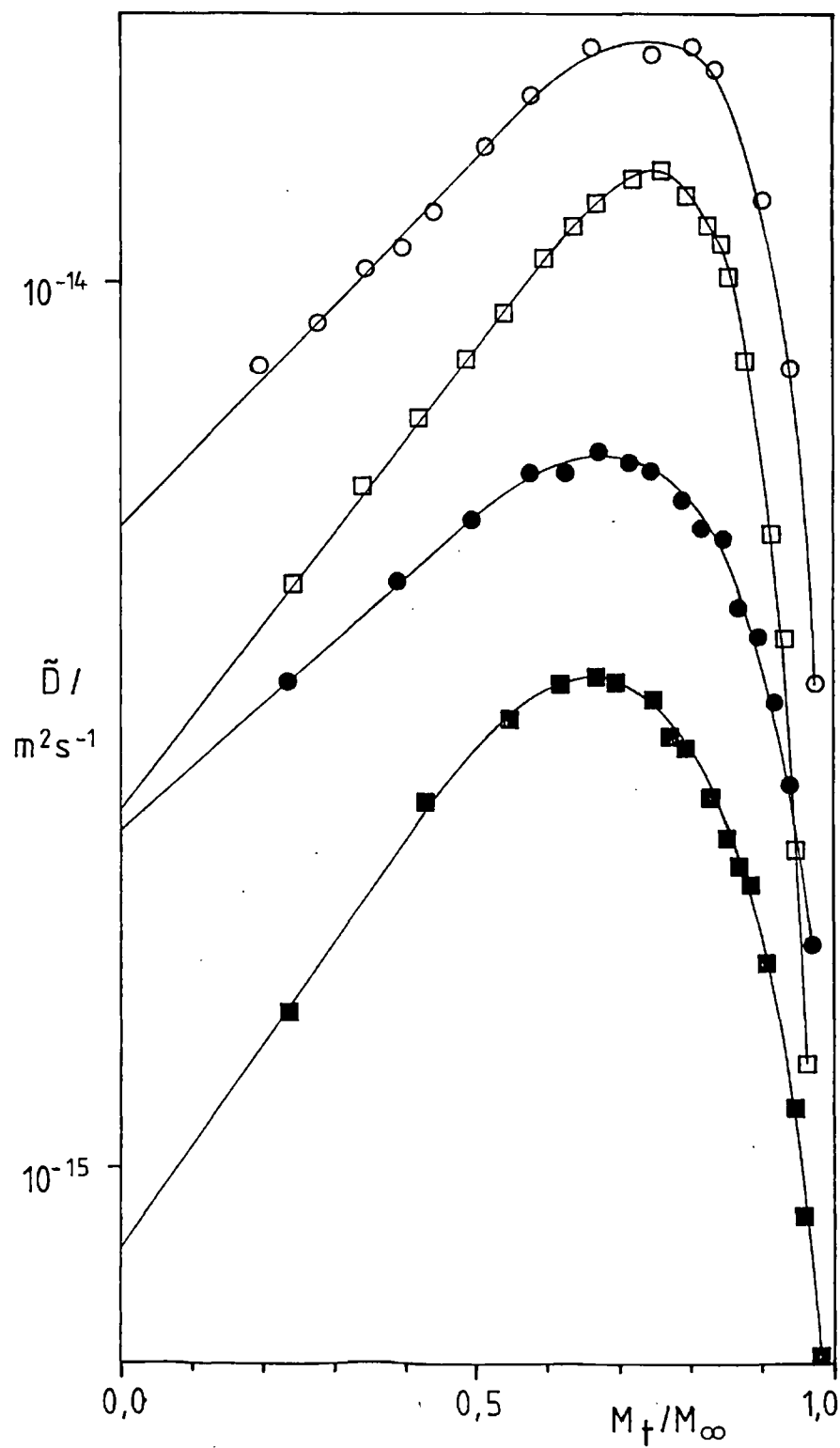


Figure 62.

- Cs-Na exchange ; $TN = 1,0 \cdot 10^{-3} \text{ N}$;
 $a_o = 6,3 \mu\text{m}$; pH 10 .
- K-Na exchange ; $TN = 1,0 \cdot 10^{-3} \text{ N}$;
 $a_o = 6,3 \mu\text{m}$; pH 10 .

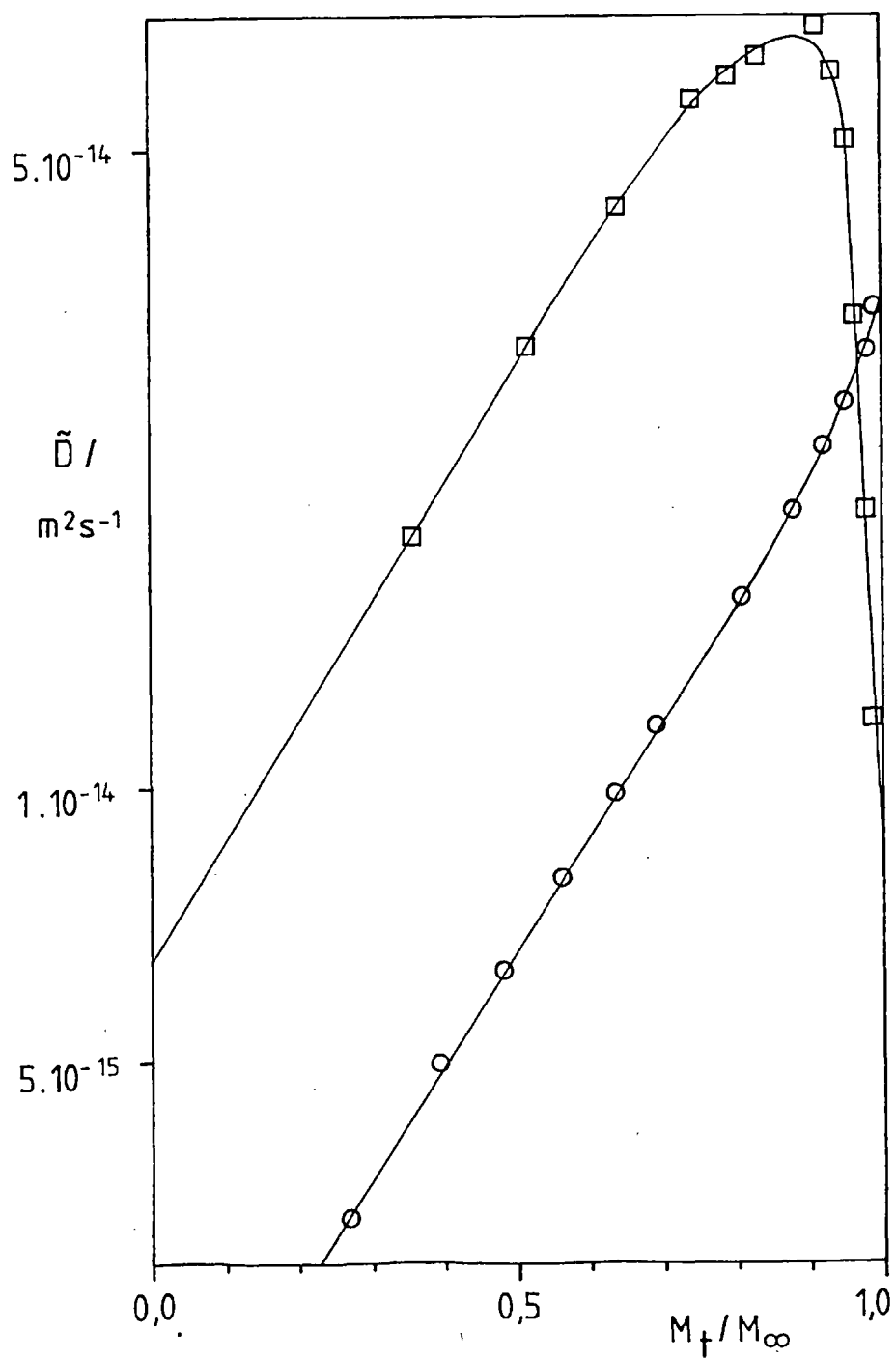
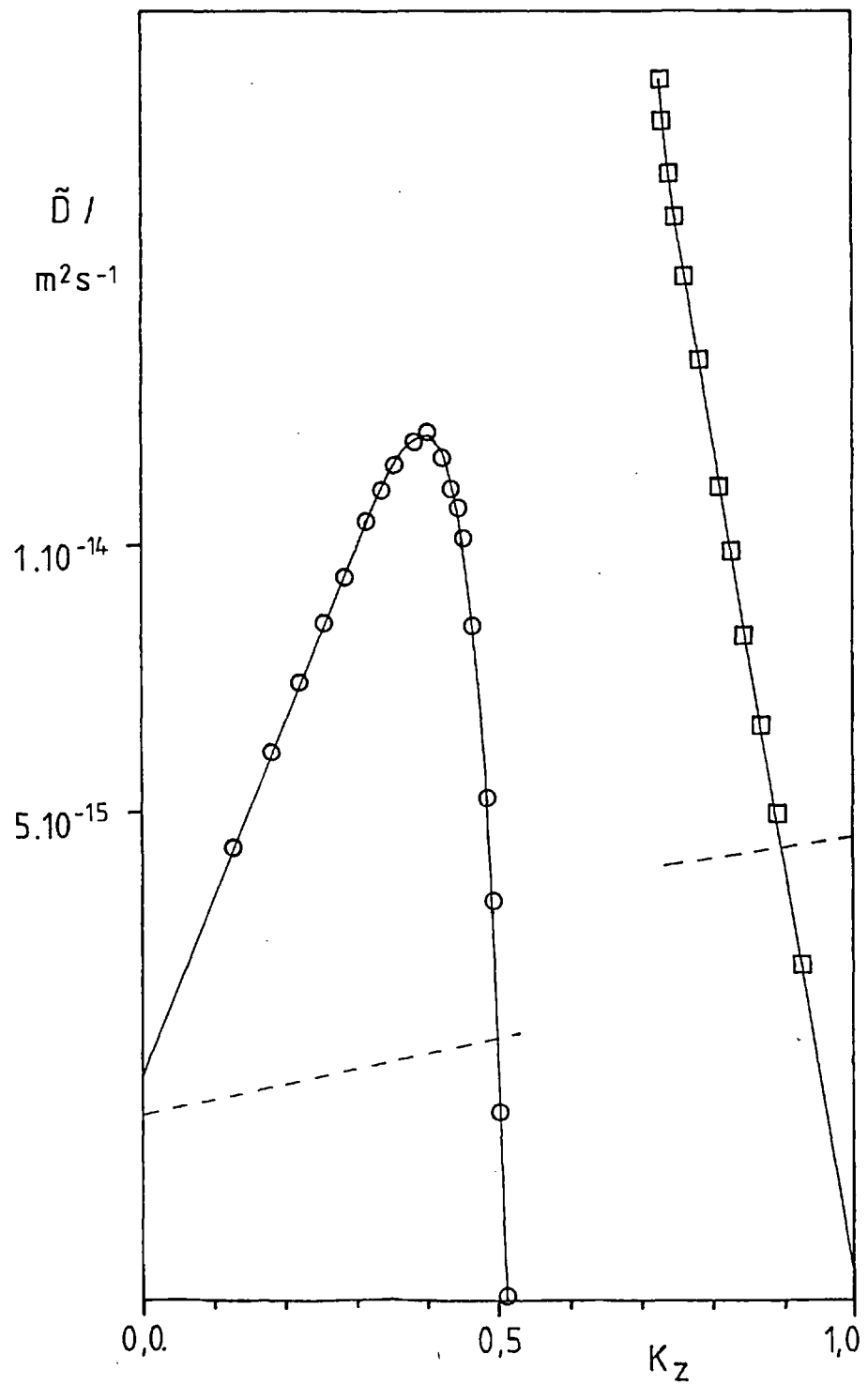


Figure 63.

- Na-K exchange ; $TN = 3,4 \cdot 10^{-3} N$;
 □ K-Na exchange ; $TN = 1,0 \cdot 10^{-3} N$;
 $a_o = 6,3 \mu m$; pH 10 .
 --- $\tilde{D}$ from Brooke & Rees.



62 and so $C_A \equiv M_t/M_\infty$. Straight line fits of the diffusion coefficients were made (ignoring the final drop for Na - K exchange) and hence the differential diffusion coefficient, $\bar{D}$, was simply calculated (see equation 2.2.14). The S factor was hence calculated by assuming that $D_{AB} \equiv \bar{D}$ (equation 2.4.6) and the values were put into the program of Brooke and Rees in tabular form. The resultant $\sqrt{t}$ plot for Na - K exchange was halfway between the experimental and the original theoretical plots. The values were therefore better than those based on self diffusion data (table 4) but still not in good agreement with the experimental data. For the K - Na exchange the increase in diffusion coefficients with $Na_z (= 1 - K_z)$ was too great and the data proved unsuitable for use in the program.

Figure 64 shows average $\sqrt{t}$ plots for Na - Cs exchange with TNs of $3,4 \cdot 10^{-3}N$ and $0,01N$ and also for Cs - Na exchange with a TN of $1,0 \cdot 10^{-3}N$ (plus $10^{-3}M$ NMe_4OH , $a_0 = 6,3\mu m$). Again the exchange with a TN of $3,4 \cdot 10^{-3}N$ used the isotherm end points and was in close agreement with the exchange with a TN of $0,01N$ which used the experimental end point. The Cs - Na exchange was faster at later stages of exchange than the Na - Cs exchange. The sodium solution concentration went through a minimum during the Cs - Na exchange (cf K - Na exchange), due to hydrolysis. Combining this with mixing effects and electrode response means that the Cs - Na exchange is probably faster than the Na - Cs exchange at all times. Figure 65 shows Cs - Na exchange measured under a number of conditions and, considering the rapidity of this exchange, the rate is again independent of TN (as was the case for Na - Cs exchange). The predicted rates (by the theory of Brooke and Rees) agree qualitatively with the experimental results ($D_{Na}^* > D_{Cs}^*$), (see table 4). Figure 66 shows the average $\sqrt{t}$ plot for Na - Cs exchange with a TN of $3,4 \cdot 10^{-3}N$, using the commercial zeolite A ($a_0 = 2,6\mu m$).

Figure 64.

Na-Cs & Cs-Na exchange ; pH 10 ; $a_o = 6,3 \mu m$.

○ Na-Cs ; $TN = 3,4 \cdot 10^{-3} N$; $Cs_{z\text{end}} = 0,34$

□ Na-Cs ; $TN = 1,0 \cdot 10^{-2} N$; $Cs_{z\text{end}} = 0,44$

● Cs-Na ; $TN = 1,0 \cdot 10^{-3} N$; $Cs_z = 0,57 \text{ to } 0,37$

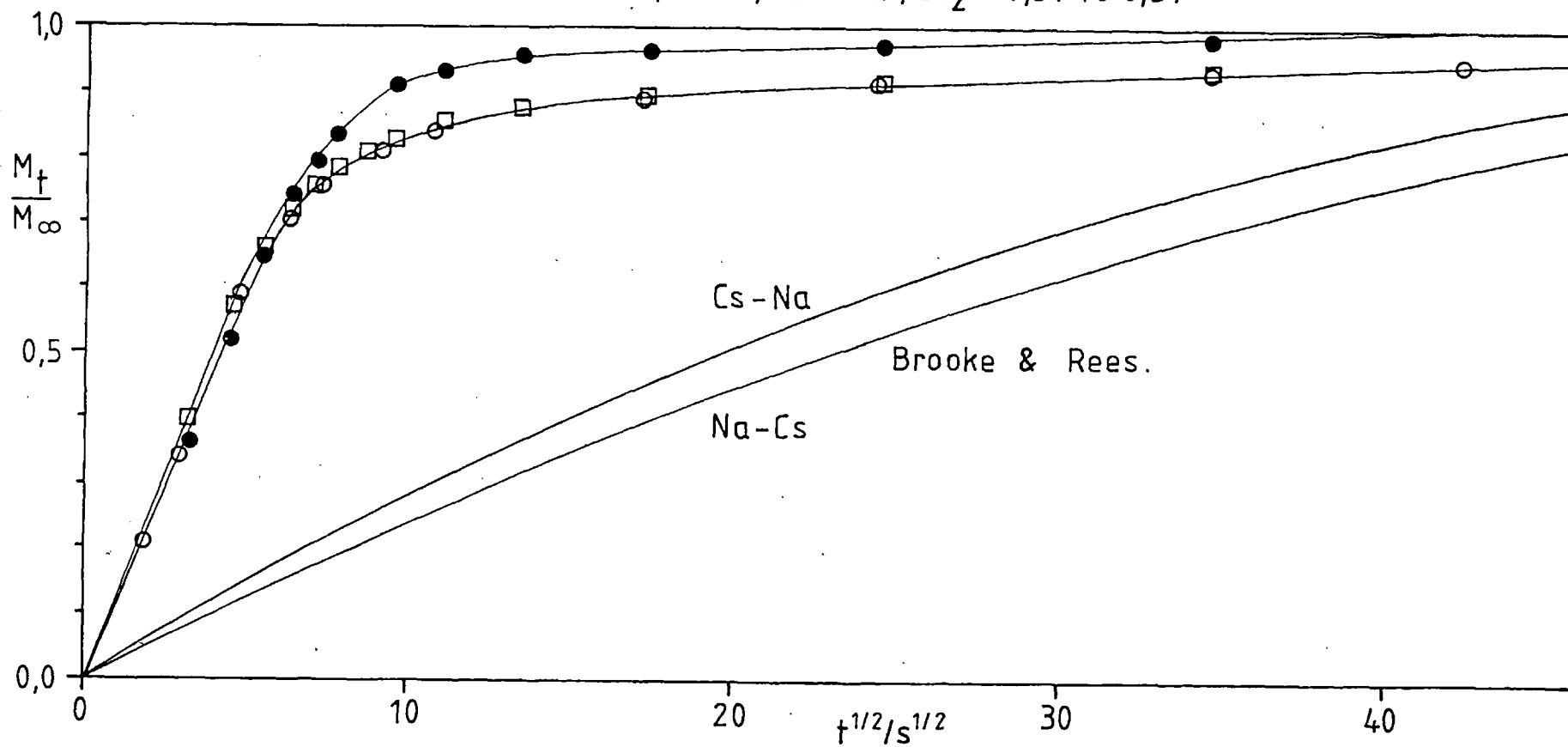


Figure 65.

Cs-Na exchange ; pH 10 ; $a_o = 6,3\mu\text{m}$.

○ $TN = 3,4 \cdot 10^{-3}N$; $M_Z/M_S = 0,711$

■ $TN = 1,0 \cdot 10^{-3}N$; $M_Z/M_S = 2,42$

◇ $TN = 1,0 \cdot 10^{-3}N$; $M_Z/M_S = 4,85$

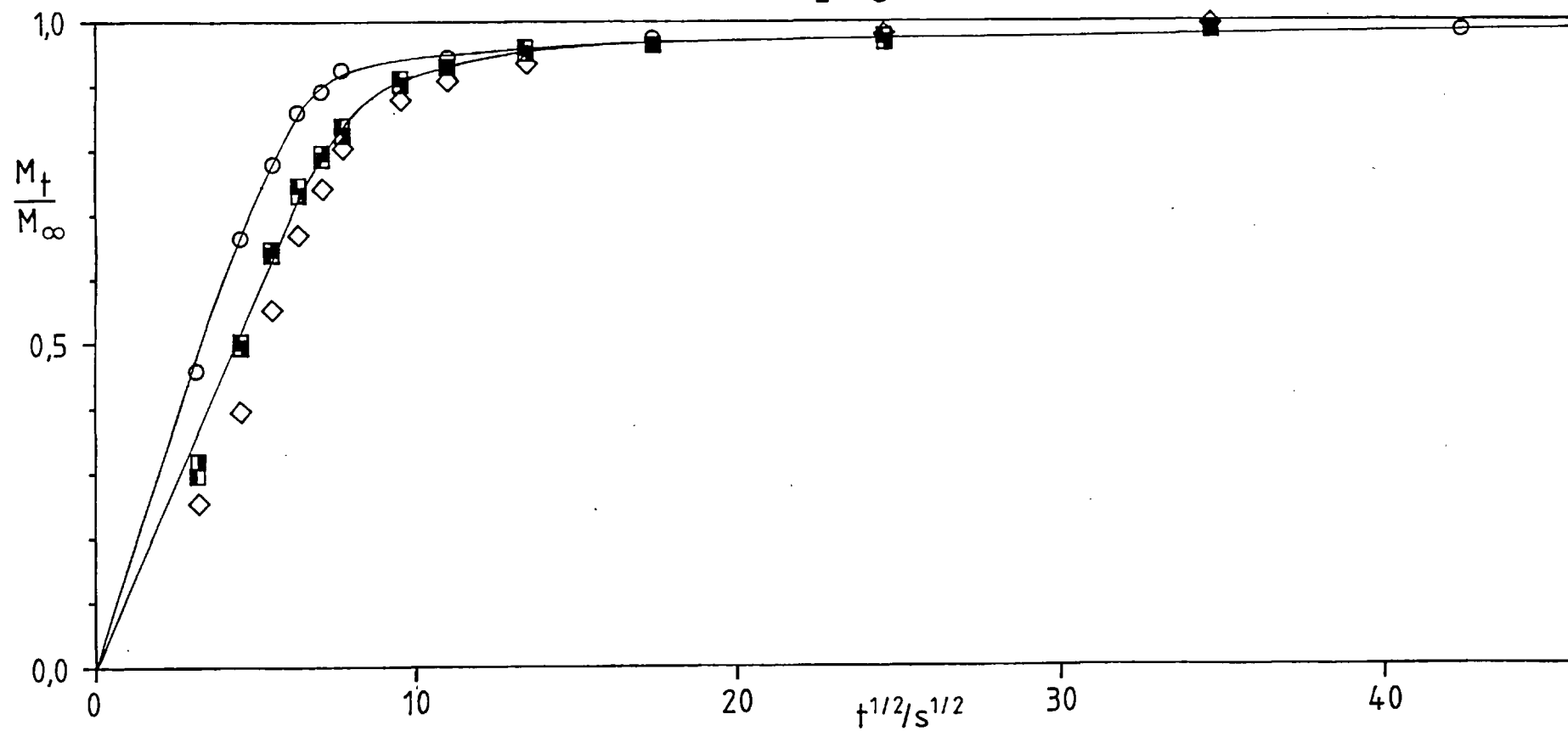
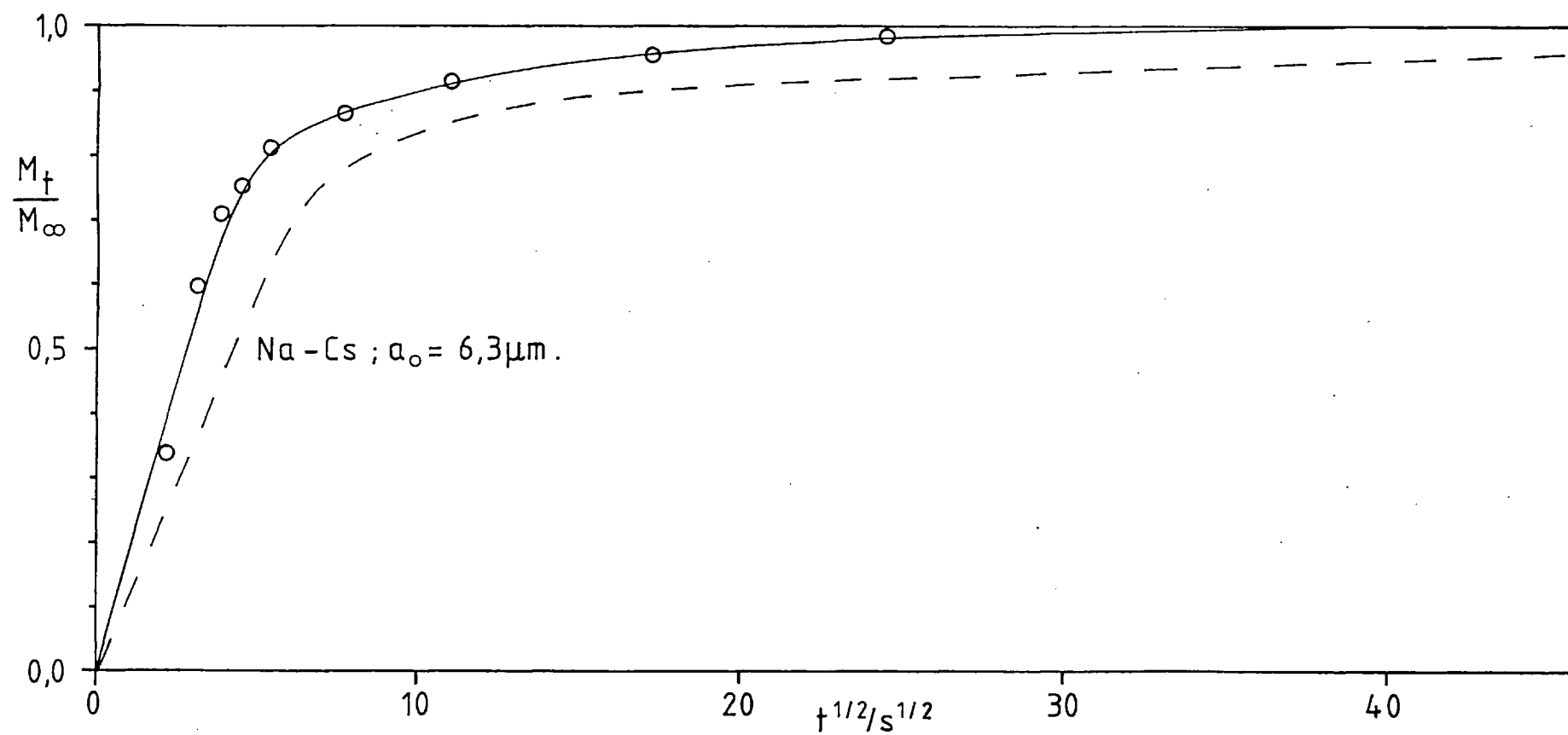


Figure 66.

Na - Cs exchange ; pH 10 ; $a_o = 2,6 \mu m$.

○ $TN = 3,4 \cdot 10^{-3} N$; $Cs_{z\text{end}} = 0,34$



The exchange is not as fast as would be expected compared with the larger crystals but with a half time of eight seconds this exchange was probably limited by mixing rate and electrode response.

This low difference in rates is reflected in the diffusion coefficient variation (figure 67) with the values for the smaller crystal being lower. The shape of the curves is the same which suggests that the rate determining step is the same (i.e. particle kinetics). Na - Cs exchange was the fastest measured and therefore gives the highest diffusion coefficients, although these coefficients are still 10^4 times lower than corresponding diffusion coefficients in the solution phase.

The diffusion coefficients for Cs - Na exchange together with those with those for K - Na exchange are shown in figure 62. The curves are remarkably similar with a difference between values of approximately four. The self diffusion coefficients of K^+ and Cs^+ , at $25^\circ C$, are very similar (45) but the zeolite phase activity coefficients are somewhat different (Table 2, 44). The Na - Cs average diffusion coefficient used in the calculation of the theoretical curve for the theory of Brooke and Rees was double the value for Na - K exchange.

Figure 68 shows the variation of diffusion coefficient with composition for the forward (Na - Cs) and reverse (Cs - Na) exchange. The two curves show a similar $\bar{D}$ variation.

Forward and reverse exchanges covering the complete range would probably give similar $\bar{D}$ variation (cf Na - K and K - Na, figure 63).

For the Na - Rb system, exchange kinetics were measured for a TN of $3.4 \cdot 10^{-3} N$, pH10, with both crystal sizes (figure 69) and diffusion coefficients calculated (figure 70). The $\bar{D}$ variation is of the same

Figure 67.

Na - Cs exchange ; pH 10 .

$\alpha_o = 6,3 \mu\text{m}$; $\circ$ $TN = 3,4 \cdot 10^{-3} \text{ N}$; $\square$ $TN = 1,0 \cdot 10^{-2} \text{ N}$.

$\alpha_o = 2,6 \mu\text{m}$; $\bullet$ $TN = 3,4 \cdot 10^{-3} \text{ N}$.

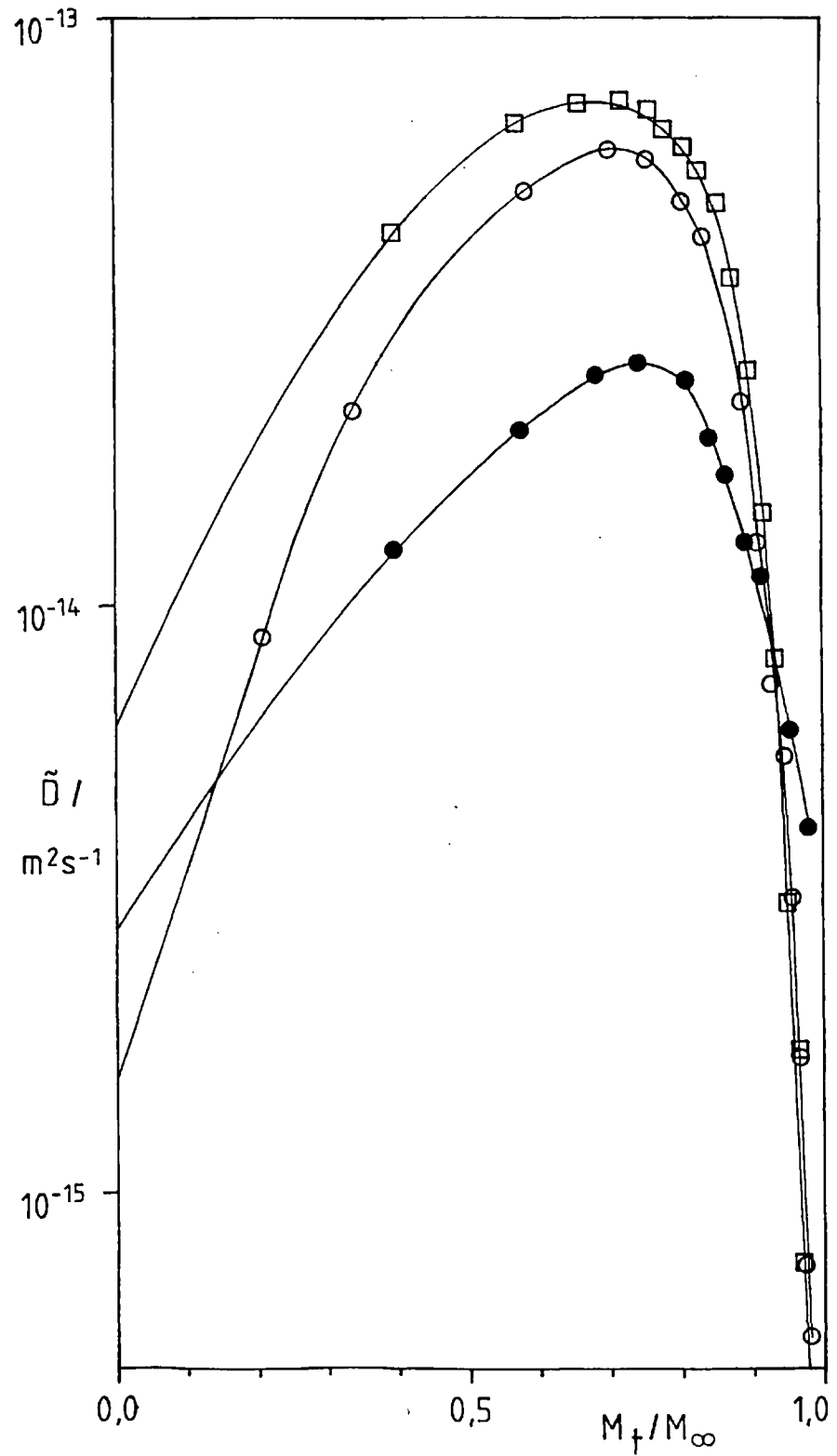


Figure 68.

○ Na-Cs exchange ; $TN=3,4 \cdot 10^{-3}N$;

□ Cs-Na exchange ; $TN=1,0 \cdot 10^{-3}N$;

$a_o=6,3\mu m$; pH 10 .

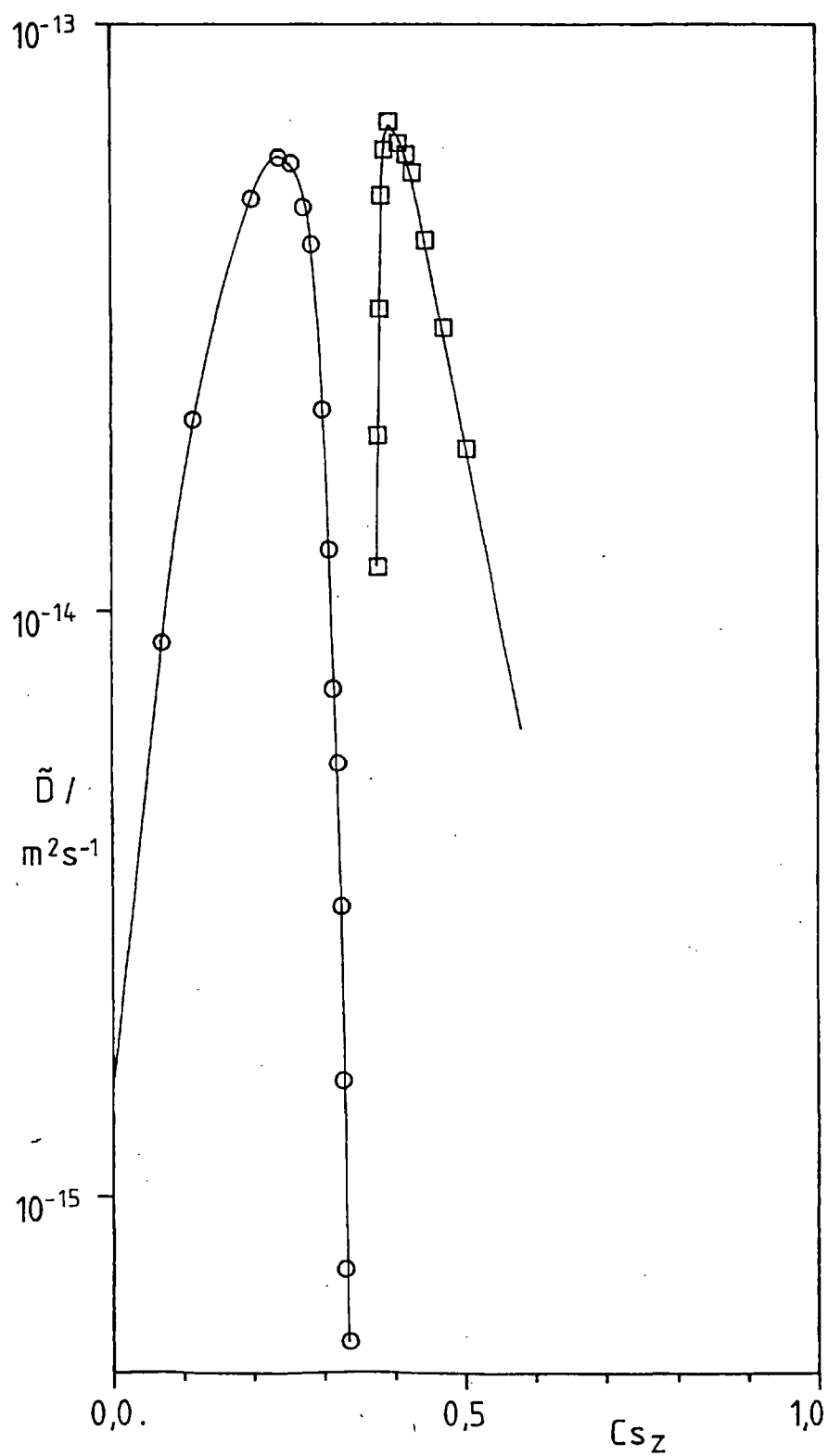


Figure 69.

Na-Rb exchange ; pH 10 ; $TN = 3,4 \cdot 10^{-3} N$; $Rb_{Z\text{end}} = 0,44$.

● $a_o = 2,6 \mu m$.

○ $a_o = 6,3 \mu m$.

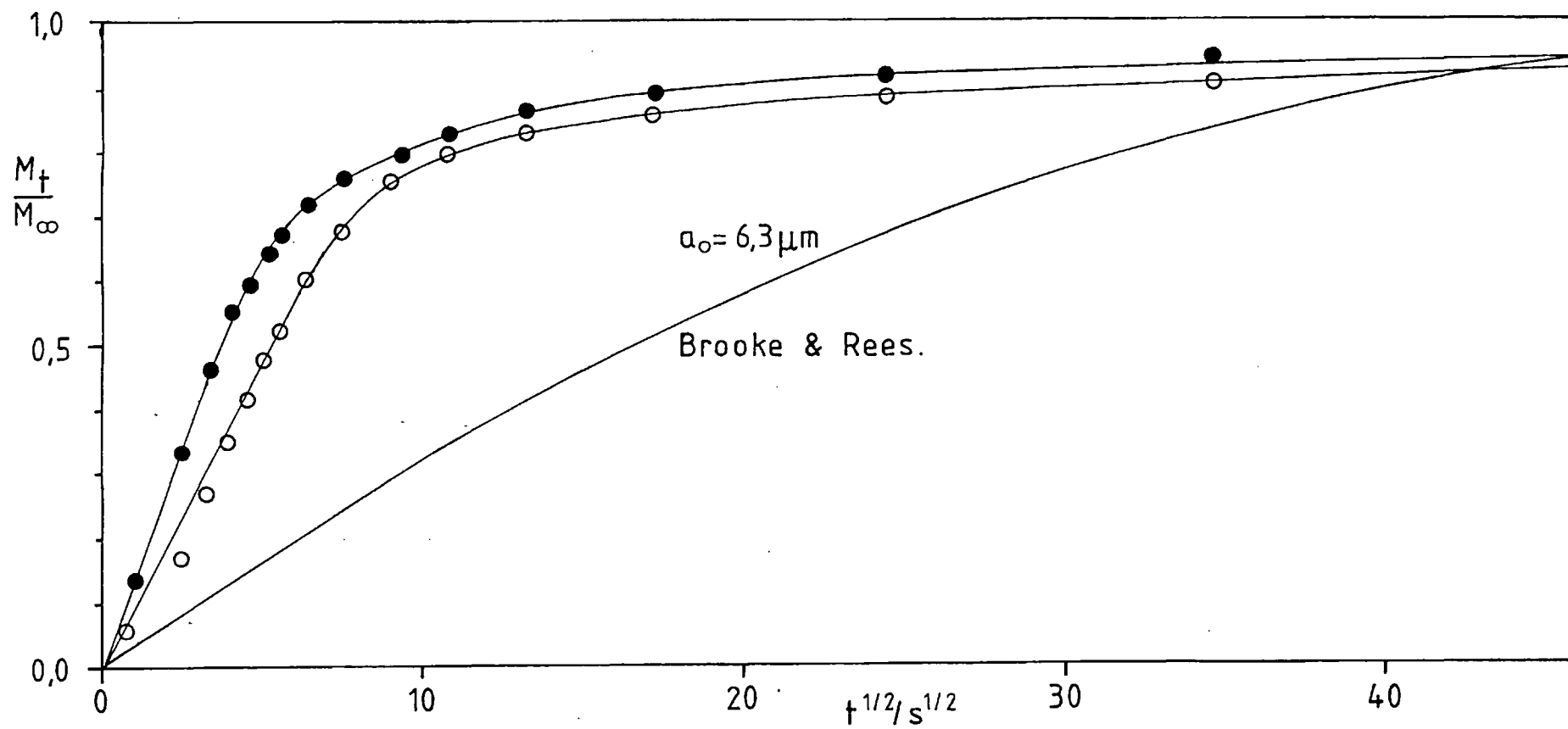
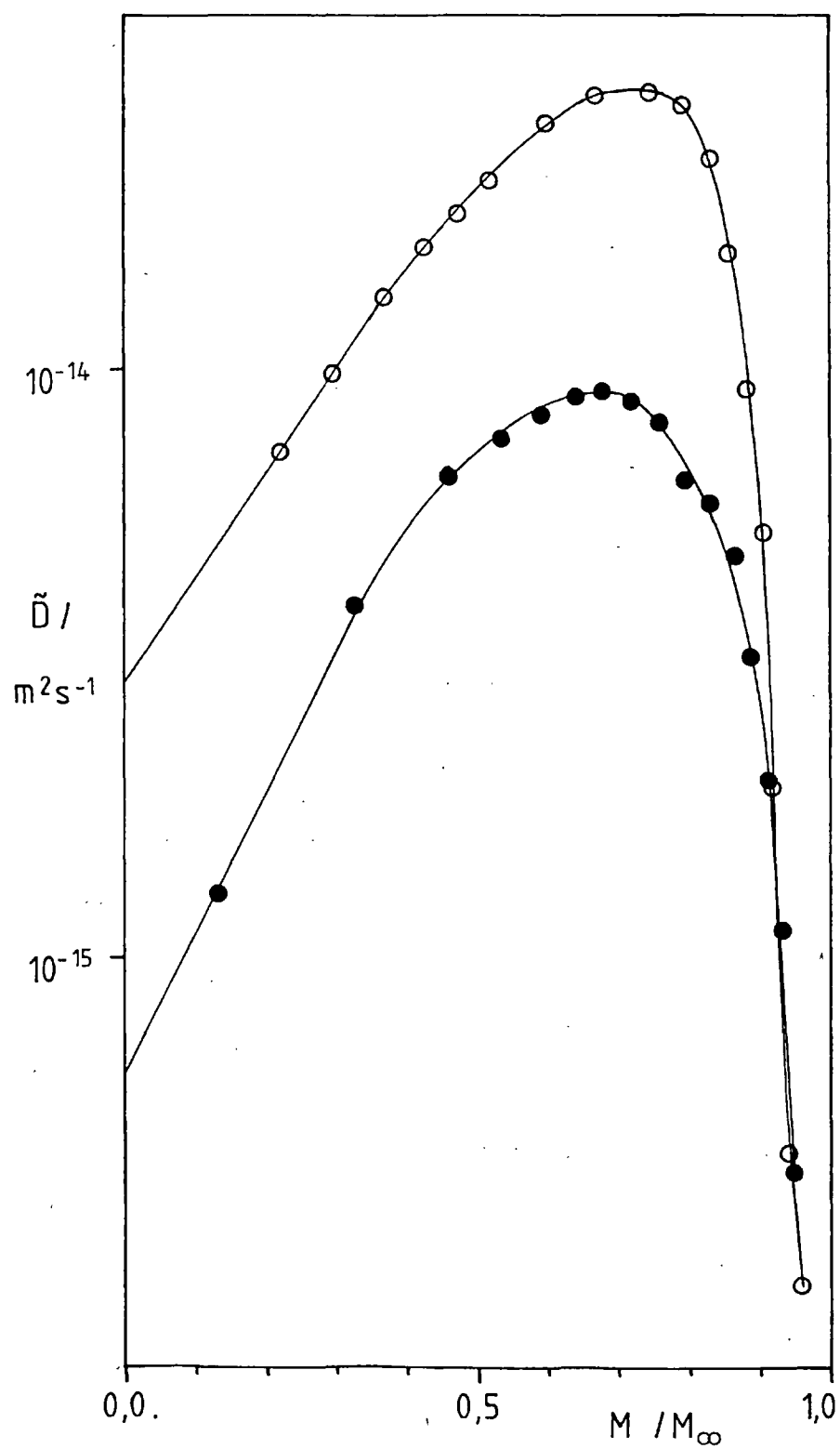


Figure 70.

Na-Rb exchange ; pH 10 ; $TN = 3,4 \cdot 10^{-3} \text{ N.}$

○ $a_o = 6,3 \mu\text{m.}$

● $a_o = 2,6 \mu\text{m.}$



form for both crystal sizes with a difference in magnitude due to agglomeration of the smaller crystal. The prediction of Brooke and Rees once again produces too slow kinetics.

For the Na - NH₄ system the exchange at pH11,5 (see figure 56) gave an unexpected degree of exchange. The $\sqrt{t}$ plot is unaffected (figure 71) and confirms that particle diffusion is rate determining for this system. The effect of crystal size on exchange rate (figure 72) and diffusion coefficient variation (figure 73) is the same as for the previous systems. A constant w value ($= M_z/M_s$) was used in the calculation of $\bar{D}$ due to a lack of isotherm data.

The theory of Brooke and Rees successfully predicted that the reverse (M - Na) kinetics would be faster than the forward (Na - M) kinetics but was not quantitative. The predicted values were "corrected" by a constant value (12,03) such that the half time for the Na - K exchange agreed with the experimental value (see table 9).

Table 9

Half times (seconds) from experiments, theory of Brooke and Rees, and corrected theory ($\div 12,03$).

System	$t_{1/2}$ expt	$t_{1/2}$ theory corr.	$t_{1/2}$ theory
Na - K	62	62	751
K - Na	31	45	538
Na - Rb	27	23	272
Na - Cs	18	44	529
Cs - Na	16	31	376

A simple factor does not suffice to give a good agreement. possible sources of the disagreement are that the theory assumes:-

Figure 71.

Na - NH_4 exchange ; $a_0 = 6,3\mu\text{m}$.

○ $\text{TN} = 3,4 \cdot 10^{-3}\text{N}$; pH 10 ; $\text{NH}_4\text{z}_{\text{end}} = 0,43$

□ $\text{TN} = 1,0 \cdot 10^{-2}\text{N}$; pH 10 ; $\text{NH}_4\text{z}_{\text{end}} = 0,66$

◇ $\text{TN} = 3,4 \cdot 10^{-3}\text{N}$; pH 11,5 ; $\text{NH}_4\text{z}_{\text{end}} = 0,07$

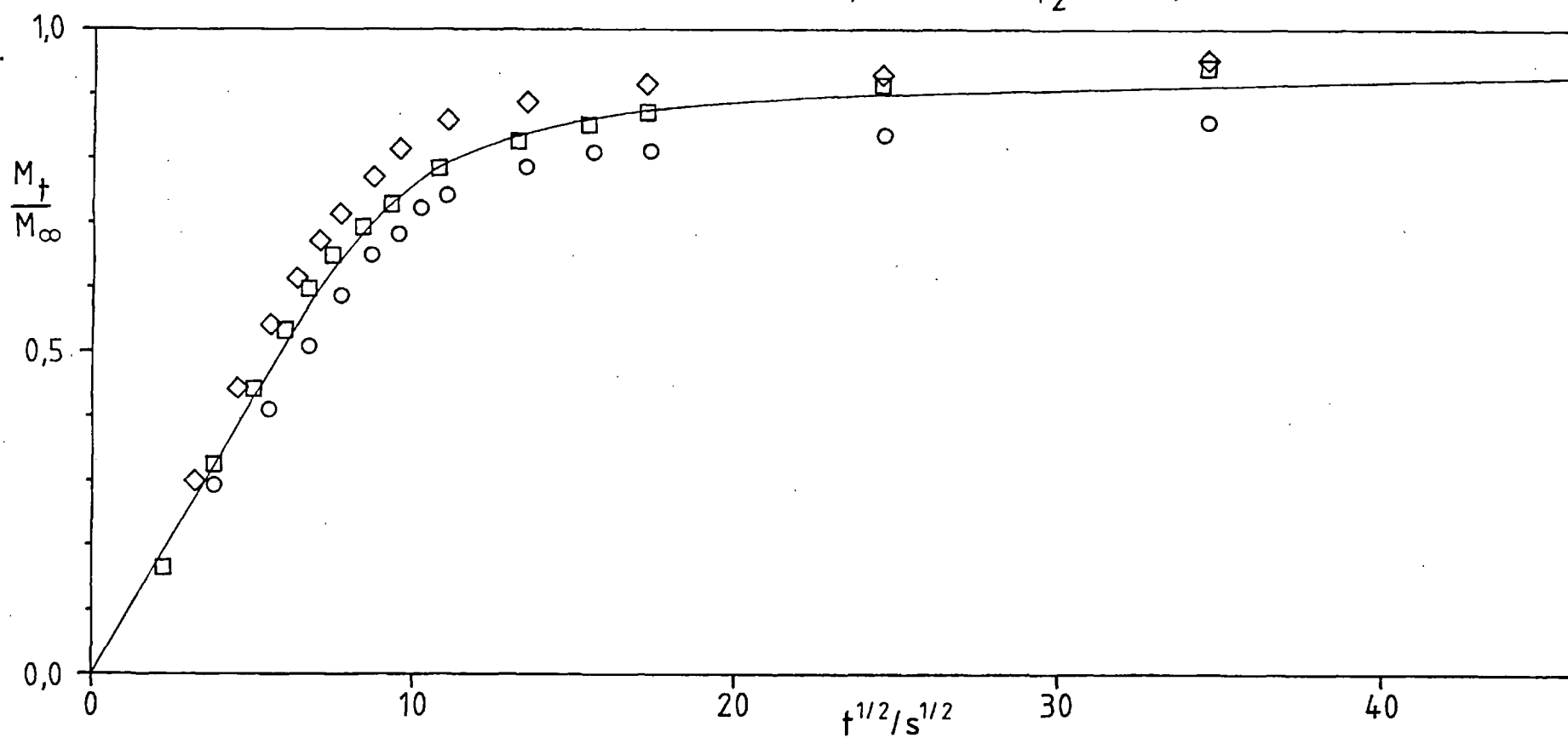


Figure 72.

Na - NH₄ exchange ; pH 10 ; a_o = 2,6 μm.

○ TN = 3,4 · 10⁻³ N ; NH₄_z end = 0,43

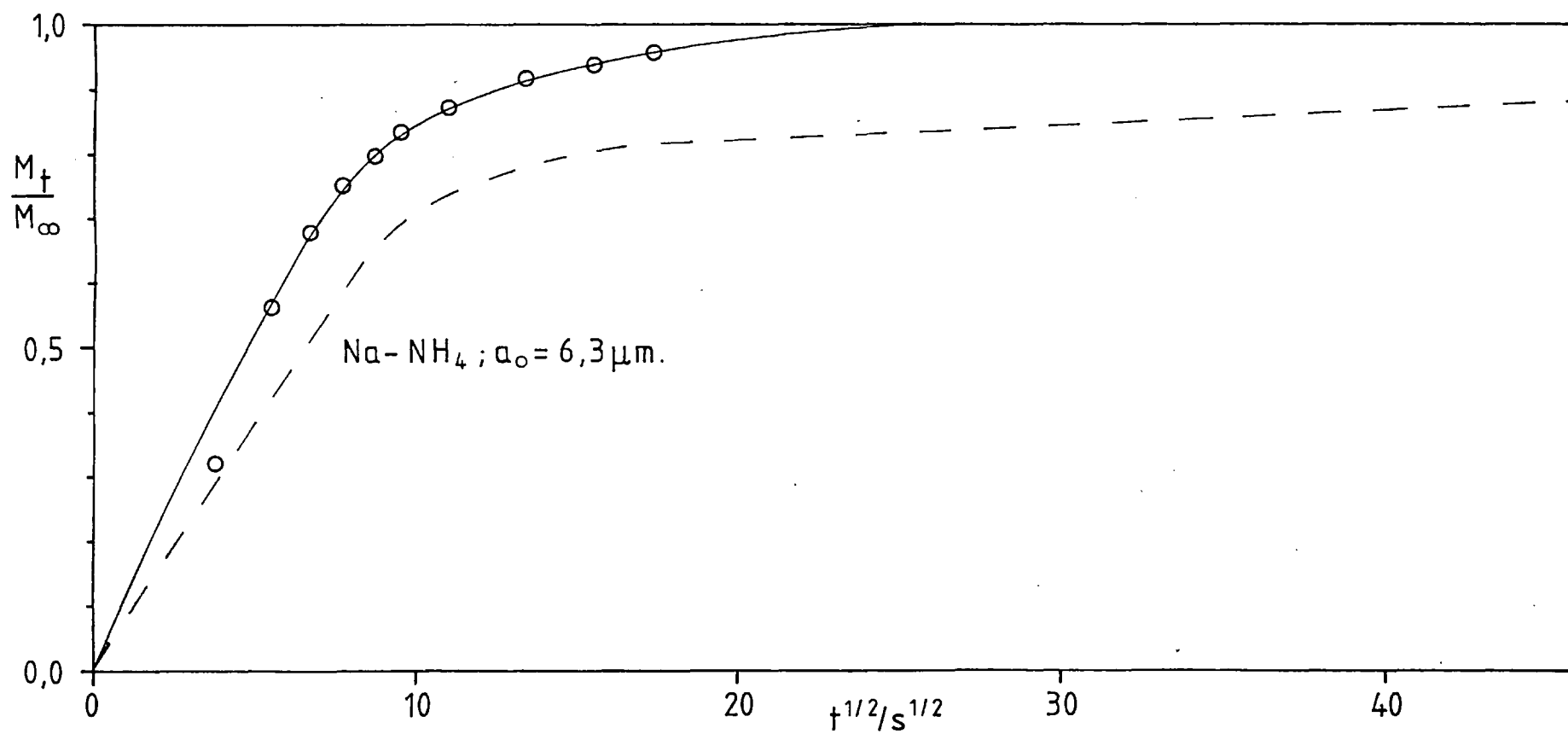
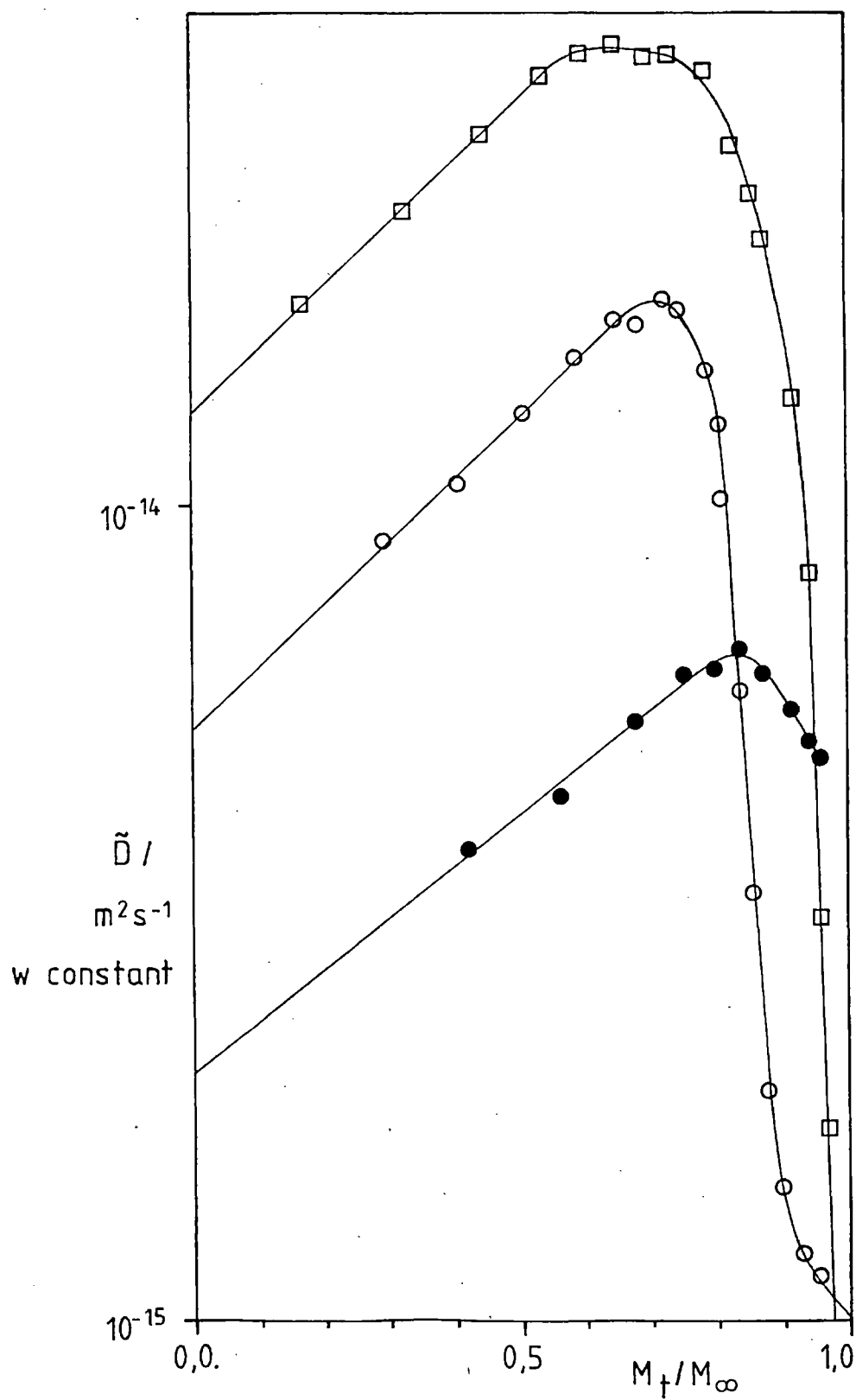


Figure 73.

Na - NH₄ exchange ; pH 10.

$a_o = 6,3 \mu\text{m}$; $\circ$ TN = $3,4 \cdot 10^{-3} \text{N}$; $\square$ TN = $1,0 \cdot 10^{-2} \text{N}$.

$a_o = 2,6 \mu\text{m}$; $\bullet$ TN = $3,4 \cdot 10^{-3} \text{N}$.



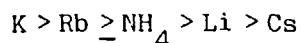
- (a) an infinite bath, i.e. does not allow for variation of concentration at the zeolite surface,
- (b) the self diffusion coefficients are independent of composition,
- (c) the self diffusion coefficients measured by Dyer et al (88) at sub zero temperatures in an alcohol/water mixture (1:1) still apply for a pure aqueous system.

Lutze and Miekeley (137), and Duffy and Rees (138, 139) considered the variation of self diffusion coefficients with composition and found that the calculated $\sqrt{t}$ plots were closer to the experimental plots than were calculations using constant self diffusion coefficients. Gaus and Lutze (87) have determined the variation of calcium, strontium and barium self diffusion coefficients with composition in zeolite A and then used a modification of the theory of Brooke and Rees to compare experimental and predicted ion exchange kinetics. The modification allowed for variable self diffusion coefficients and for the zeolite being in a non equilibrium state with water. They obtained good agreement. However, these corrections have not been applied for univalent cations due to lack of experimental measurements of the concentration dependency of self diffusion coefficients.

Lastly figure 74 shows the complete set of diffusion coefficients for sodium-univalent ion exchange with a TN of $3,4 \cdot 10^{-3} \text{N}$, pH10, $a_0 = 6,3 \mu\text{m}$. For $\text{Na} - \text{NH}_4$ exchange a constant w was used. The form and magnitude of the diffusion coefficient variation is very similar for each system. The peak diffusion coefficient decreases in the order:-

$$\text{Cs} > \text{Li} \geq \text{Rb} > \text{NH}_4 > \text{K}$$

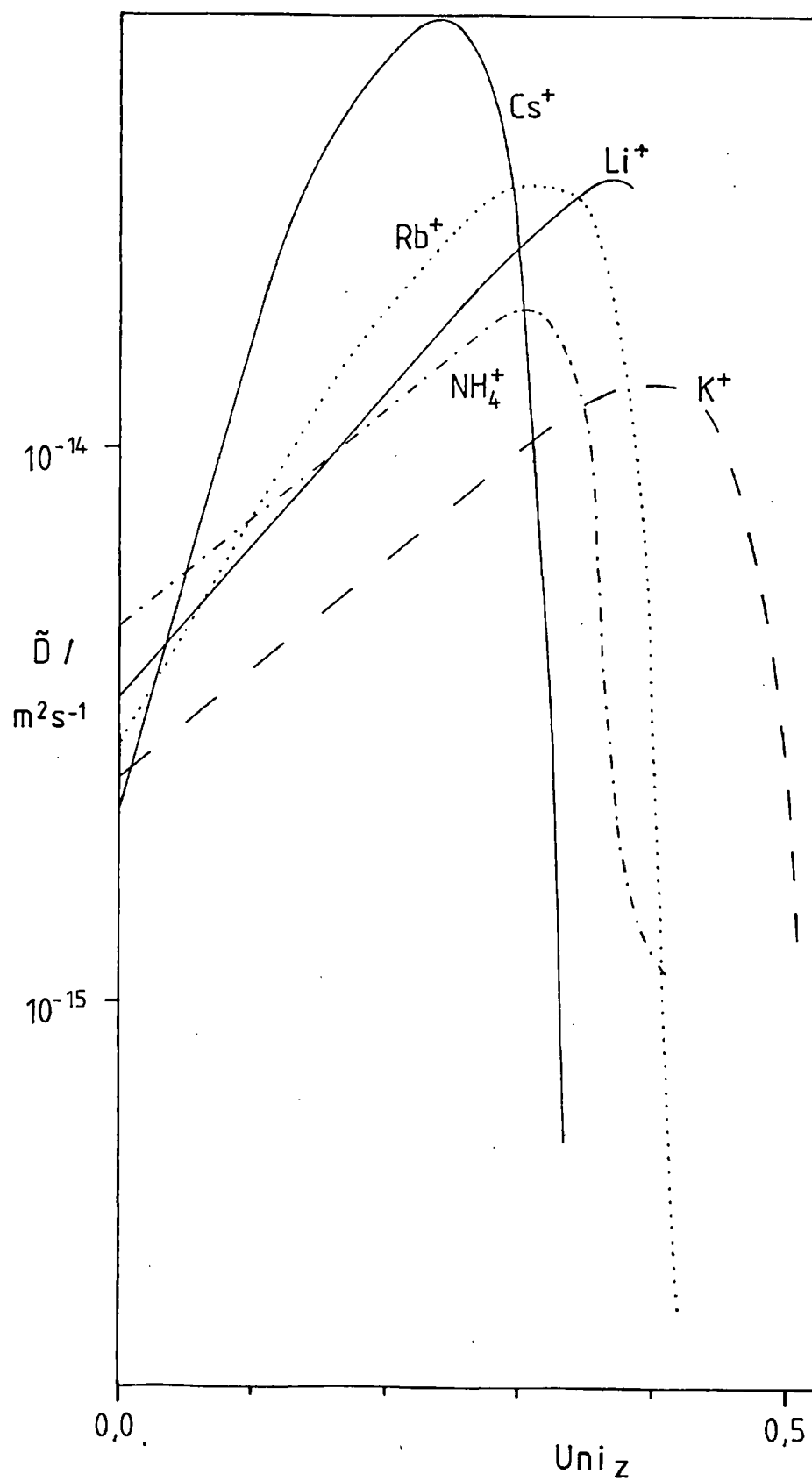
and the degree of exchange (and hence selectivity) decreases in the order



No clear implications can be drawn from this apparent relationship as the peak values are quite close. According to Helfferich (136) the ion for which the zeolite is most selective will tend to exchange into the zeolite faster than the reverse exchange. In this case the zeolite is selective for sodium and the reverse (M-Na) exchanges are the fastest but for the forward (Na-M) exchanges the least selected ion (Cs^+) enters faster. The factors of self diffusion coefficients (and their variation) and zeolite activity coefficients must be responsible for the observed trend.

Figure 74.

$\text{Na}^+ - \text{Uni}^+$ exchange ; $\text{TN} = 3,4 \cdot 10^{-3} \text{ N}$.



7. CONCLUSION

From this study of the kinetics of ion exchange several conclusions can be drawn. In all of the systems studied the ion exchange rate was independent of the exchangeable cation solution concentration which confirms that particle diffusion is rate determining for these systems. The effect of crystal size on the ion exchange rate was not quite as predicted for particle kinetics due to agglomeration of the smaller crystals and the non-ideality of the systems.

If the rapid drop in $\tilde{D}$ at the end of the exchange is considered to be an experimental artifact (due to drift effects as equilibrium is approached), the $\tilde{D}$ variation is comparatively linear, particularly for the Na - univalent ion exchange.

The "stepwise" Na - Ca exchange $\tilde{D}$ variation showed no conclusive composition effects (due to exchange at different sites) and no effects were seen in any "straight through" ion exchange system. For the Na - univalent systems the values of $\tilde{D}$ for the forward and reverse exchanges increased with M_t/M_∞ . The $\tilde{D}$ value would have been expected to drop during the reverse kinetics if the values of $\tilde{D}$ and D_{AB} are related as the variation of D_{AB} with composition is not effected by the direction of exchange. For the calculation of $\tilde{D}$ a constant diffusion coefficient is calculated for each point which is equated with the average to that point whereas D_{AB} is assumed to be variable throughout the theoretical calculations. It is not therefore possible to derive the D_{AB} variation from the experimentally determined $\tilde{D}$ variation.

If the factors effecting ion exchange kinetics are considered in terms of the theory of Brooke and Rees (97, 98) then constant self diffusion coefficients together with the activity term qualitatively predicts kinetics (reverse faster than forward for Na - univalent system).

For quantitative prediction variable diffusion coefficients together with an allowance for water diffusion are necessary (as used by Gaus & Lutze (87)). The variation in solution concentration and hence variation in zeolite outer layer composition would be difficult to incorporate in the theory of Brooke and Rees.

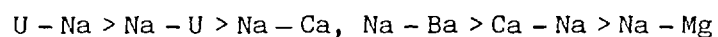
The theory of Brooke and Rees worked adequately for Sr - Ca exchange in Chabazite but not for Na - K exchange in Chabazite (97, 98). Using variable self diffusion coefficients Duffy found much better agreement for the Na - K exchange (139). Further measurements of the composition dependence of self diffusion coefficients will be needed before the results of the present study can be gainfully compared with theoretical predictions.

The effect of hydrolysis on ion exchange kinetics in zeolite A has been demonstrated. Although isotherm predicted end points gave reasonable results the best policy is to minimise hydrolysis where possible by the use of high solution concentrations and high pH.

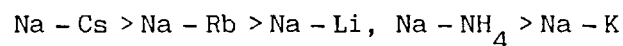
Of the Na - divalent systems the Na - Mg exchange was exceptionally slow even though the self diffusion coefficients of Mg, Ca and Ba are quite similar, (81, 88) although very recently the magnesium self diffusion coefficient has been shown to be much lower than that of calcium. The slow Na - Mg exchange was perhaps also due to magnesium's large hydration shell which has to be lost before it can enter the zeolite. This effect cannot be allowed for in theoretical calculations and would explain the observed $\tilde{D}$ variation with a possible change in rate determining step after 20% exchange (figure 46) when each Mg ion has now to share a limited number of water molecules in the confined space of zeolite A's cavities.

The ternary exchange showed the initial rate of uptake of magnesium being limited or blocked by calcium uptake but later the magnesium displaces some of the calcium. The first effect is kinetics, due to the rate of calcium uptake, and the second is equilibrium as the calcium content is brought back to the equilibrium value.

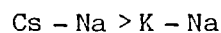
The Na - K exchange was the slowest of the Na - univalent exchanges and was predicted as such by the theory of Brooke and Rees. The relative rates observed in this study are:-



(U = univalent), also:-



and:



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Ion-Exchange Kinetics in Zeolite A

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The kinetics of Na → Ca exchange in zeolite A has been measured at 25 °C. The rates of complete replacement of Na⁺ by Ca²⁺ have been obtained and, also, the rates of small incremental replacements over the range of zeolite composition from pure sodium to 90% calcium have been measured. The kinetics of the reverse exchange has also been studied to a limited extent. All of these kinetics have been analyzed by using the Paterson solutions of the diffusion equation. In a separate study the degree of hydrolysis of zeolite A as a function of pH has been ascertained.

Introduction

Zeolite A, in its sodium form, has recently been introduced in extensive quantities as a builder in detergents. In a recent paper¹ the high selectivities of Na-A for Ca²⁺ and Mg²⁺ have been demonstrated. In this equilibrium study the thermodynamic quantities for these binary exchanges were obtained and polynomial expressions derived from which the binary isotherms at 25 and 65 °C could be calculated for any normality of solution phase. The more difficult ternary exchange was also studied for solutions which initially contained Ca²⁺:Mg²⁺ ratios of 2:1, 1:1, and 1:2. An attempt was made to predict the ternary isotherms from the binary isotherms.

Although a high selectivity for both of these divalent ions is an essential feature in the use of zeolite A as a builder in detergents, it is also necessary for the removal of the divalent ions to be extremely rapid to prevent interactions with the surfactants present. Rapid removal of Ca²⁺ ions is readily accomplished if the Na-A cubes have side lengths of ~1 μm. The Ca²⁺ ion concentration is reduced to acceptable levels in ~20 s. The removal of Mg²⁺ ions is not so rapid but the higher concentration of Mg²⁺ which still exists after ~1 min is not a serious problem.

In this paper the kinetics of Na⁺ ↔ Ca²⁺ exchange in zeolite A will be presented and the effect of the presence of Mg²⁺ ions on the exchange will be demonstrated. Also, zeolite A has one other important characteristic which enhances its suitability as a builder. It is readily hydrolyzed and so causes no environmental waste problems. The hydrolysis of zeolite A at various pH values will also be reported.

Experimental Section

In order to follow exchange times much greater than those which apply under detergency conditions, larger crystals of zeolite A were required. These large crystals were synthesized by using the Charnell method.² The

crystals obtained were well-formed cubes of side lengths in the range 15–18 μm.

The kinetics of exchange were usually followed by means of sodium or calcium ion selective electrodes but some exchange rates were also measured, or compared, radiochemically with ²²Na as the radiotracer in the zeolite phase.

The uncertainty in *F* values decreases from 6.8% to 5.9% as *F* increases and leads to a corresponding uncertainty in log *D* of 0.06–0.16. The uncertainty in the log *D* vs. *F* plots should therefore be represented by an area. However, as the uncertainty in log *D* is more significant, only error bars have been used as shown in Figure 4.

Results

In the first series of experiments Na⁺ → Ca²⁺ exchange rates were measured at three different solution normalities. In these experiments the ratio of equivalents of cation (in this case Ca²⁺) in the solution phase, *M*_s, to equivalents of cation (in this case Na⁺) in the zeolite phase, *M*_z, was also varied from 100:1 down to 1:0.8. The three rate curves obtained are shown in Figure 1. These rate curves are very similar, indicating that differences in the parameters which were varied had little effect on the rate of exchange.

The rate curves in Figure 1 were analyzed by using the Paterson³ solutions for limited volume diffusion in a manner similar to that described by Danes and Wolf.⁴ It should be noted that the Paterson solution is derived for a constant diffusion coefficient. The Danes and Wolf treatment assumes an average constant *D* over the range of *F* from zero to each given value. In these solutions the parameter *W* is required where *W* is defined as

$$W = \frac{M_z}{M_s} \frac{d[Ca]_z}{d[Ca]_s} \quad (1)$$

[Ca]_z and [Ca]_s are the equivalent cation fractions of Ca²⁺ in the zeolite and solution phases, respectively. The re-

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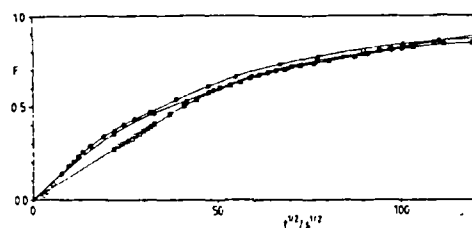


Figure 1. Rates of $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ exchange in zeolite A at three different solution-phase total normalities (TN) and three different ratios of M_2/M_1 . F is fractional attainment of equilibrium: (O) $\text{TN} = 3.4 \times 10^{-3} \text{ N}$, $M_2/M_1 = 0.81$; (●) $\text{TN} = 0.1 \text{ N}$, $M_2/M_1 = 2.7 \times 10^{-2}$; (□) $\text{TN} = 0.2 \text{ N}$, $M_2/M_1 = 1 \times 10^{-2}$.

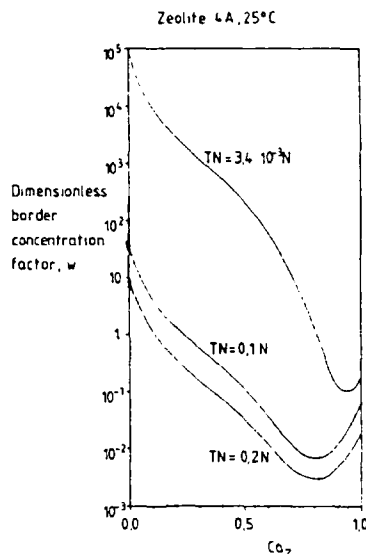


Figure 2. Dimensionless border concentration factor, W , plotted as a function of $[\text{Ca}]_1$ for three different total solution-phase normalities.

quired value of W are obtained from the slope of the isotherm at specific values of $[\text{Ca}]_1$. The values of W used in the analysis of the rate curves were calculated from the polynomial expression for the Na-Ca exchange at 25°C given by Barri and Rees¹ and are plotted in Figure 2. The isotherms for the three normalities used in these rate measurements are shown in Figure 3.

In the rate measurement for an initial solution phase of $3.4 \times 10^{-3} \text{ equiv dm}^{-3}$ of Ca^{2+} and $M_2/M_1 = 0.8$ it can be deduced from the isotherm in Figure 3 that $[\text{Ca}]_1$ at the ingoing surface of the zeolite must always be >0.90 during the time of the exchange. The values of W required for this region of $[\text{Ca}]_1$ are shown in Figure 2 to be approximately constant around a value of 0.15. In Figure 4 $\bar{D}$ is plotted against F , the fractional attainment of equilibrium for this system where $\bar{D}$ is the average diffusion coefficient operating from $F = 0$ to the value of F against which $\bar{D}$ is plotted.

The corresponding $\bar{D}$ against F plots for solutions of 0.1 and 0.2 equiv dm^{-3} are also shown in Figure 4. For these experimental conditions M_2/M_1 was 1:40 and 1:100, respectively, and $[\text{Ca}]_1$ at the ingoing surface was now always >0.975 for the first case and >0.99 for the second. The values of W required in the analysis of these rate curves

Na-Ca exchange isotherms, 25°C
--- 0.2 N, --- 0.1 N, — $3.4 \times 10^{-3} \text{ N}$

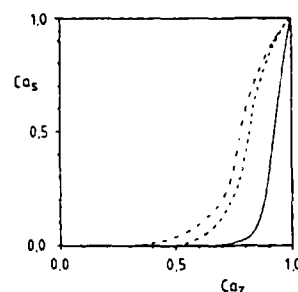


Figure 3. Na-Ca exchange isotherms at 25°C for zeolite A at three different total solution-phase normalities. $[\text{Ca}]_1$ and $[\text{Ca}]_2$ are the equivalent cation fractions of calcium in solution and zeolite phase, respectively.

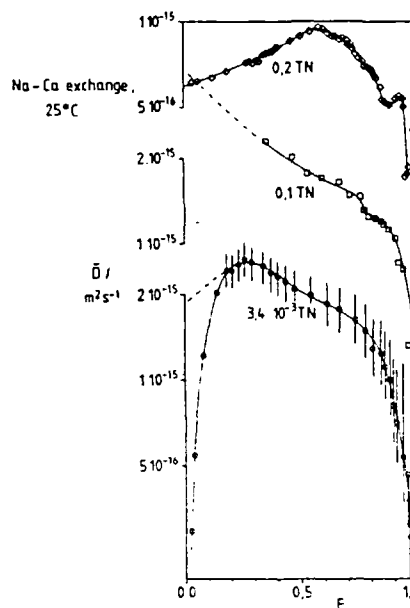


Figure 4. Plots of $\bar{D}$ against fractional attainment of equilibrium for $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ exchange in zeolite A at 25°C and three different total solution-phase normalities

can be seen from Figure 2 to be around 0.04 and 0.015, respectively.

The rate of exchange for the 0.2 equiv dm^{-3} solution was measured with a sodium-selective electrode and also radiochemically. The two $\bar{D}$ against $[\text{Ca}]_1$ (equal to F in these experiments) curves obtained from these rate measurements are shown in Figure 5. Although small differences can be seen at lower $[\text{Ca}]_1$ values, these two curves indicate that the two experimental techniques give very similar rates of exchange.

When the curves of $\bar{D}$ against F at the different solution normalities are compared (Figure 4), only minor differences are found when $F > 0.5$. At lower F values differences can be seen in these plots but not too much significance should

Ion-Exchange Kinetics in Zeolite A

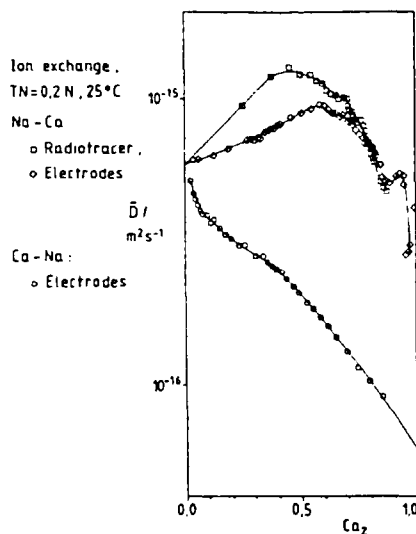


Figure 5. Plots of $\bar{D}$ against $[Ca]_s$ for zeolite A at 25 °C and total solution-phase normality of 0.2 N.

$TN = 0.2 \text{ N}$ $M_2/M_1 = 0.01$ 25°C
 • Na-Ca exchange
 • Ca-Na exchange

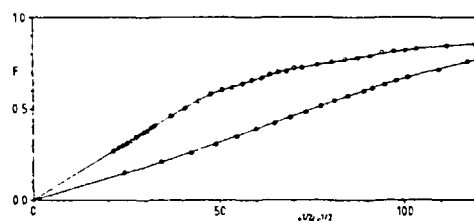


Figure 6. Rates of exchange in zeolite A at 25 °C for total solution-phase normality of 0.2 N and $M_2/M_1 = 0.01$.

be placed on these differences. The large, sudden decrease in $\bar{D}$ when $F < 0.2$ for the 3.4×10^{-3} equiv dm^{-3} solution is undoubtedly due to the response time of the ion-selective electrode at times of exchange < 60 s. The extrapolation shown in Figure 4 for this system is probably a better description of the variation of $\bar{D}$ with F in this region.

No experimental values were obtained at $F < 0.35$ with the 0.1 equiv dm^{-3} solution system. The extrapolated $\bar{D}$ values shown in Figure 4 below $F = 0.35$ were calculated from an extrapolation of the $t^{1/2}$ rate curve from $F = 0.35$ to zero.

When F is very close to 1, only very small changes in the Na^+ concentration occur and the $\bar{D}$ values calculated from the rate curves in this region are liable to large errors.

The decrease in $\bar{D}$ as F increases indicates that the differential exchange diffusion coefficient, $\bar{D}$, must decrease with increasing calcium loading of the exchanger.

The reverse exchange kinetics, i.e., $\text{Ca}^{2+} \rightarrow \text{Na}^+$, have also been measured at a solution normality of 0.2 equiv dm^{-3} . The rate curve obtained is shown in Figure 6 where it can be compared with the corresponding $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ rate curve. As the self-diffusion of sodium has been found to be much faster than that of calcium in zeolite A, these forward and reverse exchange kinetics follow the predic-

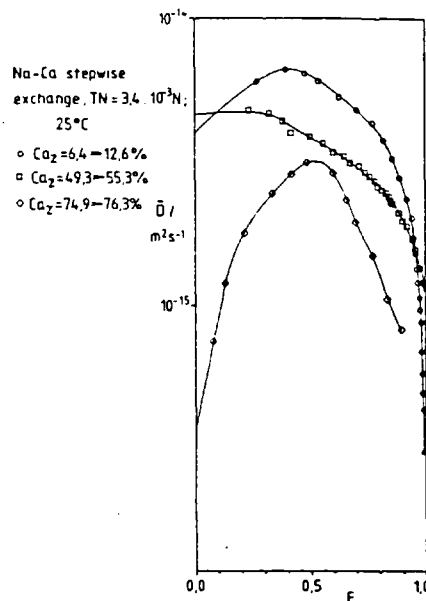


Figure 7. Plots of $\bar{D}$ against fractional attainment of equilibrium for small incremental uptakes of calcium in zeolite A at 25 °C. Total solution-phase normality is 3.4×10^{-3} N. The range of $[Ca]_s$ covered in each step is indicated. The M_2/M_1 values are as follows: $\square$, 0.559; $\diamond$, 0.477.

tions of the Helfferich and Plesset theory.⁵ In Figure 5 the variation of $\bar{D}$ with $[Ca]_s$ for the reverse kinetics may be compared with the corresponding variation for the forward kinetics. In the reverse kinetics $F = 1 - [Ca]_s$, so $\bar{D}$ now increases as the exchange proceeds, i.e., on going from pure Ca-A to pure Na-A zeolite, and correspondingly the differential diffusion coefficient $\bar{D}$ for this exchange must also increase on going from Ca-A to Na-A zeolite. Comparison of $\bar{D}$ against $[Ca]_s$ indicates, however, that for both forward and reverse kinetics $\bar{D}$ decreases with increasing calcium content of the zeolite and $\bar{D}$, at any value of $[Ca]_s$, is always greater for the forward kinetics than for the reverse kinetics.

In a second series of experiments the $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ exchange rates were measured over small 5% changes in $[Ca]_s$ from pure Na-A up to 83% Ca-A zeolite. The solution-phase concentration was maintained at a constant 3.4×10^{-3} equiv dm^{-3} . Each of the 15 rate curves obtained was analyzed as before by using Paterson's solutions. The $\bar{D}$ values obtained as a function of F from three rate curves are plotted in Figure 7. This figure includes details of the range of $[Ca]_s$ covered and the values of M_2/M_1 involved in each rate measurement. At low values of $[Ca]_s$, because of the very high selectivity of Ca^{2+} in zeolite A, the range of W covered in each rate analysis was very large; e.g., for $[Ca]_s$ going from 0.28 to 6.44%, W increased from 0.809 at small F values to 122 near the end of the run where little Ca^{2+} remained in the solution phase.

In Figure 8 the variations of $\bar{D}$ over each increment of composition covered are plotted against $[Ca]_s$ to show the overall trend in $\bar{D}$ on going from pure Na-A to almost pure Ca-A in small incremental steps. Although the trend of $\bar{D}$ against $[Ca]_s$ in this figure is similar in shape to that for

(5) Helfferich, F.; Plesset, M. S. *J. Chem. Phys.* 1958, 28, 418.

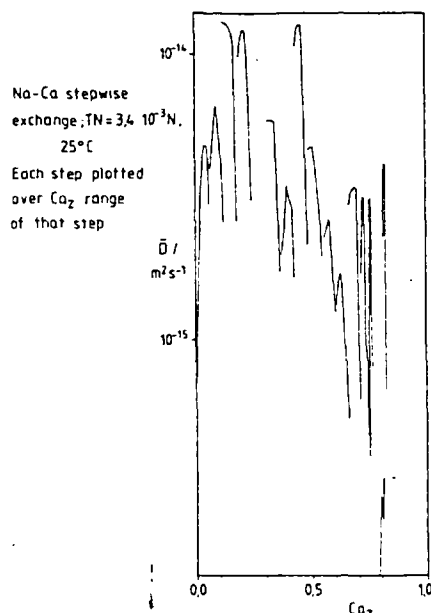


Figure 8. Variation of $\bar{D}$ over each incremental composition plotted against $[Ca]_0$ for stepwise $Na^+ \rightarrow Ca^{2+}$ exchange in zeolite A at 25 °C. Total solution-phase normality is 3.4×10^{-3} N.

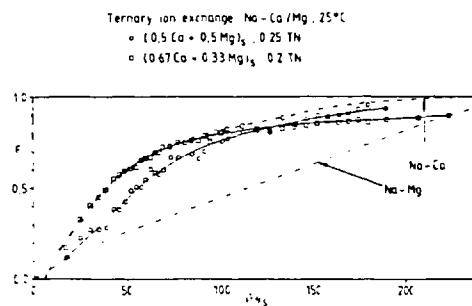


Figure 9. Ternary exchange kinetics in zeolite A at 25 °C, $Na^+ \rightarrow Ca^{2+}/Mg^{2+}$. The binary exchange kinetics are included for comparison.

the corresponding system (3.4×10^{-3} equiv dm^{-3}) in Figure 4 where exchange from pure Na-A to almost pure Ca-A is covered in one step, it is interesting to note that the $\bar{D}$ values at corresponding $[Ca]_0$ values are a little greater for the incremental uptakes.

Finally, in Figure 9 some preliminary ternary rates of exchange are presented. In these experiments pure Na-A was mixed with solutions containing 1:1 and 2:1 $Ca^{2+}:Mg^{2+}$ ratios at zero time. The rate of uptake of total divalent ion was measured as a function of time. Figure 9 shows that the rate of uptake for the 2:1 $Ca^{2+}:Mg^{2+}$ case was little different from the rate for the corresponding pure calcium solution. When the solution phase, however, was 1:1 $Ca^{2+}:Mg^{2+}$ initially, the rate of uptake of divalent ion was now somewhat slower but still much greater than the rate of uptake for the pure magnesium solution phase. Because of the very high selectivity for Ca^{2+} the composition of the zeolite phase at infinite time in both of these cases tended to be almost pure Ca-A. However, it is known from

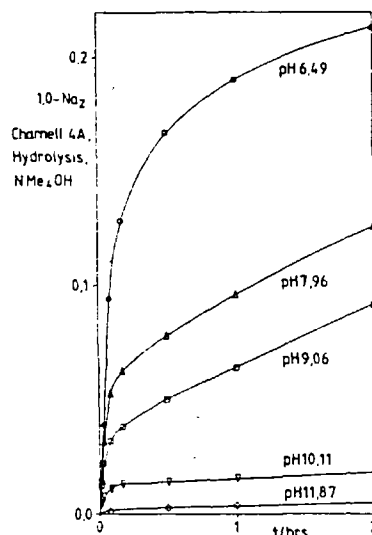


Figure 10. Rate of release of Na^+ ions at 25 °C from Na-A zeolite at various initial pH values.

equilibrium studies¹ that Mg^{2+} ions are taken up by the zeolite at low divalent ion loadings to be replaced by Ca^{2+} at high loadings even when the solution phase contains 1:1 Ca^{2+} to Mg^{2+} . The slower rate found than for the 1:1 $Ca^{2+}:Mg^{2+}$ system suggests that Mg^{2+} ions are taken up by the zeolite and block the 8-ring oxygen sites which control diffusion in the zeolite A channel system. In the 2:1 $Ca^{2+}:Mg^{2+}$ case insufficient quantities of Mg^{2+} are taken up to cause any great degree of blocking. In future rate measurements in these ternary systems all three ions will be analyzed in the solution phase as a function of time to obtain a better insight into the kinetics involved.

Hydrolysis of Zeolite A

In order to speed up the initial mixing in an ion-exchange kinetics measurement the zeolite was slurried with water at pH > 8 and then the solutions of counterion added. However, abnormally high outputs were obtained from the sodium-selective electrode which drifted upward at quite high rates before any counterion was introduced. These high concentrations of sodium in the solution phase were confirmed by atomic absorption spectroscopy. A study of this hydrolysis of Na-A zeolite as a function of pH was, therefore, carried out. In order to vary the pH of the zeolite/water slurry and exclude the possibility of ion exchange, NMe_4OH was used as the alkali. NMe_4^+ ions are too large to enter the zeolite A channels.

In Figure 10 the release of Na^+ at various initial pH values is shown as a function of time. In these experiments large crystals, synthesized by the Charnell method, were used but similar rates of release were obtained from much smaller crystals, indicating that this release was not particle diffusion controlled. In Figure 10 it can be seen that, after 2 h, 24%, 14%, and 10% of the sodium in the zeolite is released at pHs of 6.49, 7.96, and 9.06, respectively. After about 1 h the rate of hydrolysis seems to attain a constant value. The small amount of hydrolysis at pH 11.87 discounts the possibility of any entrained sodium salts being present in the zeolite channels from the synthesis process.

In the above experiments the pH was also followed as a function of time. It can be seen from Figure 11 that there

