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Cation diffusion in the natural zeolite clinoptilolite

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Abstract

The natural zeolite clinoptilolite is mined commercially in many parts of the world. It is a selective exchanger for the ammonium cation and this has prompted its use in waste water treatment, swimming pools and in fish farming. It is also used to scavenge radioisotopes in nuclear waste clean-up.

Further potential uses for clinoptilolite are in soil amendment and remediation. The work described herein provides thermodynamic data on cation exchange processes in clinoptilolite involving the NH_4, Na, K, Ca, and Mg cations. The data includes estimates of interdiffusion coefficients together with free energies, entropies and energies of activation for the cation exchanges studied. Suggestions are made as to the mechanisms of cation-exchanges involved. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Clinoptilolite; Zeolite; Cation diffusion; Ion exchange; Waste water treatment; Thermodynamic parameters

1. Introduction

The natural zeolite clinoptilolite (idealised unit cell composition $[(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O)]$ is mined commercially in many parts of the world (e.g. USA, South Africa, Bulgaria, Cuba, Hungary) [1]. Mining takes place of tuffaceous rocks that have clinoptilolite contents in the range 60–92%. Apart from its use as a cheap constructional material the major application of this zeolite is in the treatment of waste water. It has a relatively high Si/Al compositional ratio which gives it a special ion-exchange selectivity for large monovalent cations.This selectivity is used to scavenge caesium radioisotopes from aqueous nuclear waste in the SIXEP process at the BNF Sellafield site and has greatly aided post Chernobyl clean-up [2]. Another cation for which clinoptilolite has a selectivity is the ammonium ion and this has encouraged its use in water treatment plants, swimming pools and fish farming [3].

Despite this interest comparatively little data exist on the rates of cation exchange in clinoptilolite. Ames [4] used radiochemical methods to measure self-diffusion coefficients of sodium, caesium and strontium in clinoptilolite, erionite and phillipsite (as well as in the synthetic zeolites A and X). Dyer and Araya used the same technique to follow several self-diffusion processes in clinoptilolite [5]. More recently tracer diffusion coefficients of Cs and Sr into this zeolite have been estimated as part of the studies on Yucca Mountain, Nevada, which is intended as a major repository site for radioactive waste [6]. Neveu et al. [7] have used more conventional analysis to model the rates of the Na ↔ NH_4 cation exchange in clinoptilolite. Yang et al. [8] have followed Na, K, Rb and Cs diffusion in heulandite single crystals by the novel method of

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using a polarising microscope to observe changes of extinction angle caused by the compositional changes in the crystals created by ion exchange. Heulandite has the same aluminosilicate framework (HEU [9]) as clinoptilolite but has calcium as its dominant cation component in contrast to clinoptilolite which has sodium and potassium as major cations.

This work describes the use of various techniques to follow the rates of replacement of sodium, potassium, calcium (radiochemical), magnesium (atomic absorption) and ammonium (automatic Kjeldahl) from clinoptilolites. The cations of interest reflect the previously mentioned use of clinoptilolite in waste water treatment but also its potential employment for soil amendment and remediation [10].

2. Experimental

2.1. General

Clinoptilolite 1010A was supplied by Anaconda, Denver, CO, from the Death Valley Junction deposit in CA. It was purified by the method of Barrer and Townsend [11].

The purified material was converted to ion exchanged forms by treatment at 90°C, (for 2 days)-with 0.1 M solutions of the appropriate metal chloride. It must be emphasised that these conditions were chosen not to try to attain maximum exchange but to attempt a simulation of conditions not too far removed from that encountered in soil amendment and waste water treatment. To do this the time period represented a compromise, compensated by the use of a high temperature, with relatively low concentrations of the in-going ions. The alternative method involving repeated treatments with solutions of high molarity would increase the likelihood of aluminium leaching and salt imbibition taking place, and would not be representative of the likely circumstances of the uses envisaged. In the cases of Na,K and Ca exchange the solutions contained 22-Na, 42-K or 45-Ca radioisotopes of known activity. Isotopes of sodium and calcium were supplied by Amersham International, Bucks, but 42-K came from irradiation of Analar potassium nitrate in the Universities Research Reactor, Risley, Cheshire. Analyses of the cation exchanged forms were carried out by standard wet chemical methods coupled with atomic absorption or Kjeldahl methods when required. XRD checks showed that they had retained crystallinity.

2.2. Kinetic measurements

Tared amounts (~150 mg) of zeolite were placed in polythene vials with 20 ml of 0.1 M solutions of the in-going cation. The filled vials were rotated about their horizontal axis in a thermostatically controlled air oven for time periods in the range 5 min to 168 h.

At the end of the time periods the vials were taken out of the oven, centrifuged, and aliquots of solution were removed for analysis .When 42-K was the cation it was determined by Cerenkov counting , and exchanges were limited to 24 h because of the short half-life of this isotope. The other isotopes were measured by liquid scintillation counting. Experiments were carried out at 298, 303, 311, 323, and 333 K.

2.3. Interpretation of kinetic curves

Three methods were used to interpret diffusion kinetics for the systems studied. The first (CH) used the Carman–Haul [12] equation to evaluate the diffusion coefficients, D_i, for a system comprising a solid of definite shape in contact with a well-stirred fluid of limited volume. The equation can be represented as:

$$1-\frac{W_t}{W_\infty} = (1+\lambda)\left[\left\{\frac{\gamma_1}{(\gamma_1+\gamma_2)}\right\}\mathrm{e}\ \mathrm{erfc}\frac{\gamma_1}{\lambda}.\sqrt{\tau} + \left\{\frac{\gamma_1}{(\gamma_1+\gamma_2)}\right\}\mathrm{e}\ \mathrm{erfc}-3\frac{\gamma_2}{\lambda}.\sqrt{\tau}\right]-\lambda. \qquad (1)$$

For low values of $\sqrt{\tau}/\lambda$, Eq. (1) can be expressed as:

$$\frac{W_t}{W_\infty} = (1+\lambda)\frac{6}{\sqrt{\pi}}.\frac{\sqrt{\tau}}{\lambda}-\left(1+\frac{\lambda}{3}\right)\frac{9\tau}{\lambda^2} + (1+2\lambda)\times\frac{36}{\sqrt{\pi}}.\frac{\tau^{3/2}}{\lambda^3}+\cdots, \qquad (2)$$

where,

$$\tau = \frac{D_i t}{r^2}, \quad \lambda = \frac{VM}{vm},$$

$$\gamma_1 = \frac{1}{2}\left[\sqrt{\left(1+\frac{4}{3\lambda}\right)}+1\right], \quad \gamma_2 = \gamma_1 - 1,$$

and

$$\mathrm{e\ erfc}x = \exp x^2 \mathrm{erfc}x,$$

W_t is the extent of exchange at time $T = t$, and W_∞ the extent of exchange at time $T = \infty$; V is the volume of solution, M the molarity of the diffusing species with respect to the solution phase, v the volume of solid, and m the molarity of the diffusing species with respect to the solid. The clinoptilolite, after grinding and sieving, approximated to particles of radius $r = 3.0 \times 10^{-5}$ m. Plots of W_t / W_∞ with time could be constructed and elucidated to yield values of D_i, which is the interdiffusion coefficient for the cation moving through the zeolite in the presence of the counter cation and water molecules.

The second approach (BR) followed that of Boyd et al. [13] as adapted by Reichenberg [14], using;

$$\frac{W_t}{W_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}.\exp(-\beta n^2 t), \qquad (3)$$

where n is the number of diffusing species, and β (a constant) $= D_i \pi^2 / r^2$.Values of β can be estimated from a theoretically derived plot of W_t/W_∞ against βt and hence D_i.

The third method (BBK) was that of Barrer, Barri and Klinowski [15] using;

$$I_0 = \int_0^\infty \left(1 - \frac{W_t}{W_\infty}\right)\mathrm{d}t = \frac{r^2}{15 D_i}, \qquad (4)$$

where I_0 is the the area between the asymptote and the curve of W_t/W_∞ against time (t). Measurement of I_0 provided a convenient means of estimating D_i.

Activation energies (E_a), free energies (ΔG^*) and entropies (ΔS^*) for the exchange processes could be estimated from values of D_i determined when experiments were carried out at different temperatures.

3. Results and discussion

3.1. Cation forms of clinoptilolite

Table 1 lists the cation compositions of the purified parent material and the cationic forms of clinoptilolite prepared (Note; the balance is oxygen and unrecorded). Attempts to prepare a magnesium form resulted in only a small amount of exchange, under the conditions used, confirming the lack of selectivity of clinoptilolite for this cation [16]. The potassium and ammonium forms were close to homoionic but sodium was unable to displace more than about 30% of potassium from the purified material. This confirmed the observation of other workers for a sample of this zeolite from Itaya, Japan, which had a similar natural composition [5]. The calcium exchanged form also retained appreciable amounts of potassium in line with the cation selectivity series of clinoptilolite.

3.2. Kinetic measurements

3.2.1. General

Examples of the kinetic plots depicting the exchange processes are presented in Figs. 1–3. Table 2 shows examples of D_i values, for some ion-pairs, calculated by the different methods of analysing the W_t / W_∞ versus time plots at 298 K. It illustrates that diffusion coefficients calculated by the CH and BBK methods were in general agreement. Those from the BR approach were of the same order of magnitude but were less consistent. All the mathematical analyses involved the construction of a straight line plot, the slope of which generated the D_i value.

Both the CH and BR methods made use of dimensionless time plots (CH: τ vs t, BR: β vs t) and a computer program developed for the CH equation

Table 1
Composition of ion-exchanged clinoptilolites (% wt.)

Sample	Na	K	Ca	Mg	Al	Si	H_2O
Purified initial material	2.6	3.1	0.20	0.01	4.0	31.0	12.9
Na	3.5	2.0	0.10	0.01	4.0	31.6	11.7
K	0.04	3.5	0.05	0.01	4.0	30.7	10.3
Ca	0.15	0.83	1.50	0.01	4.0	29.7	8.2
NH_4	0.08	0.28	0.02	0.01	4.3	33.8	10.5
Mg[a]	1.51	1.74	0.09	0.12	4.3	30.5	10.2

[a] Prepared from the sodium form.

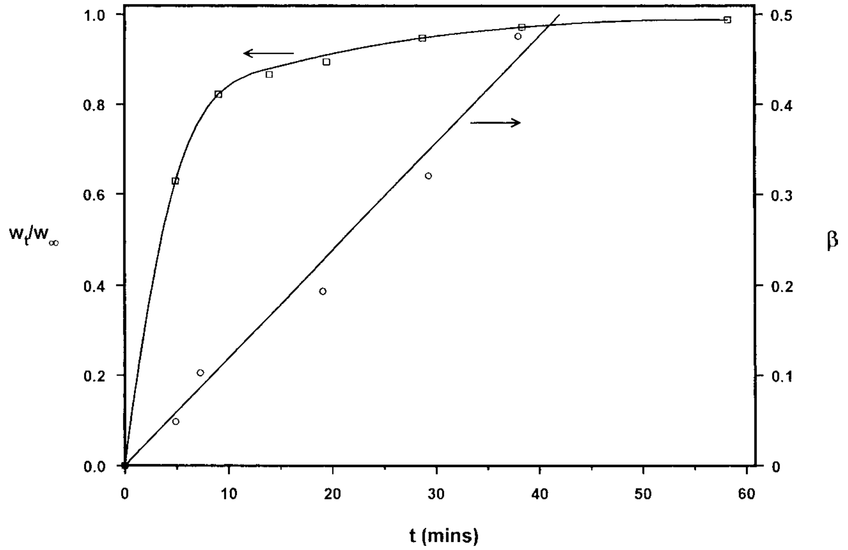

Fig. 1. Kinetic plot for the Na ↔ NH_4 exchange in clinoptilolite at 306 K. Example of the BR interpretation. □ — W_t/W_∞ versus time(t), o — β versus t.

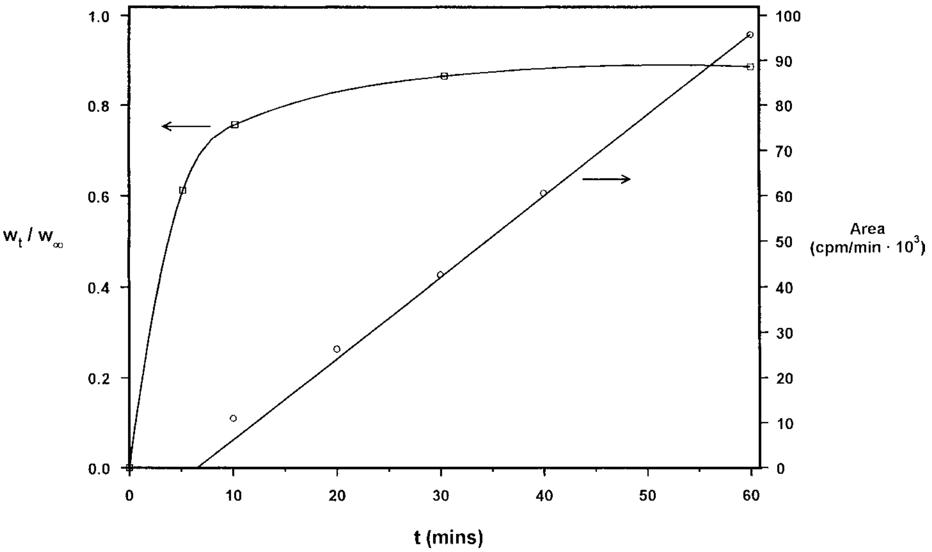

Fig. 2. Kinetic plot for the Na ↔ NH_4 exchange in clinoptilolite at 306 K. Example of the BBK interpretation. □ — W_t/W_∞ versus time (t), o — area under the W_t/W_∞ versus t curve.

evaluated the quality of fit to a straight line for the τ versus t plots prior to calculating D_i. This program is available on the University of Salford Network. When the BR method was invoked only the initial parts of the dimensionless time plots were linear (see Fig. 4 for example) and this was identified as the source of the inconsistent analysis noted above. Neveu et al. [7] also used the BR approach and showed curved β versus t plots for the Na ↔ NH_4 exchange in a homoionic Na clinoptilolite. Their original material also was supplied by the Anaconda, but no elemental composition was recorded.

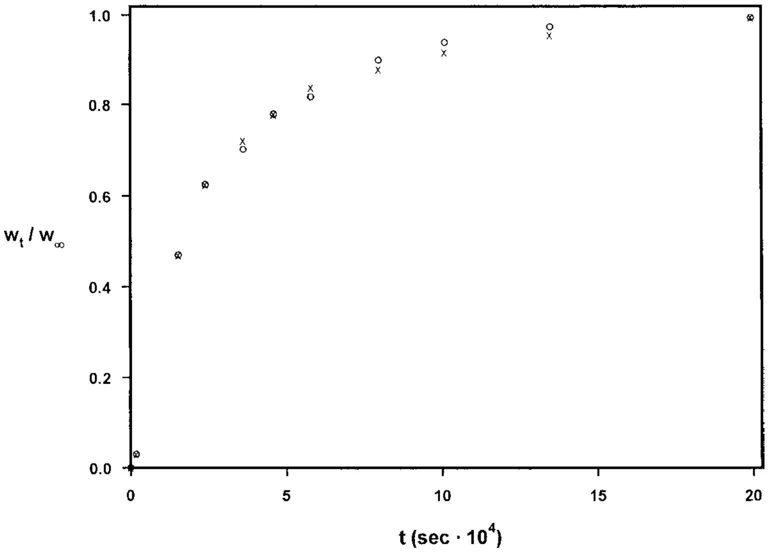

Fig. 3. Kinetic plot for the Na ↔ NH_4 exchange in clinoptilolite at 306 K. Example of the fitting of a W_t/W_∞ versus time (t) plot by the CH equation. x — experimental points, o — theoretical points.

The results of the CH analysis were used to produce E_a, ΔG^* and ΔS^* values for appropriate exchanges. These can be found in Table 3.

Table 2
Interdiffusion coefficients (D_i) estimated by different mathematical methods for cations in ion-exchange processes in clinoptilolite at 298 K

Ion exchange[a]	Interdiffusion coefficient ($10^{-13} \times m^2 s^{-1}$)		
	BBK[b]	BR[b]	CH[b]
NH_4 ↔ Na	271	107	299
NH_4 ↔ K	258	348	276
NH_4 ↔ Ca	13.1	6.3	12.6
NH_4 ↔ Mg	2.6	1.0	2.5
Na ↔ NH_4	153	138	90
Na ↔ K	207	192	190
Na ↔ Ca	6.1	123	3.4
K ↔ Na	12.4	Nc[c]	101
K ↔ NH_4	16.0	Nc	27.2
K ↔ Ca	19.1	Nc	16.0
Mg ↔ Na	9.8	Nc	0.5
Mg ↔ K	5.7	Nc	0.3
Mg ↔ NH_4	10.6	Nc	3.7
Mg ↔ Ca	10.0	Nc	0.9

[a] Ion initially present stated first.
[b] See text.
[c] Nc — not calculated.

3.2.2. Calcium ion-exchange from clinoptilolite

The isotope 45-Ca is a weak β emitter and this makes accurate assessment of its activity in aqueous solution difficult. When 45-Ca labelled clinoptilolite was the ion-exchanger being studied, calcium diffusion out of the zeolite was very slow and the conse-

Table 3
Energies (E_a), entropies (ΔS^*) and free energies (ΔG^*) of activation for ion exchange processes in clinoptilolite in the range 298–333 K based on CH data

Cation exchange process	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})
NH_4/Na	15	−47	27
NH_4/K	13	−53	27
NH_4/Ca	19	−64	35
NH_4/Mg	14	−95	39
Na/NH_4	42	35	29
Na/K	23	−26	28
Na/Ca	24	−92	48
K/Na	17	−51	29
K/NH_4	56	69	33
K/Ca	25	−38	34
Mg/Na	64	62	43
Mg/K	104	196	43
Mg/Ca	44	−20	48
Mg/NH_4	17	−80	38

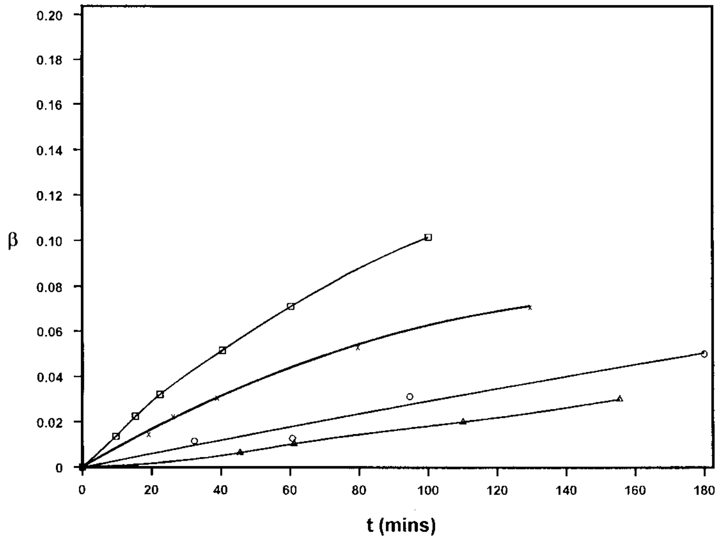

Fig. 4. Examples of β versus t plots (BR interpretation) for 1/2Ca ↔ K exchange in clinoptilolite at various temperatures. □ — 323 K, x — 311 K, o — 306 K, Δ — 298 K.

quent low levels of radioactivity in solution were hard to evaluate. They were little affected by temperature in the range chosen and no thermodynamic parameters were calculated. The diffusion of Ca out of clinoptilolite when being replaced by Na or K was approximately 5×10^{-13} m^2 s, ammonium ion ingress increased this figure by a factor of ~4. Yang et al. [8] measured the rate of exchange of calcium by sodium from a single crystal of heulandite as 2×10^{17} m^2 s^{-1} at 336 K. Even taking into account the very different method of measurement this disparity is surprising and no simple explanation can be proposed other than to comment that the method of Yang et al. is independent of crystal dimension as it makes a direct measurement of the progress of ions within the crystal.

3.2.3. Ammonium, sodium and potassium ion-exchange from clinoptilolite

Ammonium replacement: The thermodynamic parameters listed in Table 3 show that the rate controlling processes for replacement of ammonium cations by both sodium and potassium are very similar. This is also the case for the self-diffusion of these ions (see Table 4). The replacement of ammonium ions by calcium however does not correspond to that of the self-exchange of calcium, and the rate determing step may well be the movement of ammonium species through the clinoptilolite structure. Consideration of the similarity in ΔG^* values suggests that the same energy barrier controls magnesium ingress, with the larger change in entropy being a consequence of citing the hydrated magnesium in the channels of the clinoptilolite structure.

Sodium replacement: The high energy barrier seen in the ammonium exchange can be allocated to that encountered by the ammonium ion in the zeolite, i.e. larger than that previously assigned to sodium movement. Uptake of both potassium and calcium are governed by similar parameters which have some resemblance to those observed for the replacement of ammonium by the same cations. Koyama and Takeuchi [17] suggest two environments for sodium (and/or calcium), one in Channel A (M1) and one in Channel B (M2). Channels A and B are parallel to each other along the c-axis, and are both bound by 10 and 8 membered oxygen rings. It is conceivable that the thermodynamic parameters are close to those previously assigned to rate controlling steps governed by sodium or ammonium cation migration but vary because cation movements in Channels A and B meet different energy barriers. Koyama and Takeuchi state that cations in site M1 are co-ordinated to two framework oxygens and 5 water molecules, whereas in M2

Table 4
Comparisons of the parameters determined for the diffusion of cations in the HEU framework

Cation	T (K)	D/D_i ($m^2\ s^{-1}$)	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})	Reference
Self diffusion						
Na	303–345	10^{-12}	13	−36	20	[5]
K	303–345	10^{-11}	16	−17	18	[5]
Ca	303–345	$10^{-15/16}$	85	73	63	[5]
Na	323 and 343	10^{-12}	6	Nd[a]	Nd	[4]
Exchange diffusion						
Na/K/1/2Ca ↔ Cs	303	10^{-17}	Nd	Nd	Nd	[6]
Na/K/1/2Ca ↔ Sr	303	10^{-22}	Nd	Nd	Nd	[6]
Na ↔ NH_4	288	10^{-12}	Nd	Nd	Nd	[7]
1/2Ca ↔ Na	336−425	10^{-17}	79	21	Nd	[8]
Na ↔ K	329–348	10^{-13}	70	65	Nd	[8]
Na ↔ NH_4	298–333	10^{-11}	42	35	29	↑
K ↔ Na	298–333	10^{-11}	17	−51	29	This
Na ↔ 1/2Ca	298–333	10^{-13}	24	−92	48	work
1/2Ca ↔ Na/K	298–333	$\sim 10^{-13}$	Nd	Nd	Nd	↓

[a] Nd — not determined.

three framework oxygens and 5 water molecules compose the cation environments. That cations leaving site M2 should experience a slightly higher E_a to migration seems reasonable and can be suggested as the process observed here. The ΔS^* values can be explained in a similar manner to those seen in ammonium cation replacement.

Potassium replacement: The sodium exchange seems to be dependent on potassium ion migration, whereas that of ammonium depends on the in-going ion. The contrast between potassium replacement by ammonium to sodium replacement, reflected in the difference in $E_a$values, can be explained by the normal site occupancy of K in the HEU framework which is in (M3) sites in Channel C [17]. This channel runs along the *b*-axis and is composed of 8-membered rings.

The calcium exchange process seems to be controlled by cation movements in Channel B.

Magnesium replacement: The lack of exchange noted for magnesium comes from the inability of the charge on the clinoptilolite framework to strip waters of hydration from the magnesium ion. This is typical of zeolites with relatively high Si/Al ratios in their framework and explains their lack of preference for small hydrated cations in the presence of larger, less hydrated, cations [18]. Such magnesium that can enter the clinoptilolite will be expected to occupy a site unique to that cation in the framework — namely site M4 in Channel A [17]. If this is the magnesium cation site in the samples examined in this work then the high E_a, and ΔG^*, values for Na, K, and Ca exchange will come from the difficulty in removing magnesium from M4, which is a small side-pocket to the main channel. The high entropy changes for Mg ↔ Na and Mg ↔ K can be linked to the increase in disorder experienced by a magnesium ion moving from a highly specific zeolite site into solution. The negative entropy changes when calcium and ammonium are the in-going ions must be a consequence of ion hydration changes as the magnesium cations move into solution over-riding the solid state considerations.

4. Comparison to other work

Table 4 presents a comparison to other literature values with selected data from Table 3. The diffusion coefficients measured by following cation movements between solution and solid phases [4,5,7] are in good agreement. When cation movements are followed in the absence of an external chemical potential [6,8] progress through the zeolite structure is generally slower, which could be anticipated. The energy barrier to sodium self-diffusion estimated by Ames [4] is much lower than any quoted here and cannot be explained except to point out that it was estimated from measurements at only two temperatures. Other parameters cited in Table 4 come from measurements in the absence of a solution phase.

5. Summary

The choice of the CH method of interpretation was made because it had been used to gather the data for the cation self-diffusion [5] processes which have been the basis for the rate controlling steps suggested for the cation exchanges measured in this work. The BBK method gave D_i values comparable to those from the CH analyses. It was simple to use and avoided the difficulty in curve fitting encountered in the BR approach. Although the interpretation made here of the rate processes involved in the ion-exchanges studied is reasonably comprehensive it must be qualified in that a full interpretation of ion-exchange kinetics is not so simple. It requires the application of the Helffrich–Plesset (HP) equation which needs values to be known for the self-diffusion coefficients of both the ions involved as well as those for the movements of water conjoint with the exchange process [18]. Brooke and Rees [19] extensively studied Ca/Sr exchange kinetics in the zeolite chabazite using an HP approach but later work [20,21] from the same group showed that simple comparisons (such as those used in this work) can be justified without full knowledge of all the diffusion coefficients involved in the process. Full interpretation of ion-exchange kinetics will be difficult when radioisotope methods are not appropriate to measure self-diffusion coefficients, as in the case of ammonium ion movements studied here. In other instances, like magnesium, a suitable radioisotope is not easy to produce [22]. The acquisition of water self-diffusion data also has its problems particularly in those zeolites which have more open frameworks [23].

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