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Ion Exchange in Zeolites

Part 2.—Hydrolysis and Dissolution of Zeolites NaX and NaY

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Hydrolysis of zeolites NaX and NaY through H_3O^+ exchange has been studied in deionised water and $NaNO_3$ solutions. Hydrolysis was found to enhance the dissolution of silicon and aluminium from the zeolites. Equations based on the thermodynamic mass-action law were derived for the prediction of hydrolysis equilibria (Na^+ concentration and pH) over a range of different initial conditions. The agreement between predictions and observations was generally good in moderate Na^+ concentrations. At low Na^+ concentrations, however, predictions failed owing to the strong decrease of the zeolite selectivities for H_3O^+ ions with decreasing Na^+ concentration in solution. Predictions were also affected, to a small extent, by the silicate and carbonate ions present in the solutions. The carbonate ions resulted from CO_2 that had been preabsorbed by the zeolites from air. Dissolution of silicon and aluminium from the zeolites was very slow, so no equilibrium parameters for this process could be established.

Zeolites and other selective inorganic ion exchangers have a large potential for applications in aquatic pollution control and in industrial processes. The ability to calculate ion-exchange equilibria is a major step in the development of such applications. To assess empirically the performance of a large number of candidate materials for a given application over wide ranges of chemical conditions requires much experimental work. Theoretical calculations can be based on a small amount of reference measurements, or in many cases, on data already available in the literature. Calculation of equilibria is also essential for reliable process control of any ion-exchange plant.

Zeolites are hydrolysed by exchanging metal ions for hydronium ions in nearly neutral salt solutions[1,2] or deionised water.[2–4] Hydrolysis is likely to have a marked mass-action effect on concurrent metal-ion-exchange equilibria at low concentrations and effectively it can control the solution phase composition under these circumstances. By bringing hydroxide ions into solution, hydrolysis can also affect chemical equilibria, *e.g.* by dissolution of silicon and aluminium from the zeolite frameworks, or by precipitation of metal hydroxides, in the system. Thus, hydrolysis is often an unavoidable interference in other ion-exchange reactions, and in the prediction of zeolite and solution compositions at equilibrium, hydrolysis processes need to be taken into account. In addition, the study of zeolite hydrolysis is revelant to ascertain causes of decreases in selectivity observed in zeolites.[5]

So far, no studies relating to the calculation of hydrolysis equilibria and the effect of hydrolysis on concurrent ion-exchange reactions in zeolites (or in any other ion exchanger) have been reported. This paper deals with the calculation of hydrolysis equilibria; a necessary base for further studies (Parts 3 and 4 of this series) which consider the effect of hydrolysis on several trace-ion-exchange equilibria in zeolites.[6,7] In H_3O^+ exchange from water only minor conversion of the zeolites to the H_3O^+ form is likely to take place at the low and moderate solution volume to zeolite mass ratios that are normally used in ion-exchange experiments. This means that the prediction procedures[8,9] developed for the calculation of ion-exchange isotherms are not applicable to hydrolysis.

† Part 1: R. Harjula, A. Dyer, S. D. Pearson and R. P. Townsend, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1591.

Experimental

Materials

Zeolite NaX was supplied by Laporte Absorbents (Widnes, UK) and zeolite NaY by Unilever Research (Port Sunlight, UK). Their unit cell compositions were:[5] NaX: $Na_{82.6}[(AlO_2)_{87}(SiO_2)_{105}]\cdot 234\ H_2O$ and NaY: $Na_{54.2}[(AlO_2)_{56}(SiO_2)_{135}]\cdot 237\ H_2O$. The total exchange capacities were, calculated from the Al contents, 4.95 and 3.30 mequiv. g^{-1} for NaX and NaY, respectively, based on the hydrated mass of the zeolites. The stoichiometric discrepancies between the Na- and Al-contents are probably due to slight conversions of the zeolites to their H_3O^+ forms (5.1% for NaX and 3.2% for NaY). Reconversion to pure Na^+ forms was found not to be possible, as the zeolites exchanged H_3O^+ ions from water even in quite concentrated Na salt solutions. Analytical grade $NaNO_3$ was used in the solutions and deionised water was from a Millipore Q-system (pH 5.83–5.86, resistivity $<18\ M\Omega\ cm^{-1}$).

Experiments

Samples of the zeolites were equilibrated in deionised water, and in $NaNO_3$ solutions (concentration range 0.001–0.5 mol dm^{-3}), using different solution to zeolite ratios, $V:m = 10$–$500\ cm^3\ g^{-1}$. The equilibrations were carried out in polythene bottles shaken for three days. The zeolites were separated from the solution by centrifugation (15 min at 2000 G) and the pH of the solutions was measured instantly by a combined pH-electrode (Radiometer GK 2321). The solution was then removed for determination of Na, Si, Al and CO_2. Silicon was determined spectrophotometrically by the silicomolybdic acid method.[10] Na and Al were determined using an atomic absorption spectrophotometer (Perkin-Elmer Zeeman 5000). An air–acetylene flame and a graphite furnace were used for Na and Al, respectively. Total carbon content

was measured using a CO_2-sensing electrode (Orion 95-02). The uptake of H_3O^+ by the zeolites was calculated from the measurement of ion concentrations in solution (see Theory).

One sample of each zeolite was equilibrated successively six times in deionised water using a $V:m$ ratio of 100 cm^3 g^{-1}. 1 h contact times were used in each equilibration and, after centrifugation, solution pH and Na^+ concentrations measured.

The pH, and the solution concentrations of Na and Si were measured as a function of contact time (0.1–700 h) in deionised water using a $V:m$ ratio of 100 cm^3 g^{-1}. The experimental procedure was the same as in the equilibrium experiments above.

Theory

The binary ion-exchange reaction involving ions A^{z_A} and B^{z_B} may be written as

$$z_B A^{z_A} + z_A \bar{B}^{z_B} \leftrightarrows z_B \bar{A}^{z_A} + z_A B^{z_B} \quad \text{(I)}$$

where barred symbols refer to the ions in the solid phase. The corrected selectivity coefficient K_G (of Gaines and Thomas[11]) for the reaction is defined as:

$$K_G^{A/B} = \frac{\bar{E}_A^{z_B}[B]^{z_A}}{\bar{E}_B^{z_A}[A]^{z_B}}\Gamma \quad (1)$$

where $\bar{E}_A$ and $\bar{E}_B$ are the equivalent fractions of the ions in the zeolite and [A] and [B] are the concentrations of ions in the solution. The solution phase activity correction, Γ, which is the activity coefficient ratio of B and A in the binary mixture, can be calculated from the equation of Fletcher and Townsend.[12] When ion A is present in the system at much lower concentrations than B ([B] $\gg$ [A] and $\bar{E}_B \gg \bar{E}_A$), equivalent fractions are not convenient measures for the ion concentrations in the zeolite phase. Using absolute concentration units, eqn. (1) may be rewritten as:[5]

$$K_G = \frac{(z_A)^{z_B}\bar{m}_A^{z_B}\bar{M}^{z_A}[B]^{z_A}}{(z_B)^{z_A}\bar{m}_B^{z_A}\bar{M}^{z_B}[A]^{z_B}} \quad (2)$$

where $\bar{m}_A$ and $\bar{m}_B$ are the concentrations of the ions in the zeolite and $\bar{M}$ is the total equivalent content of ions A and B in the zeolite ($\bar{M} = z_A\bar{m}_A + z_B\bar{m}_B$).

Hydrolysis by Hydronium Ion Exchange

The net hydrolysis reaction of a zeolite in the B form can be written as

$$2z_B H_2O + \bar{B}^{z_B} \leftrightarrow z_B \overline{H_3O}^+ + B^{z_B} + z_B OH^- \quad \text{(II)}$$

which is obtained by combining the equations of hydronium exchange (III) and that of water dissociation (IV):

$$z_B H_3O^+ + \bar{B}^{z_B} \leftrightarrow z_B \overline{H_3O}^+ + B^{z_B} \quad \text{(III)}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{(IV)}$$

In the nearly neutral solutions discussed here, primarily H_3O^+ ions from water are exchanged and only minor conversion of the zeolite to its H_3O^+ form will occur, unless very large solution to zeolite ratios are used. Thus, in practice, the zeolite would remain in the pure B form in the exchange reaction. From this it follows that the content of H_3O^+ in the zeolite cannot be measured accurately in the solid phase. However, based on eqn. (II) and (IV), the concentration of hydronium ions in zeolite ($\bar{m}_H$) can be calculated from the changes of H_3O^+ concentration ($\Delta[H_3O^+]$), or that of B ($\Delta[B]$), in solution, *i.e.*

$$\bar{m}_H = (\Delta[H_3O^+])(V/m) \quad (3a)$$

$$= z_B(\Delta[B])(V/m) \quad (3b)$$

$\Delta[H_3O^+]$ can be calculated from

$$\Delta[H_3O^+] = [H_3O^+]_i - [H_3O^+] + [OH^-] - [OH]_i \quad (4)$$

where $[H_3O^+]_i$ and $[OH^-]_i$ are the initial hydronium and hydroxyl ion concentrations in the solutions and $[H_3O^+]$, $[OH^-]$ the corresponding equilibrium concentrations.

From eqn. (2) (A = H_3O^+), the corrected selectivity coefficient $K_G^{H/B}$ of the H_3O^+/B exchange is obtained as

$$K_G^{H/B} = \frac{\bar{m}_H^{z_B}[B]}{\bar{M}^{z_B}[H_3O^+]^{z_B}}\Gamma \quad (5)$$

since, as previously mentioned, the zeolite remains in the pure B form in the exchange reaction and thus $z_B\bar{m}_B \approx \bar{M}$. From the approximate constancy of $\bar{m}_B$ it also follows that $K_G^{H/Na}$ should be nearly constant and independent of the solution concentration of B.[8] Thus, once measured, at a given $[H_3O^+]$ and [B], $K_G^{H/Na}$ can be used to calculate $[H_3O^+]$ and Δ[B] over a range of initial conditions $[H_3O^+]_i$, $[B]_i$ and V/m.

Calculation of Hydrolysis Equilibria

Based on eqn. (3), the corrected selectivity coefficient [eqn. (5)] can be written as

$$K_H^{H/Na} = \frac{\{(\Delta[H_3O^+])(V/m)\}^{z_B}(\Delta[H_3O^+]/z_B + [B]_i)}{[H_3O^+]^{z_B}\bar{M}z_B}\Gamma \quad (6)$$

where $[B]_i$ is the initial concentration of B in solution (at equilibrium $[B] = [B]_i + \Delta[B]$). This selectivity coefficient may be determined using pH measurements alone. This might not, however, give the value defined in eqn. (5), as will be shown later. Subscript H is used therefore for this selectivity coefficient instead of G. For the calculation of solution pH at equilibrium, eqn. (6) can be solved for $[H_3O^+]$. This will lead, in the simplest case ($z_B = 1$), to a fourth-order polynomial equation. Δ[B] can be found from $z_B(\Delta[B] = \Delta[H_3O]^+)$ once $[H_3O^+]$ has been calculated from the polynomial equation. Under certain conditions the calculations can be markedly simplified and these conditions will be discussed for H_3O^+/Na^+ exchange in sodium salt solutions and pure water.

Sodium Salt Solutions at Moderate and High Concentrations

In moderate, or highly concentrated solutions of sodium salts (now B = Na^+, $\bar{M} \approx \bar{m}_{Na}$) eqn. (6) may be rewritten as

$$K_H^{H/Na} = \frac{\Delta[H_3O^+](V/m)[Na^+]_i}{[H_3O^+]\bar{m}_{Na}}\Gamma \quad (7)$$

since $[Na^+]_i \gg \Delta[Na^+]$. Now, from eqn. (7), a second-order polynomial equation is obtained for $[H_3O^+]$, *viz.*

$$\left(\frac{K_H^{H/Na}\bar{m}_{Na}}{[Na^+]_i(V/m)\Gamma} + 1\right)[H_3O^+]^2 + \left(\frac{k_w}{[H_3O^+]_i} - [H_3O^+]_i\right)[H_3O^+] - k_w = 0 \quad (8)$$

Pure Water

Calculation of pH. In pure water $[H_3O^+]_i \approx [OH^-]_i \approx 10^{-7}$ mol dm^{-3}. If the $[H_3O^+]$ of water changes by orders of magnitude during H_3O^+ exchange, then a good approx-

imation for eqn. (3*a*) is:

$$\bar{m}_H \approx [OH^-](V/m) = (k_w/[H_3O^+])(V/m) \quad (9)$$

since $\Delta[H_3O^+] \approx [OH^-]$, and at equilibrium $[Na^+] = \Delta[Na^+] \approx k_w/[H_3O^+]$, since $[Na^+]_i = 0$. The corrected selectivity coefficient thus is

$$K_H^{H/Na} = \frac{(k_w/[H_3O^+])^2(V/m)}{[H_3O^+]\bar{m}_{Na}}\Gamma \quad (10)$$

Solving eqn. (10) for $[H_3O^+]$, in logarithmic form, gives

$$-\log[H_3O^+] = pH = -\tfrac{1}{3}\log\left(\frac{k_W^2\Gamma}{K_G^{H/Na}\bar{m}_{Na}}\right) - \tfrac{1}{3}\log(V/m) \quad (11)$$

Thus, pH changes are theoretically linear with a slope of $-1/3$, as the first term in the right side of eqn. (11) is a constant ($\Gamma \approx 1$ in dilute solutions).

Calculation of Na^+ Concentration. Under the conditions discussed above

$$[H_3O^+] \approx k_w/[Na^+] \quad (12)$$

Using eqn. (12) and eqn. (3*b*), the corrected selectivity coefficient can now be written as

$$K_{Na}^{H/Na} = \frac{[Na^+]^3(V/m)}{k_w\bar{m}_{Na}}\Gamma \quad (13)$$

since $\Delta[Na^+] = [Na^+]$. Subscript Na denotes that the value of this selectivity coefficient, which may be determined from $[Na]^+$ measurements alone, may not be the same as the one obtained from eqn. (5). Solving eqn. (13) for $[Na^+]$ obtains, in logarithmic form,

$$\log[Na^+] = \tfrac{1}{3}\log[(K_{Na}^{H/Na}k_w\bar{m}_{Na})/\Gamma] - \tfrac{1}{3}\log(V/m) \quad (14)$$

Like pH, $\log[Na^+]$ changes are theoretically linear in dilute solutions.

Effects of Accompanying Dissolution Processes on Hydrolysis

(*a*) The NaOH solutions produced by hydrolysis have a great tendency to take up CO_2 from air. So if the Na^+/H_3O^+ exchange reaction is carried out in contact with air, considerable amounts of CO_2 will be dissolved in the solution. The resulting carbonic acid will then consume the hydroxyl ions, produced by hydrolysis, yielding HCO_3^- and CO_3^{2-} in solution. This neutralisation reaction will enhance the hydrolysis reaction [eqn. (II)], and so bring more Na^+ ions into solution.

(*b*) Dissolution of the zeolite framework brings silicic acid into the solution, *via*

$$Na_y[(SiO_2)_x(AlO_2)_y] + (2x + 2y)H_2O \leftrightarrow y Na^+ + x Si(OH)_4 + y Al(OH)_4^- \quad (V)$$

Like carbonic acid, silicic acid will consume OH^- ions and create silicate ions in solution. Such a conversion will enhance the dissolution of Si from the framework. Dissolution of Al from the framework will also bring Na^+ into solution, in addition to the Na^+ which has been displaced by H_3O^+.

(*c*) Taking into account all these dissolution processes, the electroneutrality condition in the solution at equilibrium will be

$$[H_3O^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Al(OH)_4^-] + [SiO(OH)_3^-] + 2[SiO_2(OH)_2^{2-}] + [L^-] \quad (15)$$

where L^- is the anion of salt NaL initially present in solution. It can be presumed that Al is present as $Al(OH)_4^-$ ions in alkaline solution. Assuming congruent dissolution, $[Na^+]_d = [Al(OH)_4^-]$, and since $[Na^+]_i = [L^-]$, the change in Na^+ concentration of solution attributable to hydrolysis ($\Delta[Na^+]_h$) becomes

$$\Delta[Na^+]_h = [Na^+] - [Na^+]_i - [Al(OH)_4^-] \quad (16a)$$

$$= [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [SiO(OH)_3^-] + 2[SiO_2(OH)_2^{2-}] \quad (16b)$$

In this case, either eqn. (16*a*) or (16*b*) must be used in eqn. (3) for the calculation of $\bar{M}_H$.

Relationship between $K_G^{H/Na}$, $K_H^{H/Na}$ and $K_{Na}^{H/Na}$

In the derivation of $K_H^{H/Na}$ and $K_{Na}^{H/Na}$ [eqn. (6), (7) and (13)] the contribution of silicate and carbonate ions to the overall hydrolysis equilibria was ignored. When carbonates and silicates form a considerable proportion of the total alkalinity of the solution, these selectivity coefficients are thus apparent selectivity coefficients. It can be shown that these apparent coefficients are related to the 'true' selectivity coefficient $K_G^{H/Na}$ by the equations

$$K_H^{H/Na} = K_G^{H/Na}\left(\frac{[OH^-]}{\Delta[Na^+]}\right)^2 \quad (17)$$

$$K_{Na}^{H/Na} = K_G^{H/Na}\left(\frac{\Delta[Na^+]}{[OH^-]}\right) \quad (18)$$

If silicate and carbonate ions are absent from solution, then $\Delta[Na^+]/[OH^-] = 1$ and $K_G^{H/Na} = K_{Na}^{H/Na} = K_H^{H/Na}$. When carbonates and silicates are present in solution however, then $\Delta[Na^+]/[OH^-] > 1$ and $K_{Na}^{H/Na} > K_G^{H/Na} > K_H^{H/Na}$.

Eqn. (17) and (18) indicate that $K_H^{H/Na}$ and $K_{Na}^{H/Na}$ can be used for the prediction of equilibrium pH and Na^+ concentrations with eqn. (8), (11) and (14), provided that $\Delta[Na^+]/[OH^-]$ remains constant, or nearly constant, over the range of conditions in which the predictions are to be made. In this case, rigorous calculations which would have to include the dissociation equilibria of carbonic and silicic acids, can be avoided.

Results and Discussion

Hydrolysis and Dissolution in Water

As expected from eqn. (11) and (14), the concentrations of OH^- and Na^+ in water equilibrated with the zeolites decreased with increasing solution to zeolite ratio (V/m) (Fig. 1). The total concentrations of Si($[Si]_T$) and Al($[Al]_T$) dissolved from the zeolite frameworks decreased with decreasing $[OH^-]$, as Si and Al were more soluble in alkaline solutions. Thus, hydrolysis affected the solubility of the zeolites. The $[Al]_T$ in solution was very close to, or at, the solubility limit of gibbsite when $V/m < 100\ cm^3\ g^{-1}$ for both NaX and NaY (Fig. 1). The measured $[Si]_T$ in solution was far below the solubility limit of amorphous silica. Silicon might, however, have precipitated as an aluminosilicate in lower concentrations and precipitation of kaolinite was also a possibility. Only in NaY at low V/m was $[Si]_T$ at the precipitation limit for kaolinite (Fig. 1).

The losses of Si and Al from the zeolite frameworks were *ca.* 0.1–0.2% for NaX and in the range 0.02–0.001% for NaY, when calculated from the measured $[Si]_T$ and $[Al]_T$ in solution. Silicon was found to be preferentially dissolved from the zeolites. For NaX (solid-phase silicon to aluminium ratio, Si : Al = 1.21) the Si : Al in solution ranged between 1.25 and 3.88, and for NaY (solid Si : Al = 2.43) it was between 15 and

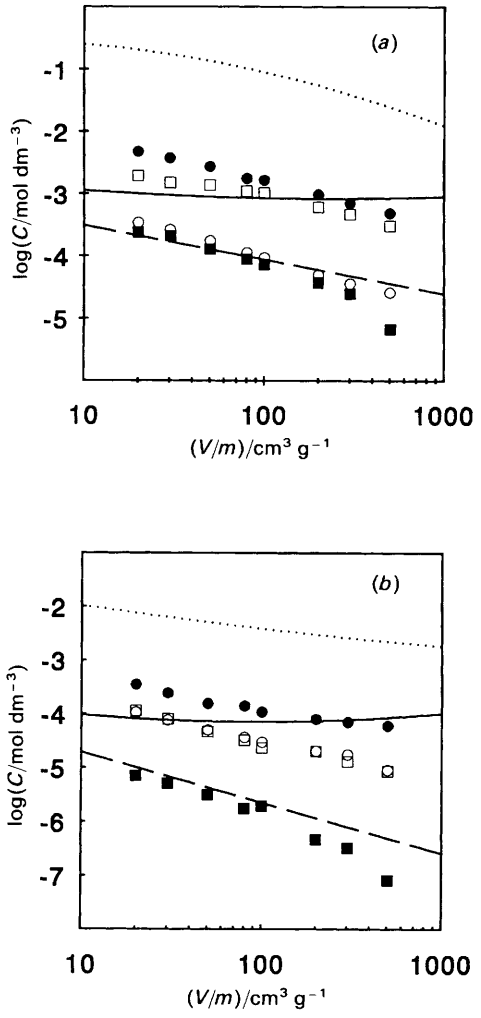

Fig. 1 Concentration of OH^- (□), Na^+ (●), total Si (○) and total Al (■) as a function of V/m for (*a*) NaX and (*b*) NaY in contact with deionised water for 3 days. Dotted and solid lines are the calculated limiting concentrations of total Si for the precipitation of amorphous silica and kaolinite, respectively. The broken line is the calculated limiting concentration of total Al for the precipitation of gibbsite. The data for the solubility calculations was taken from ref. 19.

122. This is understandable, as the solubility of Si was greater than that of Al in alkaline media. It is well known that acids dissolve Al more readily than Si from zeolite frameworks,[13] but little is known of the solubility of zeolites in water, or in nearly neutral salt solutions. Cook *et al.*[14] also found that Si dissolved preferentially from zeolite NaA into water at pH 7. The concentrations of Si they observed in solution ($V/m = 667$ cm^3 g^{-1}) were, however, one order of magnitude higher than those measured for NaX in this work ($V/m = 500$ cm^3 g^{-1}). Note that several clay minerals have been shown to be slightly soluble in water.[15]

The results described above were obtained after three days contact time. Several studies[3,16,17] have shown that the Na^+/H_3O^+ exchange reaction in neutral solutions is very rapid, equilibrium being attained in a few minutes. Kinetic experiments (0.1–700 h) during this study confirmed this, but, after *ca.* 10 h contact time, the $[OH^-]$ in solution began to decrease with concurrent increase in $[Na^+]$ and $[Si]_T$. Obviously this was caused by the increasing dissolution of the zeolites: $[Na^+]$ increasing owing to the loss of aluminium from the framework and pH decreased as dissolved silicic acid consumed OH^-. In addition, consumption of OH^- would have enhanced the hydrolysis reaction (IV), thus bringing additional Na^+ into the solution. The dissolution equilibrium of Si was not attained even after 700 h.

Electroneutrality in Solutions

Inspection of the results in Fig. 1 shows a significant anion deficiency in the solutions. The ratios of $[Na^+]$ to $[OH^-]$ for NaX and NaY were 2.50–1.48 and 13.9–3.54, respectively, in the V/m range of 20–500 cm^3 g^{-1}. In the cases where the total CO_2 in solution was measurable (detection limit 1×10^{-4} mol dm^{-3}), it was found that this deficiency consisted of carbonate, silicate and aluminate ions (Table 1). When these anions were included, the equivalent ratio of cations to anions in the electroneutrality condition of eqn. (15) was 0.98–1.20.

No detectable amounts of CO_2, or any changes in pH, were observed in the 0.001 mol dm^{-3} NaOH solutions shaken in plastic bottles in parallel with the actual experiments. It was rather surprising, therefore, that considerable amounts of CO_2 were detected in solutions after contact with NaX. The concentrations of CO_2 calculated for the zeolite phase were constant at $(1.80 \pm 0.09) \times 10^{-2}$ mol kg^{-1} over a range of experimental conditions. This indicated that the CO_2 originated from the zeolite. Obviously it had been preadsorbed from air and this was supported by the results of successive equilibrations of the zeolites in water. When the wet zeolites were allowed to be in contact with air for long periods prior to equilibrations, more Na^+ ions were released into the solution, and the $[Na^+]/[OH^-]$ ratios were higher, than in equilibrations with no pre-contact with air. This was obviously caused by carbonic acid, which decreased $[OH^-]$ and thus increased $[Na^+]$ by enhancing the hydrolysis reaction [eqn. (II)].

Selectivity of Hydronium Ion Exchange

The basic requirement for the predictions of equilibrium pH and Na^+ concentrations was the constancy of the selectivity coefficients. In order to see if this was valid, $K_H^{H/Na}$ [eqn. (6) or (7)], $K_{Na}^{H/Na}$ [eqn. (13)] and $K_G^{H/Na}$ [eqn. (5) with eqn. (3*b*) or (16*b*)] were determined over a wide range of equilibrium Na^+ concentrations for NaX and NaY. For NaY, the determination of $K_G^{H/Na}$ in most $NaNO_3$ solutions was not possible as carbonate concentrations (or $\Delta[Na^+]$) were not measurable.

Table 1 Electroneutrality in solutions[a]

sample	$[Na^+]$	$[OH^-]$	$[Al(OH)_4^-]$	$[SiO(OH)_3^-]$	$[SiO_2(OH)_2^{2-}]$	$[HCO_3^-]$	$[CO_3^{2-}]$	R_E
NaX-1	47.2	19.1	2.37	2.09	1.25	0.79	8.51	1.08
NaX-2	37.0	14.8	2.09	1.72	0.81	0.61	5.05	1.20
NaX-3	27.0	13.5	1.28	1.18	0.50	0.41	3.10	1.15
NaX-4	17.4	11.0	0.88	0.79	0.28	0.34	2.11	0.98
NaX-5	16.4	10.2	0.71	0.67	0.22	0.28	1.62	1.06
NaX-6	9.6	6.0	0.37	0.37	0.07	0.26	0.89	1.07

[a] Concentrations in 10^4 mol dm^{-3}. $R_E = [Na^+]/\{[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [SiO(OH)_3^-] + 2[SiO_2(OH)_2^{2-}] + [Al(OH)_3^-]\}$.

Mean molal activity coefficients of $NaNO_3$ and HNO_3, taken from the literature,[18] were used in the calculation of Γ.

It appeared that the assumption of constancy for $K_H^{H/Na}$ and $K_G^{H/Na}$ was reasonably valid only in moderate Na^+ concentrations (Fig. 2). In dilute solutions all the selectivity coefficients decreased with decreasing Na^+ concentration, *i.e.* with the effective total cation concentration ($[Na^+] \gg [H_3O^+]$). In order to simplify the predictions, the initial concentrations of H_3O^+ ions in the zeolites were not taken into account when deriving the equations of the selectivity coefficients. In addition, changes in zeolite composition were assumed to be negligible. The initial contents of H_3O^+ ions were 5.1% for NaX and 3.2% for NaY. In the equilibrations corresponding to the data shown in Fig. 2, the conversion of NaX to its H_3O^+ form was 5.7% in 0.5 equiv. dm^{-3} solution and increased steadily with decreasing $[Na^+]$, being 10.2% at the equilibrations with lowest $[Na^+]$. Thus the change in Na^+ content of NaX was from 94.9% to 89.8%. In NaY, the corresponding change in Na^+ content was from 96.8% to 95.6%. It was obvious that the assumption of constancy for the Na^+ contents brought very little error to the calculations of the selectivity coefficients.

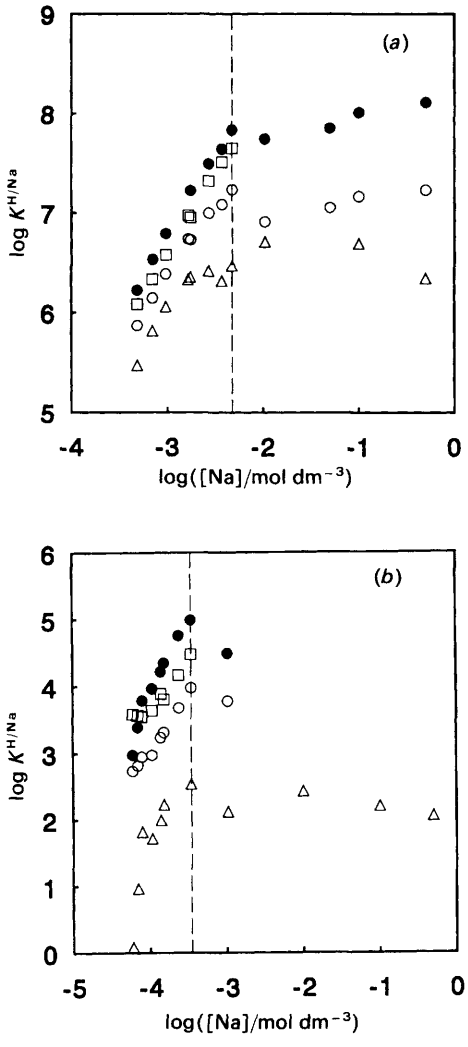

Fig. 2 Selectivity coefficients $K_G^{H/Na}$ (●) and (○), $K_H^{H/Na}$ (△) and $K_{Na}^{H/Na}$ (□) as a function of equilibrium Na^+ concentration for (*a*) NaX and (*b*) NaY. The concentration of H_3O^+ initially present in the zeolites was either ignored (open symbols) or taken into account (filled symbols) in the determinations. Datum points to the left from the broken vertical line were measured in deionised water and the equilibrium Na^+ concentration was varied adjusting V/m between 20 and 500 $cm^3\ g^{-1}$. Points to the right from the broken line were measured by adjusting the concentration of $NaNO_3$ in the solutions at constant $V/m = 100\ cm^3\ g^{-1}$.

Ignoring the initial concentrations of H_3O^+ ions in the zeolite may however, have yielded significant errors in values for $K_H^{H/Na}$, $K_{Na}^{H/Na}$ and $K_G^{H/Na}$. Because of this, the selectivity coefficients were recalculated, taking into account the initial H_3O^+ concentrations, as well as the changes of Na^+ contents in the zeolites. The recalculation had a marked effect on the magnitudes of $K_H^{H/Na}$, $K_{Na}^{H/Na}$ and $K_G^{H/Na}$. However, the general behaviour of the selectivity coefficients observed with the simplified calculations was not altered: the selectivity coefficients were effectively constant in moderate Na^+ concentrations, but decreased strongly with decreasing $[Na^+]$ in low concentrations. The recalculated values for $K_G^{H/Na}$ are shown in Fig. 2.

The changes in the Na^+ contents of the zeolites were small, *ca.* 5% for NaX and 1% for NaY, so it was unlikely that the large variations in observed selectivities arose from compositional changes in the zeolites. This conclusion was supported by the results of successive equilibrations of the zeolites in water: the corrected selectivity coefficients $K_G^{H/Na}$ for NaX and NaY did not decrease steadily with increasing conversion to the H_3O^+-form. Instead, they showed direct proportionality to the solution Na^+ concentration.

These observations were similar to those of earlier studies, in which strong decreases of selectivities, at constant zeolite compositions, were found for NH_4^+ and Mg^{2+} exchanges in NaY[1] and for Ca^{2+} exchanges in NaX and NaY.[5] In the study of Ca^{2+} exchange,[5] it was concluded that interference of concurrent H_3O^+ exchange probably was not responsible for the phenomenon, at least not *via* a direct mass-action effect. The results of this study strengthen this view, as the selectivity decrease was observed in H_3O^+ exchange. Theoretically, the observations of decreasing selectivity of zeolites for metal ions could be explained by the association of the ions with small amounts of anionic or colloidal species in solution, as the analytical methods used did not necessarily yield the concentrations of free metal ions.[5] This explanation does not apply for the H_3O^+/Na^+ exchange, however, as the measurement of solution pH in this study yielded the concentration of free H_3O^+ ions.

Calculation of pH and $[Na^+]$ at Equilibrium

Selectivity data in Fig. 2 implied that calculations of hydrolysis equilibria, based on the assumption of constant selectivity coefficients, would be possible in moderate Na^+ concentrations but were bound to fail in dilute solutions. However, a number of calculations were carried out as it was of interest to determine the magnitude of error involved and hence whether such calculations can be used for the estimation of pH and Na^+ concentration in dilute solutions. Here thermodynamic mass-action equations have been derived for the first time for the calculation of hydrolysis equilibria. To assess their validity it was necessary to compare the calculation with observation over a wide range of conditions.

The agreement between the observed and calculated pH of deionised water and $NaNO_3$ solutions equilibrated with the zeolites generally was very good (Fig. 3). Closer inspection of the gradients, however, showed some significant deviations, especially for equilibrations in deionised water at high solution to zeolite ratios, *i.e.* in solutions where the equilibrium Na^+ concentration was very low. For NaY, the calculated Na^+ concentrations in deionised water equilibrated with the zeolites corresponds well to the observed ones, but the predicted gradient of $[Na^+]$ was slightly smaller than that observed (Fig. 4). For NaX, the deviation was more marked. The contribution of Na^+ to the total Na^+ concentrations

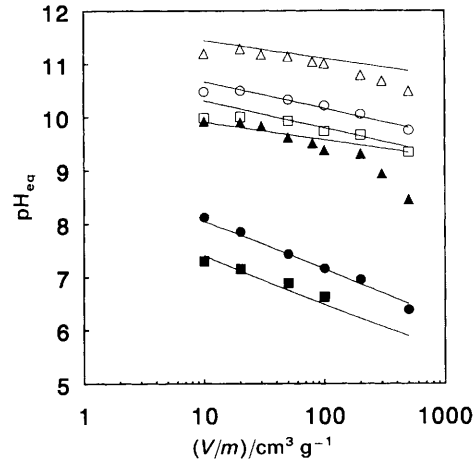

Fig. 3 Equilibrium pH (pH_{eq}) of deionised water (△), 0.1 mol dm^{-3} (○) and 0.5 mol dm^{-3} (□) $NaNO_3$ solutions equilibrated with zeolite NaX (open symbols) and NaY (filled symbols) as a function of V/m. Solid lines are the calculated values [eqn. (12) for water and eqn. (17) for $NaNO_3$]. For the calculations, $K_H^{H/Na}$ determined from eqn. (7) in 0.1 equiv. dm^{-3} $NaNO_3$ at $V/m = 50\ cm^3\ g^{-1}$ was used (log $K_H^{H/Na} = 6.63$ for NaX and 2.33 for NaY). Initial pH of water 5.85.

arising from the dissolution of Al from zeolite frameworks was in the range 1–5%, and was ignored in the calculations.

As these results show, simplified calculations based on the apparent selectivity coefficients of the H_3O^+/Na^+ exchange can be used for the calculation of hydrolysis equilibria over a wide range of conditions. However, if selectivity data measured in higher Na^+ concentrations of solution were used for predictions in very dilute solutions, the accuracy deteriorated with increasing dilution.

More rigorous calculations taking into account the effect of silicate and carbonate ions on hydrolysis equilibria brought only minor improvements to the accuracy of the predictions in dilute solutions. The deviations between calculated and observed values arose mainly from the change of the corrected selectivity coefficient $K_G^{H/Na}$, which was not affected by the presence of silicate or carbonate ions in solution.

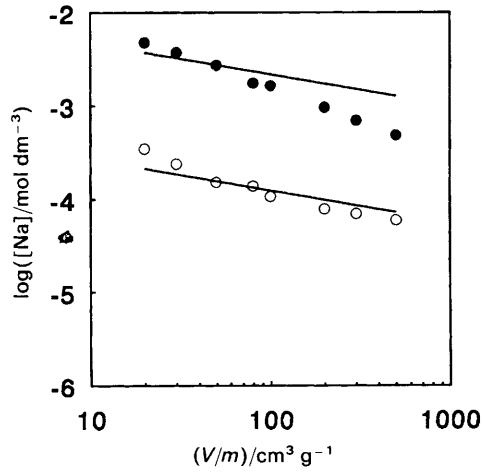

Fig. 4 Concentration of Na^+ in deionised water equilibrated with NaX (●) and NaY (○) as a function of V/m. Solid lines are calculated from eqn. (14). For the calculations, $K_{Na}^{H/Na}$ determined from eqn. (13) in deionised water at $V/m = 50\ cm^3\ g^{-1}$ was used (log $K_{Na}^{H/Na} = 7.30$ for NaX and 3.85 for NaY).

Conclusions

Predictions of hydrolysis equilibria in NaX and NaY were adequate except in dilute solutions. Here the predictions were less satisfactory owing to the strong decrease in selectivity of the zeolite for H_3O^+ ions at almost constant solid-phase composition. The partial failure of the calculations suggested that some as yet unknown phenomenon (*e.g.* chemical reaction), in addition to hydrolysis and dissolution of silicic and carbonic acids, affects the pH and Na^+ concentration in solutions. The contribution of this process becomes marked in dilute solutions only. Similar decreases in selectivity have been observed for exchanges of several divalent cations into Na zeolites, and a common factor in these exchanges was concurrent hydrolysis. The data obtained in this study demonstrated that hydrolysis was not the cause for the selectivity decreases in these univalent–divalent cation-exchange processes.

Hydrolysis of the zeolites brought considerable amounts of Na^+ ions into the solutions. Ion-exchange equilibria at dilute ionic concentrations thus will be effectively controlled by hydrolysis. For many important applications (*e.g.* separation of harmful trace ions from industrial effluents), it is therefore essential to study, and to understand, the effects of hydrolysis on ion-exchange equilibria at low ionic concentrations. Such studies would yield useful information about the selectivity decrease phenomenon and are the subject of further papers in this series.

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