DIFFUSION COEFFICIENTS OF TRANSITION METAL ION COMPLEXES IN ZEOLITES NaA, CaA, NaX*

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Ion-exchange rate curves of aqueous and ammonia transition metal ion complexes are presented together with ion-exchange isotherms of the corresponding complexes using molecular sieves as ion-exchangers. The data are treated mathematically according to Danes and Wolf procedure and the diffusion coefficients for the specific transition metal ion complexes are obtained. Finally, the variation of diffusion coefficients with the extent of ion exchange is followed.

It is well known that there are two diffusion mechanisms which may predominate during an ion exchange process[1,2]. Other factors like adsorption rates at the phase interface or the exchange rate at sites within the exchanger may, also, affect or control the kinetics. However, it is generally accepted that diffusion is the most important factor in the kinetics.

The two diffusion mechanisms are film and particle diffusion. Film diffusion involves rate control by transport through the boundary layer close to the exchange surface, while particle diffusion is concerned with the rate at which ions diffuse within the exchange matrix itself. It is the nature and properties of the intracrystalline channels and cages within the zeolite that are most important for particle diffusion control. When the ion-exchange experiment proceeds in well stirred solutions the particle controlled regime predominates.

The theoretical treatment of the rates of diffusion is based on Fick's first and second law. Fick's first law relates the flux, J_A, of species A to the concentration gradient of that species in the same direction,

$$J_A = -D \operatorname{grad} C_A . \qquad (1)$$

Fick's second law is concerned with the rate of accumulation of species within a chosen volume. The rate of accumulation is determined by equation

$$\mathrm{d}C_A/\mathrm{d}t = -\operatorname{div} J_A . \qquad (2)$$

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The diffusion coefficient D appears in both these equations. In ion exchange between two different ions there is a counter-diffusion process. The counter-diffusion coefficient is not constant even under isothermal conditions but varies in a complicated way as a function of the composition of the zeolite. This problem makes difficult the construction of an adequate model for the rates of ion exchange.

The knowledge of diffusion coefficients makes possible the calculation of the ion-exchange rate for each metal ion and therefore gives useful information for practical uses of molecular sieves. One example of such practical use is the application of zeolite A as a water softening detergent builder where a detailed knowledge of the kinetics of the ion exchange is required.

The value of the diffusion coefficient is a measure of the convenience that an entity is experiencing in travelling inside a channel which is the result of its relative size to the channel opening and its interaction with the walls of the channel. The sieving effect of ions travelling through the zeolitic structure is measured by their diffusion coefficients. On the other hand, the diffusion coefficients depend mainly on the temperature, the zeolitic structure, the size of the metal ion complex and for complexes of the same size on the interactions with the walls of the zeolitic channels.

Some research groups have been inolved in measuring the aqueous metal ion complexes self-diffusion coefficients[3-8] and interdiffusion coefficients[9-13] within the various types of zeolites. However, the ammonia metal complexes have only been studied in equilibrium state in natural zeolites[14-16].

In this work we present ion-exchange rate curves of NaX for several transition metal ion aqueous and ammonia complexes diffusing in NaX, as well as their corresponding ion-exchange equilibrium isotherms. The experimental data are treated according to Danes and Wolf[18] mathematical procedure and the average diffusion coefficient is obtained. Furthermore, we present similar diffusion experiments of cupric aqueous and ammonia complexes in NaA, CaA, and NaX molecular sieves and we obtain the diffusion coefficients. Finally, the obtained diffusion coefficients are plotted versus the extent of ion exchange.

THEORETICAL

Mathematical Formulation in Dimensionless Variables

The Paterson formulation of heating a solid sphere in a well stirred fluid is followed for the ion-exchange process, which is[17]

$$\begin{array}{lll} \partial u/\partial \tau = \partial^2 u/\partial r^2 & r < 1 & \tau > 0 \\ u = u^0 & r < 1 & \tau = 0 \\ u = u' & r = 1 & \tau = 0 \\ u' = 1 & & \tau = 0 \end{array}$$

$$\begin{array}{lll} u = u^0 & r = 0 & \text{for all } \tau \\ 3w(\partial u/\partial r - u/r) + \mathrm{d}u'/\mathrm{d}\tau = 0 & r = 1 & \tau > 0 \end{array} \qquad (3)$$

where $r = R/a$ (R is the distance from the center of the solid sphere, a radius of the solid sphere); $u = R[\mathrm{M}]_z/a[\mathrm{M}]_s^0$ (M is the incoming metal ion), $[\mathrm{M}]_z = \{[(\text{amount of substance of ionic species})/z]/\text{volume of zeolitic phase}\}$, ($z$ is the charge on the cation, $[\mathrm{M}]_s^0$ initial concentration of the incoming metal ion in solution); $u' = [\mathrm{M}]_s/[\mathrm{M}]_s^0$, $[\mathrm{M}]_s = \{[(\text{amount of substance of ionic species})/z]/\text{volume of the liquid phase}\}$ at any time, t, from the start of ion-exchange process; $w = (M_z/M_s) \, . \, (\mathrm{d}[\mathrm{M}]_z/\mathrm{d}[\mathrm{M}]_s)$ ((M_z/M_s) is the ratio of equivalents of total cations in zeolite to those in solution); $\tau = Dt/a^2$ (D diffusion coefficient; t time).

If $p \equiv -s^2$ is the Heaviside operator $\partial/\partial t$ the Eqs (*3*) transform into the equations

$$\begin{array}{l} \partial^2 u/\partial r^2 = -s^2 u \\ u = 0 \,, \quad r = 0 \\ 3w(\partial u/\partial r - u/r) - s^2(u - 1) = 0 \,, \quad r = 1 \end{array} \qquad (4)$$

Solution of the General Differential Equation

The general solution of the differential equation (*4*) is given by the formula:

$$u = \frac{s^2 \sin rs}{3w(\sin s - s \cos s) + s^2 \sin s} \equiv f(s)/F(s) \,. \qquad (5)$$

The poles s_η are roots of

$$s \operatorname{cotg} s = 1 + s^2/3w \,. \qquad (6)$$

Expansion of the Solution into Power Series

There are different methodologies for expanding the solution into series and therefore it is possible to derive different power series equations for the solution u. The Laplace transformation of solution (*5*) is given by

$$u = \mathop{\mathscr{L}}_{s \to 0} \frac{f(s)}{F(s)} + 2 \sum_{n=1}^{\alpha} \frac{f(s_\eta)}{s_\eta F'(s_\eta)} \exp\left(-s_\eta^2 \tau\right) ,$$

$$u = \frac{r}{w + 1} + 2 \sum_{1}^{\alpha} \frac{\sin(rs_\eta)}{\sin(s_\eta)} \cdot \frac{\exp\left(-s_\eta^2 \tau\right)}{3(w + 1) + S_\eta^2/3w} \qquad (7a)$$

and

$$u' = \frac{1}{w + 1} + 2 \sum_{1}^{\alpha} \frac{\exp\left(-s_\eta^2 \tau\right)}{3(w + 1) + s_\eta^2 3w} \,. \qquad (7b)$$

The series always converge but the velocity varies markedly with τ; if $\tau \geqq 1$, the entire series is negligible and $u = r/(w + 1)$ and $u' = 1/(w + 1)$, irrespective of w; but when $\tau < 1$, the speed of convergence falls off very quickly.

An alternative solution can be obtained if the s^2 is substituted by $-q^2$ and expand in powers of $\exp(-q)$. This procedure gives the following equations:

$$u = \frac{q^2}{q^2 + 3wq - 3w} \{\exp[-(1 - r) q] - \exp[-(1 + r) q] + + Q \exp[-(3 - r) q] - Q \exp[-(3 + r) q] + \ldots\} \tag{8a}$$

$$u' = \frac{q^2}{q^2 + 3wq - 3w} \{1 + (Q - 1) \exp(-2q) + Q(Q - 1) \exp(-4q) + \ldots\}, \tag{8b}$$

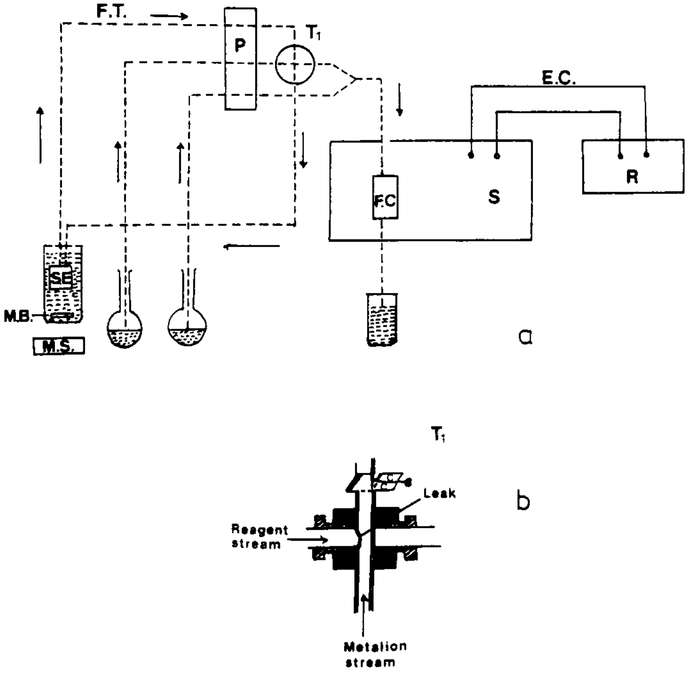

FIG. 1

Apparatus for monitoring ion exchange rate curves (a) and details of construction of the leak (b). M.S. magnetic stirrer; M.B. magnetic bar; S.E. sieving element; F.T. flow tubes; P peristaltic pump; T_1 cross-piece connector; F.C. flow cell; S spectrophotometer; E.C. electrical conducts; R recorder; and C clip where

$$Q \equiv (q^2 - 3wq - 3w)/(q^2 + 3wq - 3w).$$

The exp $(-2q)$ transforms into $1 - \mathrm{erf}(1/\sqrt{\tau})$ and the bracketed terms beyond the first two in (*8a*) and the first in (*8b*) will be negligible if $1 - \mathrm{erf}(1/\sqrt{\tau})$ is small, say $< 0{\cdot}1\%$ for $\tau \leqq 0{\cdot}1$. The Eqs (*8*) are then suitable for precise calculations the Eqs (*7*) are not in this range of τ-values.

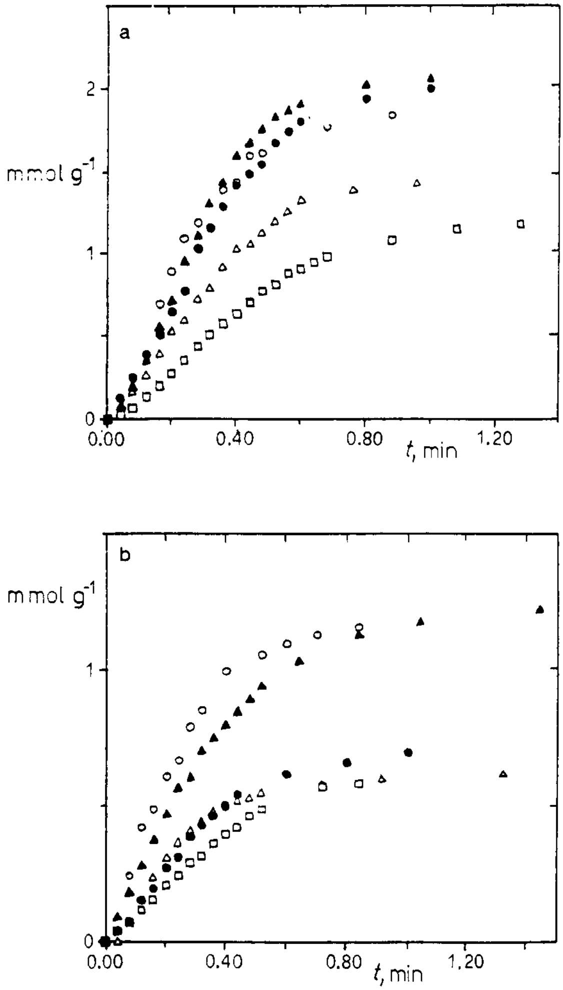

FIG. 2

Ion-exchange rate curves of aqueous (a) and ammonia (b) complexes of Cu (○); Co (△); Ni (□); Zn (●); and Cd (▲) metal ions diffusing in NaX. Uptake vs time

Relationship between the Fraction F *and* τ

As F we denote the fraction of the loss from the solution of the incoming ion at time t and the loss at time when equilibrium has been reached. Since $u' = u$ at $r = 1$ or all τ-values the F-value is defined as:

$$F = (1 - u'_\tau)/(1 - u')_{(\tau \to \alpha)}) . \tag{9}$$

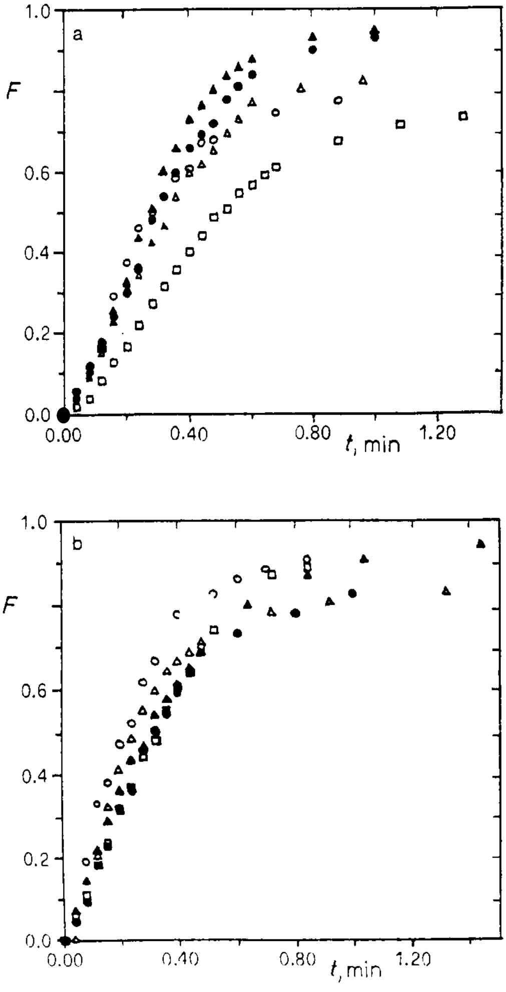

FIG. 3

Ion-exchange curves of fractional attainment of equilibrium with time of aqueous (a) and ammonia (b) complexes of Cu (○); Co (△); Ni (□); Zn (●); and Cd (▲) metal ions diffusing in NaX

The relationships of F vs τ which are derived from the different power-series solutions of u after elimination of terms of the series that are negligible compared with the rest are the following according to Danes and Wolf[18].

a) $$F = 1 - \sum_{j=1}^{n} \frac{\exp\left[-(\pi j + v_j)^2 \tau\right]}{1 \cdot 5w + \left[(\pi j + v_j)^2/6(1 + w)\right]} \quad \text{for} \quad n = 1, 2 \quad (An) \qquad (10)$$

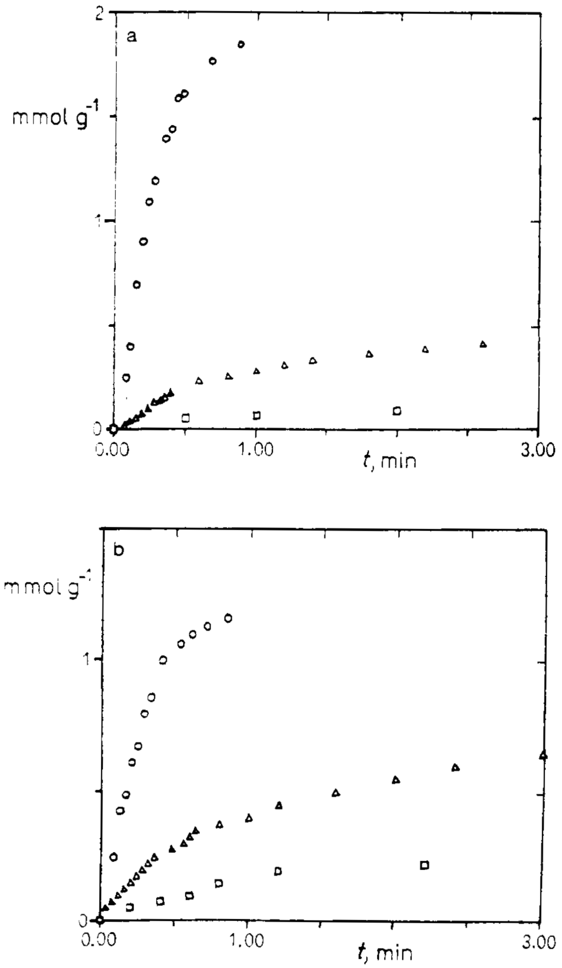

FIG. 4

Ion-exchange rate curves of Cu(II) aqueous (a) and ammonia (b) complexes diffusing in NaX (○), NaA (△), CaA (□). Uptake vs time where v_j is calculated from

$$3w = \frac{(\pi j + v_j)^2}{1 + (\pi j + v_j)\operatorname{cotg} v_j}$$

for $\tau \geqq 0{\cdot}1$ and w values $> 0{\cdot}1$.

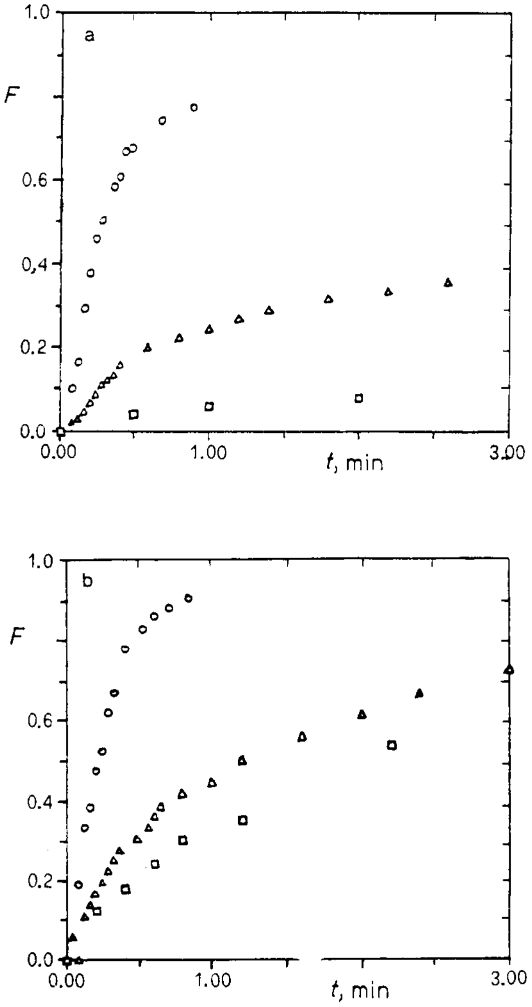

FIG. 5

Ion-exchange curves of fractional attainment of equilibrium F with time of Cu(II) aqueous (a) and ammonia (b) complexes diffusing in NaX (○), NaA (△), CaA (□)

b) $$F = \frac{1+w}{w}\left[1 - \frac{\alpha\varphi(\alpha\sqrt{\tau}) - \beta\varphi(\beta\sqrt{\tau})}{\alpha - \beta}\right] \qquad (B) \qquad (11)$$

where α, β are the roots of $(z^2/3w) + z - 1 = 0$ and $\varphi(\eta) = \exp(\eta^2)(1 - \operatorname{erf}(\eta))$ and $\operatorname{erf}(\eta) = (2/\sqrt{\pi})\int_0^\eta \exp(-\xi^2)\,d\xi$ for $w\sqrt{\tau} \leqq 0.01$.

c) $$F = 3(1+w)\sum_{j=1}^{n}(-1)^{j+1}H_j(\sqrt{\tau})^j \quad \text{for} \quad n = 1, 2, 3, 4 \qquad (Cn) \qquad (12)$$

where $H_1 = 2/\sqrt{\pi}$, $H_2 = 1 + 3w$, $H_3 = 4(2 + 3w)/\sqrt{\pi}$, $H_4 = 3w(1 + 9w + 9w^2)/2$ for $0 < w\sqrt{\tau} \leqq 0.01$ and $w \geqq 0.1$.

The value of w is calculated from the ion exchange isotherm of the specific metal ion complex by multiplying the slope of the tangent at the appropriate point of the curve by M_z/M_s. The value of F is calculated from the ion-exchange rate curves of the specific metal ions and the specific zeolitic ion exchanger by the formula:

$$F = (X_a - X_t)/(X_a - X_e)\,, \qquad (13)$$

where X_a, X_t, X_e are mole fractions (in solution) of incoming ion at the start, at time t and at equilibrium of ion-exchange process, respectively.

Calculation of the τ Values

With the values of F and w known from the experimental data we obtain the τ values easily using one of (An), (B) and (Cn) relationships (that one which gives the best approximation); the choice of the correct relationship of F vs τ (given above) depends on the range of F and w values. However, for $w \to 0$ the calculation of τ can be achieved with accuracy by using the explicit formula,

$$\tau = \tau_\beta/R^0\,, \qquad (14)$$

where τ_β is the τ value found when $w = 0$, and R^0 correction factor which is calculated from the formulas:

$$R^0 = (1+w)^2 - 1.2wF[w + 0.79 + F(0.5w + 0.2)]\,; \quad \text{if} \quad 0 < F \leqq 0.8 \qquad (15)$$

$$R^0 = 1 + w(1 - 0.4w)(2.93 - 1.6F)\,; \quad \text{if} \quad 0.8 \leqq F \leqq 0.95 \qquad (16)$$

$$R^0 = 1 + (1 - 0.46w)\left[0.608 - \frac{0.226}{\log(1-F) + 0.216}\right]; \quad \text{if} \quad 0.95 \leqq F < 1 \qquad (17)$$

When the formula used is not explicit the method of trial and error is used for obtaining the correct τ value.

Calculation of the Average Diffusion Coefficient D

From the calculation of the τ-value it is possible to calculate the average diffusion coefficient by calculating an average a-value and using the formula:

$$D_{av} = a_m^2 \tau / t \,. \tag{18}$$

The calculated D_{av}-value is varying with percentage of exchange in a complicated way.

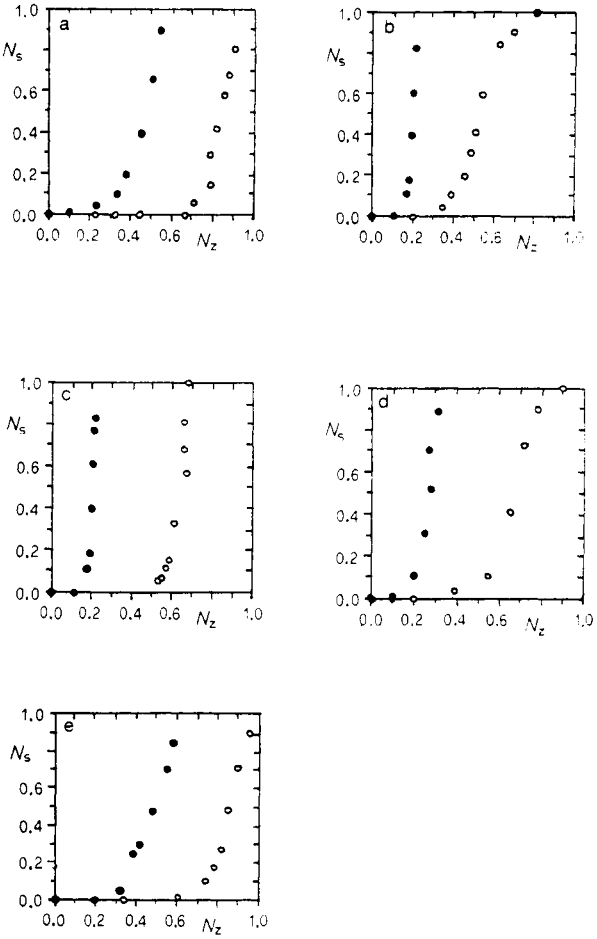

FIG. 6

Ion-exchange equilibrium isotherms at 25°C for aqueous (○) and ammonia (●) complexes of Cu (a), Co (b), Ni (c), Zn (d), and Cd (e) diffusing in NaX

The average a-value can be obtained by the formula:

$$a_m = \sum_i^n (g_i/r_i)^{-1}, \tag{19}$$

where g_i is the weight fraction with r_i radius.

EXPERIMENTAL

Materials. All salts of metal ions, ammonia and solvents used were of A.R. grade and the water used throughout this work was distilled. The molecular sieves (NaX, NaA, CaA) used were a product of Sigma in powder form with particle size less than 10 μm. The reagents and indicators used were supplied by Sigma. The standard solutions used in connection with atomic absorption spectroscopy were supplied by BDH. The preparation of standard solutions of metal ions, stock solutions of reagents and buffer solutions used in monitoring the progress of ion exchange with time are described in ref.[19] in detail.

Method of monitoring the rate curves of ion exchange. NaX (200 mg or 400 mg of NaA or CaA) were added at once into a beaker of 100 ml solution of $5 \cdot 0 \,.\, 10^{-3}$ mol l^{-1} metal ion complex, stirred with magnetic stirrer and thermostated at constant temperature (25°C ± 1). The ion-exchange solution was recycled with the aid of a peristaltic pump. The recycling solution was leaking into the stream of the metallochromic indicator which was buffered to the right pH and the absorbance of the indicator was monitored with time. The detailed procedure is described in ref.[19]. Fig. 1a shows the apparatus and the flow manifold used for obtaining the ion-exchange rate curves. Fig. 1b shows details of the construction of the leak that mixes the tiny quantity of the recycle solution with the reagent solution in the reagent stream.

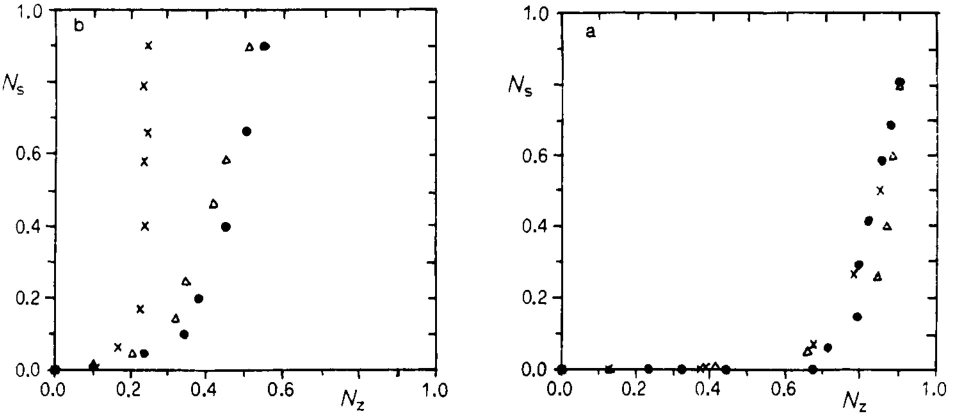

FIG. 7

Ion-exchange equilibrium isotherms at 25°C for aqueous (a) and ammonia (b) complexes of Cu ions diffusing in NaX (●), NaA (△) and CaA (×)

Method of constructing the ion-exchange isotherms. Varying volumes of 50 to 500 ml (according to the percentage of ion exchange) of $5\cdot0 \,.\, 10^{-3}$ mol l^{-1} solutions are mixed with 1·00 g of hydrated zeolite in powder form and are allowed to stand at 25°C for 48 h, under continuous stirring. The above time duration was chosen because preliminary experiments had shown that this period of time had been more than enough to reach equilibrium for the metal ion complexes studied in this work; this was also confirmed in ref.[13]. The samples were then filtered off, dissolved in concentrated mineral acid and analysed for the specific metal ion complex content using the technique of atomic absorption spectroscopy (Perkin Elmer, Model 560).

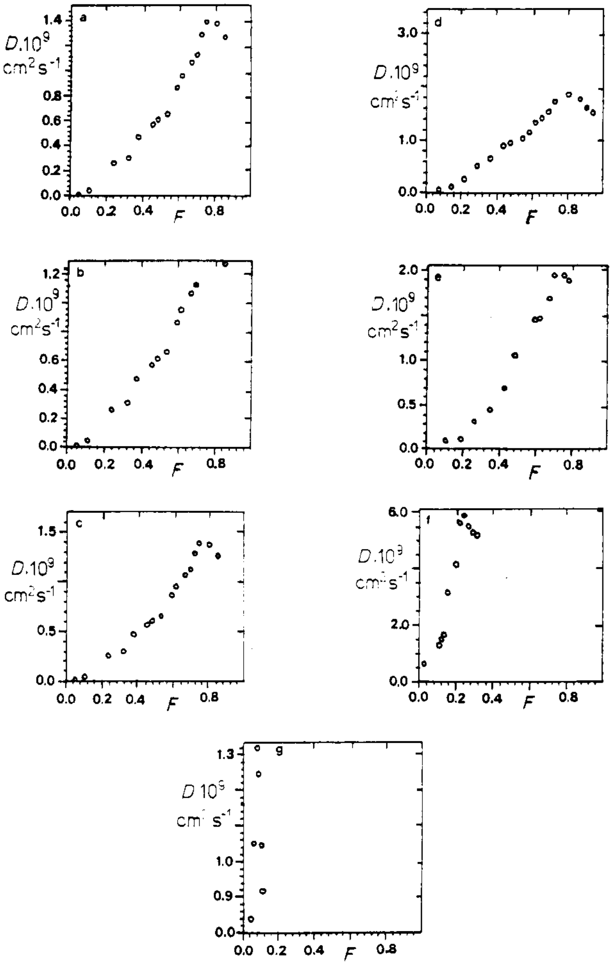

Fig. 8

D vs F curves of aqueous complexes of Co (a), Ni (b), Zn (c), Cd (d), and Cu (e) diffusing in NaX; of Cu (f) diffusing in NaA; and of Cu (g) diffusing in CaA

RESULTS

The ion-exchange rate curves obtained using the apparatus in Fig. 1 are shown in Figs 2 and 4. The corresponding plots of fractional attainment of equilibrium, F versus time are shown in Figs 3 and 5 for the rate curves from Figs 2 and 4, respectively. The ion-exchange isotherms corresponding to the rate curves are shown in Figs 6 and 7.

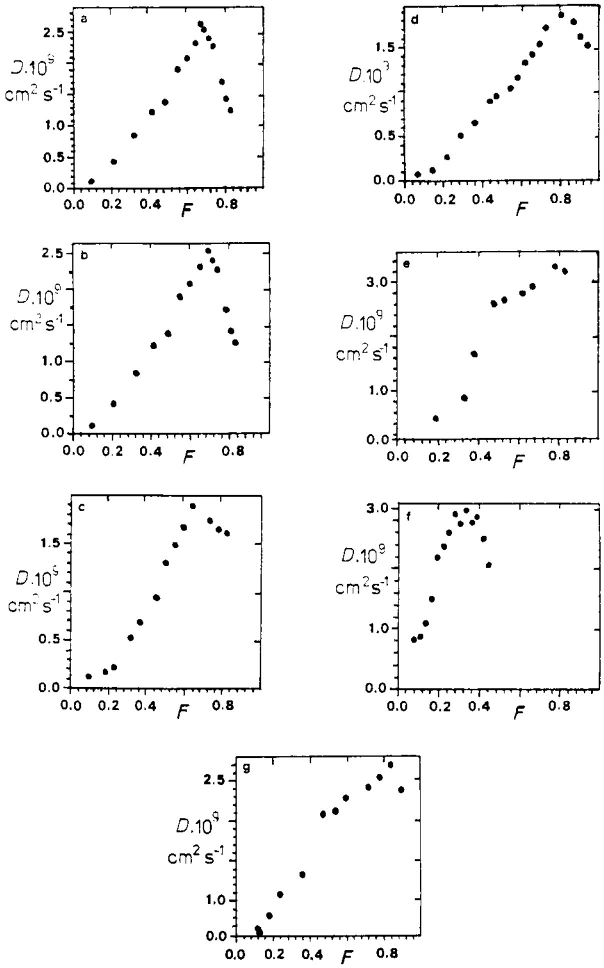

FIG. 9

D vs F curves of ammonia complexes of Co (a), Ni (b), Zn (c), Cd (d), and Cu (e) diffusing in NaX; of Cu (f) diffusing in NaA; and of Cu (g) diffusing in CaA

The treatment of the above experimental data by the mathematical procedure of Danes and Wolf[18] results in finding the average diffusion coefficients (D_{av}-values) at various F-values assuming an $a_m = 5$ μm for the zeolite particles. The variation of the D_{av}-values with the F-value is shown in Figs 8 and 9.

Figure 10 shows the w vs F relationship for the cuprammine and aqueous copper complexes diffusing in NaX zeolite. The relation has been obtained by calculating the quantity w from (M_z/M_s) $(\mathrm{d}[M]_z/\mathrm{d}[M]_s)$ at fixed F values using the isotherms of ion exchange of the corresponding complexes in NaX (Figs 6 and 7).

With the use of Fig. 10 we have obtained the w-value at fixed F-value and with the aid of Figs 8 or 9 the D_{av} at the specific F-value. Finally, we have found the corresponding ion-exchange time at the F-value from Figs 3 or 5 and the values thus obtained of w, D_{av} and t were introduced into Eq. (7b) taking only the first two terms in the summation part. The uptakes thus calculated for few fixed F-values are compared to the experimental ones found in Figs 2 or 4 and are given in Fig. 11.

From Fig. 11 it is realized that the use of Eq. (7b) gives uptake values which are very close to the experimental ones, however, at relatively low F-values the agreement of the values becomes poor. This may be explained by the inadequacy of the formula with the first two terms of the summation to approximate effectively the data at low F-values which is reasonable since other terms of the summation become significant at low F-values.

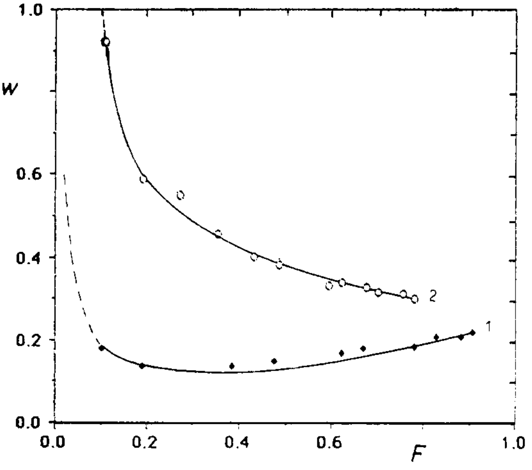

FIG. 10

w vs F curves for cuprammine (1) and aqueous (2) copper(II) complexes ion-exchanged in NaX zeolite

DISCUSSION

The diffusion coefficients calculated from the results obtained are listed in Tables I and II. From Table I it follows that in NaX molecular sieve the diffusion coefficients of aqueous complexes of the divalent metal ions studied in this work do not differ more than by factor of 2 suggesting that interactions between them and the walls of the zeolitic channels are of similar strength to all aqueous complexes studied in this work, provided that the channel openings are large enough as in NaX to

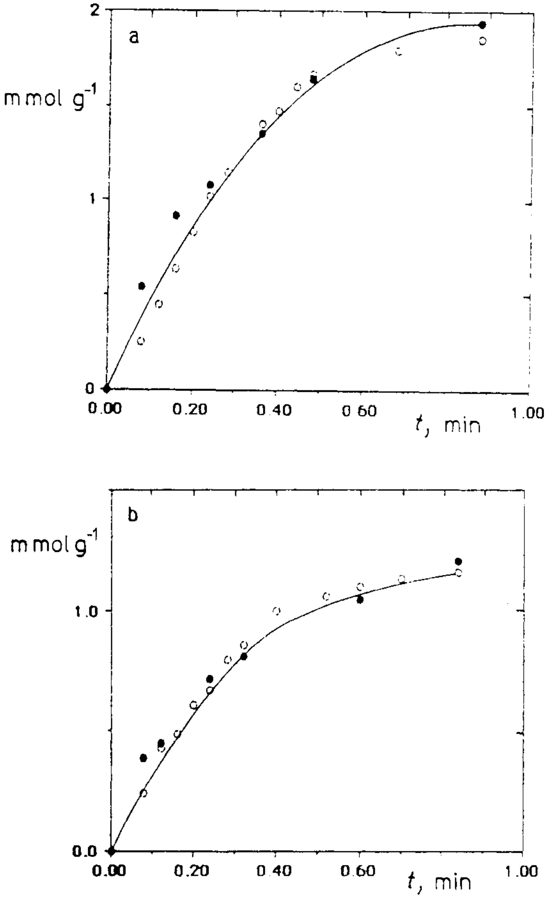

FIG. 11

Comparison of calculated uptake data (●) using Eq. (*7b*) and experimental data (○) foi the complexes of cupiammine (a) and aqueous-copper(II) (b) diffusing in NaX zeolite permit free movement to all aqueous complexes. On the other hand, the diffusion coefficients of the ammonia complexes of the same transition metal ions differ by a factor of 3 in the extreme case. This suggests that the sieving effect between the different complex ions has been improved. Finally, comparing the *D*-values between the aqueous and ammonia complexes (both of approximately the same volume size) it follows that in most cases the ammonia complexes show higher values which may be due to lower capacity of hydrogen-bonding and/or interactions to the zeolitic oxygens of the channel walls. However, this observation combined with the fact that the percentage of exchange is limited to lower values due to the partial exchange of ammonium ions allows to conclude that the ion exchange of the ammonia complexes is limited to the strongly selective sites. This would suggest that when the total number of sites is involved in the ion exchange process the overall *D*-values become lower because there is a specific *D*-value for each different group of sites in the zeolitic structure which is higher at highly selective sites.

TABLE I

Diffusion coefficients (in 10^{10} cm^2 s^{-1}) of aqueous and ammonia complexes of various transition metal ions at about 20% ion exchange of NaX

Element	Complexes	
	aqueous	ammonia
Co	2·66	4·40
Ni	2·20	3·50
Cu	1·40	5·20
Zn	2·20	1·80
Cd	1·50	2·80

TABLE II

Diffusion coefficients in (10^{10} cm^2 s^{-1}) of aqueous and ammonia complexes of Cu(II) metal ions at about 20% ion exchange of NaX, NaA and CaA

Complexes	Molecular sieve		
	CaA	NaA	NaX
Aqueous	0·01	0·42	1·40
Ammonia	0·83	2·20	5·20

From Table II it follows that the diffusion coefficients of the aqueous Cu(II com-) plexes are strongly dependent on the type of zeolite although their ion-exchange isotherms with the selected molecular sieves almost coincide (Fig. 7) and their profiles are of equally high selectivity. This suggests that the convenience of the complex to enter the zeolitic structure depends strongly on the channel opening, specifically on the ratio of the size of the window opening to the complex diameter, as well as on the type of metal ion already occupying the sites of the zeolitic structure; the metal ion due to its localization site selectivity and/or size of its hydration sphere may prevent the incoming ion to enter the zeolitic structure rapidly.

The behaviour of ammonia complexes is similar to the aqueous complexes and differs in two aspects. First, the diffusion coefficients show relatively smaller differences which are, however, still significant. Second, the ion-exchange isotherms reveal that the extent of ion-exchange of Cu(II) ammonia complex in CaA is significantly lower than in NaA and NaX zeolites suggesting a site selectivity for Ca^{2+} ions higher than for the incoming complex ions.

Comparing the ratios of the diffusion coefficients of aqueous and ammonia complexes it follows that the former are larger than the latter that again allows to suggest that the diffusion is not dependent on the size of the complex alone but on interactions between the zeolitic oxygen anions and cations or dipole molecules. These interactions must be less intense when ammonia ligands replace the water ligands.

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