CCA-1332

Self-diffusion of Cd++ Ions in Hydrated CdX Zeolite

M. B. Todorović, I. J. Gal, I. D. Paligorić, and V. M. Radak

Boris Kidrič Institute of Nuclear Sciences, Belgrade and Department of Chemistry, Faculty of Sciences, University of Belgrade, Yugoslavia

The fractional attainment of the isotopic equilibrium between a $Cd(NO_3)_2$ solution and a [115]Cd-labelled CdX zeolite has been measured as a function of time, particle size of zeolite and temperature. The experimental kinetic data have been interpreted in terms of the Brown-Sherry-Krambeck model and the self-diffusivities and diffusional activation parameters of Cd++ ions in zeolite CdX have been calculated.

INTRODUCTION

Ion-exchanged synthetic zeolites containing transition metal ions instead of sodium counter-ions are potentially useful catalysts and molecular sieves for industrial chemical processes. The thermodynamics of ion exchange in zeolites is generally well understood and in the case of Cd++—Na+ exchange has been extensivelly studied[1-4]. This however does not apply to the kinetics of ion exchange. In order to obtain fundamental data on the mobility of cations in hydrated zeolites, as, for example, the ionic self-diffusivities (self-diffusion coefficients), one depends on a suitable model which interprets the kinetics of the isotopic exchange. Thus, Dyer and coworkers[5-7] assumed that the isotopic exchange of Ca++,and Co++, Ni++ Zn++ in X and Y zeolites is governed by a single diffusion process of these ions in the solid particles, whereas Hoinkis and Levi[8-9] interpreted their isotopic exchange data on alkaline earth ions in zeolite X and A in terms of two independent diffusion processes. Later, Gaus and Hoinkis[10] modified their model by assuming a temperature dependent distribution of cations over the zeolite lattice. Brown and Sherry[11] interpreted the isotopic exchange of Na+ ions in X and A zeolite in terms of two kinetic steps: diffusion of mobile cations coupled to a intracrystalline exchange between mobile and bound cations (the Brown-Sherry-Krambeck model[12]). That model has also been applied to Zn++ in A zeolite[13] and X zeolite[14], and Cd++ in A zeolite[15].

The present paper reports the isotopic exchange kinetics of Cd++ ions measured between a $Cd(NO_3)_2$ solution and a CdX zeolite. A radio chemical technique using [115]Cd-labelled X zeolite has been applied to measure the rate of isotopic exchange. In the interpretation of data, the Brown-Sherry-Krambeck (BSK) model[12] gave good agreement with the experimental kinetic curves and allowed us to calculate the self-diffusivities of Cd++ ions in X zeolite, as well as the activation parameters for diffusion.

EXPERIMENTAL

The CdX zeolite has been prepared from 13X zeolite (BDH) by exchanging sodium ions with cadmium ions. The composition of CdX obtained by chemical analysis is shown in Table I.

TABLE I

Composition of CdX Zeolite

	Cd^{++}	Na^+	AlO_2	SiO_2	H_2O	sum
wt $^o/o$	22.17	0.19	23.80	29.61	23.95	99.73

Unit cell composition:

$$Cd_{42.1} Na_{1.8} [(AlO_2)_{86.6} (SiO_2)_{105.3}] \; 285 \; H_2O$$

Two fractions of different particle size, of mean radius 32 ± 4 μm and 20 ± 2 μm, were obtained by sieving. The preparation of the exchanged zeolite, chemical analysis and particle size determination is described in previous papers[3,13]. The CdX zeolite particles were radioactively labelled by equilibrating them with a $^{115}Cd(NO_3)_2$ solution at 90 °C for aproximately ten days. The labelled ^{115}CdX zeolite has been stored in a desiccator over a saturated solution of ammonium chloride where its water content remained constant (see Table I).

The rate of isotopic exchange between an inactive 0.01 mol dm^{-3} $Cd(NO_3)_2$ solution and a radioactive sample of CdX was followed radiometrically as described earlier[13]. The fractional attainment of isotopic equilibrium U_t is defined:

$$U_t = \frac{\overline{C_o} - \overline{C_t}}{\overline{C_o} - \overline{C_\infty}} = \frac{C_t}{C_\infty} \tag{1}$$

Here, $\overline{C_o}$, $\overline{C_t}$ and $\overline{C_\infty}$ are the concentrations of radioactive cadmium ions in the solid phase at zero time, at time t and at infinite time, when the isotopic equilibrium is established. C_o, C_t and C_∞ have the same meaning for the liquid phase ($C_o = 0$ in the present case). In the aqueous phase, C_t is measured, whereas C_∞ is calculated from the known value of $\overline{C_o}$ and the amount of Cd in both phases, assuming complete isotopic equilibrium.

The rates of isotopic exchange, U_t vs. t, are shown in Figure 1. The points are experimental data, whereas the curves represent best fits calculated with the BSK model[12] using a computer program[13].

RESULTS AND DISCUSSION

A careful check of the experimental data of Fig. 1 has shown that the rate of isotopic exchange is not a single kinetic step, nor is it controlled by the film at the phase boundary[16]. Therefore, the BSK model[12] has been applied in the quantitative interpretation, as before in the case of Zn^{++} in A[13] and X zeolite[14], and Cd^{++} in A zeolite[15]. The model has been thoroughly described[12] and often applied and discussed[13-15]. Let it here be mentioned that the BSK model assumes a two-step kinetics: diffusion of mobile cations through the openings and cages of the zeolite framework coupled to a first-order exchange process between mobile cations and cations bound to zeolite sites. In pratical application, no differentiation between different sites is made and

a single first-order »average« rate constant is used for all sites involved. Similarly, a single diffusional process is assumed over the whole lattice framework, since in an interconnected system of channels no separate diffusional paths are envisaged. According to the model, the dependence of U_t on t is given by:
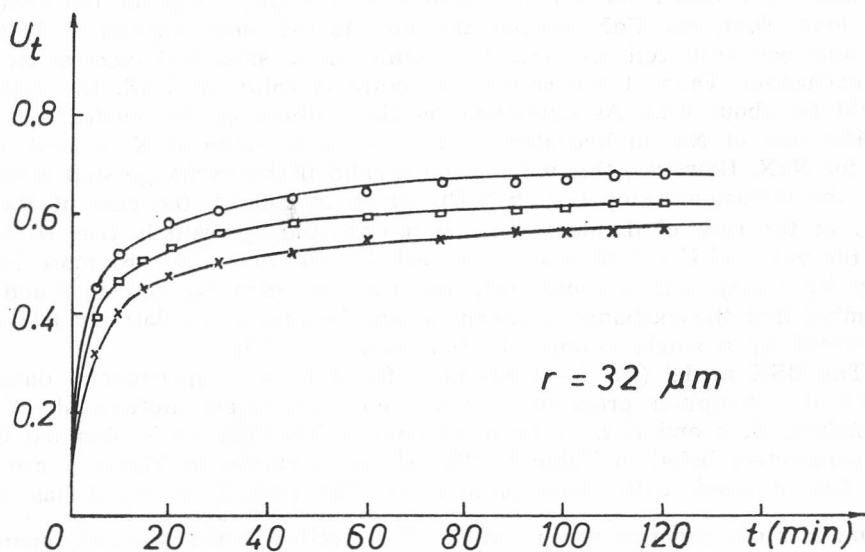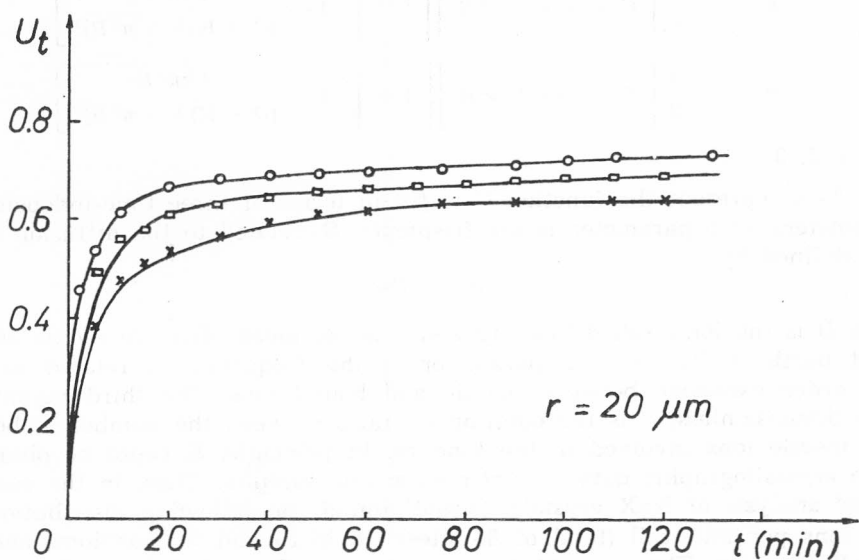

Figure 1. U_t against t at temperatures ◯, 60; ☐, 45 and x, 25 °C.

$$U_t = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2 (u_n - v_n)} \left[u_n \left(1 + \frac{v_n}{k(1+K)} \right) \exp(v_n t) - v_n \right.$$

$$\left. \left(1 + \frac{u_n}{k(1+K)} \right) \exp(u_n t) \right] \qquad (2)$$

$$u_n = -\frac{1}{2} \left[(1+K)k + n^2 B \right] \left[1 - \sqrt{1 - \frac{4 k n^2 B}{[(1+K)k + n^2 B]^2}} \right] \qquad (3)$$

$$v_n = -\frac{1}{2} \left[(1+K)k + n^2 B \right] \left[1 + \sqrt{1 - \frac{4 k n^2 B}{[(1+K)k + n^2 B]^2}} \right] \qquad (4)$$

$n = 1, 2, 3, \ldots$

Eqs. 2—4 represent the function $U_t = f(t)$ in terms of three time-independent parameters. One parameter is the frequency B, related to the diffusion step, and defined by

$$B = \pi^2 D/r^2 \qquad (5)$$

Here D is the ionic self-diffusivity and r is the mean effective radius of the solid particles. The second parameter is the frequency k, related to the first-order exchange between mobile and bound ions. The third parameter K is dimensionless, it is the equilibrium ratio between the number of bound and mobile ions involved in the kinetics. In principle, K could be obtained from crystallographic data of hydrated zeolite samples. Thus, in the case of X-ray analysis of NaX crystals, Olson[17] found the following distribution of Na^+ ions per unit cell (total of 86 sites): 16 in S_I and S_I' positions, and 24 on all S_{II} sites. The rest, 46 Na^+ ions are mobile hydrated cations in the supercage (S_{III} sites). In that case, the ratio of bound to mobile cations should be about 0.87. This ratio is not of course, necessarilly valid for the divalent Cd^{++} ions. First, our CdX sample has only 42 Cd^{++} ions instead of 43 (two Na^+ ions per until cell are probably bound on S_I sites and inaccessible for the exchange). Thus, if the above conjecture is valid for CdX, the ratio K should be about 0.83. As explained by the authors of the model[12], in the specific case of Na^+ in hydrated NaX, if a single value of K is used, it is 0.23 for NaX. However, this value is only valid if the exchange step is faster than the diffusional step (i. e. $k > B$), which is, indeed, the case of Na^+ in NaX. In the case of divalent ions, as a rule, the opposite is true ($k < B$), and the value of $K = 0.23$ is a not correct. We shall consider one more possibility by taking into account only the ratio of sites S_{II} and S_{III}, and by assuming that the exchange between S_{II} and S_I sites is a relatively fast step performed by a single »jump«. In that case, $K = 0.52$.

The BSK model (eq. 2—4) has been fitted to our experimental data by means of a computer program in which no *a priori* assumptions about the parameters B, k and K have been introduced. The best fit is obtained with the parameters listed in Table II. The U_t vs. t. curves in Figure 1 are the best fits obtained with those parameters. The sum $\sum_n$ in eq. 2 has been extended in our program up to a value of n specifed so that the next member of the sum, $(n + 1)$, gave a difference of $|U_t(n) - U_t(n + 1)| < 0.001$, which is negligible compared to the accuracy of experimental U_t values of ± 0.01—0.02.

TABLE II

Kinetic Parameters

temp/K	particle radius $r/\mu m$	$B\dagger/s^{-1}$	$k\dagger/s^{-1}$	K	$D/m^2\,s^{-1}$
298	32	8.3×10^{-4}	1.6×10^{-6}	0.7	8.64×10^{-14}
318	32	1.5×10^{-3}	1.0×10^{-5}	0.7	1.56×10^{-13}
333	32	2.1×10^{-3}	3.0×10^{-5}	0.7	2.24×10^{-13}
298	20	1.6×10^{-3}	2.5×10^{-5}	0.7	6.08×10^{-14}
318	20	3.3×10^{-3}	3.6×10^{-5}	0.7	1.33×10^{-13}
333	20	5.8×10^{-3}	5.0×10^{-5}	0.7	2.35×10^{-13}

$\dagger$ These values are accurate within about $\pm 5\%$.

As seen from Table II, the diffusional step is faster than the exchange step, since the parameter B is always about two orders of magnitude larger than k. Similar behavior has been noted in ZnX[14]. As mentioned earlier, the parameter K has been obtained without any *a priori* assumptions based on structural crystalographic data. However, one restriction has been imposed in the computer program with respect to the K value: it is a common parameter for all calculated curves U_t vs. t. (Such a restriction has not been applied, of course, to the B and k parameters.) The best fit obtained for K is 0.7, which seems to be a reasonable value, between the values of 0.8 and 0.5 discussed previously.

The ionic self-diffusivities D in Table II are obtained from the B parameters with eq. 5. They are close to the values reported for ZnX[14] (calculated with the same model), but more than an order of magnitude higher than the corresponding values of Cd^{++} in CdA zeolite, in agreement with the fact that A zeolite has smaller channels and a higher charge-density of lattice framework than X zeolite. The self-diffusivities (D) in Table 2 are self-consistent in that they depend on temperature, but not on particle size. All six D values of Table II obey a common Arrhenius type of plot as shown in Figure 2. From this plot the diffusional activation energy E_D and the parameter D_o has been obtained:

$$D = D_o \exp\left(-E_D/RT\right)$$

$$E_D = 26 \text{ kJ mol}^{-1}$$

$$D_o = 10^{-8.56} \text{ m}^2\,s^{-1}$$

The activation energy E_D is close to the corresponding values for ZnX (23.6 kJ mol^{-1}) obtained also with the BSK model[18]. However, Dyer and Townsend[6], using a single diffusion model obtained $E_D = 89.6$ kJ mol^{-1} for ZnX. With the D_o value given above, the diffusional activation entropy $\Delta S_{\pm}^D$ can be caulculated using the equation:

$$D_o = 2.718 \frac{k_B T d^2}{h} \exp\left(\Delta S_D^{\pm}/R\right)$$
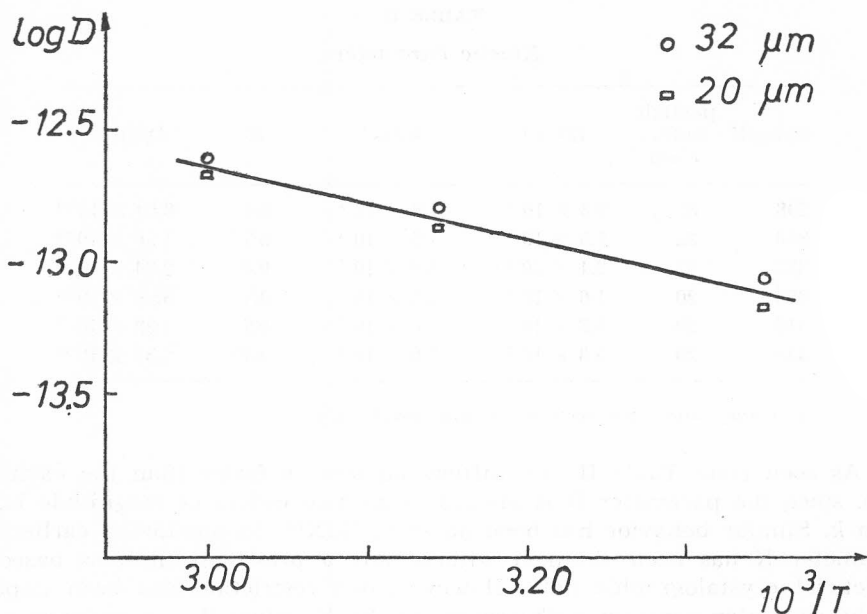
Figure 2. Arrhenius plot, log D against T^{-1}.

Here, k_B, h and R are the Boltzmann, Planck and gas constants, whereas d is the ionic jump distance (taken as $d = 0.5$ nm[13,14]). One obtains $\Delta S_D^{\neq} = -63$ J mol^{-1} K^{-1}.

The values of k in Table II show remarkable irregularities and do not obey the Arrhenius equation. This behavior seems to reflect the fact that we are dealing with several types of sites on which the Cd^{++} ions are bound. A decrease of the rate constant k implies that here exists a stronger bond of the cation to its negative site, and vice versa. In the present case, the model is simplified by taking an average value of k over all different sites on which the cations are bound, and for such an average value one can hardly expect it to obey the Arrhenius equation. In principle, to each type of sites holding cations, a specific k value should be assigned, but such a model would be too complicated and of little practical value.

REFERENCES

1. I. J. Gal, O. Janković, S. Malčić, P. Radovanov, and M. Todorović, Trans. Faraday Soc. 67 (1971) 999.
2. V. M. Radak and I. J. Gal, Proc. III Int. Conf. Molecular Sieves, Zürich 1973, p. 201.
3. I. J. Gal and P. Radovanov, J. Chem. Soc. (Faraday I), 71 (1975) 1671.
4. A. Maes and A. Cremers, J. Chem. Soc. (Faraday I), 71 (1975) 265.
5. A. Dyer and S. A. I. Barry, J. Inorg. Nucl. Chem. 39 (1977) 1061.
6. A. Dyer and R. P. Townsend, J. Inorg. Nucl. Chem. 35 (1972) 3001.
7. A. Dyer and A. B. Ogden, J. Inorg. Nucl. Chem. 37 (1975) 2207.
8. E. Hoinkis and H. W. Levi, Z. Naturforsch. A 22, (1967) 226.
9. E. Hoinkis and H. W. Levi, Ion Exchange in the Process Industries, Society of the Chemical Industry, London, 1970, p. 339.

10. E. G a u s and H o i n k i s, *Z. Naturforsch. A* **24**, (1969) 1511.
11. L. M. B r o w n, H. S. S h e r r y, *J. Phys. Chem.* **75** (1971) 3855.
12. L. M. B r o w n, H. S. S h e r r y, and F. J. K r a m b e c k, *J. Phys. Chem.* **75** (1971) 3846.
13. V. M. R a d a k, I. J. G a l, J. J. S a l a i, *J. Chem. Soc. (Faraday I)*, **72** (1976) 1150.
14. V. M. R a d a k, I. J. G a l, M. B. T o d o r o v i ć, and L. V u j i s i ć, *VI Int. Conf. Molecular Sieves, Recent Research Reports*, Chicago 1977, p. 71.
15. M. B. T o d o r o v i ć, I. J. G a l, V. M. R a d a k, and L. V u j i s i ć, *VI Int. Conf. Molecular Sieves, Recent Research Reports*, Chicago 1977, p. 104.
16. F. H e l f f e r i c h, *Ion Exchange*, Mc Graw-Hill, New York 1962, p. 255.
17. D. H. O l s o n, *J. Phys. Chem.*, **74** (1970) 2758.
18. M. B. T o d o r o v i ć, *Ph. D. Thesis*, University of Belgrade, Faculty of Sciences, Belgrade 1981.

SAŽETAK

Samodifuzija Cd^{++} jona u hidratisanom CdX zeolitu

M. B. Todorović, I. J. Gal, I. D. Paligorić i V. M. Radak

Frakciono dostizanje izotopske ravnoteže između Cd $(NO_3)_2$ u rastvoru i CdX zeolita obeleženog sa ^{115}Cd, mereno je u funkciji vremena, veličine zrna zeolita i temperature. Eksperimentalni kinetički podaci interpretirani su pomoću modela Brown-Sherry-Krambeck i izračunati su koeficijenti samodifuzije i aktivacioni parametri za proces difuzije Cd^{++} jona u CdX zeolitu.