On the Consistency of Zeolitic Self-Diffusion Coefficients

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Using a simple model for molecular, translational motion in zeolites, following Ruthven and Doetsch, a relation between self-diffusion coefficients and Henry coefficients of adsorption isotherms is presented. It is shown that on the basis of this correlation preexponential factors of both Henry constants and self-diffusion coefficients can be estimated from the activation energy of self-diffusion. Self-diffusion measurements of alcanes in NaX zeolites, using NMR pulsed field gradient techniques, are in satisfactory agreement with this result.

Comparing the data given in the literature for intracrystalline zeolitic diffusion, many inconsistencies can be stated (1–5). Very often, diffusivities calculated from sorption experiments are less by more than 2 or 3 orders of magnitude than the adequate self-diffusion coefficients obtained by means of NMR pulsed field gradient techniques (6).[1] In view of the fact that in the literature especially in the papers of Ruthven and co-workers (5, 8, 14), some of the sorption data could be interpreted and correlated on a molecular scale in quite a satisfactory way, it seems worthwhile to consider the extent to which self-diffusion coefficients are also consistent with an adequate microdynamic model. As a simple idealized description of the zeolitic microstructure we

[1] For a discussion of possible causes for this discrepancy, cf., e.g., (3, 5, 7, 10).

use the model developed by Hill (9) and first applied to zeolites by Ruthven and co-workers (5, 14).

The potential energy (U) throughout the zeolite lattice is assumed to be given by a three-dimensional, symmetric sinusoidal function

$$U = U_0 + \tfrac{1}{2}V_0 \left(1 - \cos \frac{2\pi x}{a}\right)$$
$$+ \tfrac{1}{2}V_0 \left(1 - \cos \frac{2\pi y}{a}\right)$$
$$+ \tfrac{1}{2}V_0 \left(1 - \cos \frac{2\pi z}{a}\right), \quad [1]$$

where U_0 is the potential at the minima, a is the distance, and V_0 is the energy barrier be-

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tween neighboring sites in the x-, y-, and z-coordinate directions.

In this case the oscillation frequency of molecules in the potential minima is given by

$$v_x = v_y = v_z = \left(\frac{V_0}{2ma^2}\right)^{\frac{1}{2}}, \qquad [2]$$

where m is the mass of a molecule, and the mean time interval between molecular jumps from one adsorption site to an adjacent site will be given, approximately, by

$$\tau = \frac{1}{6}\left(\frac{2ma^2}{V_0}\right)^{\frac{1}{2}} e^{V_0/kT}, \qquad [4]$$

where jumps in all directions are taken into account. According to activated diffusion theory and assuming the jump distance to be equal to the site separation a, the self-diffusion coefficient should be given by

$$D = \frac{1}{6}\frac{a^2}{\tau} = a\left(\frac{V_0}{2m}\right)^{\frac{1}{2}} e^{-V_0/kT}. \qquad [4]$$

Furthermore, subject to the additional assumption that there is no significant loss of rotational or internal vibrational freedom on sorption, the number of molecules per super-cage at low pressures p (Henry region) can be evaluated as (5)

$$n = k(T)p = \left[e^{-V_0/2kT}I_0(V_0/2kT)\right]^3 e^{-U_0/kT}$$
$$\times \frac{p}{kT}, \qquad [5]$$

where V denotes the volume of one supercage and $k(T) = k_0 \exp[E/kT]$ is the Henry coefficient; I_0 is the modified zero-order Bessel function of the first kind.

On the basis of this model a direct correlation between self-diffusion and sorption equilibrium data follows. Its consistency can be proved by evaluating the preexponential factors of the self-diffusion coefficients (D_0) and the Henry constant (k_0) from the activation energy of self-diffusion, using the equations

$$D_0 \approx a(V_0/2m)^{\frac{1}{2}}, \qquad [6]$$

$$k_0 \approx \left[e^{-V_0/2kT}I_0(V_0/2kT)\right]^3 \frac{V}{kT} \qquad [7]$$

and comparing them with the experimental results.

Evidently, the application of such a model to adsorbates with specific, i.e., short-range, interactions is dubious, so that diffusivity data of water or unsaturated paraffins (cf., e.g., (6, 10)) should not be considered in this connection. Furthermore, for paraffins adsorbed in A-type zeolites because of the relatively pronounced energy barriers in the windows between adjacent supercages, the sinusoidal function will be only a very poor approximation and another microscopic model should be applied (cf., e.g., (8)). Since the translational partition function of the adsorbed molecules (leading to the expression in the brackets of Eqs. [5] and [7]) will not be influenced by deviations from a sinusoidal energy profile in such a pronounced way as the oscillation frequencies v, Eq. [7] should also in this case give a rough approximation of the theory constant, whereas the application of Eq. [6], because of the erroneous values of v according to Eq. [2], should provide coefficients considerably higher than those actually provided.

In our estimation we put $a \approx 1°\text{Å}$ (cf., e.g., (16, 17)) and $V \approx 800$ Å for all systems. In view of the severe discrepancies between NMR and sorption data, errors, caused possibly by such a rough approximation, should be negligible.

The results are summarized in Table I. Self-diffusion data were obtained by NMR pulsed field gradient techniques. For the determination of the isotherms of cyclohexane, hexane, and heptane, isosteric and combined isosteric–isothermal methods (11, 12) were used.

It was found that for these systems even up to the lowest pressures (p $\lesssim$ 1 Pa) adsorption isotherms exhibit a slightly S-shaped pressure dependence. Within the accuracy of the model it seems to be justifiable, however, to approximate these adsorption isotherms by Henry's law and the coefficients given in Table I. The values for the adsorption isotherms of butane were taken from the literature.

TABLE I

Experimental and Theoretical Values for Self-Diffusion and Adsorption Equilibrium Data

System	$V_{0,\text{exptl}}$ (kcal/mole)	$D_{0,\text{exptl}}$ (cm²/sec)	θ	Ref.	D_0, according to Eq. [6] (cm²/sec)	$k_{0,\text{exptl}}$ (molecules/ cavity·Pa)	E_{exptl} (kcal/ mole)	Ref.	k_0, according to Eq. [7] for 300°K (molecules/ cavity·Pa)
Butane/NaX	2.2 (± 0.5)	$20\ldots60 \times 10^{-4}$	0.07	(15)	28×10^{-4}	1.5×10^{-9}	10	(13)	6.5×10^{-9}
Hexane/NaX	2.5 (± 0.8)	$20\ldots60 \times 10^{-4}$	0.07	(15)	20×10^{-4}	1.5×10^{-9}	14	(12)	3.8×10^{-9}
Heptane/NaX	3.2 (± 0.5)	$10\ldots25 \times 10^{-4}$	0.22	(16)	30×10^{-4}	2.3×10^{-9}	15	(12)	3.2×10^{-9}
Cyclohexane/NaX	3.0 (± 0.2)	$20\ldots60 \times 10^{-4}$	0.07	(15)	30×10^{-4}	1.5×10^{-9}	14	(12)	3.4×10^{-9}
Ethane/NaCaA	1.5	10^{-5}	0.02	(10)	10×10^{-3a}	6×10^{-9}	6.6	(19)	15×10^{-9}
SF₆/NaX	3.1	2.3×10^{-4b}		(18)	1.8×10^{-4c} (5)				

^{a} In agreement with the statement at the end of the passage following Eq. [7].
^{b} Estimated from relaxation time measurements.
^{c} Calculated in (5) according to Eq. [6] with V_0 obtained by best fitting of Eq. [5] to adsorption isotherms.

The agreement between the experimental values D_0 and k_0 and the theoretical values, estimated by Eqs. [6] and [7], is well within the uncertainty inherent in the rough microdynamic model. It seems remarkable that this coincidence is obtained without the use of additional parameters, which could contribute to an unjustified fitting of the theoretical values.

Further investigations based on a refined model will determine the degree of the coincidence observed between Eq. [7] and the experimental values, and the information about changes in rotational and vibrational freedom in the adsorbed phase (which had to be neglected for the derivation of Eq. [7]) that can be obtained.

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