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Evaluation of Concentration-dependent Diffusivity with Uptake Curve

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A theoretical approach to concentration-dependent diffusion has been proposed based on the constant diffusivity diffusion theory. The uncertainty function F_t was introduced to describe the diffusion process. Linear relationships have been deduced for evaluation of the diffusion coefficients at different diffusion times from the uptake curve. The diffusivity variation during the diffusion process could be represented by the time-dependent diffusivity, D_t. The applicability of the theoretical model has been tested in zeolitic adsorption systems. As an example of the applications, the diffusion of hexane, heptane and octane in NaZSM-5 zeolite has been studied.

For concentration-dependent diffusion, the diffusion equation

$$\partial c/\partial t = \mathrm{div}[D(c)\mathrm{grad}\ c] \quad (1)$$

cannot be solved because of the unknown implicated function $D(c)$. The Boltzmann–Matano method[1,2] has proved to be a useful way to deal with this sort of diffusion; however, it has its limits in cases of gases or liquids in porous solids, such as in zeolites, because it is difficult to determine the diffusant concentration distribution in solids during the diffusion process. Uptake measurement is one of the most commonly used methods to determine diffusivity. If the uptake curve is measured over a small differential change in adsorbed phase concentration the diffusivity could be considered constant, then the diffusivity may be obtained from the following simple equation.

$$\partial c/\partial t = D\ \mathrm{div\ grad}\ c \quad (2)$$

However, if diffusivity is strongly dependent on concentration, the constant diffusivity hypothesis would be a poor approximation. In the latter case, even if the uptake change is small, the influence of the concentration should be considered. The integral diffusivity is apparently not sufficient to describe this type of diffusion because the diffusivity will vary until the equilibrium of the adsorption is reached, and the concentration-dependent diffusivity $D(c)$, as shown in eqn. (1), or time-dependent diffusivity $D(t)$, should be used for the whole process. A simple way to evaluate the $D(c)$ or $D(t)$ data theoretically and experimentally is still required.

Owing to the importance of zeolites in catalysis and separation, many studies have been carried out on zeolitic intracrystalline diffusion. The diffusion coefficients in zeolite, measured by a wide variety of experimental techniques,[3] have been found to be strongly dependent on sorbate concentration. Although solving the diffusion equation[4,5] and the use of theoretical models,[6,7] including Monte Carlo simulations[8–10] provide ways to analyse adsorption kinetics, and many experimental techniques, including uptake or a modified uptake method[11] have been used to determine various types of diffusivities, there are still problems to overcome in zeolitic diffusion studies.

In the present work, a theoretical approach which deals with concentration-dependent diffusion has been proposed and tested in zeolitic diffusion systems.

Theory

Solution of the Diffusion Equation

From experimental observations on sorption kinetics, it has been found that even when D is a function of concentration, the $\sqrt{t}$ law is usually valid for small t in the form[12] $M_t/M_\infty = k\sqrt{t}$, which shows that there are some similarities in the concentration variation between concentration-dependent diffusion and constant diffusivity diffusion. Therefore, for diffusion at constant temperature and constant pressure, we assume that the solution of eqn. (1) may be represented by the combination of the solution of eqn. (2) with the same initial and boundary conditions and the uncertainty function F_t.

In the case of single-component diffusion in spherical particles, the solution of the diffusion eqn. (3) with initial and boundary conditions, eqn. (4)

$$\frac{\partial c}{\partial t} = \left(\frac{1}{r^2}\right)\frac{\partial}{\partial r}\left(r^2 D\frac{\partial c}{\partial r}\right) \quad (3)$$

$$c(r, 0) = c_0;\ c(r_0, t) = c_\infty;\ (\partial c/\partial r)_{r=0} = 0 \quad (4)$$

may be written as follows:[12]

$$\frac{\bar{c}_t - c_\infty}{c_0 - c_\infty} = F_t\left(\frac{6}{\pi^2}\right)\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_t t}{r_0^2}\right) \quad (5)$$

or alternatively

$$\frac{\bar{c}_t - c_\infty}{c_0 - c_\infty} = F_t\left\{1 - \left(\frac{6}{r_0}\right)\left(\frac{D_t t}{\pi}\right)^{1/2} \times \left[1 + 2\pi^{1/2}\sum_{n=1}^{\infty}\mathrm{ierf}\,c\frac{nr_0}{\sqrt{D_t t}}\right] + \frac{3D_t t}{r_0^2}\right\} \quad (6)$$

where $\bar{c}_t$ is the average concentration at time t in spherical particles of radius r_0; c_0 and c_∞ are the initial and final uniform concentrations, respectively; F_t is the uncertainty function which may be dependent on the diffusant concentration and the characteristic of the solid medium; D_t is the concentration-dependent diffusivity corresponding to time t or diffusant concentration $\bar{c}_t$.

During the whole process of diffusion, we can choose any time as τ; as diffusion time $t \to \tau$, then

$$F_t \to F_\tau; \quad D_t \to D_\tau \quad (7)$$

According to eqn. (5)–(7), the uptake curve could be expressed by the following three cases:

(*a*) For small t

In the case of a short diffusion time, a simpler form of eqn. (6) may be derived by the operation $[(\bar{c}_t - c_\infty)/(c_0 - c_\infty)] - [(\bar{c}_\tau - c_\infty)/(c_0 - c_\infty)]$, by considering eqn. (7) and omitting the much less significant terms

$$2\pi^{1/2} \sum_{n=1}^{\infty} \text{ierf } c \frac{nr_0}{\sqrt{D_t t}} \text{ and } (3D_t t/r_0^2).$$

$$\frac{\bar{c}_t - \bar{c}_\tau}{c_\infty - c_0} = F_\tau \left(\frac{6}{r_0}\right)\left(\frac{D_\tau}{\pi}\right)^{1/2} (t^{1/2} - \tau^{1/2}) \quad (8)$$

The F_τ function could also be obtained from eqn. (6) at time τ:

$$F_\tau = (1 - M_\tau/M_\infty) + F_\tau\left(\frac{6}{r_0}\right)\left(\frac{D_\tau}{\pi}\right)^{1/2} \tau^{1/2} \quad (9)$$

where

$$M_\tau/M_\infty = (\bar{c}_\tau - c_0)/(c_\infty - c_0) \quad (10)$$

The second term of eqn. (9) is the intercept of the line [eqn. (8)] on the time axis.

(*b*) For large *t*

$$\ln \frac{c_\infty - \bar{c}_t}{c_\infty - \bar{c}_\tau} = -\frac{\pi^2}{r_0^2} D_\tau t + \ln \frac{6}{\pi^2} + \ln \frac{F_\tau}{(1 - M_\tau/M_\infty)} \quad (11)$$

(*c*) For any diffusion time

$$\ln \frac{c_\infty - \bar{c}_t}{c_\infty - \bar{c}_\tau} = -\frac{\pi^2}{r_0^2} D_\tau (t - \tau) \quad (12)$$

By using the linear relationship of eqn. (8), (11) and (12), the concentration-dependent diffusivity D_τ and uncertainty function F_τ at time τ may be evaluated from the uptake curve. A series of D_τ values at different diffusion times could also be evaluated by altering the τ value and repeating the operation. Thus the function $D(t)$ may be obtained by regression of the $D_\tau \sim \tau$ values. With the corresponding concentration value of τ on the uptake curve, $D \sim c$ values and $D(c)$ could also be obtained in the same way.

Uncertainty Function, F_t

It can be seen that the uncertainty function F_t represents the relative deviation of the concentration at time *t* between the concentration-dependent diffusion and the constant diffusivity diffusion. If $F_t \equiv 1$, then eqn. (8), (11) and (12) will return to the same form as in constant *D* diffusion,[13] or the diffusivity is not influenced by diffusant concentration. Conversely, in the case of constant *D* diffusion, then $F_t \equiv 1$.

For a specific diffusion process, the value of F_t is related to the diffusant concentration and the interaction between diffusant and the solid medium. From eqn. (5) and (6), the value of the initial and final F_t would be:

$$F_{t=0} = 1; \quad F_{t=\infty} = 0 \quad (13)$$

which shows that diffusion may not be affected by diffusant concentration at the initial stage and may be strongly influenced by the equilibrium concentration. Thus for concentration-inhibited diffusion, the value of F_t will b the range of $1 > F_t > 0$, for concentration-enhanced diffus $F_t > 1$.

Diffusion Coefficient, D_t

D_t is the concentration-dependent diffusivity at time *t*. T variation of diffusivity with time could be shown by a seri of D_τ data at different diffusion times. Note that D_τ is a ne type of diffusion coefficient with respect to the common used integral, differential and corrected diffusivity. The rel tion between D_t and integral diffusivity $\bar{D}$ may be represent by eqn. (14).

$$\bar{D} = \int_0^\infty (D_t/t)\, dt \quad (1$$

From the above notation for F_t, it can be concluded th $D_{t=0}$ is independent of sorbate or diffusant concentration, bu these may be related to the commonly used corrected diffus vity D_0.

Experimental

The conventional gravimetric uptake method was used measure diffusivity. The diffusion experiments were carri out in a constant-volume and constant-pressure syste incorporating a Cahn–2000 electric balance to monitor th weight change of the sorbate. In order to maintain isotherm conditions, the weight of the zeolite samples was kept le than 20 mg and the samples were carefully placed on th balance pan (diameter 10 mm). Prior to the diffusion mea surements, the samples were degassed at 623 K in vacuu ($<6 \times 10^{-3}$ Pa) for at least 3 h and then cooled slowly 303 K. The step change of the uptake was about 4.0 – 6 kPa.

The zeolite crystals were synthesized in our laboratory a further identified by XRD. The crystal size was measured b electron microscopy which showed crystal uniformity. Th dimensions of the NaZSM-5 crystals are *ca.* 7 μm × 16 μm.

The diffusion coefficients were evaluated from the uptak curve using eqn. (8), (11) or (12), in which the concentratio c_0, $\bar{c}_\tau$, $\bar{c}_t$ and c_∞ were represented by the sorbate weight Q Q_τ, Q_t and Q_∞, respectively.

Results and Discussion

Validity of the Linear Relationship

Approximations have been introduced for the deduction eqn. (8), (11) and (12). Although the equations are strict tenable only when $t = \tau$, the linear relationship represent by the equations would exist as $t \to \tau$. As an extrapolati method, the diffusivity determination from the linear relatio ship is rigorous in principle.

Fig. 1 shows the plots of $(Q_t - Q_\tau)/(Q_\infty - Q_0)$ against t^{1} for C_6H_6 adsorption in NaZSM-5 zeolite at different diff

Table 1 C_6H_6 diffusion in NaZSM-5 zeolite[a]

τ/s^{-1}	M_τ/M_∞(%)	$At^{1/2} + B$: *A*	*B*	r^b	$-(B/A)\tau^{1/2}$	F_τ	$(D_\tau/r_0^2)/10^{-2}$ s^{-1}
0.433	13.27	0.408	−0.268	0.999	0.997	1.135	1.13
0.767	21.14	0.396	−0.344	0.999	0.993	1.133	1.07
1.100	27.06	0.331	−0.340	0.990	0.980	1.069	0.837
2.433	39.28	0.341	−0.529	0.997	0.994	1.136	0.786
3.767	47.15	0.207	−0.400	0.998	0.995	0.929	0.433
5.767	52.70	0.145	−0.348	0.997	0.996	0.821	0.272

[a] Results from eqn. (8). [b] Correlation coefficient.

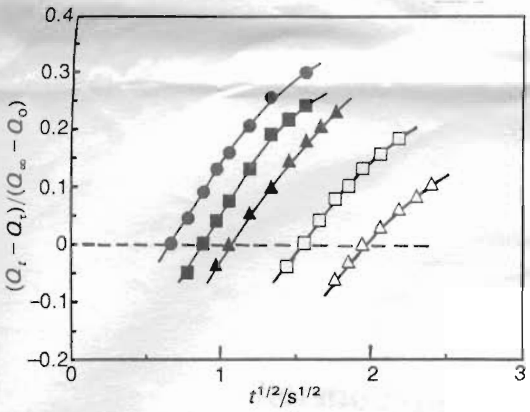

Fig. 1 $(Q_t - Q_\tau)/(Q_\infty - Q_0)$ *vs.* $t^{1/2}$ for C_6H_6 adsorption in NaZSM-5 zeolite at 303 K: ●, $\tau = 0.43$ s; ■, $\tau = 0.77$ s; ▲, $\tau = 1.10$ s; □, $\tau = 2.43$ s; △, $\tau = 3.77$ s

ion times (τ), the negative value of $(Q_t - Q_\tau)/(Q_\infty - Q_0)$ means that the diffusion time t is shorter than τ. The time of the intersection points on the $(Q_t - Q_\tau)/(Q_\infty - Q_0) = 0$ line is equal to τ. It is clear that the plot is linear as $t \to \tau$. The corresponding results are listed in Table 1. One of the features of eqn. (8) is that the slope of the line is equal to the intercept on the axis of $(Q_t - Q_\tau)/(Q_\infty - Q_0)$ multiplied by $\tau^{1/2}$, this is also shown in Table 1 by the value of $-(B/A)/\tau^{1/2}$ which is *ca.* 1. The values of the uncertainty function F_t and (D_t/r_0^2) at different diffusion times are also listed in the table, which clearly shows the variation of F_t and diffusivity in the diffusion process.

Plots of $\ln[(Q_t - Q_\tau)/(Q_\infty - Q_\tau)]$ *vs.* t for hexane adsorption in 4A zeolite are shown in Fig. 2. A linear relationship apparently exists near τ, which confirms the validity of eqn. (11) or (12) in the diffusivity determination.

A large number of zeolitic sorption systems, for example, CH_3OH, H_2O, C_6H_6, C_6–C_8 *n*-alkanes and other hydrocarbons in 4A Y-zeolites exchanged with various metal ions, ZSM-5, ZSM-11 and Mordenite, have also been used for testing the equations in our laboratory and no exceptions have been found, which shows that the theoretical approach may provide a way for the evaluation of concentration-dependent diffusivity D_t.

Diffusion of C_6, C_7 and C_8 *n*-Alkanes in NaZSM-5 Zeolite

A series of concentration-dependent diffusivities can be evaluated from the uptake curve, which would provide more information on the kinetic features of the adsorption than integral or mean diffusivity data. Examples are given for hexane,

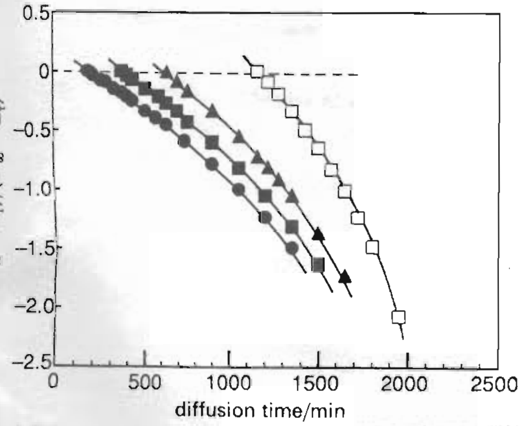

Fig. 2 $\ln[(Q_\infty - Q_t)/(Q_\infty - Q_\tau)]$ *vs.* t for hexane adsorption in 4A zeolite at 303 K: ●, $\tau = 195$ min; ■, $\tau = 390$ min; ▲, $\tau = 645$ min; □, $\tau = 1155$ min

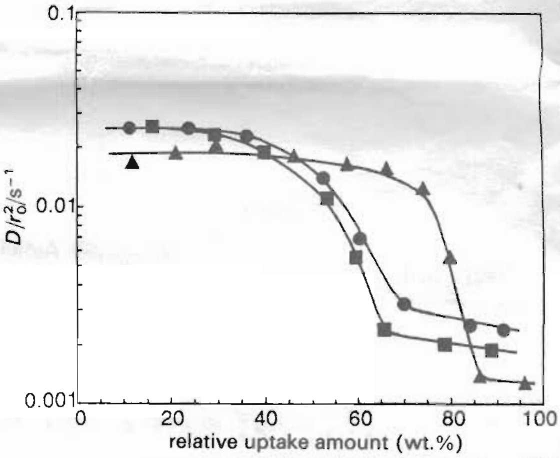

Fig. 3 Diffusivity variations of hexane, heptane and octane diffusion in NaZSM-5 zeolite at 303 K: ●, hexane; ■, heptane; ▲, octane

heptane and octane adsorption in NaZSM-5 zeolite; the variations of the diffusivity during the whole process of adsorption can be clearly seen in Fig. 3. The marked decrease in the diffusivity may be related to the manner of transportation of the alkane in ZSM-5 channels.

The size of the molecule relative to the size of the channel has been observed to have a marked effect on the value of the diffusivity; when the size of the molecule is comparable to the channel size, an oder of magnitude variation of the diffusivity would be caused by a small change of the channel size.[14] There are two types of channels in the ZSM-5 channel system, the straight channel and the sinusoidal channel. In the early stages of adsorption, the C_6, C_7 or C_8 *n*-alkane molecules are mainly transported in the straight channels[15] with high diffusivity, and after the straight channels are filled, the molecules are then mainly transported in the smaller sinusoidal channels with lower diffusivity, which may be the reason for the sharp decrease in diffusivity shown in the curves of Fig. 3. This anisotropic phenomenon is also suggested by NMR data.[16,17] The diffusivity in the straight channels is a factor of *ca.* 10 greater than that in sinusoidal channels.

Conclusions

A theoretical approach to concentration-dependent diffusion has been proposed and tested in a zeolitic adsorption system, which may allow concentration-dependent diffusivity evaluation.

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