Diffusion in Porous Solids --- A Theoretical Approach

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A theoretical approach about concentration dependent diffusion has been proposed based on the constant diffusivity diffusion theory, and its applicability for concentration dependent diffusivity evaluation from the uptake curve has been testified in zeolitic systems.

INTRODUCTION

For concentration dependent diffusion, the diffusion equation

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

can not be solved because of the implicated unknown function D(c). In the present work, a theoretical approach has been proposed for the evaluation of concentration dependent diffusivity from uptake curve.

THEORY

In the adaptation of $M_t/M_\infty = k\sqrt{t}$ law to non-constant D diffusion[1], there are some regularities of concentration variation between concentration dependent diffusion and constant diffusion. Therefor, for the diffusion at constant temperature and constant pressure conditions, we suppose that the solution of concentration dependent diffusion equation could be represented by the combination of the solution of constant D diffusion equation at the same initial and boundary conditions with a uncertain function F_t.

In case of single component diffusion in spherical particles, the solution of the diffusion equation (2) with initial and boundary conditions (3)

$$\partial c/\partial t = (1/r^2)\partial/\partial r\ (r^2 D\ \partial c/\partial r) \tag{2}$$

$$c(r\ 0) = c_0 \quad \text{and} \quad c(r_0\ t) = c_\infty \tag{3}$$

could be written as follows:

$$C_t = F_t c_0 (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-n^2\pi^2 D_t t/r_0^2) \tag{4}$$

where $C_t = \bar{c}_t - c_\infty$, F_t is the uncertain function which may relate to the diffusant concentration and the character of the solid medium, D_t is the diffusivity corresponding to time t or diffusant concentration $\bar{c}_t$, c_0 and $\bar{c}_t$ are the inatial and mean concentration at time t throughout the solid particle respectively.

RP1

When time t approaches the given time τ, there will be

$$F_t \longrightarrow F_\tau \quad \text{and} \quad D_t \longrightarrow D_\tau \tag{5}$$

According to equation(4) and (5), the variation of diffusant concentration could be obtained:

(a) for small t

$$\frac{\bar{C}_t-\bar{C}_\tau}{C_\infty-\bar{C}_\tau} = \frac{F_\tau}{(1-M_\tau/M_\infty)}\left(\frac{6}{r_0}\right)\left(\frac{D_\tau}{\pi}\right)^{\frac{1}{2}}\left(t^{\frac{1}{2}}-\tau^{\frac{1}{2}}\right) \tag{6}$$

where

$$F_t = (1-M_t/M_\infty)+F_\tau(6/r_0)(D_\tau/\pi)^{\frac{1}{2}}\ \tau^{\frac{1}{2}} \tag{7}$$

$$M_t/M_\infty=(c_\tau-c_0)/(c_\infty-c_0) \tag{8}$$

(b) for large t

$$\ln\frac{C_\infty-\bar{C}_t}{C_\infty-\bar{C}_\tau} = -\frac{\pi^2}{r_0{}^2}D_\tau t + \ln\left(\frac{6}{\pi^2}\right) + \ln\frac{F_\tau}{(1-M_t/M_\infty)} \tag{9}$$

(c) for both small or large t

$$\ln\frac{C_\infty-\bar{C}_t}{C_\infty-\bar{C}_\tau} = -\frac{\pi^2}{r_0{}^2}D_\tau\ (t-\tau) \tag{10}$$

By using the linear relationship of equation (6),(9) and (10), the D_t and F_t could be obtained experimentally.

EXPERIMENTAL RESULTS

The conventional gravimetric method[1,2] has been used to testify the applicability of the above derivation in zeolite diffusion systems, for example, CH_3OH, H_2O, C_6H_6, C_6—C_8 paraffins and other hydrocarbons in 4A, Y, ZSM-5, ZSM-11 and Mordenite, no inconsistency has been found.

As an example of the applications, the diffusion of n-hexane, n-heptane and n-octane in NaZSM-5 zeolite has been studied. The diffusivity of the paraffins in the straight channel has been observed to be 10 times of that in sinusodial channels.

CONCLUSIONS

The theoretical approach may provide a way for concentration dependent diffusivity evaluation

REFERENCES

1. R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves* Academic Press, New York, 1978
2. D.M. Ruthven, *Principles of Adsorption and of Adsorption Process*, Wiley and Sons, New York, 1984

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