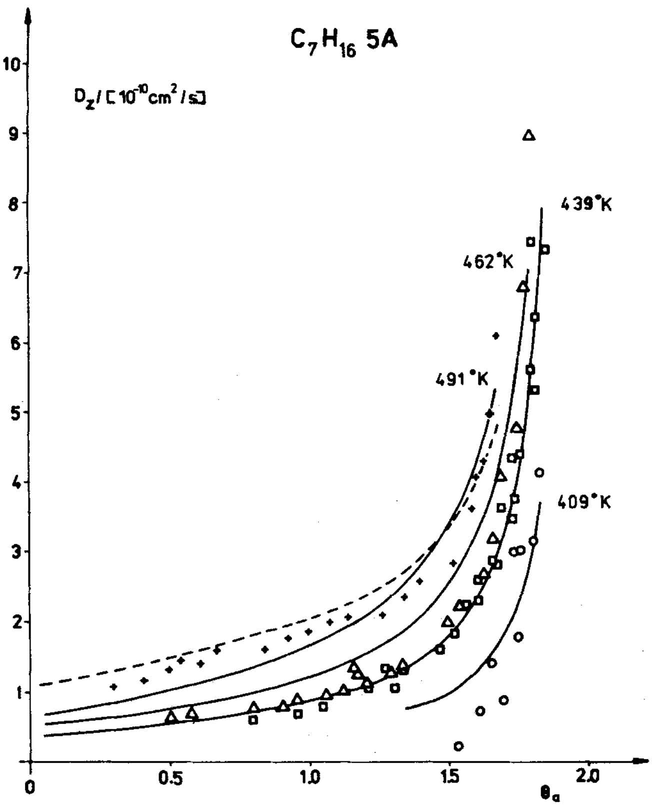

Figure 4. Effective diffusivity vs. loading for *n*-heptane/5A; —— Equation (8), --- Equation (11).

DISCUSSION OF RESULTS

Our diffusivities are defined as the jump rate per cage multiplied by the squared distance between cages. The model may be interpreted as one in which cages of given occupation levels and not individual adsorbate molecules are moving downstream. The "cage diffusivity" or jump-rate per cage is related to the self-diffusivity of the adsorbate molecules, according to Equation (6). Jump rates increase with occupation level for toluene in 13X, so that adsorbate-adsorbate intermolecular disturbances are unimportant. The jump rate remains constant for *n*-heptane in 13X, so that adsorbate-adsorbate interaction is rate limiting. This agrees with the conception that adsorbed paraffin molecules are in a coiled configuration which does not fit through the window. The probability of a molecule stretching could decrease with increased loading.

Allowing for experimental error, benzene and cyclohexane behave as toluene at low loading levels, cage-molecule interaction appearing rate-limiting, whereas closer to saturation mobility is limited by intermolecular disturbance, as with *n*-heptane. Jump rates continue to increase in the toluene system at higher loading rates than for benzene and cyclohexane, indicating relatively stronger adsorbate-lattice interaction for the alkylated ring compound.

Converting from cage diffusivities to self-diffusivities in the NaX-zeolites according to Equation (6), the self-diffusivity of toluene is independent of concentration, whereas that of *n*-heptane decreases proportional to occupation level.

Further, in the 13X studies no rate contribution has been found from jumps between cavities differing in occupation level by more than one. There is no evident reason why the $D_{i,j-1}p_i$ should be negligible. However, the $\theta_i\theta_{j-1}$, $i>j$ have been taken as the probability that a cage holding i molecules has a neighbor holding $j-1$ molecules; the θ_i are equilibrium values. The probability might be negligible during the kinetic experiment, if occupation levels were to advance in waves of cages holding one more (or less) molecule than the preceding wave. The final stage of the kinetic period would be internal rearrangement leading to the equilibrium distribution of occupation levels. Internal rearrangement does not appear to be a factor among the small-windowed 5A cages, since Equations (8) and (11) were applied successfully.

In this manner, our model Equation (4), which includes Darken's law (Equation 8) and the Ruthven model (Equation 11) as special cases, may be used to analyse adsorption rate behavior in zeolites.

NOTATION

a = sorbate concentration, mol g^{-1}
$D_{i,j-1}$ = diffusion coefficient, cm^2 s^{-1}
D_z = Fickian diffusion coefficient, cm^2 s^{-1}
E_i = energy of adsorption, J mol^{-1}
m = maximum no. of molecules per cage
N_c = total number of cavities, mol g^{-1}
P = gas pressure, Pa
P_0 = standard pressure, Pa
p_i = probability of motion
R = gas constant, J K^{-1} mol^{-1}
S_i = standard entropy, J K^{-1} mol^{-1}
T = temperature, K
T_0 = standard temperature, K
θ_a = reduced sorbate concentration
θ_i = fraction of cavities holding i molecules
μ = standard chemical potential, J mol^{-1}

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Approximate Formulae for the Dispersion Coefficients of Layered Porous Media

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Groundwater and petroleum reservoirs are composed of porous rocks. Very often these rocks constitute a layered structure. Dispersion in porous media is very important in connection with groundwater pollution (Fried 1975) and oil production by secondary recovery (Pfannkuch 1963, Fried & Combarnous 1971). Dispersion in layered porous media, represented as anisotropic in the macroscopic description, is determined by six dispersion

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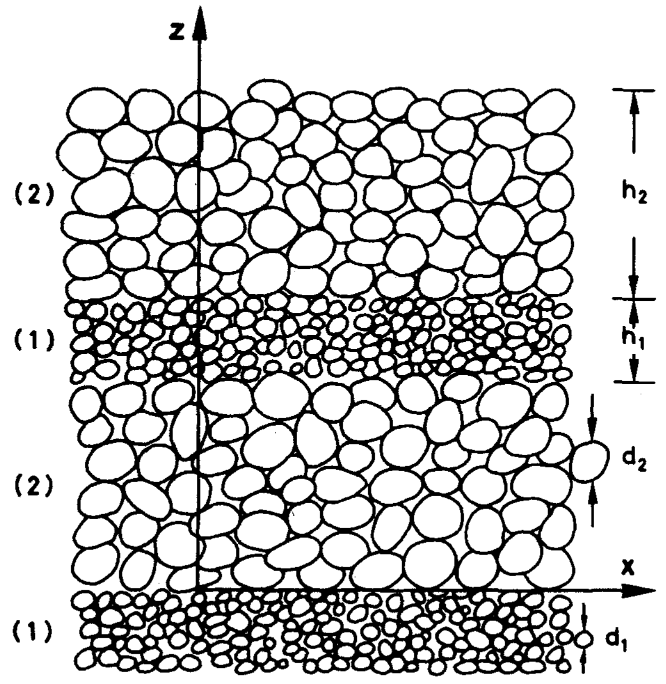

Figure 1. Sketch of the model.

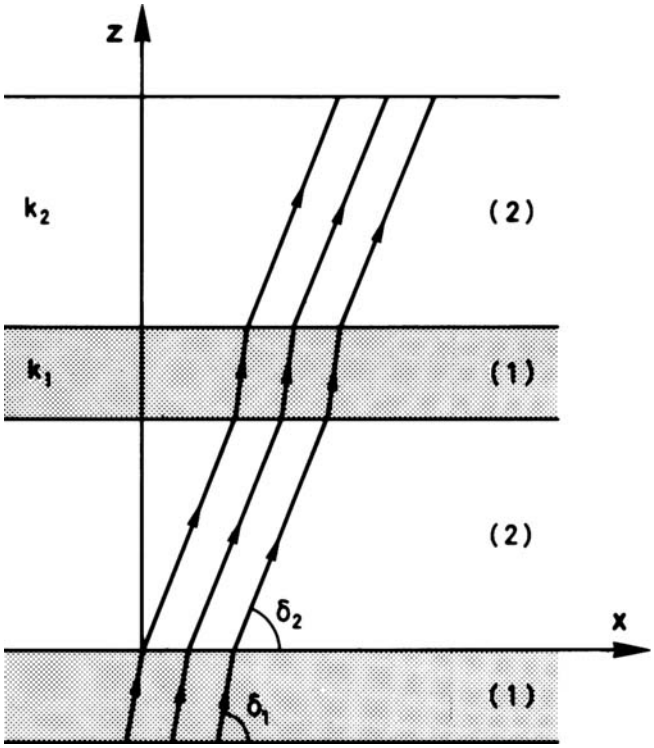

Figure 2. Uniform flow in a layered medium.

coefficients (see Moranville et al. 1977 a, b). In this note approximate, theoretical formulae for these dispersion coefficients are derived. The Péclet number is assumed large.

MODEL

Here, we consider an unbounded porous medium composed of two alternating layers (1) and (2), with constant thicknesses h_1 and h_2. Each layer is homogeneous and isotropic, and made up by grains with average diameters d_1 and d_2, respectively. The interfaces between the layers are assumed plane (Figure 1).

A cartesian coordinate system is introduced, with the xy-plane located at an interface between two layers, and the z-axis normally to the layers. The region $-h_1 < z < 0$ is occupied by a layer of type (1), and the region $0 < z < h_2$ is occupied by a layer of type (2). The orientation of the x- and y-axes will be prescribed later.

The permeability in each layer, $k_\alpha (\alpha = 1, 2)$, is proportional to the square of the characteristic grain diameter d_α. According to Bear (1972, p. 134) a general formula for the permeability k of an isotropic medium is

$$k = f_1(s) f_2(n) d^2 \tag{1}$$

where $f_1(s)$ is the shape factor, $f_2(n)$ the porosity factor and d the mean diameter of the grains.

Now the porosity in each layer is assumed equal, and the shape of the grains is assumed similar. Then the factor of proportionality, $c = f_1(s) f_2(n)$, is the same for each layer

$$k_\alpha = c\, d_\alpha^2 (\alpha = 1,2) \tag{2}$$

FLOW FIELD

A pressure-driven, uniform flow is considered. Strictly speaking, the flow is uniform only within each layer. Velocity discontinuities are usually present at the interfaces. Only the case of flow aligned in z-direction is without velocity discontinuities. The velocity $\vec{v}$ in each layer (α) is given by

$$\vec{v}^{(\alpha)} = U_\alpha \vec{i} + W_\alpha \vec{k} \quad (\alpha = 1,2) \tag{3}$$

The x-axis is thus directed along one projection of the velocity vector (Figure 2). U_1, U_2, W_1 and W_2 are constants. $\vec{i}$, $\vec{j}$ and $\vec{k}$ are unit vectors in x-, y- and z-direction, respectively.

The fluid is assumed incompressible. The continuity equation $\nabla \cdot \vec{v} = 0$ implies

$$W_1 = W_2 = W \tag{4}$$

when the porosity is constant. The angle between x-direction and the velocity vector $\vec{v}^{(\alpha)}$ in each layer is denoted by δ_α ($\alpha = 1,2$). Bear (1972, p. 156) has shown that

$$\frac{\cot \delta_1}{\cot \delta_2} = \frac{k_1}{k_2} = \frac{d_1^2}{d_2^2} \tag{5}$$

The layered porous medium can be regarded as anisotropic in a macroscopic description (Bear 1972, p. 157). The horizontal and vertical permeabilities, k_H and k_V respectively, are given by

$$k_H = \frac{k_1 h_1 + k_2 h_2}{h_1 + h_2} = c\, \frac{d_1^2 h_1 + d_2^2 h_2}{h_1 + h_2} \tag{6}$$

$$k_V = \left[\frac{\dfrac{h_1}{k_1} + \dfrac{h_2}{k_2}}{h_1 + h_2} \right]^{-1} = c\, \frac{h_1 + h_2}{\dfrac{h_1}{d_1^2} + \dfrac{h_2}{d_2^2}} \tag{7}$$

An average velocity is introduced

$$\vec{\bar{v}} = U \vec{i} + W \vec{k} = \frac{1}{h_1 + h_2} \int_{-h_1}^{h_2} \vec{v}\, d z \tag{8}$$

From Eqs. (5) and (8) it is easily shown that

$$\left.\begin{aligned} U_1 &= U\, \frac{h_1 + h_2}{h_1 + h_2 \dfrac{d_2^2}{d_1^2}} \\ U_2 &= U\, \frac{h_1 + h_2}{h_1 \dfrac{d_1^2}{d_2^2} + h_2} \end{aligned}\right\} \tag{9}$$

DISPERSION TENSORS

We will investigate the dispersion of a tracer with concentration $C(x, y, z, t)$ which has no influence on the flow field. The tracer is thus assumed not to influence the fluid density. The tracer distribution is governed by the dispersion equation

$$\frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C = \nabla \cdot (\mathscr{D} \cdot \nabla C) \tag{10}$$

The dispersion tensor in each layer is given by

$$\mathscr{D}^{(\alpha)} = a_{II}^{(\alpha)}|\vec{v}|\mathscr{E} + (a_I^{(\alpha)} - a_{II}^{(\alpha)}) \frac{\vec{v}\vec{v}}{|\vec{v}|} \tag{11}$$

see Bear (1972, p. 612). $\mathscr{E}$ is the unit tensor. Bear (1969) has shown that the dispersion coefficients a_I, a_{II} are proportional to the average pore length, which is equal to the average grain diameter in the present model

$$a_I^{(\alpha)} = A_I d_\alpha, \quad a_{II}^{(\alpha)} = A_{II} d_\alpha \tag{12}$$

A_I and A_{II} are numbers characterizing longitudinal and lateral dispersion, respectively.

Each layer is isotropic. Therefore the tortuosity (Bear, 1972, p. 615) is assumed the same in both layers. Then the numbers A_I and A_{II} are constants. The dispersion tensor in each layer may then be written

$$\mathscr{D}^{(\alpha)} = \left(A_{II}|\vec{v}|\mathscr{E} + (A_I - A_{II}) \frac{\vec{v}\vec{v}}{|\vec{v}|}\right) d_\alpha \qquad (\alpha = 1,2) \tag{13}$$

Pfannkuch (1963) determined experimentally $A_I = 1.8 \pm 0.4$. Bear (1969) proved $A_I/A_{II} > 2$. The very value of A_{II} is uncertain, but its order of magnitude is 10^{-1}, according to Fried and Combarnous (1971).

The tensors given by Eqs. (11) and (13) are valid only at large Péclet numbers

$$P^{(1)} >> 1, \quad P^{(2)} >> 1 \tag{14}$$

The Péclet numbers $P^{(1)}$ and $P^{(2)}$ are defined by

$$P^{(\alpha)} = \frac{(U_\alpha^2 + W^2)^{\frac{1}{2}} d_\alpha}{\kappa} \qquad (\alpha = 1,2) \tag{15}$$

κ is the molecular diffusivity of the tracer in the fluid.

According to Moranville et al. (1977 a) the dispersion tensor of a transversely isotropic medium at large Péclet numbers is

$$\left.\begin{aligned} \mathscr{D} = {} & a_0|\vec{v}|\mathscr{E} + a_1|\vec{v}|\vec{k}\vec{k} + a_2\frac{w^2}{|\vec{v}|}\mathscr{E} \\ & + a_3\frac{w^2}{|\vec{v}|}\vec{k}\vec{k} + a_4\frac{\vec{v}\vec{v}}{|\vec{v}|} + a_5(\vec{v}\vec{k} + \vec{k}\vec{v})\frac{w}{|\vec{v}|} \end{aligned}\right\} \tag{16}$$

in the case of vertical symmetry axis. ($w = \vec{v}\cdot\vec{k}$). Moranville et al. (1977 a) showed that the coefficients are slightly velocity dependent. In our approximate analysis, these coefficients are treated as constants.

Equation (16) is also valid for a layered porous medium, represented by average description as anisotropic. Let $\overline{\mathscr{D}}$ denote the dispersion tensor in this macroscopic description

$$\left.\begin{aligned} \overline{\mathscr{D}} = {} & (U^2 + W^2)^{\frac{1}{2}}(a_0\mathscr{E} + a_1\vec{k}\vec{k}) \\ & + \frac{W^2}{(U^2 + W^2)^{\frac{1}{2}}}(a_2\mathscr{E} + a_3\vec{k}\vec{k}) \\ & + \frac{a_4}{(U^2 + W^2)^{\frac{1}{2}}}(U\vec{i} + W\vec{k})(U\vec{i} + W\vec{k}) \\ & + \frac{a_5}{(U^2 + W^2)^{\frac{1}{2}}}W(U\vec{i}\vec{k} + U\vec{k}\vec{i} + 2W\vec{k}\vec{k}) \end{aligned}\right\} \tag{17}$$

CALCULATING DISPERSION COEFFICIENTS

Our aim is to determine a_i ($i = 0,1,2,3,4,5$), expressed by A_I, A_{II}, d_1, d_2, h_1 and h_2. Here, we consider examples of flows and tracer distributions which are suited for this purpose.

i) Consider the case $\vec{v} = W\vec{k}$, $C = C(x,t)$. A characteristic velocity for the dispersion of a concentration front in x-direction is denoted by ψ. By utilizing Eqs. (10) and (13) we estimate

$$\psi = -A_{II}d_\alpha W \frac{\partial^2 C}{\partial x^2} \Big/ \frac{\partial C}{\partial x} \qquad (\alpha = 1,2) \tag{18}$$

ψ being different in each layer gives rise to a tendency of creating a vertical gradient in C. This tendency may be significant only at time scales of the order $(h_1 + h_2)/W$ or less. We restrict our attention to cases satisfying

$$\psi << W$$

Then the time scale of dispersion is much larger than the amount of time being spent by any particle in one layer. Thus the assumption $C = C(x,t)$ is consistent. From Eq. (17) we find the relevant component of the average dispersion tensor

$$\overline{D}_{11} = (a_0 + a_2)W \tag{19}$$

The average transport of tracer mass in x-direction may be expressed in two ways

$$\overline{D}_{11}\frac{\partial C}{\partial x} = \frac{1}{h_1 + h_2}\left[\int_{-h_1}^{0} D_{11}^{(1)}\frac{\partial C}{\partial x}\,dz + \int_0^{h_2} D_{11}^{(2)}\frac{\partial C}{\partial x}\,dz\right] \tag{20}$$

From Eq. (13) we find

$$D_{11}^{(\alpha)} = A_{II}Wd_\alpha \quad (\alpha = 1,2) \tag{21}$$

This yields the formula

$$a_0 + a_2 = A_{II}\frac{d_1h_1 + d_2h_2}{h_1 + h_2} \tag{22}$$

ii) Consider the case $\vec{v} = W\vec{k}$, $C = C(z,t)$. A concentration front moves in z-direction with a characteristic velocity $W + \psi$, where

$$\psi = -A_I d_\alpha W \frac{\partial^2 C}{\partial z^2} \Big/ \frac{\partial C}{\partial z} \qquad (\alpha = 1,2) \tag{23}$$

We restrict our attention to cases satisfying $\psi << W$, which means that a "cloud" of tracer moves relatively far with the mean flow before dispersing out. Assume $\partial C/\partial z$ being approximately constant in a region of length L within the cloud, where $L >> \mathrm{Max}(h_1,h_2)$. The average transport of tracer mass due to dispersion in this region is expressed in two ways

$$\overline{D}_{33}\frac{dC}{dz} = \frac{1}{h_1 + h_2}\left[\int_{-h_1}^{0} D_{33}^{(1)}\frac{dC}{dz}\,dz + \int_0^{h_2} D_{33}^{(2)}\frac{dC}{dz}\,dz\right] \tag{24}$$

By utilizing Eqs. (13) and (17) we find

$$a_0 + a_1 + a_2 + a_3 + a_4 + 2a_5 = A_I\frac{d_1h_1 + d_2h_2}{h_1 + h_2} \tag{25}$$

iii) Consider the case $\vec{v} = U\vec{i}$, $C = C(z,t)$. The velocities are different in each layer, per Eq. (9). All exchange of fluid and tracer mass through the layer is represented by the dispersion. A stationary problem is now considered, with a constant transport of tracer mass (may be realized by "sources" and "sinks"). This requires

$$D_{33}^{(1)}\left(\frac{dC}{dz}\right)^{(1)} = D_{33}^{(2)}\left(\frac{dC}{dz}\right)^{(2)} \tag{26}$$

The average transport of tracer is expressed by

$$\bar{D}_{33}\,\overline{\frac{dC}{dz}} = \frac{1}{h_1 + h_2}\left[\int_{-h_1}^{0} D_{33}^{(1)}\left(\frac{dC}{dz}\right)^{(1)} dz + \int_{0}^{h_2} D_{33}^{(2)}\left(\frac{dC}{dz}\right)^{(2)} dz\right] \qquad (27)$$

where we have introduced the average gradient

$$\overline{\frac{dC}{dz}} = \frac{1}{h_1 + h_2}\left[h_1\left(\frac{dC}{dz}\right)^{(1)} + h_2\left(\frac{dC}{dz}\right)^{(2)}\right] \qquad (28)$$

By combining Eqs. (26)-(28) and utilizing (9), (13) and (17), we finally obtain

$$a_0 + a_1 = A_{II}\frac{(h_1 + h_2)^2}{\left(\frac{h_1}{d_1^3} + \frac{h_2}{d_2^3}\right)(d_1^2 h_1 + d_2^2 h_2)} \qquad (29)$$

iv) Consider the case $\vec{\bar{v}} = U\vec{i}$, where we assume $C = f(x)$ at the instant $t = 0$. The tracer mass transport in x-direction due to dispersion at this instant is given in two ways

$$\bar{D}_{11}\frac{\partial C}{\partial x} = \frac{1}{h_1 + h_2}\left[\int_{-h_1}^{0} D_{11}^{(1)}\frac{\partial C}{\partial x}dz + \int_{0}^{h_2} D_{11}^{(2)}\frac{\partial C}{\partial x}dz\right] \qquad (30)$$

By utilizing Eqs. (9), (13) and (17) we obtain the formula

$$a_0 + a_4 = A_I\frac{d_1^3 h_1 + d_2^3 h_2}{d_1^2 h_1 + d_2^2 h_2} \qquad (31)$$

v) Consider the case $\vec{v} = U\vec{i}$, where it is assumed that $C = g(y)$ at the instant $t = 0$. The tracer mass transport in y-direction at this instant is given in two ways

$$\bar{D}_{22}\frac{\partial C}{\partial y} = \frac{1}{h_1 + h_2}\left[\int_{-h_1}^{0} D_{22}^{(1)}\frac{\partial C}{\partial y}dz + \int_{0}^{h_2} D_{22}^{(2)}\frac{\partial C}{\partial y}dz\right] \qquad (32)$$

Eqs. (9), (13) and (17) are utilized, and we obtain

$$a_0 = A_{II}\frac{d_1^3 h_1 + d_2^3 h_2}{d_1^2 h_1 + d_2^2 h_2} \qquad (33)$$

The first dispersion coefficient in Eq. (16) is hereby determined. The second one is determined from Eq. (29)

$$a_1 = -A_{II}\frac{(d_1^3 - d_2^3)^2}{\left(\frac{d_1^3}{h_1} + \frac{d_2^3}{h_2}\right)(d_1^2 h_1 + d_2^2 h_2)} \qquad (34)$$

From Eqs. (22) and (31) we further determine

$$a_2 = -A_{II}\frac{h_1 h_2 (d_1 - d_2)^2 (d_1 + d_2)}{(h_1 + h_2)(d_1^2 h_1 + d_2^2 h_2)} \qquad (35)$$

$$a_4 = (A_I - A_{II})\frac{d_1^3 h_1 + d_2^3 h_2}{d_1^2 h_1 + d_2^2 h_2} \qquad (36)$$

To determine a_3 and a_5, we have only one equation (25). One more relation is needed. A more refined analysis than the present one must then be applied. A flow with both U and W non-zero must be considered, and the velocity influence on the coefficients a_i must be taken into account. In order to get a consistent theory, all the previous results would have to be modified. This is left for future work.

Moranville et al. (1977 a) found these constraints for the dispersion coefficients of layered media

$$a_0 + a_1 + a_2 + a_3 + a_4 + 2a_5 > 0 \qquad (37)$$

$$a_0 + a_1 > 0 \qquad (38)$$

$$a_0 + a_2 > 0 \qquad (39)$$

$$a_0 + a_4 > 0 \qquad (40)$$

$$a_4 > a_1 \qquad (41)$$

$$a_0 > 0 \qquad (42)$$

$$a_2 + a_3 + a_4 + 2a_5 > 0 \qquad (43)$$

$$a_1 + a_2 + a_3 + 2a_5 < 0 \qquad (44)$$

Our results are in perfect accordance with all eight constraints (37)-(44). Thus the limitations of our approximations are concealed.

CONCLUSIONS

Expressions for the dispersion coefficients of layered porous media have been derived. The analysis is approximate, based on the assumption that the velocity influence on these coefficients may be neglected. We found agreement with eight constraints derived by Moranville et al. (1977 a).

A general theory of dispersion in anisotropic media was developed by Bear (1969). A serious disadvantage is the central role of tortuosity in his theory, which causes obscure relations to observable quantities. Directly applicable theories in this field are still lacking. Crude approximations, like the present one, may be useful to provide preliminary information.

NOTATION

a_i = dispersion coefficients of transversely isotropic media ($i = 0,1,2,3,4,5$)
a_I = $A_I d$ = longitudinal dispersion coefficient of isotropic porous medium
a_{II} = $A_{II} d$ = lateral dispersion coefficient of isotropic porous medium
A_I, A_{II} = numbers characterizing longitudinal and lateral dispersion, respectively, in an isotropic medium
c = $f_1(s) f_2(n)$ = proportionality factor defined by Eq. (2)
$\underline{C}$ = concentration of tracer
$\bar{C}$ = average concentration of tracer
d_α = average grain diameter of layer α ($\alpha = 1,2$)
$\bar{D}_{ij}$ = component of average dispersion tracer; indices i and j taking values (1,2,3) corresponding to (x, y, z)-directions
$\underline{\mathcal{D}}$ = dispersion tensor
$\bar{\mathcal{D}}$ = $\sum_{i,j} \bar{D}_{ij}\vec{i}_i\vec{i}_j$
$\mathcal{E}$ = $\vec{i}\vec{i} + \vec{j}\vec{j} + \vec{k}\vec{k}$ = unit tensor
$f_1(s)$ = shape factor
$f_2(n)$ = porosity factor
h_1 = height of layer (1)
h_2 = height of layer (2)
$\vec{i}$, $\vec{j}$, $\vec{k}$ = unit vectors in x, y, z-direction
k_1 = permeability of layer (1)
k_2 = permeability of layer (2)
k_H = average horizontal permeability
k_V = average vertical permeability
$P^{(1)}$ = $(U_1^2 + W^2)^{1/2} d_1/\kappa$, Péclet number in layer (1)
$P^{(2)}$ = $(U_2^2 + W^2)^{1/2} d_2/\kappa$, Péclet number in layer (2)
$\vec{\bar{v}}$ = $U\vec{i} + W\vec{k}$ = average velocity
$\vec{v}^{(1)}$ = $U_1\vec{i} + W_1\vec{k}$ = velocity in layer (1)
$\vec{v}^{(2)}$ = $U_2\vec{i} + W_2\vec{k}$ = velocity in layer (2)
x, y, z = cartesian coordinates

Greek Letters

δ_1 = angle between velocity vector in layer (1) and x-direction
δ_2 = angle between velocity vector in layer (2) and x-direction

κ = molecular diffusivity of tracer in fluid
ξ = k_H/k_V = ratio between average permeabilities
ψ = velocity for the dispersion of a concentration front

Superscripts

(1) = quantity related to layer (1)
(2) = quantity related to layer (2)

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Kinetics of Parallel Dehydrogenation and Dehydration of Cyclohexanol on NiO-Al$_2$O$_3$ Catalyst Systems

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Although several investigators (Emelyanov et al. 1972, Rovskii et al. 1973, Ratnaswamy et al. 1970, Pillai and Kuloor 1974, Viswanathan and Yeddanapalli 1974) have studied of cyclohexanol decomposition, the reaction is more complex than had been recognized (Athappan 1979). The decomposition of cyclohexanol leading exclusively either to cyclohexene or to cyclohexanone has frequently been used as a model reaction in studying the mechanism of dehydration or dehydrogenation and in testing corresponding catalysts (Morita et al. 1970, Kuriacose et al. 1968). A quantitative study of the kinetics and mechanisms of the coupled systems, in general, where both reactions proceeded as parallel reactions has attracted little attention (Klissurskii et al. 1971, Jambor and Beranek 1975, Beranek 1975).

From the literature, it is evident that no systematic quantitative analysis of the experimental data on decomposition of cyclohexanol over NiO-Al$_2$O$_3$ system has been reported. Also, values of the rate coefficients and adsorption coefficients are unknown. Accuracy of the experimental data is of no guarantee of successful kinetic analysis when the experimental program suffers from lack of insight into the effect of different variables. Froment (1975) discussed in detail the estimation of parameters and emphasized the necessity of statistically testing the results.

In this investigation, increased emphasis is placed on model discrimination and parameter estimation. The reaction was studied at atmospheric pressure in the temperature range of 300-350°C where the homogeneous reaction was negligible. The experimental results are analyzed on the basis of Langmuir-Hinshelwood kinetics, with statistical interpretation to show the real significance of mechanism determination with precise experimental data.

CATALYST PREPARATION AND CHARACTERIZATION

Alumina supported catalysts containing up to 20 wt. % NiO were prepared by impregnating the alumina with an aqueous solution of nickel nitrate hexahydrate and dried at 110°C for 2 hours. The catalyst was then made into the cylindrical pellets, activated at 450°C for 12 hours. The entire characterization of the catalyst system by means of X-ray, i.r, d.t.a, t.g.a., electron microscopy and B.E.T. Studies has been reported elsewhere (Athappan 1979). The composition of the catalyst was chosen on the basis of Athappan's study, where it was established that the activity passed through a maximum over a catalyst composition of about 15% by weight of NiO on alumina calcined at 450°C for 12 hours. All runs in this study were performed exclusively with the catalyst of this composition (surface area = 87 m^2/g). Catalytic activity was defined as the number of moles of cyclohexanone formed/unit time/unit weight of the catalyst under the following conditions: feed liquid, pure cyclohexanol; W/F = 50 g/(gmole)(hr)$^{-1}$; cylindrical pellets (3 mm in diameter by 3 mm in length).

APPARATUS AND PROCEDURE

The flow system with general experimental procedures and method of analysis were described by Athappan (1979). To establish the experimental conditions for which the reaction rate was not influenced by external and internal diffusion, the influence of space velocity, catalyst mass and particle size was studied as in the usual manner (Ross and Walsh 1961). As a result of these preliminary studies, the kinetic measurements were performed at flow rates from 0.57-5.7 moles hr^{-1} (N.T.P.).

The cyclohexanol was fed by the calibrated metering pump into a preheater, where it was mixed with diluent N$_2$ gas and vaporized. The vapor was then led to the reactor containing the catalyst bed. The temperature of the catalyst bed was measured by an iron-constantan thermocouple located in a coaxial thermowell. Temperature control was achieved by diluting the catalyst bed with inert porcelain beads, in the ratio of 1:5 by volume. The main stream of the effluents from the reactor was cooled by condenser. The liquid condensate was analyzed by gas-chromatography and the gaseous products were metered.

A 254 mm long, 12 mm diameter, copper tube packed with 20% Carbowax 20M on Chromosorb P. (30-100 mesh) was used as an analyzing column in the chromatograph. Nitrogen was

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