ON THE CONCENTRATION DEPENDENCY OF INTRAPARTICLE EFFECTIVE DIFFUSIVITY FOR TETRAHYDROFURAN-ACTIVATED CARBON SYSTEM

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To make clear the mechanism of intraparticle diffusion at relatively high concentration ranges, the values of intraparticle diffusivity, Diq, of tetrahydrofuran (THF) within activated carbon pellets were measured at 308 K by use of two methods, i.e., the steady-state diffusion method and the flow method for fixed-bed adsorption. The two values of Diq obtained agreed with each other fairly well. Surface and pore diffusivities were calculated from Diq based on a concept of simultaneous occurrence of transfer through pore spacings and through surfaces. The value of surface diffusivity, Ds, thus calculated was almost equal to those reported for solvent vapor-activated carbon systems in lower concentration ranges. The value of pore diffusivity, Dp, calculated was close to that evaluated from molecular diffusion theory combined with Knudsen diffusion. It became clear that breakthrough curves numerically estimated using the values of Diq, variable with the change in amount adsorbed, fitted the experimental breakthrough curves more closely than those estimated by use of the values of diffusivity assumed to be constant irrespective of amount adsorbed for specific experimental runs.

Introduction

Adsorption of organic solvent from air at relatively low concentration, such as less than 0.1 vol%, by passing through a fixed bed of activated carbon is well known as a technique of solvent recovery. Under these conditions, it has already been pointed out that surface diffusion is predominant for intraparticle effective diffusion, i.e., transport of solvent within activated carbon particles,5,6,10) and methods of estimating the diffusivity from breakthrough curves have been developed by a number of investigators.2,3,6) Using values of the effective diffusivity, adsorbers can be designed and their performance can be predicted for a range of operating conditions. The estimation of the intraparticle effective diffusivity from breakthrough curve leads to comparatively large error; thus the values of diffusivity have to be compared with those obtained by other methods.

In recent years, the concentration of solvent vapors in the air treated by carbon bed often reaches as high as 0.5 to 2 vol%. In these cases, the values of intraparticle effective diffusivity, Diq, empirically obtained clearly increase with increasing amount of solvent adsorbed on carbon particles.

For the case where diffusion through pore spacings, i.e., pore diffusion, and that through pore surfaces, i.e., surface diffusion, take place simultaneously within adsorbent particles, Diq is expressed as follows12):

\[ Diq = Ds + Dp/(dq/dc)p \] (1)

where c denote adsorbate concentration of fluid, q is amount adsorbed in equilibrium with c, and dq/dc means differential coefficient of isotherm. Ds and Dp denote surface- and pore-diffusivity, respectively, and \( \rho_p \) is particle density.

Even if the information for q and c obtained from the analysis of fixed-bed breakthrough curves and/or from the steady-state diffusion method gives the mean values over the cross-sectional area of the fixed bed or in the particles of the adsorbents, it is evident that the value of dq/dc estimated from the values mentioned above decreases and thus the second term in the right-hand side of Eq. (1) increases, with increasing c in bulk phase, when favorable isotherm systems such as organic solvent vapor-activated carbon systems are considered.

For such systems, therefore, the concentration dependency of the intraparticle effective diffusivity Diq is also explained by the change in dq/dc with concentration.

The purpose of the present paper is to obtain the values of intraparticle effective diffusivity of tetrahydrofuran (THF) vapor within Takeda HGW 750 activated carbon by use of a method of steady-state diffusion and from the analysis of fixed-bed adsorption breakthrough curves, respectively, and to present a method of estimating effective surface diffu-
sivity and effective pore diffusivity based on a concept of simultaneous occurrence of transfer through pore spacings and through surfaces. Furthermore, breakthrough curves were calculated using the intraparticle diffusion equation based on the variable \( D_{iq} \) depending on the amount adsorbed, and were compared with experimental curves.

1. Equations

Regarding steady-state diffusion through pellets, the relation between the mass flow rate of adsorbate through the pellets, \( N \), and \( D_{iq} \) is expressed by Eq. (2).

\[-N = D_{iq}qAq(S/L)/l \]  
(2)

where the difference in the amount adsorbed \( (\Delta q) \) between a distance \( L \) is taken as the driving force. \( S \) denotes the surface area per unit length of pellets which contributes to diffusion, and \( l \) means the total length of pellets.

Assuming that intraparticle mass transfer takes place due to surface diffusion and pore diffusion, Eq. (2) can be written as follows.

\[-N = D_s qAq(S/L)/l + D_p qAq(S/L)/l \]  
(2')

Comparison of Eq. (2') with Eq. (2) brings about the following equation.

\[ D_{iq} = D_s + D_p qAq(S/L)/l \]  
(3)

where \( \Delta q \) and \( \Delta c \) are the difference of the amount adsorbed and the concentration at both sides of pellets, respectively. The value of particle density, \( \rho_s \), can easily be measured and is listed in Table 1.

The value of \((S/L)\) can be numerically obtained from Eq. (4) together with boundary conditions in the same manner as described elsewhere. The steps in evaluating \((S/L)\) are as follows:

1) Calculate distribution of amount adsorbed within a pellet by use of Eq. (4).

\[ r^2 \frac{\partial^2 q}{\partial r^2} + r \frac{\partial q}{\partial r} + \frac{\partial q}{\partial \theta} = 0 \]  
(4)

boundary conditions

\[ q = q_1 \quad \text{for} \quad \theta_1 < \theta < \frac{\pi}{2} \]

\[ \left( \frac{\partial q}{\partial r} \right)_{r=b} = 0 \quad \text{for} \quad -\frac{\pi}{2} < \theta < \theta_1 \]

\[ q = q_2 \quad \text{for} \quad -\frac{\pi}{2} < \theta < -\theta_2 \]

where \( r \) denotes radial length and \( b, x, y \) and \( \theta \) are shown in Fig. 1.

2) Estimate mean values of amount adsorbed at \( y = y_1 \) and \( y = -y_2 \) from the distribution and cross section.

3) Determine \((S/L)\) from Eq. (2) together with \( \Delta q \) obtained from boundary conditions and value of \(-N/D_{iq}qAq(S/L)/l\) which can be calculated from the values of amount adsorbed at \( y = y_1 \) and \( y = -y_2 \), and the diffusion area.

Therefore, the values of \( D_{iq} \) can be easily determined from Eq. (2) together with empirical values of \( \Delta q \), \( l \), \( \rho_s \) and the numerical value of \((S/L)\) mentioned above.

For fixed-bed adsorption, the effective intraparticle diffusivity can be obtained from breakthrough curves. The bed length for each run needs to be larger than that of the adsorption zone to apply the constant pattern concept. In fact, the constant length of adsorption zone, \( Z_a \), is usually formed when the bed length is larger than \((2-3)Z_a \) and the mass balance between fluid and particles can be expressed by the operational line during adsorption on adsorbent particles from fluid. Thus, substituting the slope of the operational line, \( \beta \) to mean value of \( dq/dc \) in Eq. (1), the following equation can be derived.

\[ D_{iq} = D_s + D_p qAq(S/L)/l \]  
(5)

Therefore, \( D_s \) and \( D_p \) can be determined from the values of the intercept and the slope in the linear relation between \( D_{iq} \) and \( \Delta c/\Delta q \) as Eq. (3) for the steady-state diffusion method, and the relation between \( D_{iq} \) and \( 1/\beta \) as Eq. (5) for fixed-bed adsorption, provided \( D_s \) is constant irrespective of the change in value of amount adsorbed throughout each run. For a system of strongly favorable isotherm, such as solvent vapor-activated carbon systems, the amount adsorbed \( q \) approaches a constant value rapidly with increasing concentration \( c \), and for higher concentration ranges, \( D_s \) seems to be almost constant even if \( q \) changes slightly with the change of \( c \).

Regarding estimation of breakthrough curves
Based on the simultaneous pore- and surface-diffusion concept, the numerical procedure is essentially similar to that for the case of surface diffusion controlling except that \( D_{\text{aq}} \) must be varied with the concentration in the pore spacings. That is, constant temperature, constant influent flow rate, plug flow (no radial concentration gradient in bulk phase), no gradient in solid-phase concentration for a certain cross section of the bed consisting of uniform spherical particles, simultaneous occurrence of both surface diffusion and pore diffusion within adsorbent particles, Langmuir-type isotherm, and equilibrium momentarily established on the pore surface of particles are assumed. Then the mathematical description of fixed-bed adsorption is given by the following equations.

Material balance in the bed

\[
\frac{\partial c}{\partial z} + \frac{\partial \bar{c}}{\partial t} + \gamma \frac{\partial \bar{q}}{\partial t} = 0
\]  

(6)

Rate equations

for fluid film transfer

\[
\frac{\partial \bar{q}}{\partial t} = k_f a_v (c - c_s)
\]

(7)

for transfer at interface

\[
\frac{\partial \bar{q}}{\partial t} = -D_{\text{aq}} \rho \rho_v \left( \frac{\partial q}{\partial r} \right)_{r=b}
\]

(8)

for intraparticle diffusion

\[
\frac{\partial q}{\partial t} = D_{\text{aq}} \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right)
\]

(9)

Equilibrium (Isotherm)

\[
q = \frac{q_a K c}{1 + K c}
\]

(10)

where \( \gamma \) is bed bulk density, \( e \) is void fraction of bed, \( k_f \) denotes fluid-film mass transfer coefficient, \( a_v \) is external area of particles, \( c_s \) is bulk concentration at the geometrical surface of particles, \( q_a \) and \( K \) are Langmuir constants, and the superscript bar denotes the mean value.

The procedure to obtain the fixed-bed breakthrough curves is almost the same as that previously reported,\(^{11}\) except that \( D_{\text{aq}} \) must be varied depending on \( c \) and \( q \).

Since the isotherm is given by Eq. (10), the term \( dq/dc \) in Eq. (1) can easily be obtained and \( D_{\text{aq}} \) can be calculated for further calculation of breakthrough curves by use of Eqs. (8) and (9). In the calculation of Eq. (8), an iteration method was used and for the calculation of amount adsorbed at next time \( t+\Delta t \) and radial position \( r \), the amount adsorbed derived from the term with respect to \( D_{\text{aq}} \) is original Eq. (8) was replaced by the value obtained from the previous iteration. The iterative calculation of Eq. (8) was discontinued when the increment for the amount adsorbed at each iteration became less than either 0.001% of the amount adsorbed at previous time or \( 10^{-10} \) kg/kg-adsorbent, whichever was larger.

2. Experimental

2.1 Steady-state diffusion

Activated carbon pellets, HGW 750 produced by TAKEDA Chem. Ind. and extra pure grade tetrahydrofuran (THF) were used as adsorbent and solvent, respectively, throughout the study. Physical properties of the sample are presented in Table 1.

The apparatus to measure steady-state diffusion is a so-called diffusion cell. The cell unit made of stainless steel had a diaphragm and two chambers, as shown in Fig. 2. Nine carbon pellets were horizontally fixed in holes in the diaphragm by use of epoxy resin. To decrease fluid-to-particle diffusion resistance, the linear velocity of air in both chambers must be increased. The volume of each chamber was about \( 2.4 \times 10^{-6} \) m\(^3\) and flow rate on both sides was maintained about \( 6.7 \times 10^{-6} \) m\(^3\)/s. The diffusion cell was thermostated at 308 K.

The pressure was maintained constant on both sides of the pellets. THF-laden air was introduced into the upper chamber, THF-free air into the lower chamber.

Concentration of THF in both air streams of constant flow rate was determined by passing them to a shorter bed and measuring the weight increase due to adsorption of THF for a certain period (before the breakthrough of THF took place). The equilibrium amount adsorbed for the respective streams was determined in the same way as above, except that a small amount of the activated carbon pellets was exposed to the streams until equilibrium was established.

2.2 Fixed-bed adsorption

HGW 750 carbon was crushed and a fraction of 8/12\# particles, i.e. mean particle diameter of \( 1.83 \times 10^{-3} \) m, was obtained and then dried with a nitrogen stream for 2 h or more at 413 K. The carbon particles were packed in a glass column of 2.2 \times 10^{-2} m i.d. and about 5 \times 10^{-2} m long.

As shown in Fig. 3, THF-laden air of constant concentration was supplied to the fixed bed of carbon particles and then THF concentration in the effluent was measured by a flame ionization detector (FID). Because the FID responds sensitively to change of THF concentration and to change of flow rate of the fluid introduced to the detector, the ratio of effluent concentration to influent concentration, \( c/c_0 \), was determined by the FID continuously at a scheduled flow rate of 0.3 m/s at 308 K, maintained precisely constant. The concentration of THF at equilibrium
was measured by an interferometer when the concentration of THF was rather high. However, when the influent concentration, \( c_0 \), was lower, \( c_0 \) was determined by exposing a short column filled with activated carbon to a THF-laden stream of \( c_0 \) for a certain time and then by measuring the increase in weight.

3. Results and Discussion

Concentrations of THF in the two streams from a diffusion cell were determined and the value of \( \Delta q \) was evaluated from the procedure mentioned above. The mass flow rate of THF through pellets, \( N \), was obtained from the concentration of THF and the flow rate on the side of lower concentration.

The values of intraparticle effective diffusivity, \( D_{iq} \), were determined from Eq. (3) or Eq. (5) based on those values with respect to various THF concentrations. The obtained values of \( D_{iq} \) and experimental conditions are summarized in Table 2.

Values of intraparticle diffusivity, \( D_{iq} \), were evaluated from breakthrough curves by use of the methods developed by the authors\(^2\) and/or by Kawazoe\(^6\) because the adsorption isotherm for the THF-HGW 750 system was well expressed by a Langmuir-type equation over the entire range of influent concentration studied here. The Langmuir constants, \( K \) and \( q_\infty \), for this system are 184 m\(^3\)/kg and 0.383 kg/kg-adsorbent, respectively.

From the results presented in Tables 2 and 3, it is clear that the values of \( D_{iq} \) obtained from the two methods mentioned above are almost the same and that they increase with increasing \( \Delta C/\Delta q \) or \( 1/\beta \). When \( D_{iq} \) listed in Tables 2 and 3 are expressed against \( \Delta C/\Delta q \) or \( 1/\beta \), an approximately linear relationship can be obtained, as shown in Fig. 4. From the positive slope of the straight line and the significant size of the second term in Eqs. (3) and (5) under conditions listed in Tables 2 and 3, it is clear that an appreciable amount of pore diffusion occurs simultaneously under the experimental conditions.

The value of effective surface diffusivity, \( D_s \), obtained from the intercept of the figure is \( 3.74 \times 10^{-10} \) m\(^2\)/s. It is almost the same order of magnitude as the values reported for organic solvents of almost the same molecular weight to THF-activated carbon systems.\(^6\) On the other hand, the value of effective pore diffusivity, \( D_p \), determined from the slope of the line is \( 1.05 \times 10^{-6} \) m\(^2\)/s. From a well-known method for estimating effective intraparticle pore diffusivity based on molecular diffusivity,\(^9\) Knudsen diffusivity\(^12\) and parallel and tortuous pore model, and taking tortuosity \( k^2 \) to be 3,\(^7\) the value becomes to be \( 1.12 \times 10^{-6} \) m\(^2\)/s. Therefore, the value of \( D_p \) estimated from Fig. 4 seems to be reasonable.

For the examination of mathematical validity of the present concept, the relative importance of the first term to the second in the right-hand sides of Eq. (3) and (5) must be further checked. Therefore, the ratio \( D_s/(D_p \Delta C/\Delta q \beta) \) or \( D_s/(D_p \beta \rho_p) \) is listed in Tables 2 and 3. The results range from 1 to 15 and the values indicate that the present concept can be applicable to analyze the concentration dependency of intraparticle effective diffusivity under the condition discussed here.

An alternative method to test the present diffusion concept will be performed by comparing the fixed-bed breakthrough curves with numerical results obtained, changing successively the value of \( D_{iq} \) in Eqs. (8) and (9) with the change of bulk concentration and amount adsorbed within the pore of adsorbents, respectively.

Although a number of papers have been presented for gaseous and/or aqueous systems under the condition of surface diffusion controlling,\(^1,2,6,11,12\) none of them has taken into account the dependence of \( D_{iq} \) on bulk and solid concentration in the pores due to simultaneous contribution of both surface diffusion and pore diffusion in non-linear isotherm systems, except Fleck's\(^1\) and Mansour's\(^6\) papers. Fleck estimated fixed-bed breakthrough curves under constant contribution of pore diffusion to overall transfer of...
adsorbate through pores of adsorbent particles. Because the value of \( dq/dc \) and thus the contribution of pore diffusion remarkably changes with solvent concentration in the pores for favorable isotherm systems such as THF-activated carbon discussed here, the numerical method presented by Fleck cannot be applied to the present system. Mansour briefly studied the contribution of pore-diffusion.

It is necessary to examine if the values of \( D_s \) and \( D_p \) obtained from the mean values during adsorption are useful for the estimation of \( D_{iq} \) at each point on the pore surface of the adsorbent. Therefore, breakthrough curves were calculated using Eqs. (6) to (10) for both cases, namely a) \( D_{iq} \) changes with the changes of bulk concentration and amount adsorbed based on the present concept and b) \( D_{iq} \) is constant. Figure 5 shows an example. The values of \( D_{iq} \) used in the calculation of curve b) were estimated by use of \( \beta \) as the mean value of \( dq/dc \) over the whole concentration range.

It will be concluded that concentration dependency of intraparticle diffusivity exists due to simultaneous surface diffusion and pore diffusion under the condition examined.

4. Conclusion

The values of intraparticle effective diffusivity, \( D_{iq} \), were determined from the measurement of steady-state diffusion and from the analysis of fixed-bed adsorption breakthrough curves for the tetrahydrofuran-activated carbon system. From the analysis of \( D_{iq} \) obtained on the basis of the simultaneous surface diffusion and pore diffusion concept for various concentrations of tetrahydrofuran in bulk fluid, the effective surface diffusivity, \( D_s \), was determined to be \( D_s = 3.74 \times 10^{-6} \text{ m}^2/\text{s} \) and the effective pore diffusivity, \( D_p \), as \( 1.05 \times 10^{-6} \text{ m}^2/\text{s} \) at 308 K.

The breakthrough curves will be calculated with better accuracy than by the previous methods when one uses the values of \( D_{iq} \) estimated from Eq. (3) or Eq. (5).

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Nomenclature

\[
a_v = \text{external area of particles per unit bed volume} \quad \left[ \text{m}^2/\text{m}^3\text{-bed} \right]
\]

\[
\text{Table 2. Experimental conditions and results for THF diffusion at 308 K}
\]

<table>
<thead>
<tr>
<th>Run</th>
<th>( c_0 \times 10^3 ) [kg/m³]</th>
<th>( c_{low} \times 10^3 ) [kg/m³]</th>
<th>( N \times 10^6 ) [kg/s]</th>
<th>( \Delta q ) [kg/kg]</th>
<th>( \Delta c/\Delta q ) [kg/m³]</th>
<th>( D_{iq} \times 10^{10} ) [m²/s]</th>
<th>( D_i(D_{iq}/\Delta q) ) [—]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>2.15</td>
<td>0.554</td>
<td>0.742</td>
<td>0.306</td>
<td>0.0703</td>
<td>4.85</td>
<td>3.34</td>
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<tr>
<td>P-2</td>
<td>4.00</td>
<td>0.851</td>
<td>1.14</td>
<td>0.323</td>
<td>0.124</td>
<td>5.75</td>
<td>1.90</td>
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<td>P-3</td>
<td>8.54</td>
<td>1.20</td>
<td>1.61</td>
<td>0.356</td>
<td>0.240</td>
<td>7.74</td>
<td>0.980</td>
</tr>
</tbody>
</table>

\( I = 0.0485 \text{ m}, S/L = 1.44 \).

\[
\text{Table 3. Experimental conditions and results for THF adsorption by fixed bed at 308 K}
\]

<table>
<thead>
<tr>
<th>Run</th>
<th>( c_0 \times 10^3 ) [kg/m³]</th>
<th>( u ) [m/s]</th>
<th>( 1/\beta ) [kg/m³]</th>
<th>( D_{iq} \times 10^{10} ) [m²/s]</th>
<th>( D_i(D_{iq}/\beta \rho \phi) ) [—]</th>
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<tr>
<td>F-1</td>
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<td>F-4</td>
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<td>0.31</td>
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</table>

Fig. 5. Comparison of an experimental breakthrough curve with calculated ones based on two diffusion models.
FLOWGRAPH REPRESENTATION OF THE MULTISTAGE PROCESS PROBLEM SOLUTION

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Key Words: Evaporation, System Engineering, Multistage Process, Flowgraph Representation, Process Simulation

Flowgraph representation for the solution of a multistage process problem is studied. The flowgraph unit is a graph which consists of vertex and directed edge, respectively, corresponding to variable and calculation technique (equation, matrix, and others). An algorithm for the construction of the overall flowgraph, which consists of all flowgraph units appearing in the problem, is proposed and applied to a multiple-effect evaporator process problem. The resulting overall flowgraph provides a visual inspection of essential aspects of the problem as well as the difficulty of the solution and calculation scheme. An example of computable flowgraph construction is included.

Introduction

In recent years, the application of computers to the analysis, design and operation of chemical process systems has been accepted as a basic tool. In this regard, much research effort has been devoted to obtaining an algorithm to solve the large-scale system of equations. However, in contrast to the works on partitioning and tearing of the system equations, published works on the representation of the calculation scheme are meager. We can see the concepts of the graph of flow in the studies of Steward\(^6\) and Himmelblau.\(^3\)

Recently, studies\(^4,7\) with graph application have