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QUARTERLY PROGRESS REPORT
ON
CONFIGURATIONAL DIFFUSION OF
ASPHALTENES IN FRESH AND
AGED CATALYST EXTRUDATES

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James A. Guin
A. Ray Tarrer

Chemical Engineering Department
Auburn University
Auburn, AL 36849

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Statement of Work

Configurational Diffusion of Asphaltenes in Fresh and Aged Porous Catalyst Extrudates

Objective: The objective of this research is to determine the relationship between the size and shape of coal and petroleum macromolecules and their diffusion rates i.e., effective diffusivities, in catalyst pore structures. That is, how do the effective intrapore diffusivities depend on molecule configuration and pore geometry.

Task 1. Relationship Between Effective Intrapore Diffusion Coefficients, Molecular Size and Pore Geometry.

Finite bath-type diffusion experiments will be performed using both coal and petroleum-derived macromolecular species, e.g. asphaltenes, as well as model compounds, e.g. porphyrins, polymers, of known molecular size. By monitoring the concentration of solute macromolecules in the bath, the effective intrapore diffusion coefficients will be determined through application of the appropriate diffusion equations. Macromolecular species concentrations will be monitored by size exclusion chromatography (SEC). Relationships will be sought between the size, and shape, e.g. planar, coil, of the diffusing solutes and the pore geometry (pore size distribution) of the catalyst support. The effects of molecule configuration and catalyst pore size distribution on the effective intrapore diffusivity will be examined. Specially prepared laboratory catalysts with very narrow pore size distributions and other model porous media, e.g. porous Vycor glass, will be utilized in the experiments. Pore structures of all catalysts and other porous media will be characterized by mercury porosimetry and surface area (BET) analysis.

Task 2. Effects of Solvent Composition, Solute Concentration, and Temperature on the Molecular Configuration and Diffusion Rate of Coal and Petroleum Asphaltenes in Catalyst Pores.

Diffusion experiments such as in Task 1 will be performed with varying solvent compositions, i.e., paraffinic-aromatic mixtures, to examine the effects of the state of molecular aggregation (self-assemblies) on the rates of diffusion of coal and petroleum asphaltenes in the catalyst pores. Similar experiments will be performed to study the effect of *temperature* and solute (macromolecule) *concentration* on the state of molecular configuration and aggregation on the resulting pore diffusivity.

Task 3. Assessment of Diffusional Limitations in Aged Catalysts

Diffusivity measurements such as conducted in Task 1 will be performed with both model compound and coal-derived macromolecular species using extrudate-type aged catalysts from laboratory experiments as well as aged catalysts obtained from actual coal liquefaction pilot plants such as the Wilsonville, AL Advanced Coal Liquefaction R & D Facility. From the experimental diffusivities so obtained, an evaluation of effects of changes in catalyst pore structure, e.g. tortuosity, pore plugging, shall be made. The changes in pore diffusivities associated with the pore structural changes caused by coke and metals deposition will be investigated, as compared with the fresh catalysts. An assessment of the relationship of increased diffusional limitations to coke and metals deposition in the catalyst pores will be made based on the results of the diffusivity measurements. The degree to which pore diffusivities can be restored to their original values by carefully controlled oxidation and/or extractive catalyst regeneration techniques also will be explored. The practical importance of these findings to coal liquefaction technology will be evaluated.

Summary

This quarter, we developed a mathematical diffusion model for catalyst with a nonuniform pore structure during the adsorptive diffusion process due to the adsorbed layer of solute molecules on the catalyst pore walls. Diffusion experiments with quinoline and polystyrene were performed. Effective diffusivities were obtained by fitting the experimental data with a diffusion model. Results showed that the uniform pore model did not satisfactorily represent the diffusion behavior of larger polystyrene molecules, which gave rise to very high tortuosity values. The shrinking pore model better represented the adsorptive diffusion uptake behavior of a solute from the surrounding bath, especially for a diffusing solute with larger molecule size. Adsorption of solute molecules on the catalyst pore walls further restricts the diffusion rate due to increased steric and hydrodynamic hindrance factors. The tortuosity factor could also increase during adsorptive diffusion process due to the increased constrictions caused by the adsorbed solute molecules.

Modeling and experiments for diffusion and adsorption with multi-component systems are still in progress.

Planned Work

Next quarter experiments using binary or multiple solute systems will be continued. A mathematical diffusion model with these binary or multiple solute systems will be developed, the numerical solution will be obtained. The diffusion behavior will be studied by fitting the experimental data with the diffusion model.

Effects of Solute Adsorption on Hindered Diffusion

Uptake Rates in Finite Bath Experiments

ADSORPTIVE DIFFUSION MODEL

When porous catalyst particles are immersed in a finite well stirred bath with constant volume containing solute and solvent, the solute molecules diffuse into the porous particle where they are adsorbed onto the solid surface. As a result of this diffusion-adsorption process, the concentration of solute in the surrounding bath is depleted. By monitoring the disappearance of solute in the bath, the diffusion parameters can be determined. A mathematical model was developed to describe the diffusion controlled uptake process.

Generally, in studies of this type, properties of the porous solid are considered to be uniform throughout the particle during adsorptive diffusion process. This assumption is valid if the adsorbed layers of solute do not significantly change the pore diameter, e. g., small solute molecule and/or low amounts of adsorption. However, in the model developed here, it is assumed that the values of porosity and pore size in the porous particle may be functions of time and radial position. This assumption results in an effective diffusivity which is also a function of time and radial position inside the particle. Thus, the model developed here is somewhat more general than previously used models which assumed constant average values for catalyst properties and a resulting constant effective diffusivity⁽¹⁻⁴⁾.

According to mass balance, the following mathematical model can be derived.

The solute mass balance in the porous particle is:

$$\frac{\partial (K_p \epsilon C)}{\partial t} + \frac{\partial (\rho_p Q)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 D_e \frac{\partial C}{\partial r}) \quad (1)$$

with initial and boundary conditions:

$$C|_{t=0} = 0 \quad (2)$$

$$\frac{\partial C}{\partial r}|_{r=0} = 0, \quad C|_{r=R} = C_b(t) \quad (3)$$

A material balance for the solute in the bath yields:

$$\frac{d(V_b C_b)}{dt} = -4\pi R^2 k (D_e \frac{\partial C}{\partial r})|_{r=R} \quad (4)$$

with the initial condition:

$$C_b|_{t=0} = C_{b1} \quad (5)$$

In the above equations, D_e is the effective diffusivity defined as

$$D_e = \frac{\epsilon K_p K_r}{\tau} D_m \quad (6)$$

in which K_p and K_r factors are restrictive diffusion parameters due to steric and hydrodynamic factors, respectively. These two factors were estimated by the following two expressions derived for spherical solutes diffusing in cylindrical pores⁽⁶⁻⁹⁾

$$K_p = (1 - \lambda)^2 \quad (7)$$

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (8)$$

where λ is the ratio of solute molecular diameter to catalyst pore diameter

$$\lambda = \frac{D_m}{D_p} \quad (9)$$

By defining the following dimensionless variables and constants, the above

equations can be put into dimensionless form, where the "0" subscript denotes properties of the original porous particle without adsorbed solute used as a reference state.

$$\xi = \frac{r}{R}, \quad t^* = \frac{K_{r0} D_{AB}}{\tau R^2} t, \quad \theta = \frac{C}{C_{b1}}, \quad \theta_b = \frac{C_b}{C_{b1}}, \quad \theta_q = \frac{Q}{Q_1} \quad (10)$$

$$g_1 = \frac{K_p e}{K_{p0} e_0}, \quad g_2 = \frac{K_p K_r e}{K_{p0} K_{r0} e_0}, \quad E_e = \frac{\rho_p Q_1}{K_{p0} e_0 C_{b1}}, \quad E_m = \frac{\rho_p Q_m}{K_{p0} e_0 C_{b1}}, \quad F = \frac{V_b \rho_p}{W_c K_{p0} e_0} \quad (11)$$

Functions g_1 and g_2 embody the radial dependence of catalyst properties, and reflect the *local* degree of pore clogging due to the adsorption of solute molecules on the pore walls. Constants E_e and E_m indicate the ratios of equilibrium adsorption capacity and monolayer adsorption capacity to catalyst pore fluid accumulation capacity, respectively, evaluated at initial diffusion conditions. F is the ratio of surrounding bath volume to the available catalyst pore volume.

Use of the above variables and constants gives the dimensionless model as

$$\frac{\partial (g_1 \theta)}{\partial t^*} + E_e \frac{\partial (\theta_q)}{\partial t^*} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(g_2 \xi^2 \frac{\partial \theta}{\partial \xi} \right) \quad (12)$$

$$\left(\frac{\partial \theta}{\partial \xi} \right) \Big|_{\xi=0} = 0, \quad \theta \Big|_{\xi=1} = \theta_b(t^*) \quad (13)$$

$$\theta \Big|_{t^*=0} = 0 \quad \xi < 1 \quad (14)$$

$$\frac{d\theta_b}{dt} = -\frac{3}{F} \left(g_2 \frac{\partial \theta}{\partial \xi} \right) \Big|_{\xi=1} \quad (15)$$

$$(\theta_b) \Big|_{t^*=0} = 1 \quad (16)$$

In the above equations, θ_q is the dimensionless solute adsorption. In this work,

the solute adsorption equilibrium was fitted by the Freundlich isotherm, viz.,

$$Q = mC^{\frac{1}{n}} \quad (17)$$

in which case, equation (12) can be expressed as

$$\frac{\partial (g_1 \theta)}{\partial t^*} + E_s \frac{\partial (\theta^{\frac{1}{n}})}{\partial t^*} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} (g_2 \xi^2 \frac{\partial \theta}{\partial \xi}) \quad (18)$$

Using experimental parameters E, F, and n, along with local expressions for g_1 and g_2 , the above equations were solved numerically using the Method of Lines and the IVPK subprogram in the IMSL package.

In the above model, if it is assumed that the pore structure of the catalyst is uniform and unchanged during the adsorption-diffusion process, then

$$\lambda = \lambda_0, \quad K_p = K_{p0}, \quad K_r = K_{r0}, \quad \epsilon = \epsilon_0, \quad \tau = \tau_0, \quad D_s = D_{s0} \quad (19)$$

and thus,

$$g_1 = 1, \quad g_2 = 1 \quad (20)$$

In this simple case, the numerical solution can be expressed as

$$\theta_b = \theta_b(t^*, E_s, F, n) \quad (21)$$

The diffusion model for this case is termed the *uniform pore model* which we used before.

On the other hand, if a significant layer of solute molecules adsorbs on the catalyst pore walls, this process will modify the pore structure through which the remaining molecules diffuse. In another words, the adsorbed solute molecules will further restrict the diffusion process by decreasing the local pore size. In this case, g_1 and g_2 are functions of time and radial position inside the particle. The mathematical diffusion model based on these assumptions is termed the *shrinking pore model*.

To obtain local expressions for g_1 and g_2 in the shrinking pore model, the

following assumptions were made. For convenience and simplicity, the pores in the porous particle were modeled as cylindrical capillaries with uniform cross sections, with the local pore cross-section area being linearly dependent on the amount of local solute adsorption, viz.,

$$A = A_0 - (A_0 - A_m) \frac{Q}{Q_m} = A_0 \left[1 - \left(1 - \frac{A_m}{A_0} \right) \frac{Q}{Q_m} \right] \quad (22)$$

In equation (22), A_m represents the pore cross section area with an adsorbed monolayer of solute molecules q_m . For a monolayer of spherical molecules of diameter D_m in a pore of diameter D_{p0} we have

$$A_m = \frac{\pi}{4} (D_{p0} - 2D_m)^2 \quad (23)$$

Hence, for the Freundlich adsorption isotherm, the *local* pore diameter can be expressed as

$$D_p = D_{p0} \left[1 - 4\lambda_0 (1 - \lambda_0) \frac{E}{E_m} \theta^{\frac{1}{n}} \right]^{\frac{1}{2}} \quad (24)$$

The local ratio of molecule size to pore size will be given by

$$\lambda = \lambda_0 \left[1 - 4\lambda_0 (1 - \lambda_0) \frac{E}{E_m} \theta^{\frac{1}{n}} \right]^{-\frac{1}{2}} \quad (25)$$

The ratio of local to initial porosity is

$$\frac{e}{e_0} = \frac{\lambda_0^2}{\lambda^2} = 1 - 4\lambda_0 (1 - \lambda_0) \frac{E}{E_m} \theta^{\frac{1}{n}} \quad (26)$$

and thus, functions g_1 and g_2 can be expressed as

$$g_1 = \frac{K_p e}{K_{p0} e_0} = \frac{\lambda_0^2}{\lambda^2} \frac{(1 - \lambda)^2}{(1 - \lambda_0)^2} \quad (27)$$

In this case, the local pore diffusivity is given by

$$g_2 = \frac{K_p K_r e}{K_{p0} K_{r0} e_0} = \frac{\lambda_0^2}{\lambda^2} \frac{(1-\lambda)^2}{(1-\lambda_0)^2} \frac{1-2.104\lambda+2.089\lambda^3-0.948\lambda^5}{1-2.104\lambda_0+2.089\lambda_0^3-0.948\lambda_0^5} \quad (28)$$

$$D_e = \frac{g_2 \tau_0}{\tau} D_{e0} \quad (29)$$

To avoid undue complexity, the tortuosity factor τ is considered as an average constant value independent of time and radial position, although the average value of τ during the adsorptive diffusion process will generally differ from the original value τ_0 prior to any solute adsorption.

By inserting equations (25), (27) and (28) into equations (12) to (16), the shrinking pore model can be solved numerically, and the solution will be given by

$$\theta_b = \theta_b(t^*, E_e, F, n, E_m, \lambda_0) \quad (30)$$

Comparison of the solutions for the uniform and the shrinking pore models, as shown in equations (21) and (30), respectively, shows that two additional model parameters are required for shrinking pore model, namely, E_m and λ_0 .

When the monolayer adsorption q_m (thus E_m) is much larger than the initial equilibrium adsorption q_i (thus E_e), and/or when the ratio of molecular size to initial pore size λ_0 is small, the shrinking pore model reduces to the uniform pore model. Physically, when the amount of monolayer adsorption is small, and/or when the solute molecule size is small, the effects of solute adsorption on the pore structure of a porous particle are negligible. For better understanding of this phenomenon, Figures 1 and 2 show the numerical solutions for typical values of E_e , F and n at different E_m and λ_0 , respectively. From Figure 1 it can be seen that for small values of E_m , the solutions for the uniform and

shrinking pore models are far apart. As E_m increases, the shrinking pore model approaches the uniform pore model. Similarly, as shown in Figure 2, when λ_0 is small, the shrinking pore model approaches the uniform pore model. Both Figures 1 and 2 show that the effect of an adsorbed layer of solute molecules acts to slow the diffusional uptake of solute from the bath, i. e., C_b/C_{bi} declines at a slower rate.

EXPERIMENTAL

1. Materials

Chemicals. Quinoline (99+%, Aldrich Chemical Company) and Polystyrene ($M_w=2514$, $M_w/M_n=1.09$, Aldrich Chemical Company) were used as solutes, HPLC grade cyclohexane (99.9+%, Fisher Scientific) was used as solvent. Quinoline and cyclohexane were pretreated with 4A molecular sieves prior to use to remove impurities and water.

Catalyst. A commercial NiMo/Al₂O₃ catalyst, Criterion 324, developed by Criterion Catalyst Company(formerly Shell), was used in this study. Catalyst samples were calcined at 573 K for 12 hours prior to use in diffusion experiments.

2. Apparatus and Procedures

Catalyst Properties. Catalyst pore volume, particle density and porosity were measured by pycnometry. Catalyst surface area was determined by the single point BET method using N₂. Pore size distribution was determined by Hg porosimetry to 60,000 psia.

Equilibrium Adsorption Isotherms. Equilibrium adsorption experiments were performed to measure solute uptakes by the catalyst at different equilibrium concentrations. Solutions

of 25 cc of quinoline or polystyrene in cyclohexane at various concentrations were placed in bottles containing $-45\ \mu\text{m}$ (-325 mesh) weighed catalyst particles. The bottles were placed in an environmental shaker for 2 weeks until equilibrium was attained. Temperature was controlled at 303 and 308 K for quinoline and polystyrene, respectively. Equilibrium concentrations of quinoline and polystyrene were determined by UV spectrophotometry at 274 nm and 262 nm, respectively.

Diffusion Experiments. Diffusion experiments were performed using the adsorptive uptake of solute (quinoline or polystyrene) from a finite bath surrounding the catalyst pellets. This approach has been used by a number of investigators⁽¹⁻⁴⁾. Experiments were performed in a magnetically stirred glass diffusion cell containing a wire screen basket for holding catalyst particles⁽¹⁾. Temperature was controlled at 303 and 308 K for quinoline and polystyrene, respectively. Catalyst samples were presaturated with cyclohexane before diffusion runs, during which the uptake of quinoline or polystyrene was monitored periodically by UV spectrophotometry.

RESULTS AND DISCUSSION

1. Adsorption Isotherms and Model Parameter Estimation

In order to fit the diffusion model with the experimental data, adsorption isotherms and certain properties of the diffusion system were required. Adsorption isotherms were obtained by fitting equilibrium data with the Freundlich equation (17). Figure 3 shows the isotherms for the adsorption of quinoline and polystyrene from cyclohexane, and Table 1 gives the corresponding Freundlich isotherm parameters m and n for these systems.

Figure 4 shows the pore size distribution for the Criterion 324 catalyst obtained by mercury injection. It can be seen that the catalyst has a fairly narrow unimodal pore size distribution, which can be represented reasonably well by an average pore diameter. The average pore diameter based on the pore volume and surface area measurements was estimated by equation (32)

$$D_p = \frac{4 V_p}{S} \quad (31)$$

Catalyst pore volume, particle density and porosity were measured by pycnometry, and catalyst surface area was determined by the single point BET method, and results are given in Table 1. The critical diameter of quinoline was calculated as 6.9 °A, based on the bond lengths, bond angles and atomic radii of the molecular structure. The hydrodynamic diameter of polystyrene in cyclohexane at 35 °C was estimated by the Mark-Houwink equation⁽⁵⁾ to be 23.2 °A. Molecular diffusivities of quinoline and polystyrene in cyclohexane were calculated by the Wilke-Chang and Stokes-Einstein equations, respectively. The monolayer adsorption q_m was estimated geometrically by the assumption of a equilateral-triangular arrangement of spherical molecules on the cylindrical pore walls of the catalyst.

2. Diffusion Experiments and Data Fitting with the Uniform Pore Model

Adsorptive diffusional uptake experiments for both quinoline and polystyrene from cyclohexane with Criterion 324 catalyst were performed. Table 2 gives the dimensionless model parameter values for these systems as calculated from equations (10) and (11). Figure 5 shows experimental data for the solute uptake in the surrounding bath

as a function of time, together with the curves fitted from the numerical solution using the *uniform pore model* with a tortuosity τ_0 of 1.9.

From Table 2, the ratios of E_c to E_m for quinoline and polystyrene are 0.41 and 0.62, respectively, and the values of λ_0 are 0.055 and 0.186, respectively. According to the discussions in the theoretical section, these values of E_c/E_m and λ_0 show that for the quinoline system, the effects of adsorption on catalyst pore structure during the uptake process will be less than those with the polystyrene system. As shown in Figure 5, the uniform pore model, which does not consider the effects of solute adsorption on the process, fits the experimental data for the diffusion of quinoline quite well with a tortuosity value of 1.9. However, when the uniform pore model is used for fitting the diffusion of polystyrene, with the same τ_0 of 1.9, a much faster uptake is predicted than is actually evidenced by the experimental data. In fact, as shown in Figure 5, the uniform pore model solution predicts that the quinoline and polystyrene uptake curves should lie very close together, when in reality, as shown by the experimental data points, the uptake of polystyrene is much slower, taking about 4 times as long as quinoline to decline to a C_b/C_{bi} value of 0.4. If the uniform pore model is forced to fit the experimental polystyrene data by adjusting the tortuosity value, a satisfactory fit is obtained by using an adjusted tortuosity of 7.6, as shown in Figure 5. This value is 4 times greater than the value of 1.9 used for quinoline system. Since the same catalyst is used for both quinoline and polystyrene systems, one might expect to a first approximation that the tortuosity would be about the same for both cases. On the other hand, there is reason to believe that in the hindered diffusion region, the tortuosity is a function of both the catalyst pore structure and the diffusing molecule size. This later

consideration would allow the use of two different tortuosity values, however, the value of 7.6 for polystyrene system is significantly greater than 1.9 and is at the upper limit of observed tortuosity values for the type of pore structure in alumina supported catalysts^(18,19). In light of this observation, a more reasonable rationale was sought for the relatively slower uptake of polystyrene as compared to quinoline. In particular, it was hypothesized that the slower uptake rate observed with the larger polystyrene solute resulted at least partly from a relatively thicker layer of adsorbed solute on the pore walls, with associated increased hindrance factors, rather than simply an increase in pore tortuosity, as required by the uniform pore model.

3. Application of Shrinking Pore Model

As discussed above, the slower than predicted uptake of polystyrene might be due to the adsorbed layer of polystyrene on the pore walls of the catalyst, thus decreasing the available pore size, and thereby further restricting the diffusion rate. In another words, due to the adsorbed polystyrene layer, the local pore diameter would be decreased, and λ increased. This would cause a reduction in the local values of the porosity and the hindrance factors K_p and K_r (equations (7) and (8)), with a corresponding decrease in effective diffusivity (equation (6)). A model incorporating these effects was developed earlier in the theoretical section and was termed the *shrinking pore model*.

Figure 6 shows the resulting fit of the same experimental data by the shrinking pore model for the diffusion of quinoline and polystyrene in cyclohexane with the Criterion 324 catalyst. Comparison of the fitted results in Figures 5 and 6 shows that for the quinoline

solute system, both the uniform and the shrinking pore models fit the experimental data equally well using a tortuosity value of 1.9. This behavior results from the small values of λ_0 (0.055) and E_e/E_m (0.41) evidenced by the quinoline system. As noted in the theoretical section, when the monolayer adsorption capacity q_m (thus E_m) is much larger than the initial equilibrium adsorption q_i (thus E_e), and/or the ratio of molecular size to the initial pore size λ_0 is quite small, the shrinking pore model reduces to the uniform pore model. Physically, this result derives from the fact that quinoline is a small molecule, and the amount of adsorption at the concentration level used in these experiment is much less than a monolayer.

For the diffusion of the polystyrene solute, comparison of the results in Figures 5 and 6 shows that the shrinking pore model using tortuosity of 1.9 fits the experimental data much better than the uniform pore model with the same value of tortuosity, even though the actual uptake is still somewhat slower. By adjusting the tortuosity value from 1.9 to 2.8, the shrinking pore model will satisfactorily fit the experimental data, as shown in Figure 6. In light of the previous discussion regarding the dependence of tortuosity on both the pore structure and the size of the diffusing molecule, such an increase from 1.9 to 2.8, a factor of only 1.5, seems reasonable. Furthermore, a tortuosity value of 2.8 is closer to normally observed values for catalysts of this type than the value of 7.6 required by the uniform pore model.

As discussed above, for the best fit of the experimental data, the *uniform pore model* required the tortuosity values of 1.9 and 7.6 for quinoline and polystyrene, respectively, with an average of 4.8. On the other hand, the *shrinking pore model* required

the tortuosity values of 1.9 and 2.8 for quinoline and polystyrene, respectively, with an average of 2.4. Since for the same catalyst, the tortuosity value should be about the same. If it is used the average tortuosity values of 4.8 and 2.3 for the uniform and shrinking pore models, respectively, the results are shown in Figure 7. It can be seen that the shrinking pore model much better described the experimental data than the uniform pore model, even though the fit is still not so satisfactory.

Table 3 compares the fitted results with the uniform and the shrinking pore models. For quinoline diffusion system, the initial values of λ and ϵ at the outer surface of the catalyst particles with the *shrinking pore model* are nearly the same as compared to those with the *uniform pore model*, and the fitted effective diffusivities are not far apart, 2.9 and $2.8 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. However, in the case of polystyrene, due to its larger molecular size and E_c/E_m ratio, the porosity ϵ with the *shrinking pore model* decreased to a very low level, even though the fitted effective diffusivities from *uniform* and *shrinking* pore models are not so significantly different, 0.088 and $0.11 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. Due to increased hindered diffusion effects, including steric and hydrodynamic, the effective diffusivity for polystyrene, $0.11 \times 10^{-6} \text{ cm}^2/\text{s}$, is much lower than that for quinoline, $2.8 \times 10^{-6} \text{ cm}^2/\text{s}$.

Conclusions

The shrinking pore model better represents the adsorptive diffusion uptake behavior of a solute from a surrounding bath, especially for a diffusing solute with larger molecule size. Adsorption of solute molecules on the pore walls of the catalyst further restricts the diffusion rate due to increased steric and hydrodynamic hindrance factors. The

tortuosity factor could also increase during adsorptive diffusion process due to the increased constrictions caused by the adsorbed solute molecules.

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Table 1. Measured and Estimated Parameters of Diffusion Systems

Properties of Criterion 324 catalyst	
shape	cylindrical
ratio of particle length to diameter	2.3
support	unimodal Al_2O_3
metals, wt%	
Ni	3.7
Mo	13.2
average pore diameter D_p , °A	125
porosity ϵ_p , cc/cc	0.66
pore volume, cc/g	0.47
particle density ρ_p , g/cc	1.40
surface area, m^2/g	150
initial tortuosity τ_0	1.9
Properties of quinoline/cyclohexane/Criterion 324 system	
molecular diameter D_m , °A	6.9
molecular diffusivity D_{AB} , $\cdot 10^5 \text{ cm}^2/\text{s}$	1.16
monolayer adsorption q_m , mg/g	77.9
Freundlich isotherm constant m	52.4
Freundlich isotherm constant n	7.03
Properties of polystyrene/cyclohexane/Criterion 324 system	
molecular diameter, °A	23.2
molecular diffusivity, $10^6 \text{ cm}^2/\text{s}$	2.42
monolayer adsorption q_m , mg/g	133.6
Freundlich isotherm constant m	97.7
Freundlich isotherm constant n	5.34
Diffusion conditions	
temperature, K	$(303 \pm 1)/(308 \pm 1)$
bath volume, cc	150
stirring speed, rpm	> 800

Table 2. Dimensionless Model Parameters for the Diffusion Systems

diffusion model parameters	solute	
	quinoline	polystyrene
n	7.03	5.34
E	2512	658
F	2357	473
E_m	6147	1068
λ_0	0.055	0.186
$q_i/q_m(E_c/E_m)$	0.41	0.62

Table 3. Fitted Results with the Uniform and Shrinking Pore Model for Quinoline/ and Polystyrene/Cyclohexane Systems

parameters	quinoline/CH/Criterion		polystyrene/CH/Criterion	
	uniform pore	shrinking pore	uniform pore	shrinking pore
λ	0.055	0.058 ^(a)	0.18	0.23 ^(a)
ϵ	0.66	0.60 ^(a)	0.66	0.41 ^(a)
τ	1.9	1.9	7.6	2.8
$D_e \cdot 10^6 \text{ cm}^2/\text{s}$	2.9	2.8 ^(a)	0.088	0.11 ^(a)

(a) Evaluated at outer surface of the catalyst particle at initial diffusion conditions

Fig. 1 C_b/C_{bi} vs. t^* at different E_m for Shrinking Pore Model with $E=1000$, $F=1000$, $n=3$, $\lambda_s=0.1$

Fig. 2 C_b/C_{bl} vs. t' for Shrinking Pore Model at different λ , with $E=1000$, $F=1000$, $n=3$, $E_m=1500$

Fig. 3 Equilibrium Adsorption Isotherms for Quinoline and Polystyrene in Cyclohexane with Criterion 324 Catalyst

Fig. 4 Differential Pore Size Distribution for the Criterion 324 Catalyst Obtained from Mercury Injection

Fig. 5. Fit of Experimental Data with Uniform Pore Model for the Uptakes of Quinoline and Polystyrene in Cyclohexane on Criterion 324 Catalyst

Fig. 6. Fit of Experimental Data with Shrinking Pore Model for the Uptakes of Quinoline and Polystyrene in Cyclohexane on Criterion 324 Catalyst

Fig. 7. Fit of Experimental Data with Same Value of τ Using Shrinking and Uniform Pore Models

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