Hindered Diffusion of Asphaltenes at Evaluated Temperature and Pressure

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Abstract

During this time period, we performed experiments to examine the effects of solvent composition on the diffusion controlled uptake of quinoline into alumina catalyst pellets. Of particular interest was the effect of solvent aromaticity on the diffusive uptake process. The uptake experiments were performed at a temperature of 300°C for the adsorptive diffusion of quinoline in a solvent mixture of mineral oil and 1-methyl naphthalene onto alumina catalyst pellets. These experiments were conducted in a 40 cm³ microautoclave, the use of which is more economical from both a purchasing and waste disposal standpoint due to the small quantities of solvents and catalysts utilized, and is also significantly safer at the higher temperatures. In order to study the effect of aromaticity of the solvent on the hindered diffusion-adsorption process, the experiments were performed at different volume fractions of 1-methyl naphthalene. Detailed calculations were made to estimate the effects of aromaticity, i. e., as reflected by the percentage of 1-methyl naphthalene in the solvent, on the diffusive properties of the solute. Model simulation results were then performed which showed that the mathematical model incorporating diffusion and adsorption mechanisms satisfactorily fitted the adsorptive diffusion of quinoline onto the alumina catalyst at 300°C with various solvent aromaticities. The logarithm of the adsorption constant at a particular volume fraction of 1-methyl naphthalene, obtained by simulating the experimental data with the model solution, was found to be linearly dependent on an aromaticity factor.

HINDERED DIFFUSION OF ASPHALTENES AT ELEVATED TEMPERATURE AND PRESSURE

Table of Contents

<u>Disclaimer</u>	1
<u>Abstract</u>	2
<u>Objectives</u>	4
<u>Executive Summary</u>	5
<u>Introduction</u>	6
<u>Experimental Section</u>	6
1. Materials	
2. Apparatus and Procedures	
<u>Results and Discussion</u>	8
Quinoline/(Mineral oil + 1-methyl naphthalene) System	8
1. Molecular weight estimation of mineral oil	
2. Viscosity of the mixture	
3. Effective and molecular diffusivities	
4. Experimental data	
5. Adsorption constant	
6. Equilibrium adsorption time	
7. Effect of aromaticity on hindered diffusion	
<u>Conclusions</u>	20
<u>Nomenclature</u>	26
<u>References</u>	27
<u>Planned Work</u>	52

Objectives

1. To investigate the hindered diffusion of coal and petroleum asphaltenes in the pores of catalyst particles at elevated temperature and pressure.
2. To examine the effects of concentration, temperature and solvent type on the intraparticle diffusivity of asphaltenes.

Executive Summary

A very recent article, relating to planning for the future at DOE labs, has noted the need for increased understanding of the interactions between catalyst pore sizes and asphaltene sizes (Chem. and Eng. News, March 29, 1999). In this paper, researchers at the Argonne Laboratory have noted that the size of asphaltene molecules is very dependent on the temperature, and this has a direct bearing on the optimal sizes of pores for supported catalysts. Our project seeks to investigate the relation between these two size factors as they relate to pore diffusion inside the catalyst pellets at various temperatures. In the current time period we have used the model compound quinoline to examine certain factors relating to pore diffusion, in particular, the aromaticity of the solvent at an elevated temperature of 300° C. Specifically, we performed experiments to examine the effects of solvent composition, in particular, the aromaticity, on the diffusion controlled uptake of quinoline into alumina catalyst pellets. The hindered diffusion of quinoline in a mixture of 1-methyl naphthalene and mineral oil into the pores of catalyst particles at a temperature of 300°C was studied. Experiments were conducted in a microautoclave system at varying volume fractions of 1-methyl naphthalene. The adsorption constant was determined by fitting the experimental diffusion uptake data with a mathematical model. As a result of the simulation, it was found that the logarithm of the adsorption constant was linearly dependent on the aromaticity of the system, and as the volume fraction of 1-methyl naphthalene increased, the degree of adsorption decreased. This is believed to be the result of competitive adsorption of the aromatic solvent on the surface of the catalyst. Parameter estimation calculations were performed to estimate properties of the diffusive system as a function of solvent composition. The simulation results showed that the mathematical model satisfactorily fitted the adsorptive diffusion of quinoline onto alumina at temperature of 300°C.

It is expected that the current MS student, Mr. Surya Vadlamani, working on the research project will graduate during the next time period, and it is planned to begin a new MS student on the project in the next few weeks, in order to allow for a period of overlap and training.

Introduction

Because many catalytic reactions are carried out at relatively high temperatures and pressures, it is advantageous to seek to understand diffusion and adsorption behavior at elevated temperatures and pressures in order to provide reasonable judgment in catalyst design and process development (Chem. and Eng. News, March 29, 1999). However, due to the experimental difficulties involved, very few investigators have studied pore diffusion and surface adsorption at high temperatures and pressures. In one study along this line, Seo and Massoth (1985) investigated effects of temperature on hindered diffusion of polyaromatic model compounds into alumina. These investigators concluded that the hindrance factor $K_r K_p$ was a function of temperature; however, their temperature covered a rather limited range of from 25°C to 50°C. Our work has extended the temperature range up to 300° C and in this report we have investigated the effects of solvent composition on the uptake process.

Thus, in the current time period, diffusion experiments were performed to investigate the effect of solvent composition on the adsorptive uptake of the solute in a binary mixture. The effect of introducing aromaticity in the solvent was also studied. This was effected by conducting experiments with quinoline as the solute and a mixture of mineral oil and 1-methyl naphthalene as the solvent. Experiments were conducted varying the percentage of 1-methyl naphthalene in the binary mixture.

Experimental Section

Materials

In adsorptive diffusion experiments, quinoline (Aldrich) was used as solute and a mixture of light mineral oil (Humco) and 1-methyl naphthalene (Aldrich) was used as solvent. A commercial alumina catalyst (Johnson Mathey, Lot #A27E03), with a cylindrical shape, 0.33 cm in diameter and 0.36 cm in length, and having a surface area of 100 m²/g, was used as the adsorption-diffusion medium. Additional properties of the catalyst are given in Table 1.

Apparatus and Procedures

The effect of solvent composition on the adsorptive uptake of quinoline in a mixture of mineral oil and 1-methyl naphthalene as the solvent was studied. The binary mixed solvent was prepared at volume fractions of 0.25, 0.50 and 0.75 of 1-methyl naphthalene. The molecular weight of mineral oil had to be estimated as the effective diffusivity of quinoline in the binary mixture of mineral oil and 1-methyl naphthalene depended on the mole fraction of mineral oil. The molecular weight of mineral oil was estimated by GC analysis described in the next section. The diffusion-controlled adsorptive uptake of quinoline in the mixture of 1-methyl naphthalene and mineral oil was carried out in a microautoclave batch reactor where the alumina particles were supported on a wire mesh which avoided direct contact with the solution until the experiment was begun by immersing the microautoclave in a heated fluidized sand bath. Prior to immersion, the microautoclave was purged with helium 5 times to remove any air in the system and was pressurized up to 300 psig with helium.

The microautoclave was attached to a horizontal agitator and lowered into a fluidized sand bath at the desired temperature which was controlled by a thermostat and runs were made at fixed time intervals with an initial solute (quinoline) concentration corresponding to 100 ng N/ μ L. The catalyst particles were initially in a dry condition and experiments were conducted for various time intervals, following which the liquid phase was collected and analyzed to determine the concentration of solute remaining in the liquid.

The adsorptive uptakes were conducted at a temperature of 300°C. The composition of the solvent was varied from 25 - 75% (volume) of 1-methyl naphthalene. A nitrogen analyzer was used to determine quinoline concentration remaining in the liquid phase following the uptake experiments in order to determine the amount of solute adsorbed onto the catalyst surface.

Results and Discussion

Properties of the Quinoline/(Mineral oil + 1MN) System

In order to perform model simulations of the diffusion-controlled uptake process, it is necessary to have properties of the diffusing system such as viscosities and densities. In this section we discuss the various estimation techniques, and experimental methods which were used to obtain this information for the quinoline/(mineral oil + 1MN) system.

Molecular weight estimation of mineral oil

The molecular weight of mineral oil was estimated since the molecular diffusivity of quinoline in the binary mixture of 1-methyl naphthalene and mineral oil depended on the mole fraction of mineral oil in the mixture. The mineral oil used in our work is a mixture of a range of hydrocarbons with different weight fractions. To estimate its composition, the mineral oil was analyzed on a gas chromatograph via ASTM D-2887 whereby a boiling point distribution as a function of the cumulative weight percent was obtained as shown in Figure 1. This data was then reduced to weight percents in five discrete temperature ranges as plotted in Figure 2. Then the individual weight fractions in these five ranges were related to the carbon number using the data available in ASTM (D2887-89) which gave the boiling points of normal paraffins from C₂ to C₄₅. This particular boiling point data is plotted in Figure 3 where it is observed that there exists a linear dependence between the logarithm of the carbon number and the boiling point, viz.

$$\ln(n) = 0.0042T + 1.5403 \quad (1)$$

From the above sets of data the weight percent distribution of mineral oil as a function of carbon number was obtained and is shown in Figure 4. Using this distribution, the average molecular weight of our mineral oil was then estimated to be 296 which corresponds to a carbon number of 21 indicating that the average boiling point of the mineral oil would be approximately 350°C. This average boiling point is in fairly good agreement with the 50% cut point in Figure 1. Utilization of this average molecular weight allows computation of the solvent compositions on a molar basis, as needed for several correlation equations in the following sections.

Estimation of viscosity of the mixture

In order to perform the model simulation calculations for the adsorptive uptake of quinoline in the mixture of 1MN and mineral oil, it is necessary that the effective diffusivity of quinoline in the mixture be estimated. This property depends on the viscosity of the solvent mixture through which the quinoline is diffusing. Since the amount of quinoline is negligible (mole fraction of quinoline = 1.85×10^{-3}) the solvent is assumed to be of pseudo-binary composition. The effective diffusivity of a solute in a binary solvent depends on the viscosity of the mixture which in turn is dependent on the individual viscosities. Hence the viscosity of the solvent at different volume fractions of 1MN has to be estimated. To calculate the mixture viscosity Lobe's equation (Lobe, 1973) is used which for binary mixtures is expressed as

$$u_m = \Phi_A u_A e^{\Phi_B a_A^*} + \Phi_B u_B e^{\Phi_A a_B^*} \quad (2)$$

where

v_m = kinematic viscosity of the mixture η/ρ , cSt

ϕ_j = volume fraction of the component j

α_j^* = dimensionless constant for the component j

If A is chosen as the component with lesser viscosity then

$$a_A^* = -1.7 \ln \frac{u_B}{u_A}$$

$$a_B^* = 0.27 \ln \frac{u_B}{u_A} + \left(1.3 \ln \frac{u_B}{u_A} \right)^{1/2}$$

The viscosity of the mixture at 300°C can be obtained if the individual kinematic viscosities at 300°C are known. The viscosity of mineral oil at 300°C is given in Table 2, the value being 0.2865 cP. The viscosity of 1-methyl naphthalene at 300°C is obtained from Yaws Handbook of Viscosity (Yaws, 1995) as 0.22 cP. Since the viscosity of 1MN is less than that of mineral oil, component A is chosen to be 1MN. It is assumed that the sum of the volume fractions of mineral oil and 1MN is equal to one since the mole fraction of quinoline is negligible. Substituting the

values of the parameters in the Lobe's equation for the viscosity of the mixture equation (2) can be written as

$$\mathbf{u}_m = 0.533\mathbf{f}_{MN} \exp(-0.8762\mathbf{f}_{MN}) + 0.345(1 - \mathbf{f}_{MN}) \exp(-0.7494\mathbf{f}_{MN}) \quad (2.1)$$

where ϕ_{MN} is the volume fraction of 1MN.

The expression obtained for the kinematic viscosity of the mixture is plotted as a function of ϕ_{MN} in Figure 5.

The density of the mixture is a function of the individual densities and the volume fractions of 1MN and mineral oil. Assuming a simple mixing rule for the volumes ie., the volume of the mixture is equal to the sum of the individual volumes, the expression for the density of the mixture of mineral oil and 1MN can be given by

$$\mathbf{r}_m = \mathbf{r}_{MN}\mathbf{f}_{MN} + \mathbf{r}_{MO}\mathbf{f}_{MO} \quad (2.1.a)$$

The densities of 1MN and mineral oil are shown in Tables 2 and 3, the values being 0.999 g/cc and 0.835 g/cc respectively. The density of the mixture can be expressed as

$$\mathbf{r}_m = 0.835\mathbf{f}_{MO} + 0.999\mathbf{f}_{MN} \quad (2.1.b)$$

But since the mole fraction of quinoline in the present system is negligible (approximately equal to 1.85×10^{-3}) it can be said that the sum of the volume fractions of mineral oil and 1MN is equal to one. i.e.,

$$\mathbf{f}_{MN} + \mathbf{f}_{MO} = 1 \quad (2.1.c)$$

Substituting for the volume fraction of mineral oil from equation (2.1.c) into equation (2.1.b) an equation for the density of the mixture of mineral oil and 1MN can be obtained in terms of the volume fraction of 1MN and is given by

$$\mathbf{r}_m = 0.83 + 0.17\mathbf{f}_{MN} \quad (2.2)$$

In the above equations, the units for ρ_m are g/cc.

Since the kinematic viscosity is related to the viscosity by the following expression

$$\nu = \eta / \rho$$

the mixture viscosity η_m is given by the following expression

$$\mathbf{h}_m = (0.533\mathbf{f}_{MN} \exp(-0.8762\mathbf{f}_{MN}) + 0.345(1 - \mathbf{f}_{MN}) \exp(-0.7494\mathbf{f}_{MN})) (0.83 + 0.17\mathbf{f}_{MN}) \quad (2.3)$$

The above expression for the viscosity is plotted as a function of the volume fraction of 1MN in Figure 6. The mole fraction of 1MN can be expressed in terms of the volume fraction as follows

$$x_{MN} = \frac{\frac{r_{MN} f_{MN}}{M_{MN}}}{\frac{r_{MN} f_{MN}}{M_{MN}} + \frac{r_{min} (1 - f_{1MN})}{M_{MO}}} \quad (2.4)$$

where ρ_{MN} and ρ_{MO} are the densities of 1MN and mineral oil respectively. M_{MN} and M_{MO} are the molecular weights of 1MN and mineral oil respectively. Substituting for the densities and the molecular weights, equation (2.4) can be written as

$$x_{1MN} = \frac{0.696 f_{MN}}{0.28 + 0.416 f_{MN}} \quad (2.4.a)$$

From equations(2.3) and (2.4) it is possible to obtain an expression for the mixture viscosity in terms of the mole fraction of 1MN in the form of

$$h_m = f(x_{MN}) \quad (2.4.b)$$

The viscosity of the mixture is obtained using equation (2.3) for different volume fractions of 1MN. Equation (2.4.b) is plotted against the mole fraction of 1MN in Figure 7. Because equation (2.4b) is a fairly complex functional form if written out completely, a simpler curve fitted relationship was derived by plotting the logarithm of the viscosity of the mixture vs. the reciprocal of the mole fraction of mineral oil. As shown in Figure 8 the true mixture viscosities as obtained from equation (2.4.b) agree relatively well with this relation expressed as:

$$-\ln(\eta_m) = 44.677 / X_{MO} - 55.105 \quad \text{for } X_{MO} > 0 \quad (2.5)$$

But since $X_{MO} + X_{MN} = 1$ for relatively small mole fractions of quinoline equation(2.5) can be expressed in terms of the mole fraction of 1MN as:

$$-\ln(\eta_m) = 44.677 / (1 - X_{MN}) - 55.105 \quad \text{for } X_{MN} < 1 \quad (3)$$

These empirical relationships can be used to estimate the viscosities of the mixture at different mole fractions of mineral oil.

Effective and molecular diffusivities for the system of quinoline as solute and a mixture of 1MN and mineral oil as solvent

A key parameter needed in order to perform the model simulation calculations for the diffusive system is the effective diffusivity of the solute, quinoline, in the catalyst pores. In the present system a case of multicomponent diffusion occurs because the solute (quinoline) diffuses through a homogenous solution of mixed solvents, mineral oil and 1-methyl naphthalene. Since the solute is dilute, there are no concentration gradients for the solvent species and one can speak of a single solute diffusivity with respect to the mixture D_{Am}^0 . Perkins and Geankoplis (Perkins and Geankoplis, 1969) evaluated most of the methods to evaluate D_{Am}^0 with available data and suggested the following correlation

$$D_{Am}^0 h_m^{0.8} = \sum_{\substack{j=1 \\ j \neq A}}^n x_j D_{Aj}^o h_j^{0.8} \quad (4)$$

where

D_{Am}^0 = effective diffusion coefficient for dilute solute A into mixture

D_{Aj}^o = infinite-dilution binary diffusion coefficient of solute A into solvent j

x_j = mole fraction of j

h_m = mixture viscosity, cP

h_j = pure component viscosity, cP

The molecular diffusivity of quinoline in neat mineral oil is given in Table 2, as 6.08×10^{-5} cm²/s. The molecular diffusivity of quinoline in pure 1MN is estimated according to the Scheibel relation (Scheibel, 1954) which is a modification of the Wilke-Chang equation eliminating the association factor and is given by

$$D_{AB}^o = \frac{KT}{h_B V_A^{1/3}} \quad (5)$$

where K is determined by

$$K = 8.2 \times 10^{-8} \left[1 + \left(\frac{3V_B}{V_A} \right)^{2/3} \right] \quad (6)$$

and

D_{AB}^o = mutual diffusion coefficient of solute A at very low concentrations in solvent B, cm²/s

T = absolute temperature

h_B = viscosity of solvent B, cP

V_A = molal volume of solute A at its normal boiling temperature, cm³/g-mol

V_B = molal volume of solute B at its normal boiling temperature, cm³/g-mol

Both V_B and V_A are calculated according to Tyn and Calus method (Tyn and Calus, 1975) where the molar volume at the normal boiling point is related to the critical volume by the following expression

$$V_b = 0.285 V_c^{1.048} \quad (7)$$

It has been found that the critical volumes of 1MN and quinoline are 437cc/g-mol and 445cc/g-mol respectively (Reid, Prausnitz and Sherwood, 1977). The molecular diffusivity of quinoline in 1MN is estimated from equations (5), (6) and (7), to be 1.205×10^{-4} cm²/s. The molecular diffusivity of quinoline in the mixture of 1MN and mineral oil can now be expressed by equation (4) as

$$D_\infty = \frac{X_{1MN} D_{\infty, MN} h_{MN}^{0.8} + X_{MO} D_{\infty, MO} h_{MO}^{0.8}}{h_m^{0.8}} \quad (8)$$

Substituting the values of the individual molecular diffusivities and viscosities and since $X_{MO} + X_{MN} = 1$, the preceding expression can be written as

$$D_\infty = \frac{2.2366 + 1.353 X_{MN}}{h_m^{0.8}} \times 10^{-5} \text{ cm}^2/\text{s} \quad (8.1)$$

The dependence of the mixture viscosity on the mole fraction of 1MN can be obtained from equations (2.3) and (2.4.a) and the molecular diffusivity of quinoline in the mixture of 1MN and mineral oil is calculated using equation (8.1) for different mole fractions of mineral oil. The resulting molecular diffusivity as given by equation (8.1) is plotted as a function of the mole fraction of 1MN in Figure 9.

The effective pore diffusivity D_e is estimated using the following equation

$$D_e = \frac{K_p K_r e}{t} D_\infty \quad (9)$$

where K_p and K_r are hindered diffusion model parameters due to steric and hydrodynamic factors respectively. For spherical solutes diffusing in cylindrical pores they are given by

$$K_p = (1 - \lambda)^2 \quad (9.1)$$

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (9.2)$$

Here $\lambda = d_m/d_p$, where d_m is the solute molecule diameter and d_p is the catalyst pore diameter. Substituting the values of K_p , K_r , ε and τ in equation (9), the effective diffusivity of quinoline in the mixture of 1MN and mineral oil can now be expressed as

$$D_e = \frac{0.388 + 0.2347 X_{MN}}{h_m^{0.8}} \times 10^{-5} \text{ cm}^2/\text{s} \quad (10)$$

The above equation for the effective diffusivity is plotted vs. the mole fraction of 1MN in Figure 10 where it is observed to increase with increases in the mole fraction of 1MN.

The effective diffusivity of quinoline in the mixture of 1MN and mineral oil is plotted against the mole fraction of mineral oil as shown in Figure 11. By performing a curve fit procedure as shown in Figure 11, a relatively simpler empirical quadratic dependence can be determined to exist between the effective diffusivity, D_e and the mole fraction of mineral oil as given by

$$D_e \times 10^6 = 7.159 X_{MO}^2 - 17.164 X_{MO} + 20.63 \quad (11)$$

where D_e is in cm^2/s . Tables 4-6 give a summary of the parameter values as estimated in the previous sections for the diffusing system considered in the present work.

Comparison of Experimental Diffusion Uptake Data with Model Simulations

The experimental data obtained in the uptake studies during this time period are shown in Tables 7 and 8. The experimental data shown in Table 7 for the effect of solvent composition on the adsorptive uptake of quinoline in a mixture of mineral oil and 1-methyl naphthalene at volume fractions of 0.25, 0.50 and 0.75 of 1-methyl naphthalene at 300°C was compared to model simulations as shown in this section. The volume fractions correspond to mole fractions of 0.453, 0.713 and 0.881 of 1-methyl naphthalene respectively. Figure 12 shows a comparison between experimental data and model simulation at three different values of K (5, 2.9 and 1cc/g) for the adsorptive uptake of quinoline in a mixture of 25% 1MN and 75% mineral oil onto alumina at 300°C. The value of K which best fits the experimental data for the quinoline / (25% 1MN, 75% Mineral oil) system at 300°C obtained from least square analysis is 2.9 cc/g. In order to further validate and confirm this value of K, additional validation experiments were performed for each solvent mixture at a different solution volume/catalyst weight (V/W) ratio. Figure 13 shows such a validation of the value of K for the above conditions. The experimental data at 50 and 75% 1MN was compared with model simulations for different values of K as shown in Figures 14 and 16, respectively. The values of K later obtained from a least square analysis were validated for the respective systems in Figures 15 and 17 respectively. The values of K obtained for the quinoline/ (50% 1MN, 50% Mineral oil) system and the quinoline/ (75% 1MN, 25% Mineral oil) were 1 and 0.5cc/g respectively.

Behavior of Adsorption Constant

As shown in the previous section, the adsorption constant, K for the given system of quinoline/1MN/Mineral oil was estimated at 0.25, 0.50 and 0.75 volume fractions of 1MN by comparison of the experimental data with the simulation model. A least squares analysis was done to estimate the value of K for the given volume fraction of 1MN and the resulting K values are summarized in Table 9 and are plotted against the mole fraction of 1MN in Figures 18 and 19. From these results it is apparent that the adsorption constant for the given system decreases and the effective diffusivity of quinoline in the mixture of 1MN and mineral oil increases as the concentration of 1MN increases. In one sense, this implies that an increase in aromaticity of the system causes effects somewhat, although not entirely, similar to an increase in temperature.

From the results shown in Figures 18 and 19, the following dependencies of the adsorption constant on the mole fraction of 1MN were found to exist. These are:

$$K = 7.6507 X_{MN}^2 - 15.594 X_{MN} + 8.2582 \quad (12)$$

and

$$\ln(K) = 2.2323 - 3.1848 X_{MN} \quad (13)$$

In both the above equations it is assumed that $X_{MO} + X_{MN} = 1$ since $X_{quinoline}$ is negligible (approximately equal to 1.85×10^{-3}).

Equilibrium Adsorption time

Effect of Composition

In Figures 12-17 it can be seen that most of the adsorption occurs early in the process and that the concentrations reach equilibrium rather quickly. This process can be examined by focusing on the expression for the dimensionless time t^* in the hindered diffusion model development which is given by

$$t^* = \frac{D_e}{(K_p e + r_p K) R^2} t \quad (14.1)$$

If we let

$$A = \frac{1}{1 + \frac{K r_p}{K_p e}} \quad (14.2)$$

then equation (14.1) can be solved for the actual diffusion time as

$$t = \frac{K_p e R^2 t^*}{D_e A} = \frac{F}{D_e A} \quad (14.3)$$

where F is a constant equal to $K_p e R^2 t^*$

The denominator of equation 14.3 is a function of system temperature and composition. It was seen from equation (10) previously that the effective diffusivity increased with increases in the mole fraction of 1MN. It can also be seen from equation (14.2) that A increases with increases in the mole fraction of 1MN because the adsorption constant K decreases. Since both factors in the product $D_e A$ in equation (14.3) increase with increases in the mole fraction of 1MN, the actual time taken for the adsorption process decreases with increases in the mole fraction of 1MN.

In light of these results, the actual time required for the system to reach adsorption equilibrium as a function of solvent composition was examined in greater detail. Since the adsorption system under consideration i.e., Quinoline/(Mineral oil + 1MN) theoretically takes infinite time to reach complete equilibrium, the time taken to achieve finite amounts of 75 and 95% of the equilibrium adsorption was obtained by incorporating the following equation into the computer program which gives the time taken to achieve a given percentage of equilibrium adsorption for a given temperature and a given value of V/W for the quinoline/mineral oil system.

$$\left(1 - \frac{C_b}{C_i}\right)_t = \frac{p}{100} \left(1 - \frac{C_b}{C_i}\right)_{t=\infty}$$

Here p is the percentage of equilibrium adsorption for which the time is desired to be estimated. Figure 20 shows the time taken for 75 and 95% of equilibrium adsorption to take place for the Quinoline/ (25% 1MN + 75 % Mineral oil) and Quinoline/ (50% 1MN + 50% 1Mineral oil) respectively. It can be observed that both t_{75} and t_{95} decrease as the volume fraction of 1MN increases in the system. For a typical value of V/W of 10, 95% of equilibrium adsorption is attained in about 0.55 hours for the system containing 25% of 1MN and is attained in about 0.25 hours for the system containing 50% of 1MN. These short values for the equilibrium times can be explained in terms of the adsorption constants and the diffusivity coefficients by looking at the expressions detailed in equations (14.1), (14.2) and (14.3). As noted above, as the concentration of 1MN in the solvent increases, the value of K decreases (A increases) and the effective diffusivity of quinoline in the solvent increases. Hence the system attains equilibrium very quickly.

Effect of Temperature

Based on our work in earlier reports, we have found that the effect of temperature on the equilibrium adsorption time is more significant than the effect of composition. Temperature effects both key parameters in the hindered diffusion model, the effective diffusivity D_e and the adsorption constant K. Based on our previously reported work, we have found that an increase in temperature increases the effective diffusivity and lowers the adsorption constant. A decrease in the adsorption constant K results in an increase in the constant A as shown in equation (14.2). Therefore, an increase in the temperature increases the product $D_e A$ and as shown in equation (14.3) the actual time for the system to reach equilibrium decreases. Results of calculations based

on the simulation model at different temperatures are shown in Figures 21 and 22, respectively illustrating the effect of temperature on the time taken for 75 and 95% of equilibrium adsorption (Vadlamani , 1999). It can be seen from these two figures, that the effect of temperature on the rate of approach to equilibrium is quite dramatic.

Effect of aromaticity

Solvent composition as embodied by the aromaticity can play an important role in the process of hindered diffusion-adsorption under consideration. To explore this solvent composition factor, in the present work, variable amounts of aromaticities were introduced into the solvent in the form of 1-methyl naphthalene. To model the system, we have assumed that the base solvent, mineral oil, is a mixture of a range of paraffins and hence does not contribute to the aromaticity in the system. In this context an aromaticity factor is defined for the system. The aromaticity factor f_a for a solute/solvent system is defined to be the ratio of the number of aromatic carbons to the total number of carbons in the solvent. 1- methyl naphthalene which has a chemical formula of $C_{10}H_7CH_3$ has the following structural representation

As can be seen above 1- methyl naphthalene has a methyl group attached to one of the benzene rings. The number of aromatic carbons in 1MN is ten. It may be recalled that the molecular weight of mineral oil was estimated to be 296 which corresponds to a formula of $C_{21}H_{44}$. For a basis of 100 moles of a mixture of 1MN and mineral oil the aromaticity factor f_a is given by the following formula

$$f_a = \frac{100x C_{aromatic}(1MN)}{100x C_{total}(1MN) + 100(1-x) C_{total}(min)} \quad (15)$$

Where

x = mole fraction of 1MN

$C_{\text{aromatic}}(1\text{MN})$ = Number of aromatic carbon atoms in 1MN = 10

$C_{\text{total}}(1\text{MN})$ = Total number of carbon atoms in 1MN = 11

$C_{\text{total}}(\text{min})$ = Total number of carbon atoms in mineral oil = 21

The aromaticity factor values can now be calculated for different volume fractions of 1MN. For a given volume percent ϕ_{MN} of 1MN the mole fraction of 1MN can be estimated by the formula given in equation (2.4). The values of the aromaticity factors obtained by the above procedure are plotted against the adsorption constant K , for the particular volume fraction of 1MN. Following this procedure, the adsorption constant K , was found to decrease exponentially with the aromaticity factor as shown in Figure 23. The dependence of the adsorption constant K on the aromaticity factor can thus be expressed as

$$K = 8.1505 \exp (- 3.9703 f_a) \quad (16)$$

The logarithm of the adsorption constant K is plotted against the aromaticity factor f_a in Figure 24. As shown in the figure, the logarithm of the adsorption constant decreases linearly with increase in the aromaticity factor. A similar dependence of the logarithm of the adsorption constant was found previously to exist with temperature. Thus, earlier experiments conducted on the Quinoline/Cyclohexane system and Quinoline/Mineral oil system revealed that the logarithm of the adsorption constant decreased linearly with increase in temperature (Vadlamani , 1999). It should be recalled that the present experiments on the Quinoline/(Mineral oil + 1MN) system were done at a constant temperature of 300°C with the volume fraction of 1MN being a variable. It can be observed that the increase in solvent aromaticity plays a somewhat similar role to an increase in temperature for the present system. This behavior can be attributed to the increase in diffusivity and decrease in the adsorption constant values with increase in aromaticity.

Conclusions

In this time period the adsorption-diffusion behavior of quinoline, in a mixture of mineral oil and 1-methyl naphthalene onto alumina in a microautoclave batch reactor has been studied for volume fractions of 0, 0.25, 0.5 and 0.75 of 1MN. Solvent composition as embodied in the effect of aromaticity on the hindered diffusion-adsorption process has been studied. The logarithm of the adsorption constant was found to be linearly dependent on the aromaticity factor which is defined to be the ratio of the number of aromatic carbons to the total number of carbons in the solvent system. As the volume fraction of 1MN increased, the aromaticity factor increased and the value of adsorption constant decreased. On the other hand the effective diffusivity increased with increase in the volume fraction of 1MN. Both of these factors shorten the time for the uptake experiment to reach equilibrium. Simulation results showed that the mathematical model satisfactorily fitted the adsorptive diffusion of quinoline from a mixture of mineral oil and 1MN onto alumina at a temperature of 300°C.

Table 1. Properties of Alumina

shape	cylindrical
diameter, cm	0.33
length, cm	0.36
equivalent radius, cm	0.17
surface area, m ² /g	100
particle density, g/cm ³	1.47
pore volume, cm ³ /g	0.45
porosity, cm ³ /cm ³	0.66
average pore diameter, nm	15.6

Table 2. Parameter values for quinoline/mineral oil system at 300⁰C

Density	0.835 g/cc
Kinematic viscosity	0.345 cP-cc/g
Viscosity ^(a)	0.2865 cP
Molecular diffusivity ^(b)	60.8 x 10 ⁻⁶ cm ² /s
Effective diffusivity ^(c)	10.554 x 10 ⁻⁶ cm ² /s

- (a) Obtained from Maxwell's hand book (Maxwell, 1962)
(b) Calculated from Scheibel relation (Perry and Green, 1984)
(c) Obtained from equation (7.1) assuming a tortuosity factor of 3.

Table 3. Parameter values for quinoline / 1 methyl naphthalene system at 300⁰C

Density	0.999 g/cc
Kinematic viscosity	0.222 cP-cc/g
Viscosity ^(a)	0.22 cP
Molecular diffusivity ^(b)	$1.2054 \times 10^{-4} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$2.0917 \times 10^{-5} \text{ cm}^2/\text{s}$

- (a) Obtained from Yaws handbook of Viscosity
- (b) Calculated from Scheibel relation (Perry and Green, 1984)
- (c) Obtained from equation (7.1) assuming a tortuosity factor of 3.

Table 4. Parameter values for the quinoline / (25% 1MN - 75% mineral oil) system at 300⁰C

Density	0.87375 g/cc
Kinematic viscosity	0.3216cP-cc/g
Viscosity ^(a)	0.2810 cP
Molecular diffusivity ^(b)	$7.831 \times 10^{-5} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$1.3586 \times 10^{-5} \text{ cm}^2/\text{s}$

- (a) Calculated from equation (2)
- (b) Calculated from equation (4)
- (c) Obtained from equation (7.1) assuming a tortuosity factor of 3

Table 5. Parameter values for the quinoline / (50% 1MN - 50% mineral oil) system at 300⁰C

Density	0.9125 g/cc
Kinematic viscosity	0.2906 cP-cc/g
Viscosity ^(a)	0.2651 cP
Molecular diffusivity ^(b)	$9.2217 \times 10^{-5} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$1.6 \times 10^{-5} \text{ cm}^2/\text{s}$

- (a) Calculated from equation (2)
(b) Calculated from equation (4)
(c) Obtained from equation (7.1) assuming a tortuosity factor of 3

Table 6. Parameter values for the quinoline / (75% 1MN - 25% mineral oil) system at 300⁰C

Density	0.9512 g/cc
Kinematic viscosity	0.2574 cP-cc/g
Viscosity ^(a)	0.2448 cP
Molecular diffusivity ^(b)	$10.5495 \times 10^{-5} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$1.8303 \times 10^{-5} \text{ cm}^2/\text{s}$

- (a) Calculated from equation (2)
(b) Calculated from equation (4)
(c) Obtained from equation (7.1) assuming a tortuosity factor of 3

Table 7. Experimental data for the Quinoline/(Mineral oil + 1MN) system at 300°C

V = 5.8ml W = 0.455gm 1MN = 25%		V = 3.75ml W = 0.533gm 1MN = 50%		V = 2.75ml W = 0.0.533gm 1MN = 75%	
Time, hrs	C _b /C _i	Time, hrs	C _b /C _i	Time, hrs	C _b /C _i
0	1	0	1	0	1
0.5	0.833	0.5	0.885	0.5	0.914
1	0.82	1	0.884	1	0.916
2	0.82	3	0.878	1.5	0.918
3	0.822	5	0.887	2	0.917

Table 8. Validation data for the Quinoline/(Mineral oil + 1MN) system at 300°C

V = 3.75ml W = 0.533gm 1MN = 25%		V = 2.75ml W = 0.533gm 1MN = 50%		V = 1.75ml W = 0.0.533gm 1MN = 75%	
Time, hrs	C _b /C _i	Time, hrs	C _b /C _i	Time, hrs	C _b /C _i
0	1	0	1	0	1
0.5	0.721	0.5	0.845	0.25	0.878
1	0.716	1	0.849	0.5	0.884
2	0.719	3	0.85	1	0.877
3	0.719	5	0.851	2	0.879
4	0.714				

Table 9. Adsorption constant values for the Quinoline/(Mineral oil + 1MN) system

Volume fraction	Mole fraction ^(a)	Adsorption constant, cc/g	Aromaticity factor ^(b) , f_a
0	0	8.25	0
25	0.4426	2.9	0.0267
50	0.7043	1	0.0504
75	0.8774	0.5	0.0717

(a) Calculated from equation (2.4)

(b) Calculated from equation (15)

Nomenclature

Letters

C_0	solute bath concentration at the centre of the particle, g/cm ³
C_b	solute bath concentration, g/cm ³
C_i	initial solute bath concentration, g/cm ³
C_s	solute bath concentration at the surface of the particle, g/cm ³
D_∞	solute molecular diffusivity, cm ² /s
D_e	solute effective diffusivity, cm ² /s
f_a	aromaticity factor
k	Boltzmann constant, 1.38×10^{-16} erg/K
K	linear adsorption constant, cc/g
K_p	partition factor
K_r	restriction factor
M_{IMN}	molecular weight of IMN
M_{min}	molecular weight of mineral oil
N	carbon number
P	percentage of equilibrium adsorption
T	absolute temperature, K
V	catalyst pellet volume, cc
V_b	bath volume, cc
V_p	catalyst pore volume, cc
W	catalyst weight

Greek

ε	catalyst porosity
η	solvent viscosity, g/cm-s
α	dimensionless constant in Lobe's equation
ν_m	mixture Kinematic viscosity, cm ² /s
ϕ_A	volume fraction of A, cm ³ /cm ³
τ	tortuosity factor

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Figure 1. Boiling point distribution of mineral oil with respect to the cumulative weight percent.

Figure 2. Boiling point distribution of mineral oil.

Figure 3. Plot of the logarithm of the carbon number against the boiling point for normal paraffins from C₂ to C₄₅.

Figure 4. Distribution of the weight of mineral oil with respect to the carbon number.

Figure 5. Dependence of the kinematic viscosity of the mixture of mineral oil and 1MN on the volume fraction of 1MN.

Figure 6. Dependence of the viscosity of the mixture of 1MN and mineral oil on the volume fraction of 1MN.

Figure 7. Dependence of the viscosity of the mixture of 1MN and mineral oil on the mole fraction of 1MN.

Figure 8. Linear dependence of the logarithm of the viscosity of the mixture of mineral oil and 1MN on the reciprocal of the mole fraction of MO.

Figure 9. Dependence of the molecular diffusivity D_{∞} of quinoline in the mixture of mineral oil and 1MN at 300°C.

Figure 10. Dependence of the effective diffusivity D_e of quinoline in the mixture of mineral oil and 1MN at 300°C.

Figure 11. Dependence of the effective diffusivity D_e of quinoline in a mixture of mineral oil and 1MN on the mole fraction of mineral oil at 300°C.

Figure 12. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in 25% 1MN / 75% mineral oil.
($V=5.8\text{ml}$, $W=0.455\text{g}$, $T=300^\circ\text{C}$)

Figure 13. Validation of the value of K for the adsorptive uptake of quinoline in 25% 1MN, 75% mineral oil ($V=3.75\text{ml}$, $W=0.533\text{g}$, $T=300^\circ\text{C}$).

Figure 14. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in 50% 1MN / 50% mineral oil.
($V=3.75\text{ml}$, $W=0.533\text{g}$, $T=300^\circ\text{C}$)

Figure 15. Validation of the value of K for the adsorptive uptake of quinoline in 50% 1MN / 50% mineral oil ($V=2.75\text{ml}$, $W=0.533\text{g}$, $T=300^\circ\text{C}$).

Figure 16. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in 75% 1MN / 25% mineral oil.
(V=2.75ml, W=0.533g, T=300°C)

Figure 17. Validation of the value of K for the adsorptive uptake of quinoline in 75% 1MN / 25% mineral oil ($V=1.75\text{ml}$, $W=0.533\text{g}$, $T=300^\circ\text{C}$).

Figure 18. Dependence of the adsorption constant, K for the adsorptive uptake of quinoline in a mixture of 1MN and mineral oil as a function of the mole fraction of 1MN.

Figure 19. Linear dependence of the logarithm of the adsorption constant, K for the adsorptive uptake of quinoline in a mixture of 1MN and mineral oil on the mole fraction of 1MN at 300°C.

Figure 20. Comparison of the equilibrium times for the (25% MN, 75% MO) and the (50% MN, 50% MO) system.

Figure 21. Model simulated time taken to achieve 75% of the equilibrium adsorption at different temperatures for the quinoline/mineral oil system at a V/W value of 10cc/g.

Figure 22. Model simulated time taken to achieve 95% of the equilibrium adsorption at different temperatures for the quinoline/mineral oil system at a V/W value of 10cc/g.

Figure 23. Dependence of the adsorption constant, K on the aromaticity factor f_a .

Figure 24. Linear dependence of the logarithm of the adsorption constant on the aromaticity factor f_a .

Planned Work

During the next time period it is expected that the current MS student, Mr. Surya Vadlamani will graduate and a new student will continue the work. The new student will concentrate his efforts in working with the diffusion of asphaltenes at various temperatures and in a range of solvents. In addition, the utilization of catalyst supports with a different range of pore sizes than has been considered in previous work will allow the relationship between pore diameter and asphaltene size to be more fully investigated.