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THE DIFFUSION OF LIQUIDS IN PORES

MARTEN TERNAN
HYDROCARBON PROCESSING RESEARCH LABORATORY

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by

Marten Ternan

Energy Research Laboratories/CANMET
Energy, Mines and Resources Canada
Ottawa, Ontario, K1A 0G1, Canada

ABSTRACT

An equation for the diffusion of solute molecules in pores filled with liquids has been developed. It has been found to represent the diffusion of a variety of materials, from simple molecules to fractions of petroleum asphaltenes.

KEY WORDS: diffusion, pore, liquid property, catalyst

For several years, work in our laboratory has been directed toward the conversion of oil sand bitumen and heavy oils into usable fuel products. When conventional hydrocracking catalysts are used, the reaction rate is normally influenced by the rate of diffusion of the large carbonaceous molecules, within the catalyst pores. In the present work, an equation for the effective diffusivity in liquid filled pores was developed and compared with literature data.

There have been a number of studies (Beck and Schultz, 1970; Prasher and Ma, 1977; Prasher et al, 1978; Thrash and Pildes, 1981; Deen et al, 1981; Galiasso and Morales, 1983) which have reported effective diffusivities of liquids within the pore structure of catalysts and other solids. The data in some studies (Satterfield et al, 1973; Chantong and Massoth, 1983; Baltus and Anderson, 1983; Seo and Massoth, 1985) have generally been correlated by empirical equations of the type indicated in Equation 1.

$$\frac{D_{eff}}{D_B} = \frac{A \epsilon}{\tau} \exp(-B\lambda) \qquad (1)$$

D_{eff} is the effective diffusivity of the solute molecule in a pore filled with a liquid phase solution. D_B is the diffusivity of the same solute molecule in the bulk phase of the same solution. A and B are empirical parameters. ϵ is the porosity of the solid. τ is the tortuosity. $\lambda = r_m/r_p$, where r_m is the radius of the diffusing solute molecule and r_p is the pore radius.

Theoretical Approach

In this work, the effective diffusivity of a solute molecule in a pore filled with liquid is obtained by applying a series of correction factors, CF_i, to the diffusivity of the solute molecule in a bulk phase liquid, as indicated in Equation 2.

$$D_{eff} = D_B \left(\prod_i CF_i \right) \qquad (2)$$

Any phenomenon which influences diffusion will be treated as a correction factor and therefore will be included in the effective diffusivity. The two correction factors considered are related to the concentration of the solute in the pore, and to the influence of the pore wall on the solvent viscosity.

Concentration Effect

The first correction factor, CF_1, was termed the steric partitioning coefficient by Anderson and Quinn (1974). It was originally suggested by Ferry (1936) on the basis of geometrical considerations. The centerline of the solute molecules cannot occupy the region $r_p - r_m$ of the pore. In contrast, smaller solvent molecules can occupy this region. This effect decreases the concentration of the solute in the pore in comparison with its concentration immediately outside the pore in the bulk liquid. The cross sectional area of the pore available to the solute molecule divided by the total cross sectional area of the pore is the first correction factor, CF_1, (steric partitioning coefficient).

$$CF_1 = \frac{\pi(r_p - r_m)^2}{\pi r_p^2}$$

$$= (1.0 - \lambda)^2 \tag{3}$$

Pore Wall Effect

In principle, the force field from the pore wall could alter some of the factors which influence diffusivity in the bulk liquid.

Bulk liquid diffusivities can be calculated from the Stokes-Einstein equation, Equation 4,

$$D_B = \frac{RT}{6\pi\mu r_m} \tag{4}$$

or from the Eyring theory of transport phenomena (Hirschfelder et al, 1954), Equation 5.

$$D_B = \frac{n^{1/3}kT}{\mu} \tag{5}$$

With the exception of viscosity, all of the terms in the above two equations are constants for a given solute-solvent system (assuming the diffusion occurs isothermally).

The well known equation, Wilke and Chang (1955), for estimating the bulk liquid diffusivity is shown in Equation 6.

$$D_B = 7.4 \times 10^{-8} \frac{(\Phi M)^{1/2}T}{\mu V^{0.6}} \tag{6}$$

Recently, Hayduk and Minhas (1982) developed an improved correlation for estimating liquid diffusivity, which is shown in

Equation 7.

$$D_B = 6.916 \times 10^{-10} \frac{T^{1.7} R_B^{0.2}}{\mu^{0.8} R_A^{0.4}} \qquad (7)$$

Again, with the exception of viscosity, all of the terms in the above two predictive equations are also constants.

On this basis, the viscosity will be the only solution property considered to be altered by the proximity of the pore wall. It is hypothesized that the field force (Van der Waals forces) emanating from the pore wall will make solvent in its vicinity more viscous than the solvent further away from the pore wall. An increase in viscosity would cause a decrease in diffusivity. The second correction factor, CF_2, is obtained by replacing the bulk solvent viscosity in the above equations with a solvent viscosity typical of the liquid within the pore.

$$CF_2 = \frac{\mu_B}{\mu_p} \qquad (8)$$

The viscosity μ_p in the pore is assumed to consist of two parts, the bulk viscosity, μ_B, and an incremental viscosity, $\Delta\mu_W$, caused by the proximity of the pore wall. The centers of very large pores may contain solvent having a viscosity identical to that of bulk liquid. In contrast, there would be solvent of greater viscosity near the walls of the pores. It is known that the force field will decrease with increasing distance from the wall. Therefore

the viscosity should also decrease with distance from the wall until it becomes equal to the bulk viscosity. There is probalbly an exponential decrease in solvent viscosity with distance from the pore wall. However to simplify matters, the viscosity variation with distance will be represented by a viscosity increment having a constant value, $\Delta\mu_w$, as shown in Figure 1. It is assumed that there are only two viscosities, μ_B, the bulk solvent viscosity and $(\mu_B + \Delta\mu_w)$, an enhanced viscosity in the proximity of the pore wall. The viscosity in the pore, μ_p, is taken as a volume average of these two.

Let r_w be the distance from the pore wall, in which the enhanced viscosity solvent resides. Then consider those solute molecules within the zone of enhanced viscosity. Their centers will be within the distance $r_w + r_m$ of the pore wall. For circular pores, the portion of the pore cross sectional area, XA, containing enhanced viscosity solvent, which influences the solute, will be,

$$XA = \pi r_p^2 - \pi(r_p - r_m - r_w)^2 \qquad (9)$$

The viscosity in the pore can be obtained by summing the volumes of the two regions which are accessible to the solute molecules.

$$\pi r_p^2 L \mu_p = \pi r_p^2 L \mu_B + (XA) L \Delta\mu_w \qquad (10)$$

In the above, L is the pore length. By rearranging Equation 10 with $\beta = r_w/r_p$, Equation 11 is obtained.

$$\mu_p = \mu_B + (2\lambda + 2\beta)\Delta\mu_w \qquad (11)$$

Equation 11 can be combined with Equation 8 to obtain,

$$CF_2 = \frac{1}{1 + P\lambda} \tag{12}$$

where

$$P = 2(1 + \frac{r_m}{r_w})\frac{\Delta\mu_w}{\mu_B} \tag{13}$$

The field force has been used to successfully explain physical adsorption of several layers of adsorbed molecules on a solid wall (Ternan, 1973). This indicates that the field force extends further than a single molecule and that r_m/r_w in Equation 13 can be taken as less than 1. If r_m/r_w is ignored in Equation 13, then for a given solvent, P will be a constant and will not vary with the solute.

The final equation is obtained by substituting Equations 3 and 12 into Equation 2 to obtain,

$$\frac{D_{eff}}{D_B} = \frac{(1 - \lambda)^2}{1 + P\lambda} \tag{14}$$

Equation 14 has been compared with experimental data in

Figures 2 to 4. In each case, a least squares estimate of the
parameter P was obtained by minimizing the sum of the squares of the
residuals.

Figure 2 shows the data of Satterfield et al (1973). They
measured liquid phase diffusivities of pure component solutes having
molecular weights from 58 to 1143, in a silica alumina catalyst having
a median pore diameter of 3.2 nm. They used several solvents, hexane,
cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane and water. The
best fit of their data was obtained with a value of the parameter P
equal to 16.26 .

Figure 3 shows the data of Chantong and Massoth (1983). They
measured liquid phase diffusivities of the following pure component
molecules, naphthalene, coronene, octa-ethylporphyrin, and
tetra-phenylporphyrin, in four gamma alumina materials having average
pore diameters from 4.9 to 15.4 nm. Cyclohexane was used as the
solvent in all cases. The best fit of their data was obtained with a
value of the parameter P equal to 11.04 .

Figure 4 shows the data of Baltus and Anderson (1983). They
measured the liquid phase diffusivities of several Kuwait petroleum
asphaltene fractions which were prepared by gel permeation
chromatography. The polystyrene equivalent molecular weights of these
solutes varied from 2000 to 64,000. The porous materials were mica
membranes each of which had pores of a uniform size. The pore sizes
varied from 7 to 218 nm (Baltus, 1982). Tetrahydrofuran was used as
the solvent in all cases. The best fit of their data was obtained
with a value of the parameter P equal to 2.017 .

Equation 14 represents the experimental data well, for solutes
having a wide range of molecular weights. It has only one adjustable
parameter, compared with two adjustable parameters used in empirical
equations of the type indicated in Equation 1. It satisfys two
necessary conditions for any valid theoretical equation. It predicts

$D_{eff} = 0$ when the diffusing solute molecule radius is equal to the pore radius, $\lambda = 1$. None of the empirical equations satisfy this condition. It predicts $D_{eff} = D_B$ when the pore size is large compared with the dimension of the diffusing solute molecule, $\lambda = 0$. The only empirical equation to satisfy this condition is the one by Baltus and Anderson (1983). These features make Equation 14 more suitable for representing effective diffusivity than any of the existing empirical equations.

The parameter P is a function of viscosity (Equation 13). The field from the pore wall would be expected to influence polar solvents (such as tetrahydrofuran) differently than non-polar solvents (such as cyclohexane). Since a variety of solvents were used in making the measurements shown in Figures 1 to 3, a correlation between P and viscosity cannot be expected using these data.

Effect of Temperature

To consider the influence of temperature on diffusivity, the Significant Structure Theory of Liquids (Eyring and Marchi, 1963) was used to model the solvent. It has been successful in predicting the viscosities of liquids (Ree et al, 1972; Eyring, 1936). According to the theory

$$\mu = K \ exp(\Delta G/RT) \tag{15}$$

Both $\Delta\mu_w$ and μ_B can be expressed in terms of Equation 15 and substituted into Equation 13 to obtain,

$$\ln P = \ln[(2K_w/K_B)(1 + r_m/r_w)] + (\Delta G_w - \Delta G_B)/RT \tag{16}$$

Equation 16 indicates that $\ln(P)$ should be proportional to the inverse of the temperature. Seo and Massoth (1985) have measured liquid diffusivities as a function of temperature. Their data are plotted in Figure 5. They used the same porous aluminas and the same solutes as Chantong and Massoth (1983). Equation 14 was fitted to their data and the resulting P values are plotted in Figure 6 as a function of inverse temperature. The shape of the line in Figure 6 is in general agreement with that predicted by Equation 16. This indicates that the variation of the diffusivity parameter, P, with temperature is consistent with the expected variation of viscosity with temperature. Furthermore, it supports the relationship between P and viscosity as shown in Equation 13.

Equation 14 should be useful in several applications. One would be diffusion in the pores of membranes, used in reverse osmosis or in ultrafiltration (Matsuura et al; 1981). Another is the catalytic hydrocracking of residuum (Ternan, 1986). For example, the radius of diffusing asphaltene micelles has been estimated at approximately 1 nm (Speight 1981). If D_{eff} is to be within 80 % of D_B, then from Figure 4, r_m/r_p must be 0.05 or less. According to these numbers the catalyst pore radius would have to be 20 nm or larger. It should be noted that hydrocracking reaction conditions (high temperature and concentrated solutions) are considerably different than the conditions used to develop Equation 14 (close to ambient temperatures and extremely dilute solutions). Nevertheless the estimate of 20 nm is close to the pore radius in some recently described residuum hydrocracking catalysts.

The shape of the molecule is also important. Hayduk and Buckley (1972) have shown that for the same molar volume, linear molecules have greater diffusivities in bulk liquids than spherical molecules. Similarly Deen, Bohrer and Epstein (1981) have shown that linear polymers have much greater diffusivities through porous membranes than do more condensed globular molecules. In hydrocracking applications bitumen and heavy oil molecules are often considered to

be composed of a nucleus of condensed aromatic rings that have several linear side chains at their extremities. Some of the side chains are removed during the reaction. Thus the reactant molecules diffusing into a catalyst pore may have a different shape than the product molecules diffusing out of a catalyst pore. Although all of the uncertainties have not been resolved, Equation 14 is a definite improvement over the empirical correlatons in the current literature.

Acknowledgement

Nomenclature

A = empirical parameter in Equation 1

B = empirical parameter in Equation 1

CF = correction factor

D_{eff} = effective diffusivity of a solute molecule in a pore filled with liquid

D_B = diffusivity of a solute molecule in a bulk phase solution

ΔG_B = activation energy for bulk viscosity in Equation 15

ΔG_W = activation energy for incremental wall viscosity in Equation 15

k = Boltzmann's constant

K_B = pre-exponential factor for bulk viscosity in Equation 15

K_W = pre-exponential factor for incremental wall viscosity in Equation 15

L = pore length

M = molecular weight of solvent

n = number density of molecules

P = parameter in Equation 13

r_m = radius of solute molecule

r_p = pore radius

r_w = distance from pore wall in which solvent has enhanced
viscosity

R = universal gas constant

R_A = radius of gyration of the solute molecule

R_B = radius of gyration of the solvent molecule

T = temperature

V = molar volume of solute

λ = r_m/r_p

β = r_m/r_w

ϵ = porosity

π = 3.1416

Φ = association factor

τ = tortuosity

μ = viscosity

μ_B = viscosity of bulk solvent

μ_p = representative viscosity of solvent in the pore

$\Delta\mu_w$ = enhanced viscosity increment of solvent in the
proximity of the pore wall

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CAPTIONS FOR FIGURES

Figure 1: Illustration of viscosity variation near the
pore wall caused by the field force from the wall

Figure 2: (Pore to Bulk) Diffusivity Ratio Versus
(Molecule to Pore) Radius Ratio. Data are from
Satterfield et al (1973). Solid line is Equation 14
with P = 16.26
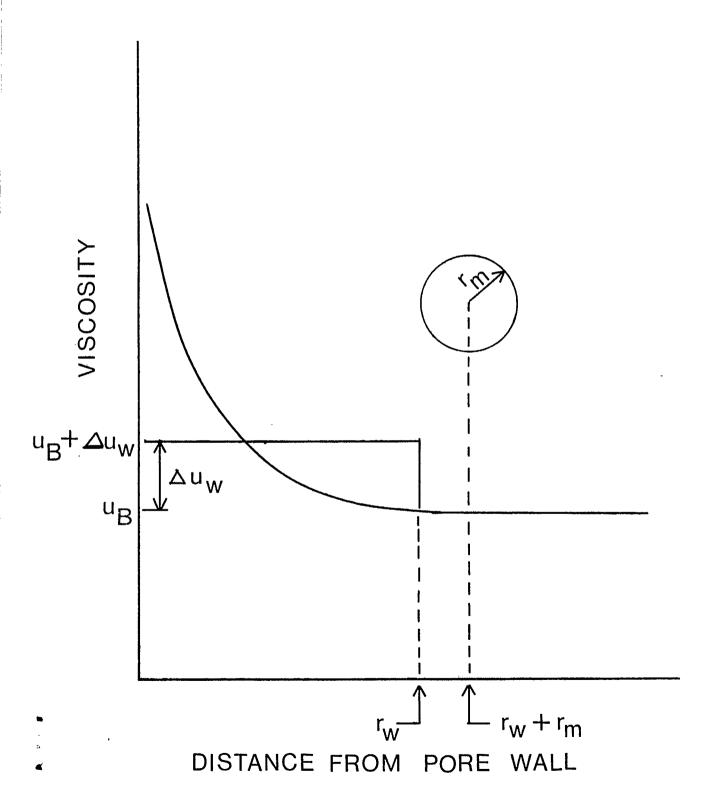
Figure 3: (Pore to Bulk) Diffusivity Ratio Versus

(Molecule to Pore) Radius Ratio. Data are from
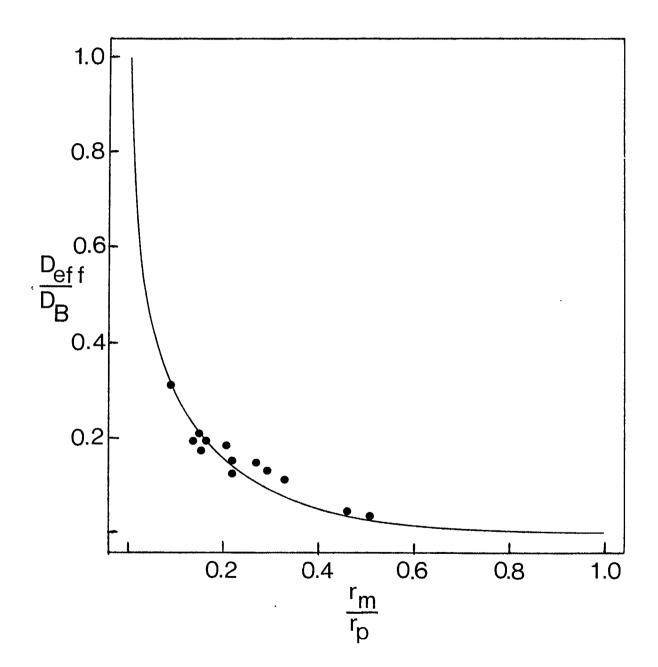Chantong and Massoth (1983). Solid line is Equation 14
with P = 11.04
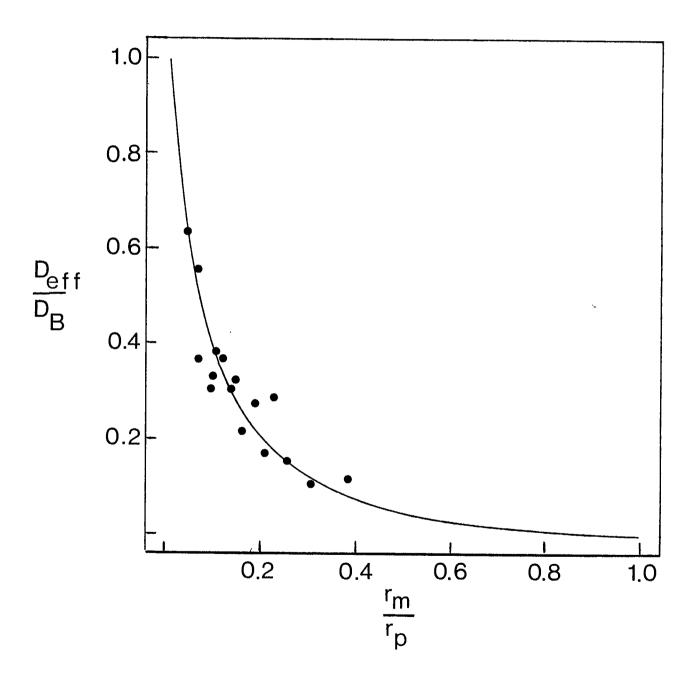
Figure 4: (Pore to Bulk) Diffusivity Ratio Versus
(Molecule to Pore) Radius Ratio. Data are from
Baltus and Anderson (1983). Solid line is Equation 14
with P = 2.017

Figure 5: (Pore to Bulk) Diffusivity Ratio Versus
(Molecule to Pore) Radius Ratio. Data are from
Seo and Massoth (1985). The solid lines are
for P values of 19.80, 10.64, and 6.53 at 298 K,
313 K, and 333 K respectively.

Figure 6: Parameter P versus Inverse Temperature K^{-1}.

VISCOSITY

$u_B + \Delta u_w$

Δu_w

u_B

r_m

r_w

$r_w + r_m$

DISTANCE FROM PORE WALL

4.