Partitioning and Adsorption of Aromatic Compounds on Microporous Silica Gel

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When the size of a molecule is comparable to the pore, through which it is diffusing, a reduction in the rate of diffusion is observed. This phenomenon is known as hindered diffusion and has been the focus of a great deal of study (Anderson and Quinn, 1974; Deen, 1987). Hindered diffusion is believed to be a combination of two effects: equilibrium partitioning and hydrodynamic effects. Other effects such as van der Waals and electrostatic interactions may also have some influence on a molecule's motion through a micropore (Deen and Smith, 1982).

The equilibrium partitioning of solute molecules from the bulk solution into a porous medium is defined as the ratio of the concentration of the solute in the pores, C_p, to the concentration at equilibrium of the solute in the bulk solution, C_b

$$K_p = \frac{C_p}{C_b} \tag{1}$$

Ferry (1936) arrived at the following expression for rigid spheres in well-defined cylindrical pores from geometric considerations,

$$K_p = (1 - \lambda)^2 \tag{2}$$

where λ is the ratio of the radius of the solute to the radius of the pore. Ferry deduced that there was a region in the cylindrical pore that the center of the "hard sphere" solute molecule could not access. The steric exclusion effect occurred due to the fact that the rigid molecule could never get closer to the pore wall than a distance equal to its own radius. Giddings et al. (1968) obtained expressions for the partition coefficient from a thermodynamic viewpoint. Inside the pore, certain molecular configurations cannot occur since they would overlap the pore wall, this leads to a reduction in configurational entropy for the solute molecules. Therefore, K_p can be thought of as a ratio of the number of accessible configurations inside the pore to the number of configurations in a nonrestricted solution. When appropriate restrictions are imposed, the analysis of Giddings et al. (1968) reduces to Eq. 2. Theoretical expressions for K_p have also been developed for the partition coefficient to account for such effects as solute-solute interactions, solute-solvent interactions, and repulsion by the pore wall (Cassassa, 1967; Glandt 1980 and 1981; Limbach et al., 1989).

Limbach and Wei (1990) state that in defining λ for nonspherical molecules and noncircular pores the appropriate characteristic molecular size is the mean projected molecule radius r_m (Baltus and Anderson, 1984). The appropriate pore size is the pore hydraulic radius (V_{sp}/A_s). With these definitions of the characteristic lengths, λ in Ferry's equation may be written as:

$$\lambda = r_m/2(V_{sp}/A_s) \tag{3}$$

Limbach et al. (1989) examined using Monte Carlo simulations the partitioning of axisymmetric molecules in neutral various-shaped pores typical of fibrous and granular materials. Their results show that even at large values of λ (defined by Eq. 3), Eq. 2 represented the partitioning exceptionally well. They concluded that Eqs. 2 and 3 would be suitable for estimating small molecule partitioning in granular materials.

There have been several experimental studies that have investigated the partitioning of molecules in porous materials (Satterfield et al., 1973; Colton et al., 1975; Prasher and Ma, 1977; Prasher et al., 1978; Baltus and Anderson, 1983, 1984). A wide range of substances have been utilized in these studies, such as various types of hydrocarbons, latex particles, polymers and proteins. Of interest here are those studies in which solute adsorption may have influenced the observed value of the partition coefficient. Satterfield et al. (1973) performed equilibrium studies on a variety of hydrocarbon solutes and solvents as well as aqueous solutions of salt and sugars on silica-alumina

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supports. The results of their investigation showed that saturated hydrocarbons and aqueous salt and sugar solutions exhibited partitioning coefficients on the order of unity, whereas aromatic compounds had partitioning coefficients that were substantially greater than unity. These results are in direct contrast to the predictions of the simple steric exclusion model proposed by Ferry, as well as results they later obtained for macromolecules (Colton et al., 1975) which showed reasonable agreement with Ferry's equation. Although there was no clear explanation for why the saturated hydrocarbons and the aqueous salt and sugar solutions differed with Ferry's model, it was concluded that the high values of K_p for the aromatic hydrocarbons was due to adsorption. Subsequent work by Prasher and Ma (1977) and Prasher et al. (1978) have also resulted in results similar to Satterfield et al. (1973). In these equilibrium studies (Prasher and Ma, 1977; Prasher et al., 1978) with a wide variety of hydrocarbon solutions in porous alumina, the values of K_p ranged from 0.6 to 2. They concluded that K_p is only minimally affected by λ, the major influence being that between the solute molecule and the support surface.

Unless accounted for separately in the solute mass balance, the partition coefficient defined in Eq. 1 will include in the solute pore concentration the effect of any solute adsorption. This can result in K_p values greater than unity for adsorbing solutes such as aromatic hydrocarbons as shown in the studies discussed above. The solute concentration in the pore should represent a balance between equilibrium partitioning caused by steric exclusion and equilibrium adsorption on the support surface. Interpretation of equilibrium partitioning data through a solute mass balance requires that each of these phenomena be considered separately. The objective of this paper is to illustrate how adsorption effects can be separated from steric exclusion effects for several strongly adsorbing aromatic compounds on silica gel supports. The results show remarkable agreement with Ferry's equation when λ is defined by Eq. 3, and support the Monte Carlo simulations of Limbach et al. (1989).

Solute Mass Balance Equation

If porous particles are placed in a well-mixed solution, the solute mass balance is:

$$C_{bi} V_{si} = C_b V_s + C_p V_{sp} M_s \tag{4}$$

where C_{bi} is the initial bulk concentration of solute and V_{si} is the initial bulk fluid volume. The terms C_b and C_p are the bulk and pore concentrations, respectively, at some later time after equilibrium has been reached. The support loading is M_s (in g) and V_{sp} is the specific pore volume (cm^3/g support). The term V_s is the final bulk fluid volume and can be written as:

$$V_s = V_{si} - V_{sp} M_s \tag{5}$$

Combining Eqs. 4 and 5 with the definition of the partition coefficient shown in Eq. 1 results in the following expression.

$$\frac{(C_{bi} - C_b) V_{si}}{V_{sp} C_b} = (K_p - 1) M_s \tag{6}$$

All the terms on the lefthand side of Eq. 6 are known or can be measured in a solute partitioning experiment. If the initial solute concentration and mass of support used are varied for several experiments a plot of the lefthand side of Eq. 6 vs. M_s will result in a line with a slope equal to $(K_p - 1)$. The resulting partition coefficient should be thought of as a *lumped term* since it represents not only solute molecules in the pore, but adsorbed solute molecules as well. This would be the partition coefficient reported by previous investigators and for adsorbing solutes can be greater than unity. C_p is really an effective pore solute concentration which may also include the amount of solute "lost" to the support surface by adsorption.

Adsorption effects can be separated from partitioning effects by rewriting the mass balance shown in Eq. 4.

$$C_{bi} V_{si} = C_b V_s + C_p V_{sp} M_s + C_a M_s A_s \tag{7}$$

where C_a is the concentration of adsorbed solute molecules per square meter of support, and A_s is the specific surface area of the support. The solute mass balance now includes separate terms for the amount of solute contained in the pore and the amount adsorbed on the support surface. Since the majority of the surface area of the particle is in the pore, it can be assumed that solute adsorption takes place only in the pores. The pore concentration (C_p) can be related to the adsorbed solute concentration C_a' through an adsorption isotherm, for example, the Freundlich equation:

$$C_a' = m C_p^{1/n} \tag{8}$$

where m and n are constants that must be determined experimentally and C_a' is the grams of solute adsorbed per gram of support. C_a' and C_a are related by the following eqs.:

$$m' = m/A_s, \quad C_a = C_a'/A_s \tag{9}$$

m' places the adsorbed solute on a per unit area of support basis to account for the variation in specific surface area of supports with different average pore size (Table 1).
Hence,

$$C_a = m' C_p^{1/n} \tag{10}$$

Combination of Eqs. 5, 7 and 10 results in the following expression:

$$C_{bi} V_{si} = C_b V_{si} - C_b M_s V_{sp} + C_p V_{sp} M_s + m' M_s A_s C_p^{1/n} \tag{11}$$

Further rearrangement and use of Eq. 1 yields:

$$\frac{(C_{bi} - C_b) V_{si}}{C_b V_{sp}} = \left\{ (K_p - 1) + \frac{m' A_s}{C_b V_{sp}} (K_p C_b)^{1/n} \right\} M_s \tag{12}$$

Table 1. Physical Properties of the Silica Gel Particles

Avg. Pore Dia. (nm)	BET Surface Area (m^2/g)	Pore Vol. (cm^3/g)
2.3	653	.38
4.0	668	.72
6.0	567	.83
21.0	272	1.43
30.0	247	1.85

Equation 12 states the solute mass balance in terms of the separate effects of equilibrium partitioning and solute adsorption. In the absence of adsorption this equation simplifies to Eq. 6. If a series of experiments are performed in which the initial solute concentration and the mass of support are varied, then a plot of the lefthand side of Eq. 12 vs. M_S should be linear with the term in braces equal to the slope. The term in braces includes both the effect of steric exclusion and adsorption. The next section describes the experimental approach that was used to determine the partition coefficient and the parameters which describe the adsorption isotherm.

Experimental Studies

The equilibrium partitioning and adsorption studies (Al-ishusky, 1990) were carried out in 25 cm^3 stainless steel Parr bombs. Each vessel was kept at constant temperature and well-mixed by a modified Cole-Parmer Corp. "Magna-4" stirrer/heater unit. The design of the stirrer/heater unit allowed four bombs to be stirred and heated simultaneously. In all the adsorption runs, the bombs were maintained at 25°C and at ambient pressure. Silica gel particles (W. R. Grace Co.) with average pore sizes ($4V_{sp}/A_s$) of 2.3, 4.0, 6.0, 14.7 and 30.0 nm were used as the support material. Silica gel was selected for its range in average pore diameter and its narrow pore size distribution. Table 1 summarizes the physical properties of the silica gel support as determined by a Quantasorb adsorption/desorption analyzer. The silica gel was first calcined in a Lindberg Sola Basic furnace at 650°C for 6–8 hours. This was done to remove any moisture and organic impurities that might have deposited in the pores during storage. After the calcination was completed, the silica gel was transferred to sealed storage containers so that exposure to the laboratory atmosphere was minimized. The silica gel particles ranged in size from 100–250 μm in diameter.

The solutes were naphthalene, phenanthrene, and fluoranthene. Their mean projected radius was estimated from their major and minor axis dimensions taken from molecular models and using formulas given by Baltus and Anderson (1984). Their respective mean projected radii are 0.33, 0.38 and 0.42 nm. The experimental matrix for each solute consisted of four solute concentrations (0.25, 0.50, 0.75 and 1.00 wt. %) and four support loadings (1, 2, 4 and 6 g) for each support pore size. This provided 16 data points fot the determination of K_p by either Eq. 6 or 12 for a given value of λ. The regression coefficient (r^2) for Eq. 6 or 12 in all cases was greater than 0.91.

The samples withdrawn from the bombs were analyzed using a Hewlett-Packard 5890A gas chromatooraph. The gas chromatograph was linked to a Hewlett-Packard 3392A Integrator. A flame ionization detector was used for the analysis. The column was a 10 ft × 1/8 in. (3 m × 3.2 mm) stainless steel packed column of 10% SP-2100 methyl silicone supported on 100/120 Supelcoport. Nitrogen was used as the carrier gas at a flow rate of 20 mL/min. The injector temperature was 250°C and a sample size of 0.1 μL was used. Hydrogen and air flow rates were 40 mL/min and 450 mL/min, respectively. The oven temperature profile was as follows: maintain oven temperature at 100°C for 2 minutes, increase oven temperature to 300°C at a rate of 6°C/min, hold oven temperature at 300°C for 5 minutes.

Before the partitioning and adsorption studies were performed, the length of time required for solute partitioning and adsorption to reach equilibrium was determined. To accomplish this, 1 g samples of the 30 nm support were exposed to solutions containing each of the solutes at an initial concentration of 1 wt. %. Equilibrium for all three solutes was reached in about 10 hours. To ensure that partitioning and adsorption was complete during the ensuing studies, a sample time of 24 hours was used for this investigation.

Since it is likely that these solutes will adsorb, the adsorption isotherms were first determined. The 30.0 nm pore size support was used in the isotherm determination since partitioning as predicted by Ferry's model (Eq. 2) would be expected to be quite small. This assumes that the adsorption isotherm is the same for each support and is not affected by the pore size. The resulting plots for the solutes used in this study are shown in Figure 1.

The Freundlich isotherm was chosen to represent the solute adsorption isotherms

$$C_a = \frac{m}{A_s(dp = 300)} (K_p C_b)^{1/n} \qquad (13)$$

Assuming that K_p is unity for the 30.0 nm support, a plot of $\ln(C_a)$ vs. $\ln(C_b)$ will result in a line with:

$$\text{Slope} = \frac{1}{n} \qquad (14)$$

and

$$\text{Intercept} = \ln\left[\frac{m}{A_s(dp=300)}\right] \qquad (15)$$

Since the equilibrium partition coefficient is actually slightly less than unity, Eq. 12 can be used to determine the actual value of K_p for the current values of m and n and the process repeated until convergence. The Freundlich constants obtained in this manner for the 30 nm support are summarized in Table 2, whereas Figure 1 also compares the Freundlich isotherm to the adsorption data.

Results and Discussion

The partitioning and adsorption studies for naphthalene, phenanthrene and fluoranthene when analyzed according to Eq.

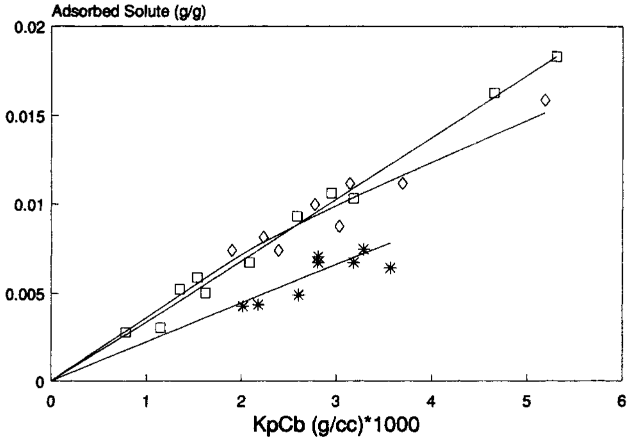

Figure 1. Adsorption isotherms (30 nm support).
* naphthalene, □ phenanthrene, ◇ fluoranthene

Table 2. Constants for the Freundlich Isotherm

Solute	m	n
Naphthalene	1.768	1.04
Phenanthrene	2.095	1.10
Fluoranthene	1.285	1.212

6 are consistent with the results for aromatic compounds of previous investigators (Satterfield et al., 1973; Prasher and Ma, 1977; Prasher et al., 1978). As in those studies, the aromatic solutes in this investigation exhibited *lumped* partition coefficients greater than unity, as shown by the data and trend lines in Figure 2, where λ is defined by Eq. 3.

The lumped partition coefficients indicate an adsorption effect that is masking the solute partitioning as described by Ferry's steric exclusion model shown in Eq. 2. For each solute we observe that the lumped K_p increases with increasing λ. As λ increases, the pore size decreases and the surface area of the particle increases as shown in Table 1. Therefore, at higher values of λ, there exists more surface area available for adsorption which increases the lumped value of K_p even in the presence of an increasing steric exclusion effect.

When the adsorption isotherm (Table 2) was included in the solute mass balance (Eq. 12), the resulting partition coefficients for all three solutes were in excellent agreement with Ferry's Eq. with λ defined by Eq. 3 as shown in Figure 3. This agreement also supports the Monte Carlo simulation results in granular materials obtained by Limbach et al. (1989) which showed that Ferry's equation can be used to describe partitioning in porous materials when λ is defined by Eq. 3. These results also support the assumption that at least for silica gel the adsorption isotherm on a per unit area of support basis is for the most part independent of the pore size.

The difference between the lumped K_p's and those obtained when adsorption effects are properly accounted for is evidence that for aromatic compounds, solute adsorption not only counterbalances steric exclusion of the solute molecule, but masks the effect entirely. The results obtained in this investigation show that even in a strongly adsorbing system, Ferry's equation with λ defined by Eq. 3 provides an excellent prediction of the partitioning of the solute between the bulk solution and the pore provided that the adsorption isotherm is known beforehand. On the other hand, adsorption data in supports of various average pore size where partitioning may be important, should be analyzed according to Eq. 12 modified to incorporate the desired adsorption isotherm model, where Ferry's equation and Eq. 3 can be used to describe the partitioning coefficient. Equation 12 can then be solved for the parameters describing the adsorption isotherm.

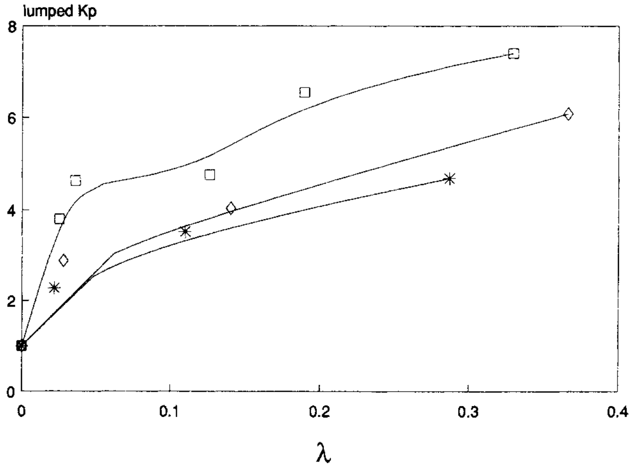

Figure 2. Lumped partition coefficients.

* naphthalene, □ phenanthrene, ◇ fluoranthene, —— trendlines

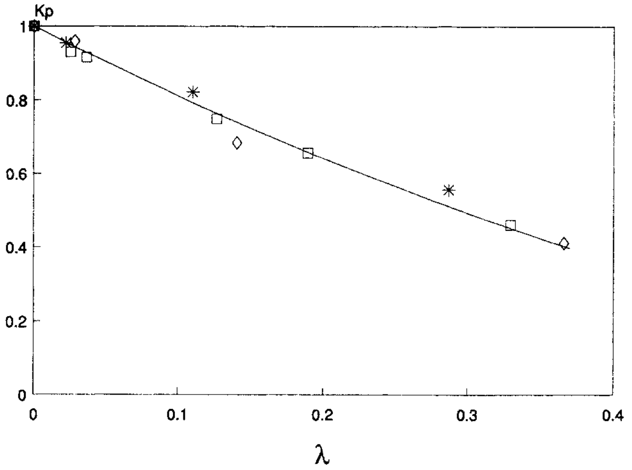

Figure 3. Partition coefficients.

* naphthalene, □ phenanthrene, ◇ fluoranthene, —— Eqs. 2 and 3

Acknowledgment

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Notation

A_S = support surface area
C_a = concentration of adsorbed solute per unit area
C_a' = concentration of adsorbed solute per unit mass
C_b = bulk solute concentration
C_p = pore solute concentration
K_p = partition coefficient
M_s = support mass
m, n = Freundlich constants
r_m = mean projected molecule radius
V_{sp} = support pore volume
V_s = bulk fluid volume

Greek letter

λ = defined by Eq. 3

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Errata

- *In the paper titled "Competitive Hydrodesulfurization and Hydrogenation in a Monolithic Reactor" (May 1990, p. 750), Table 2 should read as follows:*

Table 2. Estimated Values of Parameters in Model 2 with Approximate 95% Confidence Limits

ΔH (J/mol) · site r	
CH	$(-4.82 \pm 0.46) \times 10^4$
H	$(-5.41 \pm 0.93) \times 10^4$
T	$(-4.89 \pm 0.42) \times 10^4$
E_a (J/mol)	
CH	$(1.10 \pm 0.16) \times 10^5$
T	$(8.40 \pm 1.20) \times 10^4$
THT	$(8.53 \pm 2.31) \times 10^4$
k^o (mol/s · kg cat.)	
CH	$(4.22 \pm 2.06) \times 10^{-3}$
T	$(2.82 \pm 1.12) \times 10^{-3}$
THT	$(2.69 \pm 1.99) \times 10^{-3}$

- *In the paper titled "Effective Kinetic Modeling of Multistep Homogeneous Reactions" (August 1990, p. 1200), the following corrections are made:*

Lefthand column of p. 1203, line 6 of paragraph "Rate and Yield-Ratio Equations. . . ," replace "for" by "with."

Righthand column of p. 1207, line under matrix equation, replace "order $k = j - l$" by "order $k - j - 1$."

- *In the paper titled "Stability of Multilayer Extrusion of Viscoelastic Liquids" (May 1990, p. 710)*, a term $i\alpha Re_j u''_{sj}\phi_j$ should be added to the righhand side of Eq. 17. Also, the second term on the righthand side of Eq. 19c should read $2i\alpha\tau_{xxsj}\phi'_j$, instead of $2i\alpha\tau_{xxsj}\phi_j$. The corrected forms of these equations were already considered in subsequent derivations and computations of the paper. We would like to acknowledge gratefully the assistance of Professor Bamin Khomami, at The Washington University, in bringing the errors to our attention.