

J. Non-Equilib. Thermodyn.
2005 · Vol. 30 · pp. 1–20

Effects of adsorbed phase on diffusion of subcritical hydrocarbons in activated carbon at low pressures

Jun-Seok Bae and Duong D. Do*

Division of Chemical Engineering, the University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

*Corresponding author (duongd@cheque.uq.edu.au)

Abstract

Diffusions of free and adsorbed molecules of subcritical hydrocarbons in activated carbon were investigated to study the influence of adsorbed molecules on both diffusion processes at low pressures. A collision reflection factor, defined as the fraction of molecules undergoing collision to the solid surface over reflection from the surface, is incorporated into Knudsen diffusivity and surface diffusivity in meso/macropores. Since the porous structure of activated carbon is bimodal in nature, the diffusion of adsorbed molecules is contributed by that of weakly adsorbed molecules *on* the meso/macropore surfaces and that of strongly adsorbed molecules *in* the small confinement of micropores. The mobility of adsorbed molecules on the meso/macropore surface is characterized by the surface diffusivity $D_{\mu 2}$, while that in the micropore is characterized by $D_{\mu 1}$. In our study with subcritical hydrocarbons, we have found that the former increases almost linearly with pressure, while the latter exhibits a sharp increase at a very low-pressure region and then decreases beyond a critical pressure. This critical pressure is identified as a pressure at which the micropores are saturated.

1. Introduction

Transport of molecules in both gas and adsorbed phases through porous media has been a subject of great interest because of its significance in many applications such as separation technology, catalyst design, sorption process design and optimization, as well as solid characterization [1–3]. In particular, diffusion through activated carbon has received good attention since it consists of a wide pore-size distribution ranging from micropores where most adsorption occurs, to macropores where gas phase transport dominantly takes place.

It has been known that molecular transport through activated carbon at a given pressure gradient is attributed to gas phase diffusion (i.e., Knudsen diffusion and viscous flow), adsorbed phase diffusion, and condensate flow [4]. The first and third

mechanisms are relatively well established and understood. However, the surface diffusion is still far from being completely understood since there have been no rigorous theoretical methods to directly determine its contribution to total mass transport in porous solids. Conventional methods (i.e., Eq. [1]) to calculate the permeability of the surface diffusion of subcritical hydrocarbons have been questioned and proven to be inadequate [5].

$$B_{\mu} = B_{T_observed} - B_{T_predicted}, \quad (1)$$

where B_{μ} is the surface diffusion permeability of adsorbate, and $B_{T_observed}$ and $B_{T_predicted}$ are the total permeabilities obtained from adsorbate experiments and predicted from inert gas experiments, respectively.

The common assumption in the literature that gas phase diffusion and surface diffusion are additive and parallel processes is questionable [5]. Transport of molecules within the pores depends on the pore geometry and topology, the physical properties of permeating molecules, the interaction force between diffusing molecules and pore surface atoms [6], as well as the presence of adsorbed phase on the solid surface [7]. The transport of adsorbate, therefore, requires information on adsorbed concentration on the surface and potential energy of fluid–solid interaction. Brown and co-workers [7, 8] made attempts to describe their experimental observations that showed significant effects of the presence of adsorbed molecules on the gas phase diffusion and on the adsorbed phase diffusion. They derived gas–adsorbate momentum exchange, which takes into account interactions between the gas phase and the adsorbed phase. Although they were unable to describe the diffusion behavior satisfactorily, they pointed out the importance of the coupling between gas phase diffusion and adsorbed phase diffusion. Because of the surface potential energy between diffusing molecules and surface atoms, the collision to and rebound from the surface for gas phase diffusion is influenced by dispersion force fields to some degree. Shindo et al. [9] have stressed that the attraction potential force near the solid atoms bends the trajectories of gas phase molecules, giving rise to less gas phase flux than in the case where there is no attraction force. However, they did not take into account the effect of the presence of adsorbed molecules. Furthermore, some molecular dynamics simulations have demonstrated that the surface diffusion process may be remarkably affected by the collision of gas phase molecules on the solid surface [10, 11]. Therefore, both gas phase diffusion and surface diffusion are affected by the presence of adsorbed phase. In our previous study [5], the effect of the presence of adsorbed phase on gas phase diffusion was taken into account by introducing a collision reflection factor (which is a function of adsorbed concentration) to the Knudsen diffusivity of adsorbate.

Among the transport mechanisms in porous media, the importance of surface diffusion has been stressed because surface diffusion contributes significantly to the total mass flow rate through the solids and yet its mechanism still remains little understood. Conventionally, surface diffusion flux (J_{μ}) has been described by a Fickian type equation as follows:

$$J_{\mu} = -D_{\mu} \frac{dC_{\mu}}{dz}, \quad (2)$$

where D_μ is the surface diffusivity, which is a function of the local adsorbed concentration C_μ and solid properties. This surface diffusivity D_μ is a lumped parameter and its functional form has been the subject of an ongoing debate in theoretical and experimental studies. The review on the functional forms for surface diffusivity can be found elsewhere [12].

In this paper, the effect of adsorbed phase concentration on both gas and adsorbed phase diffusions will be incorporated into the Knudsen diffusivity and the surface diffusivity in meso/macropores. Since the activated carbon used in this study has bimodal pore size distribution (i.e., micropore and meso/macropore), the surface diffusion is expected to occur in both pores. Using experimental data of transport of various adsorbates in activated carbon, we first derive the functional form of surface diffusivity ($D_{\mu 2}$) in meso/macropores and then the surface diffusivity ($D_{\mu 1}$) in micropores.

2. Theory

In this paper, condensate flow is not considered since we deal with the transport of molecules at low pressures where the capillary condensate flow is absent. Gaseous viscous flow is a well-known process and can be easily described from the properties of permeating species as well as the porous medium, provided that the presence of adsorbed phase has a negligible effect on gaseous viscous flow [5]. Thus our emphasis is placed on two transport processes: Knudsen diffusion and surface diffusion.

2.1. Knudsen diffusivity as a function of loading

In our earlier study on diffusion and flow of subcritical fluids in activated carbon, we studied the dependence of Knudsen diffusion on pressure (i.e., loading) by introducing a pressure-dependent collision reflection factor f_M [5]. The collision reflection factor is defined as the fraction of molecules undergoing collision to the solid surface over reflection from the solid surface. Thus, it is logical to expect that when there are no adsorbed molecules on the surface this factor may be different from that in the presence of adsorbed molecules. That is, the collision and reflection of molecules during the course of Knudsen diffusion must be influenced by the presence of adsorbed species on the pore surfaces. Figure 1 illustrates schematically the effect of adsorbed molecules on the Knudsen diffusion process. As the adsorption loading increases, the fraction of molecules reflected from the surface is greater, resulting in a decrease of the collision reflection factor. It is logical to assume that this factor decreases linearly with the fractional loading θ_M in meso/macropores where most gas phase diffusion takes place:

$$f_M = f_\infty \theta_M + f_0(1 - \theta_M), \quad (f_\infty < f_0), \quad (3)$$

where f_∞ and f_0 are the collision reflection factors at high pressure (close to the vapor pressure, P_0) and at the limit of zero pressure, respectively, in meso/macropores. Note that the parameters defined in Eq. (3) for Knudsen diffusion are associated

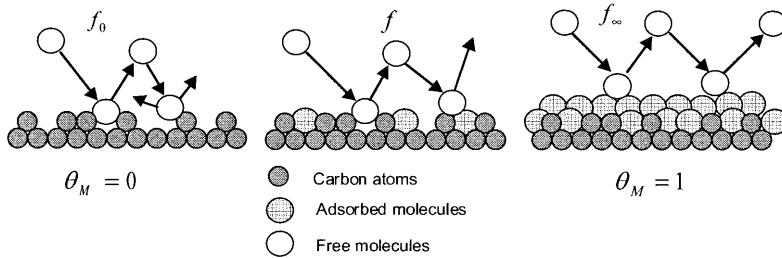


Figure 1 Schematic illustration of the effect of adsorbed molecules on the collision reflection factor. θ_M is the fractional loading in meso/macropores. As adsorbed molecules are built up, the collision reflection factor decreases because of reduction in activation energy for surface diffusion.

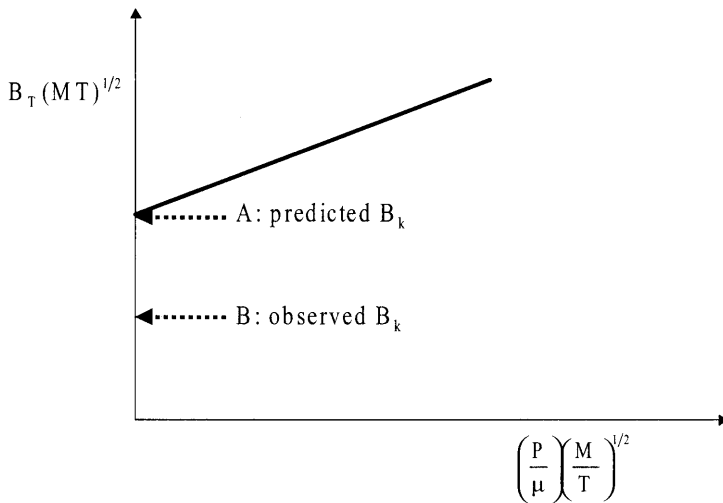


Figure 2 Schematic illustration to determine the collision reflection factor f_0 in the limit of zero pressure for strongly adsorbing vapors in activated carbon. Having known the intercepts A and B in this figure, we can obtain the value of f_0 according to Eq. (4).

with meso/macropores as the gas phase transport in micropores is not possible. As shown in Figure 2, the observed Knudsen diffusion permeability (B_k) for adsorbates is much lower than the B_k predicted from the inert gas experiments, which was based on the dispersive fluid–solid interaction. With the value of f_0 for inert gases chosen to be unity, the value of f_0 for adsorbates can be obtained by matching the predicted B_k against the experimental value at zero loading:

$$B_{K_predicted} \left(\frac{2 - f_0}{f_0} \right) = B_{K_observed} \quad (4)$$

When the dispersive interaction between permeating molecules and solid surface atoms is negligible, which is assumed to be the case for inert gases, the Knudsen diffusivity (D_k^0) is given by

$$D_k^0 = \frac{4K_0}{3} \sqrt{\frac{8R_g T}{\pi M}}, \quad (5)$$

where K_0 is the Knudsen diffusion parameter, which is a solid characteristic. Consequently, the Knudsen diffusivity (D_k^a) for adsorbing vapors at any surface loading takes the following form:

$$D_k^a = \frac{4K_0}{3} \sqrt{\frac{8R_g T}{\pi M}} \left(\frac{2 - f_M}{f_M} \right), \quad (6)$$

where f_M is calculated from Eq. (3). Thus it is seen that the Knudsen diffusivity is a function of adsorbed concentration in the meso/macropores. To delineate the adsorption in meso/macropores and that in micropores, we deconvolute the adsorption equilibrium isotherms into two, using a dual Langmuir equation as the correlating equation:

$$\begin{aligned} C_\mu &= C_{\mu 1} + C_{\mu 2} \\ &= C_{\mu m 1} \frac{b_1 P}{1 + b_1 P} + C_{\mu m 2} \frac{b_2 P}{1 + b_2 P} \end{aligned} \quad (7)$$

The first term of RHS in Eq. (7) corresponds to adsorption in micropores while the second term is due to adsorption in meso/macropores ($b_1 > b_2$). The fractional loading (θ_M) in large pores (which is used in Eq. [3]) can be obtained from the above equation as follows:

$$\theta_M = \frac{C_{\mu 2}}{C_{\mu m 2}} = \frac{b_2 P}{1 + b_2 P} \quad (8)$$

Having discussed the Knudsen diffusivity as a function of loading of the meso/macropores, we now propose a general mechanism of transport of adsorbing vapors in activated carbon. For a given pressure gradient imposed across two ends of a porous medium, the total permeability of permeating molecules through the solid at low pressures can be described by three processes, Knudsen diffusion, viscous flow, and surface diffusion, which are assumed to be additive. Because of the distinct bimodal pore size distribution in activated carbon, we can describe the transport as a sum of four separate processes as follows:

- (i) Knudsen diffusion in meso/macropores
- (ii) Gaseous viscous flow in meso/macropores
- (iii) Diffusion of adsorbed molecules in meso/macropores
- (iv) Diffusion of adsorbed molecules in micropores

It is emphasized that the first three processes occur in meso/macropores while the last occurs in micropores where Knudsen diffusion and viscous flow are absent because of the small confinement of micropores. Since gaseous viscous flow is a streamline flow, mainly taking place in the inner core of meso/macropores, it is reasonable to assume that the presence of adsorbed species does not affect the viscous flow. On

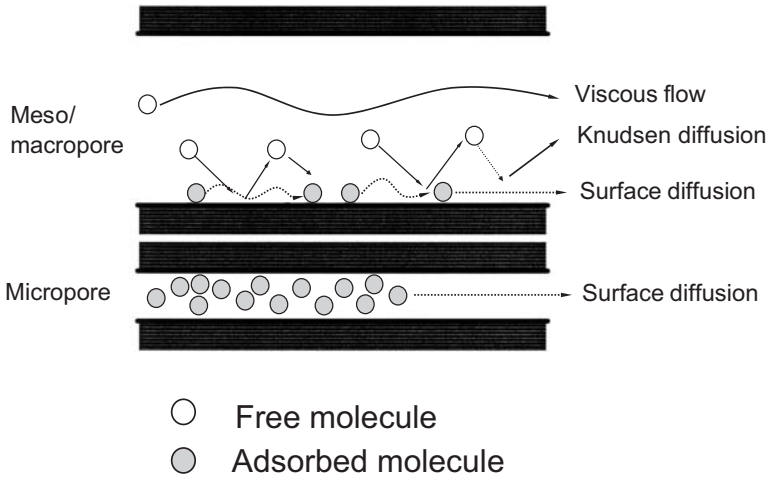


Figure 3 Schematic diagram of transport processes of strongly adsorbing vapors in activated carbon. The Knudsen diffusion and the surface diffusion in meso/macropores are coupled with the coupling factor being the adsorbed concentration in meso/macropores, $C_{\mu 2}$.

the other hand, in the region adjacent to the meso/macropore surface, Knudsen diffusion and surface diffusion are coupled with the coupling factor being the adsorbed concentration. Figure 3 illustrates schematically the above processes. Thus the total permeability (B_T) is given by

$$B_T = \underbrace{\frac{16K_0}{3\sqrt{2\pi MR_g T}} \left(\frac{2 - f_M}{f_M} \right) + \frac{B_0 P}{\mu R_g T}}_{\text{meso/macropore}} + B_{\mu 2} + \underbrace{B_{\mu 1}}_{\text{micropore}}, \quad (9)$$

where B_0 is the viscous flow parameter of the medium and μ is the gas phase viscosity. Here, K_0 and B_0 can be obtained from inert gas experiments. The last two terms in the RHS of Eq. (9) are the surface diffusion permeabilities in meso/macropores and in micropores, respectively. It is generally accepted that adsorption in activated carbon is a transition process from gas phase molecules to liquid-like molecules in the pores [13]. The diffusion of adsorbed molecules is contributed by weakly adsorbed molecules in meso/macropores and by strongly adsorbed molecules in micropores, and it will be discussed in the next section.

2.2. Description of surface diffusion with loading

Knowing the total permeability (B_T) experimentally, and subsequently the Knudsen diffusion permeability (B_K) and the viscous flow permeability (B_V), we can determine the surface diffusion permeability (B_μ) as follows:

$$B_\mu = B_T - (B_K + B_V) \quad (10)$$

This surface diffusion permeability is contributed by the mobility of adsorbed molecules in micropores and meso/macropores and can be described by $B_{\mu 1}$ and $B_{\mu 2}$, respectively, as given below:

$$B_{\mu} = B_{\mu 1} + B_{\mu 2} = D_{\mu 1} \frac{dC_{\mu 1}}{dP} + D_{\mu 2} \frac{dC_{\mu 2}}{dP}. \quad (11)$$

Here we have assumed that those two diffusions are additive. The diffusivities, $D_{\mu 1}$ and $D_{\mu 2}$, are the surface diffusivities in micropore and meso/macropore, respectively, and they are a function of their respective adsorbed concentrations, that is, $D_{\mu 1} = D_{\mu 1}(C_{\mu 1})$ and $D_{\mu 2} = D_{\mu 2}(C_{\mu 2})$. They will be determined experimentally. Knowing the transport surface diffusivity, the “corrected” surface diffusivity (D_{μ}^*) can be obtained from the following Darken’s equation,

$$D_{\mu}^* = \frac{D_{\mu}}{\left(\frac{\partial \ln P}{\partial \ln C_{\mu}} \right)}, \quad (12)$$

where $(\partial \ln P / \partial \ln C_{\mu})$ is a thermodynamic correction factor that increases linearly with pressure for the Langmuir equation. For the two regions of micropores and macropores of activated carbon, the thermodynamic correction factors can be calculated from Eq. (7). The transport diffusivities for these two regions are

$$D_{\mu 1} = \frac{D_{\mu 1}^*}{(1 - C_{\mu 1}/C_{\mu m 1})} = D_{\mu 1}^*(1 + b_1 P) \quad \text{and} \quad (13a)$$

$$D_{\mu 2} = \frac{D_{\mu 2}^*}{(1 - C_{\mu 2}/C_{\mu m 2})} = D_{\mu 2}^*(1 + b_2 P). \quad (13b)$$

If the Darken theory holds (constant corrected diffusivity D_{μ}^*) for strongly adsorbing vapors in activated carbon, the surface diffusivity D_{μ} would be proportional to pressure. Such a concentration independence of the corrected diffusivity (D_{μ}^*) has not been proven for strongly adsorbing vapors in activated carbon. In general, one would expect this corrected diffusivity to be a function of adsorbed concentration, and we will show this dependence in Section 4. Also, since the Knudsen diffusion and the surface diffusion in meso/macropores take place simultaneously, as mentioned earlier, the surface diffusivity as well as the Knudsen diffusivity will be linked in terms of adsorbed concentration in meso/macropores.

3. Experimental

The transport processes of subcritical hydrocarbons through a commercial activated carbon were investigated by using a differential permeation method. The hydrocarbons studied and the physical properties are listed in Table 1. The activated carbon used in this investigation is cylindrical in shape with a diameter of 1/16 inch and has

Table 1 Physical properties of adsorbates studied at 293 K.

	Molecular weight (g mol ⁻¹)	Liquid molar volume (m ³ kmol ⁻¹)	Liquid self diffusivity [15] (m ² s ⁻¹)	Liquid viscosity (N s m ⁻²)	Vapor viscosity (N s m ⁻²)
Carbon tetrachloride	153.82	0.0969	1.945×10^{-9}	9.739×10^{-4}	9.820×10^{-6}
Benzene	78.11	0.0893	3.100×10^{-9}	6.108×10^{-4}	7.442×10^{-6}
<i>n</i> -Hexane	86.18	0.1291	5.172×10^{-9}	3.100×10^{-4}	6.355×10^{-6}

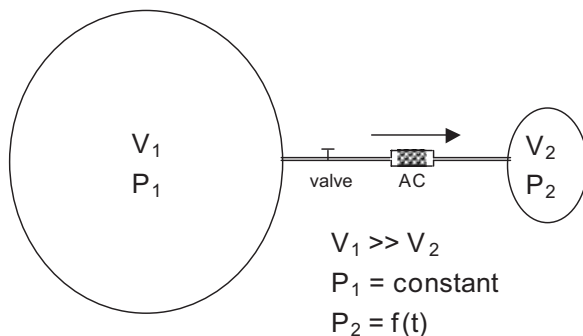


Figure 4 Schematic diagram of a differential permeation setup. The reservoir V_1 is much larger than V_2 so that the pressure P_1 remains practically unchanged during the course of adsorption and diffusion. The pressure change in the reservoir V_2 was measured and used to calculate the total flux through activated carbon according to Eq. (14).

a microporosity of 0.40 and a macroporosity of 0.3. The mean macropore size is 0.8 μm . The experimental setup is shown schematically in Figure 4, and more details can be found elsewhere [14].

The apparatus consists of two main compartments which are separated by the porous medium. The LHS reservoir is much larger in volume than the RHS one (i.e., $V_1 \gg V_2$) such that the pressure of the LHS reservoir is practically constant during the course of diffusion and adsorption. After a small dose of gas or vapor is filled in the LHS reservoir and at $t = 0^+$, opening the isolation valve between the LHS reservoir and the sample cell allows molecules to diffuse through the medium. When P_1 and P_2 have approached an equilibrium pressure (P^*), the isolation valve is closed. Subsequent runs can be conducted by increasing the pressure in the LHS reservoir incrementally from P^* to $P^* + \Delta P$, where $\Delta P \ll P^*$, until P^* is close to the vapor pressure of the permeating species. In each run, the pressure (P_2) of the RHS reservoir is recorded with respect to time, from which we can calculate the flux and hence the total permeability (B_T). This total permeability is determined from Eq. (14) by plotting $\ln[(P_1 - P^*)/(P_1 - P_2)]$ versus time (t):

$$\ln\left(\frac{P_1 - P^*}{P_1 - P_2(t)}\right) = B_T \left(\frac{AR_g T}{V_2 L}\right) t, \quad (14)$$

where V_2 is the RHS reservoir volume, A is the cross-sectional area of the sample, and L is the sample length.

4. Results and discussion

4.1. Equilibrium isotherms

The equilibrium adsorption isotherms of benzene, carbon tetrachloride, and n -hexane were obtained at three different temperatures. The relationships between the amount adsorbed and pressure were described reasonably well with the dual Langmuir equation (Eq. [7]). The optimal parameters, $C_{\mu m1}$, b_1 , $C_{\mu m2}$, and b_2 , obtained from the fitting of the equation against the experimental data are listed in Table 2. The equilibrium isotherms for each adsorbate are divided into adsorbed concentrations $C_{\mu 1}$ (in micropores) and $C_{\mu 2}$ (in meso/macropores) and plotted with respect to pressure in Figure 5. The micropore capacity, $C_{\mu 1}$, increases sharply with pressure at very low pressures while the meso/macropore capacity, $C_{\mu 2}$, which is used to calculate the collision reflection factor, increases moderately. From the behavior of $C_{\mu 1}$ with respect to pressure, one would expect that the contribution of surface diffusion in micropores to the total permeability diminishes once micropores are completely filled at low pressure.

4.2. Total permeability

The total permeability of inert gases such as helium can be described by the first two terms in the RHS of Eq. (9) since inert gas adsorption in activated carbon at moderate temperatures and pressures is negligible. The total permeability of inert gases exhibits a linear dependence on pressure, from which the solid characteristics, K_0 and B_0 , were found to be 7.069×10^{-8} m and 2.578×10^{-14} m², respectively. If there is *no surface diffusion for adsorbates*, one can predict the total permeability of adsorbates from their physical properties such as molecular weight and viscosity. The ratio of the total permeability ($B_{T,observed}$) of adsorbates observed from experiments over the total permeability ($B_{T,predicted}$) predicted from inert gas experiments is plotted

Table 2 Optimal parameters of the dual Langmuir isotherm equation for strongly adsorbing vapors in activated carbon.

Parameter	Temp. (K)	Benzene	CCl ₄	n -Hexane
$C_{\mu m1}$ (mol m ⁻³)	293	3.325×10^3	3.208×10^3	2.790×10^3
	303	2.923×10^3	2.746×10^3	2.577×10^3
	312	2.603×10^3	2.388×10^3	2.400×10^3
b_1 (Pa ⁻¹)	293	2.128×10^{-1}	2.900×10^{-1}	3.319×10^{-1}
	303	2.035×10^{-1}	2.308×10^{-1}	2.505×10^{-1}
	312	1.959×10^{-1}	1.903×10^{-1}	1.975×10^{-1}
$C_{\mu m2}$ (mol m ⁻³)	293	2.524×10^3	1.868×10^3	1.084×10^3
	303	2.636×10^3	2.056×10^3	1.156×10^3
	312	2.741×10^3	2.242×10^3	1.226×10^3
b_2 (Pa ⁻¹)	293	2.525×10^{-3}	2.475×10^{-3}	9.861×10^{-4}
	303	2.204×10^{-3}	2.769×10^{-3}	1.099×10^{-3}
	312	1.965×10^{-3}	3.045×10^{-3}	1.204×10^{-3}

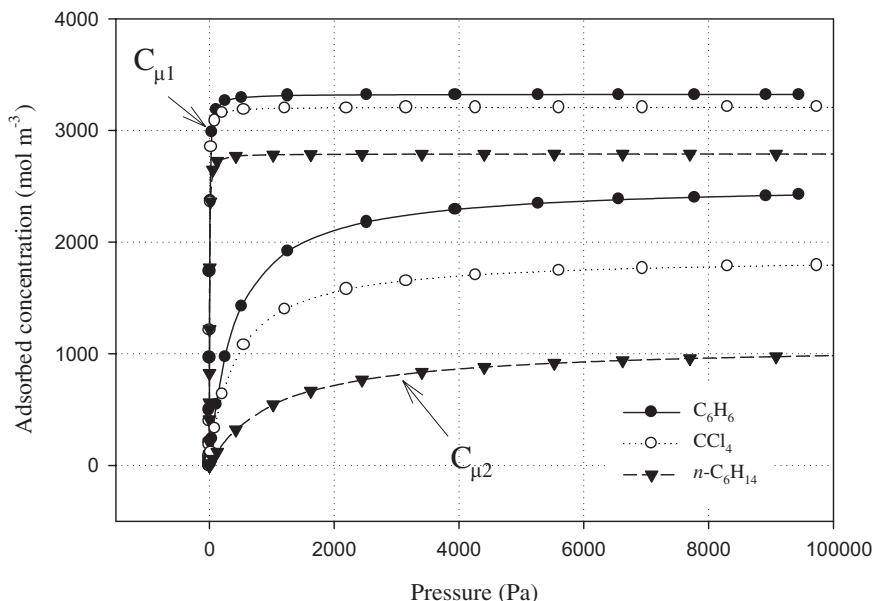


Figure 5 Equilibrium isotherms of benzene, carbon tetrachloride, and *n*-hexane in micropores ($C_{\mu 1}$) and in meso/macropores ($C_{\mu 2}$) of activated carbon at 293 K, obtained from the dual Langmuir equation (Eq. [7]).

against reduced pressure at three temperatures in Figure 6. From this plot, we derive two significant points.

1. At very low pressures, the ratio is very low and increases sharply with pressure, approaching greater than unity for the cases of *n*-hexane and benzene. This phenomenon, which will be discussed further in the following sections, should be related to the interplay between Knudsen diffusion and surface diffusion, since gaseous viscous flow is negligible at this range of pressure.
2. At reduced pressure ranging from 0.1 to 0.8, the ratio decreases linearly with reduced pressure regardless of temperature and type of adsorbate. This suggests that the sum of Knudsen diffusion and surface diffusion permeability should decrease linearly with pressure since viscous flow is a linear function of pressure.

However, care should be taken because the effect of adsorbed molecules on both Knudsen diffusion and surface diffusion has not been taken into account yet. Neglecting the effects of the presence of adsorbed species and fluid–solid interactions on diffusion processes may lead to erroneous conclusions [6]. Thus, we need to firstly determine the Knudsen diffusion permeability for adsorbate before we elaborate further the behavior of surface diffusion permeability in activated carbon.

4.3. Knudsen diffusion permeability

To calculate the Knudsen diffusion permeability, firstly the collision reflection factor in Eq. (3) was obtained with the fractional loading in meso/macropores. The initial

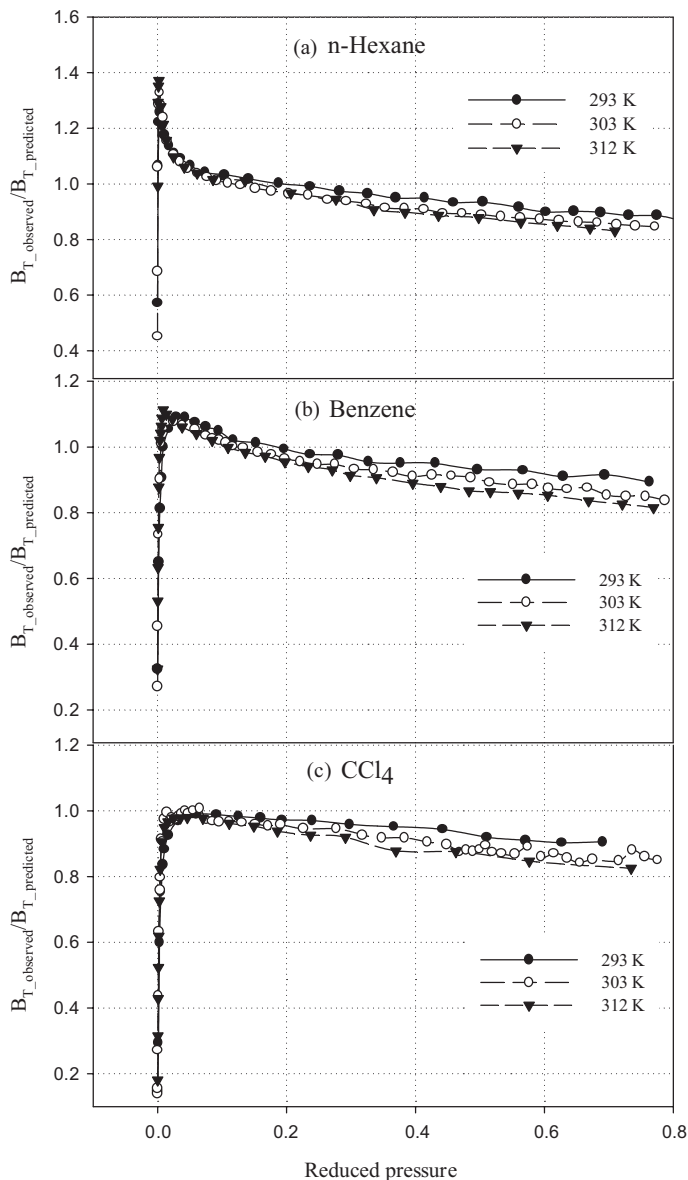


Figure 6 Relative total permeability of adsorbates in activated carbon at three temperatures (293 K, 303 K, and 312 K): (a) *n*-hexane, (b) benzene, and (c) carbon tetrachloride. $B_{T_observed}$ and $B_{T_predicted}$ are the total permeabilities obtained from adsorbate experiments and predicted from inert gas experiments by taking the first two terms in Eq. (9) with f_M being unity, respectively.

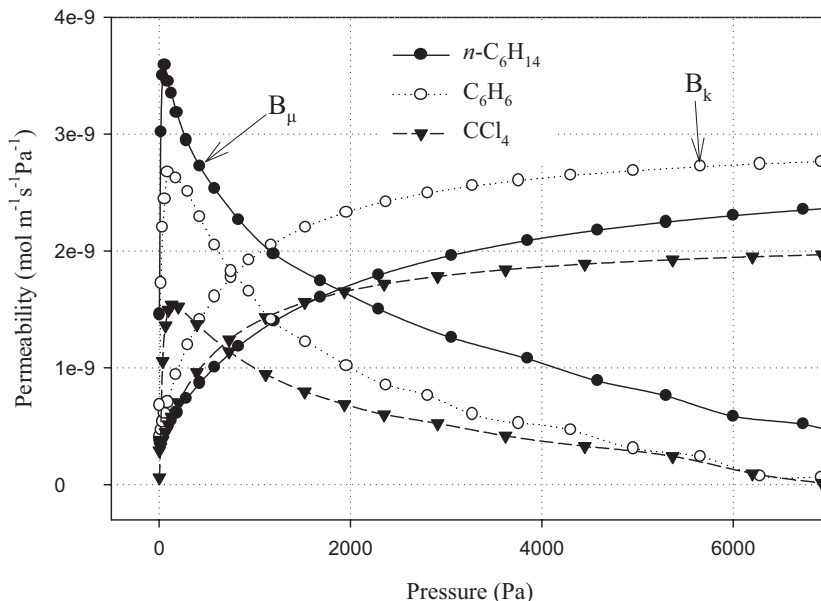


Figure 7 Knudsen diffusion permeability (B_k) and surface diffusion permeability (B_μ) of *n*-hexane, benzene, and carbon tetrachloride in activated carbon at 293 K. The effect of adsorbed molecules on Knudsen diffusion was taken into account in the calculation of B_k . According to Eq. (10), the surface diffusion permeability B_μ was obtained.

value (f_0) of the collision reflection factor for adsorbates can be calculated from the two intercepts in the plots of $B_T(MT)^{0.5}$ versus $(P/\mu)(M/T)^{0.5}$ for inert gases and adsorbates as schematically shown in Figure 2. From Eq. (4), the value f_0 was found to be 1.79 for all adsorbates studied. The collision reflection factor (f_∞) at high pressure (close to the vapor pressure, P_0) was 1.06, which was estimated by fitting our previous model [16] against experimental data. This value f_∞ at high loadings is close to unity, suggesting the collision and reflection of adsorbate is similar to that of inert gases. By incorporating the effect of adsorbed phase into the collision reflection factor, the Knudsen diffusion permeability (B_k) for each adsorbate was calculated and plotted in Figure 7. We see that the behavior of Knudsen diffusion permeability with loading is different from the description of Eq. (5). For example, for pressures up to about 2 kPa, the B_k of *n*-hexane is smaller than that of carbon tetrachloride, which cannot be predicted from only the ratio of its inverse square root of molecular weight as required by Eq. (5). Thus, neglecting the effect of adsorbed molecules on Knudsen diffusion may give rise to incorrect results. The conventional calculation of Knudsen diffusivity does not take into account the interaction force between colliding molecules and surface atoms and the effect of the presence of adsorbed phase. Here, the collision reflection factor takes these points into account implicitly. It is, however, noted that the effects of temperature, types of adsorbate, and molecular structure on the collision reflection factor are not accounted for in this paper since the temperature range studied is relatively narrow and all adsorbates used adsorb strongly in activated carbon.

4.4. Surface diffusion permeability

According to Eq. (10), the surface diffusion permeability (B_μ) of each adsorbate was calculated and plotted in Figure 7. The B_μ increases drastically at very low pressures, indicating the significance of surface diffusion in this region. The mechanism for surface diffusion at very low pressures can be explained as follows. Adsorbed molecules occupy progressively onto lower energy sites where the mobility is greater, resulting in the higher contribution of surface diffusion to the total permeability and hence a sharp increase in the observed total permeability. Once pressure approaches a critical pressure, P^* , at which micropores are saturated, the adsorbed phase flux through micropores decreases because of the reduction of chemical potential gradient inside those pores. As a result, the contribution of surface diffusion in micropores to the total permeability becomes less and less as pressure increases beyond P^* . Then the significance of surface diffusion in meso/macropores to the total permeability becomes apparent for pressures greater than P^* . The respective contribution of surface diffusion in both pores will be discussed in the following section.

4.5. Determination of surface diffusivity

It is noted that our methodology to determine surface diffusivity is based on experimental observations. Before we derive a functional form of surface diffusivity, here we recall the observations that are essential for us to quantify the four processes that we have proposed in Eq. (9):

1. The observed Knudsen diffusion permeability of adsorbate at zero loading is lower than the calculated values (from inert gas permeability), and the surface diffusion should be negligible at zero loading, indicating that the collision reflection factor of adsorbate *is not* the same as that of inert gases.
2. The observed total permeability increases sharply at low pressures, indicating the significance of surface diffusion. Since under this condition adsorption only occurs in micropores, this surface diffusion is attributed to adsorbed molecules in micropores.
3. The ratio ($B_{T,observed}/B_{T,predicted}$) reduces to unity, suggesting that the surface diffusion of adsorbed molecules in micropores becomes negligible.
4. The slope of the total permeability of adsorbate versus pressure is less than that calculated from inert gases over the range of reduced pressure of 0.1–0.8, suggesting that the surface diffusion permeability decreases with loading.

Having described the mechanism of surface diffusion in Section 4.4, in which we have shown that the relative contributions of surface diffusion in micropores and in meso/macropores are different in a different range of pressure, we will determine these surface diffusions based on the above observations. First we will consider that in the meso/macropore regions.

4.5.1. Surface diffusivity in meso/macropores We make an assumption that the surface diffusion permeability ($B_{\mu 2}$) in meso/macropores is similar in pattern to the behavior of B_μ versus loading. This assumption is reasonable as we expect the surface

diffusion in micropores to be significant only in the very low pressure range as discussed earlier. This pattern of B_μ versus loading follows the form of $\theta_M(1 - \theta_M)$. So we can write

$$B_{\mu 2} = \alpha \theta_M (1 - \theta_M), \quad (15)$$

where α is constant of proportionality. Knowing this surface diffusion permeability, the surface diffusivity can be calculated according to Eq. (11) and given by

$$D_{\mu 2} = \frac{B_{\mu 2}}{dC_{\mu 2}/dP} = \alpha \left(\frac{\theta_M}{1 - \theta_M} \right). \quad (16)$$

This result suggests that the surface diffusivity increases with loading much faster than the Darken theory because of the presence of θ_M in the numerator of the above equation (recall the Darken theory: $D_\mu \propto 1/[1 - \theta]$). Knowing the transport surface diffusivity as given in Eq. (16), the corrected surface diffusivity in meso/macropores is

$$D_{\mu 2}^* = \alpha \theta_M. \quad (17)$$

Thus we can propose a functional form for the corrected surface diffusivity as

$$D_{\mu 2}^* = a + \alpha \theta_M. \quad (18)$$

The reason for the introduction of the parameter a is because at zero loading adsorbed molecules should exhibit some intrinsic mobility. We denote this intrinsic mobility at zero loading as $D_{\mu 2}^{*(0)}$. Then the equation for the corrected surface diffusivity at any loading in meso/macropores will become

$$D_{\mu 2}^* = D_{\mu 2}^{*(0)} (1 + b \theta_M). \quad (19)$$

The remaining parameter to be discussed in the above equation is b . We know that at zero loading and at high loading the collision reflection factors are f_0 and f_∞ , respectively, as discussed earlier in Section 2.1, and that the Knudsen diffusivities (D_{k0} and $D_{k\infty}$, respectively) at these two extremes are

$$D_k^{a(0)} = \beta \left(\frac{2 - f_0}{f_0} \right) \quad \text{and} \quad D_k^{a(1)} = \beta \left(\frac{2 - f_\infty}{f_\infty} \right), \quad (20)$$

where β is the Knudsen diffusivity for inert gases as defined in Eq. (5). We argue that the mobility of adsorbed molecules is related to the magnitude of Knudsen diffusivity because of the momentum exchange between the free molecules and the adsorbed molecules [7, 8]. We rewrite Eq. (19) as follows:

$$D_{\mu 2}^* = D_{\mu 2}^{*(0)} (1 - \theta_M) + D_{\mu 2}^{*(1)} \theta_M, \quad (21)$$

where $D_{\mu 2}^{*(1)}$ is the corrected surface diffusivity at saturation of mesopores. As loading increases, the interaction between the adsorbed molecules and the surface is weaker, leading to greater mobility. Hence we expect that the following inequality is true:

$$D_{\mu 2}^{*(1)} > D_{\mu 2}^{*(0)} \tag{22}$$

Let us stress that at high loadings, the collision reflection factor is lower due to the weaker interaction with the surface, and the following inequality has been obtained in Section 2.1:

$$D_k^{a(1)} > D_k^{a(0)} \tag{23}$$

We see that the Knudsen diffusivity and the corrected surface diffusivity follow the same trend, resulting from the coupling of the momentum exchange between the free molecules and the adsorbed molecules. Then it is reasonable to assume that

$$D_{\mu 2}^{*(0)} \propto D_k^{a(0)} \quad \text{and} \quad D_{\mu 2}^{*(1)} \propto D_k^{a(1)}. \tag{24a,b}$$

Using Eq. (6), we can write the following expressions for the corrected surface diffusivity at zero loading and high loadings:

$$D_{\mu 2}^{*(0)} \propto \left(\frac{2 - f_0}{f_0} \right) \quad \text{and} \quad D_{\mu 2}^{*(1)} \propto \left(\frac{2 - f_\infty}{f_\infty} \right). \tag{25a,b}$$

Therefore, the final equation for the corrected surface diffusivity in meso/macropores is

$$\begin{aligned} D_{\mu 2}^* &= \alpha \left\{ \left(\frac{2 - f_0}{f_0} \right) (1 - \theta_M) + \left(\frac{2 - f_\infty}{f_\infty} \right) \theta_M \right\}, \\ &= D_{\mu 2}^{*(0)} (1 + b \theta_M) \\ \text{where } b &= \left(\frac{2(f_0 - f_\infty)}{f_\infty(2 - f_0)} \right). \end{aligned} \tag{26}$$

Eq. (26) reduces to the HIO model when b is equal to zero, in which the corrected surface diffusivity is a constant. For subcritical hydrocarbon in activated carbon, however, the value of β is found to be 6.56, indicating that the corrected surface diffusivity is a linear function of loading. Consequently, we have the transport surface diffusivity in meso/macropores as follows:

$$D_{\mu 2} = D_{\mu 2}^{*(0)} \left[1 + (1 + b) \left(\frac{\theta_M}{1 - \theta_M} \right) \right] \tag{27}$$

We have completed the derivation of the necessary equations for the description of surface diffusion in meso/macropores. The only parameter that we need to derive

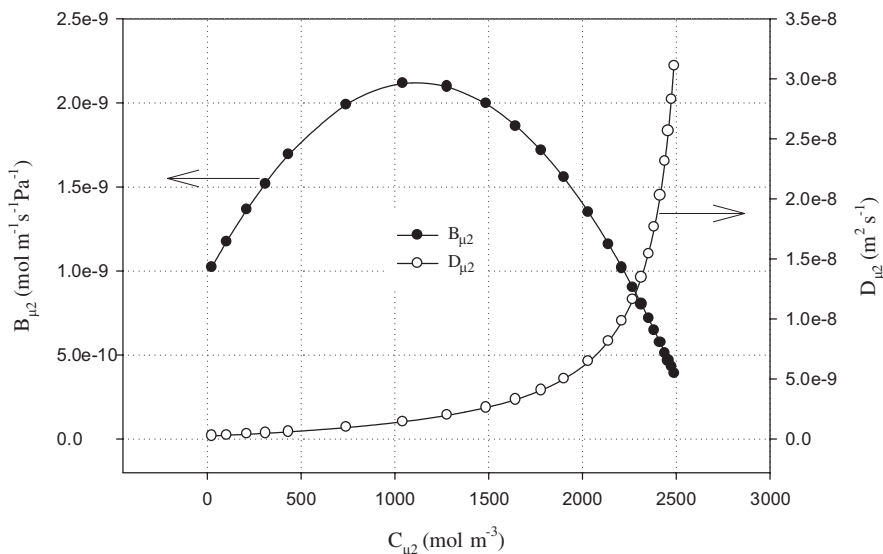


Figure 8 Plots of surface diffusion permeability and surface diffusivity with respect to adsorbed concentration $C_{\mu 2}$ for benzene in the meso/macropores of activated carbon at 293 K. The surface diffusivity $D_{\mu 2}$ was calculated according to Eq. (26).

from the experimental surface permeability is the corrected surface diffusivity at zero loading, $D_{\mu 2}^{*(0)}$. According to the above equation, the corrected surface diffusivities $D_{\mu 2}^{*(0)}$ in the limit of zero loading at 293 K were found to be 2.428×10^{-10} , 1.577×10^{-10} , and $1.043 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for benzene, carbon tetrachloride, and *n*-hexane, respectively. The surface diffusion permeability ($B_{\mu 2}$) and the transport diffusivity ($D_{\mu 2}$) of benzene at 293 K are depicted with respect to the adsorbed concentration ($C_{\mu 2}$) in meso/macropores in Figure 8.

4.5.2. Surface diffusivity in micropores The surface diffusivity ($D_{\mu 1}$) in the micropores of activated carbon is far from being completely understood because of the complexity in the energy distribution, the pore structure and geometry of micropores, and the dispersion interaction force between adsorbed molecules and solid surface atoms. One would argue that the surface diffusion permeability ($B_{\mu 1}$) in micropores behaves like $\theta_{\mu}(1 - \theta_{\mu})$, like the way we did for surface diffusion permeability in meso/macropores. However, we do not find that this is the case, suggesting that the functional form of $D_{\mu 1}$ in micropores should be different from that of $D_{\mu 2}$, possibly due to the geometric confinement in micropores. To find this functional form experimentally, we can calculate the $B_{\mu 1}$ from Eq. (11). The surface diffusion permeability of each adsorbate is deconvoluted to $B_{\mu 1}$ and $B_{\mu 2}$ for micropores and for meso/macropores, respectively, and plotted against gas phase pressure in Figure 9. In the case of *n*-hexane, the surface diffusion in micropores plays more significant roles in the transport of adsorbed molecules, compared to that in meso/macropores at very low pressures. On the other hand, in the cases of benzene and carbon tetrachloride, $B_{\mu 2}$ contributes to the total permeability more significantly

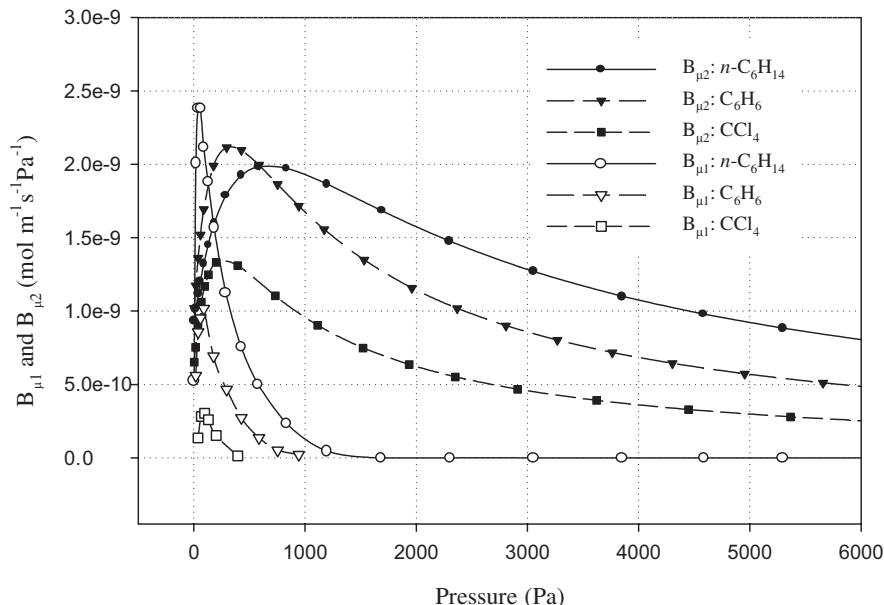


Figure 9 Surface diffusion permeabilities in micropores ($B_{\mu 1}$) and meso/macropores ($B_{\mu 2}$) of *n*-hexane, benzene, and carbon tetrachloride in activated carbon at 293 K. Knowing the $B_{\mu 2}$, the $B_{\mu 1}$ was calculated from the relation of $B_{\mu 1} = B_{\mu} - B_{\mu 2}$.

than the $B_{\mu 1}$ over a whole range of pressures. This suggests that the mobility of adsorbed *n*-hexane molecules in micropores may be higher than that of the others. Another possible reason is that lack of local thermodynamic equilibrium at the pore mouth may have a significant effect on the surface diffusion permeability [17]. According to Do’s structural model on surface diffusion [18], a possible mechanism for surface diffusion is for molecules to penetrate the pore mouth, to diffuse along the pore, and to evaporate from the pore. Of these three steps, the penetration and evaporation steps are limiting steps, suggesting that the assumption of local thermodynamic equilibrium may break down at the pore entry and exit. Since *n*-hexane is linear chain molecules in structure, it may enter micropores more easily than the others, resulting in its greater contribution to surface diffusion flux compared to the other two adsorbates.

In geometrically restricted pores such as micropores, transport phenomena may be different from conventional description in surface diffusion [19]. Knowing the $B_{\mu 1}$, the surface diffusivity ($D_{\mu 1}$) was calculated from Eq. (11). Figure 10 illustrates the behavior of surface diffusivity of benzene in micropores with respect to the adsorbed concentration ($C_{\mu 1}$) in micropores. The $D_{\mu 1}$ increases with loading similarly to the behavior of $D_{\mu 2}$ up to a critical fractional loading, θ_{μ}^* , at which micropores are saturated. Beyond this critical loading, we observe a sudden decrease of $D_{\mu 1}$. This phenomenon was observed for all three adsorbates studied. More research on the surface diffusion in a confined pore is required to determine theoretically the functional form of the surface diffusivity in micropores.

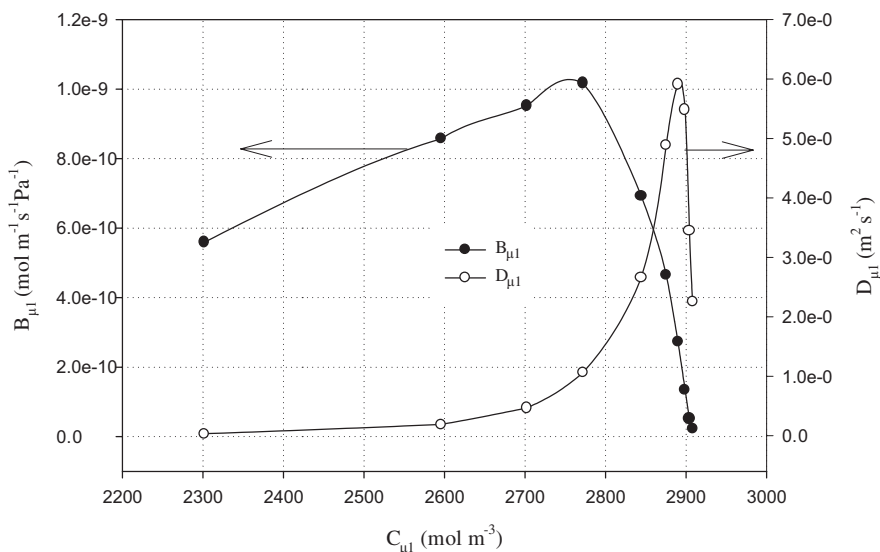


Figure 10 Plots of surface diffusion permeability and surface diffusivity with respect to adsorbed concentration $C_{\mu 1}$ for benzene in the micropores of activated carbon at 293 K. The surface diffusivity $D_{\mu 1}$ was calculated from the relation of $D_{\mu 1} = B_{\mu 1}/(dC_{\mu 1}/dP)$ according to Eq. (11).

5. Conclusions

In this paper, Knudsen diffusion and surface diffusion are associated with the presence of the adsorbed phase by incorporating the collision reflection factor into both diffusion processes. Considering a bimodal pore size distribution of activated carbon, the surface diffusivity of subcritical hydrocarbons was determined for the meso/macropores of activated carbon. This surface diffusivity increases with loading, as typically illustrated in Figure 8. The surface diffusivity in micropores exhibits a similar increasing behavior with respect to loading for loading up to a critical value, beyond which it decreases very sharply (Figure 10). This critical value is identified as the saturation point of micropores. At low pressures, surface diffusion in micropores dominates the transport of adsorbed molecules, whereas after the critical loading most surface diffusion takes place in meso/macropores.

Appendix

Nomenclature

B_0	viscous flow parameter [m ²]
B_k, B_v	permeabilities for Knudsen diffusion and viscous flow, respectively [mol m ⁻¹ s ⁻¹ Pa ⁻¹]
B_T, B_{μ}	total permeability and surface diffusion permeability [mol m ⁻¹ s ⁻¹ Pa ⁻¹]
$C_{\mu}, C_{\mu m}$	adsorbed concentration, maximum adsorbed concentration, respectively [mol m ⁻³]

D_k^0, D_k^a	Knudsen diffusivity for inert gas and adsorbate, respectively [$\text{m}^2 \text{s}^{-1}$]
D_μ, D_μ^*	surface diffusivity and corrected surface diffusivity, respectively [$\text{m}^2 \text{s}^{-1}$]
f_M	collision reflection factor in meso/macropores
K_0	Knudsen diffusion parameter [m]
P, P_0	gas phase pressure and vapor pressure, respectively [Pa]
R_g	gas constant [$\text{J K}^{-1} \text{mol}^{-1}$]
T	temperature [K]

Greek letters

α, β	constants in Eqs. (15) and (19), respectively
θ_μ, θ_M	fractional loading in micropores and in meso/macropores, respectively

Acknowledgements

The support from the Australian Research Council is gratefully acknowledged.

References

- [1] Baker, R.W., Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res.*, 41 (2002), 1393.
- [2] Lerou, J.J., Ng, K.M., Chemical reaction engineering: A multiscale approach to a multi-objective task, *Chem. Eng. Sci.*, 51 (1996), 1595.
- [3] Rutherford, S.W., Characterization of carbon adsorbents by permeation methods, Ph.D., Chemical Engineering, The University of Queensland, 1999.
- [4] Do, H.D., Do, D.D., A new diffusion and flow theory for activated carbon from low pressure to capillary condensation range, *Chem. Eng. J.*, 84 (2001), 295.
- [5] Bae, J.-S., Do, D.D., Surface diffusion of strongly adsorbing vapors in activated carbon by a differential permeation method, *Chem. Eng. Sci.*, 58 (2003), 4403.
- [6] Reyes, S.C., Sinfelt, J.H., DeMartin, G.J., Diffusion in porous solids: The parallel contribution of gas and surface diffusion processes in pores extending from the mesoporous region into the microporous region, *J. Phys. Chem. B*, 104 (2000), 5750.
- [7] Bell, W.K., Brown, L.F., Kinetic theory approach to simultaneous gas and surface diffusion in capillaries, *J. Chem. Phys.*, 61 (1974), 609.
- [8] Spencer, J.L., Brown, L.F., Experimental observations of gas phase-adsorbed phase interactions during counterdiffusion in porous alumina, *J. Chem. Phys.*, 63 (1975), 2882.
- [9] Shindo, Y., Hakuta, T., Yoshitome, H., Inoue, H., Gas diffusion in microporous media in Knudsen's regime, *J. Chem. Eng. Jpn.*, 16 (1983), 120.
- [10] Zeiri, Y., Tracer surface diffusion at high pressures: Molecular-dynamics study, *J. Chem. Phys.*, 113 (2000), 3868.
- [11] Asscher, M., Zeiri, Y., Surface processes induced by collisions, *J. Phys. Chem. B*, 107 (2003), 6903.
- [12] Do, H.D., Do, D.D., Prasetyo, I., On the surface diffusion of hydrocarbons in microporous activated carbon, *Chem. Eng. Sci.*, 56 (2001), 4351.
- [13] Rudzinski, W., Panczyk, T., Phenomenological kinetics of real gas-adsorption-systems: Isothermal adsorption, *J. Non-Equilib. Thermodyn.*, 27 (2002), 149.
- [14] Bae, J.-S., Do, D.D., Study on diffusion and flow of benzene, *n*-hexane and CCl_4 in activated carbon by a differential permeation method, *Chem. Eng. Sci.*, 57 (2002), 3013.
- [15] Dullien, F.A.L., Predictive equations for self-diffusion in liquids: a different approach, *AIChE J.*, 18 (1972), 62.

- [16] Bae, J.-S., Do, D.D., A unique behavior of sub-critical hydrocarbon permeability in activated carbon at low pressures, *Korean J. Chem. Eng.*, 20 (2003), 1097.
- [17] Nelson, P.H., Auerbach, S.M., Modeling tracer counter-permeation through anisotropic zeolite membranes: From mean field theory to single-file diffusion, *Chem. Eng. J.*, 74 (1999), 43.
- [18] Do, D.D., A model for surface diffusion of ethane and propane in activated carbon, *Chem. Eng. Sci.*, 51 (1996), 4145.
- [19] Gupta, V., Nivarthi, S.S., McCormick, A.V., Davis, H.T., Evidence for single file diffusion of ethane in the molecular sieve AIPO4-5, *Chem. Phys. Lett.*, 247 (1995), 596.

Paper received: 2003-11-05

Paper accepted: 2004-09-09