A Unique Behavior of Sub-critical Hydrocarbon Permeability in Activated Carbon at Low Pressures

Jun-Seok Bae and Duong D. Do[†]

Division of Chemical Engineering, University of Queensland, St. Lucia, Qld 4072, Australia

Abstract—In our study on sub-critical hydrocarbon permeation in activated carbon, a minimum in the total permeability (B_T) at low pressure has been observed for only long-chain hydrocarbons such as *n*-hexane and *n*-heptane. Such an observation suggests that the minimum appearance depends on the properties of permeating vapors as well as the porous medium. In this paper a permeation model is presented to explain the minimum behavior with the allowance of the collision-reflection factor in the Knudsen diffusivity to be a function of surface loading. Surface diffusion was found to be very significant compared to other transport mechanisms such as Knudsen diffusion and gaseous viscous flow at low pressures. Since the gaseous viscous flow contributes negligibly to the B_T at low pressures, the minimum appearance in the B_T is mainly attributed to the interplay between Knudsen diffusion and surface diffusion. Also, the molecular structure of adsorbates plays an important role in the minimum appearance.

Key words: Permeability, *N*-hexane, Activated Carbon, Surface Diffusion, Hydrocarbon

INTRODUCTION

In adsorption processes, including separation and purification in porous materials, it is essential to develop reliable methods for estimation in process performance and design parameters. This requires accurate information on the adsorption kinetics and equilibrium characteristics. For example, chromatography [Schneider and Smith, 1968], frequency response [Yasuda, 1982], and differential adsorption beds [Mayfield and Do, 1991] have been proposed to measure dynamic parameters. Furthermore, Do [1995] has developed a constant molar flow (CMF) method which has been applied by Do and co-workers. Due to the lesser accuracy of the CMF method at high relative pressure, a differential permeation (DP) method, which is used in this paper, has recently been applied [Bae and Do, 2002; Prasetyo, 2000].

Transport of adsorbing vapors through porous media such as activated carbon is generally described by Knudsen diffusion, gaseous viscous flow, surface diffusion and capillary condensate flow [Do and Do, 2001; Do et al., 2001]. Each of these mechanisms plays an important role in the mass transfer of the adsorbates through the medium, generally characterized by permeability which depends on the properties of adsorbates as well as adsorbents. Knudsen diffusion is free molecular diffusion, describing the transport of molecules colliding and bouncing back from the porous solid wall. Due to a total pressure gradient between both ends of the medium, gaseous viscous flow takes place. Also an adsorbed concentration gradient is a driving force for adsorbed phase diffusion on the surface, commonly known as surface diffusion. At high pressure where capillary condensation occurs, there is capillary condensate flow. Since activated carbon is known to possess micropores as well as meso/macropores, one would expect that surface diffusion is significant in micropores where most adsorption occurs while gaseous diffu-

sion and flow mainly takes place in meso/macropores. In this paper we are dealing with permeability at low pressures where the capillary condensate flow is absent.

In diffusion and flow of adsorbing gases or vapors through capillaries, a minimum at low pressure has been reported in the plot of flow rate versus pressure, with an argument that it appears when the mean free path (λ) is comparable to the capillary radius (r) [Adzumi, 1937; Carman, 1950; Knudsen, 1909]. For the tortuous and irregular capillaries of porous media, on the other hand, the minimum is not expected to appear as reported theoretically and experimentally [Carman, 1950; Pollard and Present, 1948; Wicke and Vollmer, 1952]. However, in our permeation study of sub-critical hydrocarbons through activated carbon, a minimum appearance in the total permeability (B_T) at low pressure depends on the type of adsorbate and it is persistent with a given adsorbate (*i.e.*, if the minimum occurs for a given adsorbate at one temperature it will occur at other temperatures as well) [Bae and Do, 2002]. In our investigation *n*-hexane and *n*-heptane, which are linear-chain molecules in structure, show a clear minimum in the B_T at low pressure while there is no minimum for other nonlinear structured molecules such as benzene, carbon tetrachloride and 2,3-dimethylbutane. Such an observation suggests that the existence of the minimum depends on the properties of permeating vapors as well as the porous medium. Here we argue that the interplay of the above three transport mechanisms may determine the appearance of the minimum in the total permeability. In this paper we develop a permeation model which introduces a collision-reflection factor to take into account the adsorption effect on Knudsen diffusion permeability. Surface diffusion is treated in such a way that the mobility of molecules on the surface increases with surface concentration due to the reduction of energy barrier for the diffusion of adsorbed molecules with the progress of adsorption. This paper will present a better description of the three diffusion mechanisms and feasible reasons for the minimum appearance in the total permeability of sub-critical hydrocarbon through activated carbon.

[†]To whom correspondence should be addressed.
E-mail: duongd@cheque.uq.edu.au

PROBLEM FORMULATION ON PERMEABILITY

For a given pressure gradient across a porous medium, the mass balance equation can be described as follows, provided that Knudsen diffusion, viscous flow and surface diffusion are additive to the total flux.

$$\varepsilon\frac{\partial}{\partial t}\left(\frac{P}{R_g T}\right)+(1-\varepsilon)\frac{\partial C_\mu}{\partial t}=\frac{\partial}{\partial z}\left\{\left[\frac{\varepsilon D_p}{R_g T}+\frac{\varepsilon B_0 P}{\mu R_g T}+(1-\varepsilon)D_\mu\frac{\partial C_\mu}{\partial P}\right]\frac{\partial P}{\partial z}\right\} \quad (1)$$

where ε is the porosity of the particle, P is the intraparticle pressure and C_μ is the adsorbed phase concentration. At steady state the terms in the square bracket of the RHS of Eq. (1) are corresponding to Knudsen diffusion permeability (B_k), viscous flow permeability (B_v) and surface diffusion permeability (B_μ), respectively. The pore diffusivity (D_p), which is assumed to follow Knudsen mechanism, takes the form of Eq. (2) for non-overlapping cylindrical pore of radius r.

$$D_P^0=\frac{D_k^0}{\tau_k}=\frac{2r}{3\tau_k}\sqrt{\frac{8R_g T}{\pi M}} \quad (2)$$

Here D_p^0 and D_k^0 are the pore diffusivity and Knudsen diffusivity, respectively, when there is no dispersive interaction between permeating molecules and solid surface atoms (*i.e.*, the molecule behaves as a hard sphere and the surface as a hard surface). For adsorbing gases or vapors these parameters can be estimated from inert gas permeation experiment. Since we are dealing with permeability at moderate temperature and pressure, adsorption of inert gases on activated carbon is negligible (*i.e.*, $B_\mu=0$). Thus only two terms (B_k and B_v) describe the total permeability (B_T) for inert gases. By plotting $B_T(MT)^{0.5}$ against $(P/\mu)(M/T)^{0.5}$ from the following relationship [Eq. (3)] for inert gases

$$B_T\sqrt{MT}=\frac{8\varepsilon r}{3\tau_K\sqrt{2\pi R_g}}+\frac{\varepsilon r^2}{8\tau_v R_g}\left(\frac{P}{\mu}\sqrt{\frac{M}{T}}\right) \quad (3)$$

we have an intercept of 1.617×10^{-8} which should be the same for adsorbing vapors because of the following reasons:

1. In the limit of zero pressure the contribution of gaseous viscous flow to the total permeability is negligible.
2. The surface diffusion is also insignificant since adsorbed molecules tend to reside at highest energy sites where the mobility is extremely low. Thus, the total permeability (B_T) for adsorbing vapors in the limit of zero pressure is practically the Knudsen diffusion permeability (B_k).

With these points in mind, the value of the first term of RHS in Eq. (3) should be universal for any permeating molecules for a given porous solid as it contains only solid properties. However, we have found experimentally that the intercept for adsorbing vapors is consistently much lower than that of inert gases [Bae and Do, 2002]. We attribute this to the interaction potential energy between adsorbing molecules and surface atoms, which is different from that for inert gases, giving rise to the difference in the intercept of Eq. (3). To take this effect into account, we introduce a collision-reflection factor (*f*), which is the fraction of molecules undergoing collision to the solid surface over reflection from the surface, to Knudsen dif-
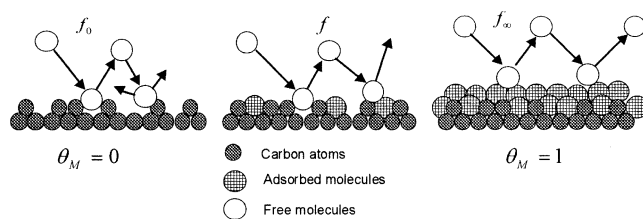
Fig. 1. Schematic illustration of the effect of adsorbed molecules on the collision reflection factor.

fusivity. Subsequently, the pore diffusivity (D_p) for adsorbing vapors takes the following form;

$$D_P=\frac{D_k}{\tau_k}=\frac{2r}{3\tau_k}\sqrt{\frac{8R_g T}{\pi M}}\left(\frac{2-f}{f}\right) \quad (4)$$

One would expect that the value *f* should be different between the case when there are no adsorbed molecules on the surface and the case when the surface is covered with adsorbed molecules. Consequently, the collision and reflection of molecules during Knudsen diffusion must be affected by the presence of adsorbed species on the surface. Here we argue that the presence of adsorbed species affects the Knudsen diffusion through the collision reflection factor, which should be a function of loading. Fig. 1 schematically illustrates the effect of the presence of adsorbed species on the collision reflection factor. As it is expected that the value *f* decreases with an increase of loading, we propose the following dependence form of the value *f* on surface loading:

$$f=f_\infty\theta_M+f_0(1-\theta_M) \quad (5)$$

where f_0 and f_∞ are the values at the limit of zero pressure and at high pressure (close to vapor pressure), respectively, which will be obtained directly from experiments, and θ_M is the surface coverage in meso/macropores.

The surface diffusivity (D_μ) is known to be a function of adsorbed phase concentration [Do and Do, 2001; Moon et al., 1990] and is equal to the corrected diffusivity (D_μ^*) multiplied by a thermodynamic correction factor ($\partial\ln P/\partial\ln C_\mu$).

$$D_\mu=D_\mu^*\frac{\partial\ln P}{\partial\ln C_\mu} \quad (6a)$$

This corrected diffusivity is assumed to follow an Arrhenius form $D_\mu^*=D_\infty^*\exp(-E_\mu/R_g T)$, where E_μ is the energy barrier for surface diffusion. As pressure increases, adsorption takes place progressively on lower energy sites, resulting in the reduction of energy barrier for surface diffusion which is assumed to have the following function with loading [Do et al., 2001]:

$$E_\mu=E_\mu^0\left(1-\frac{\beta C_\mu}{1+\beta C_\mu}\right) \quad (6b)$$

where E_μ^0 is the activation energies for surface diffusion at the limit of zero pressure. The larger the parameter β is, the faster E_μ decreases with adsorbed concentration. When $\beta=0$, Eq. (6) reduces to the classical Darken equation. With the energy barrier as given in Eq. (6b), the corrected diffusivity takes the following functional form with respect to adsorbed concentration:

Table 1. Physical properties of adsorbates studied at 303 K

	Molecular weight (g/gmol)	Liquid molar volume (m³/kgmol)	Liquid viscosity (N·s/m²)	Surface tension (N/m)
Carbon tetrachloride	153.82	0.0977	8.450×10^{-4}	2.567×10^{-4}
Benzene	78.11	0.0900	5.638×10^{-4}	2.755×10^{-4}
n-Hexane	86.18	0.1322	2.846×10^{-4}	1.743×10^{-4}
2,3Dimethylbutane	86.18	0.1320	3.251×10^{-4}	1.637×10^{-4}
n-Heptane	100.20	0.1480	3.650×10^{-4}	1.927×10^{-4}

$$D_\mu^* = D_{\mu\infty}^* \exp\left[-\left(\frac{E_\mu^0}{R_g T}\right)\left(1 - \frac{\beta C_\mu}{1+\beta C_\mu}\right)\right]$$

$$= D_{\mu 0}^* \exp\left[\left(\frac{E_\mu^0}{R_g T_0}\right)\left(1 - \frac{T_0}{T}\right)\right] \exp\left[\left(\frac{E_\mu^0}{R_g T}\right)\left(\frac{\beta C_\mu}{1+\beta C_\mu}\right)\right] \quad (7)$$

where $D_{\mu\infty}^*$ is the corrected surface diffusivity (D_μ^*) at the infinite temperature and $D_{\mu 0}^*$ is the D_μ^* in the limit of zero pressure at the reference temperature (T_0).

EXPERIMENTAL

A differential permeation method was used to determine diffusion kinetics of strongly adsorbing vapors through an Ajax activated carbon (type 976) (which has particle density of 733 kg/m³, micropore porosity 0.40, macropore porosity 0.31 and mean macropore size 0.8 μm). An activated carbon pellet was carefully mounted in a copper block, separating two reservoirs. One reservoir is much larger in volume than the other, and is used as the supply reservoir. Thus the supply reservoir was maintained practically at constant pressure during the course of diffusion and adsorption. The physical properties of adsorbates studied are listed in Table 1.

The flux of each adsorbate through the porous solid was measured with respect to time. Knowing the receiving reservoir volume (V), the cross-sectional area (A) and the length (L) of the particle, we can determine the total permeability (B_T) from Eq. (8) which gives us a straight line passing through the origin with a slope of $B_T (AR_g T/VL)$ in a plot of $\ln[(P_1-P_2^0)/(P_1-P_2)]$ versus time.

Fig. 2. Total permeability of *n*-hexane, benzene and carbon tetrachloride in activated carbon.

$$\ln\left(\frac{P_1-P_2^0}{P_1-P_2(t)}\right) = \left(B_T \frac{AR_g T}{VL}\right)t \quad (8)$$

where P_1 is the pressure in the supply reservoir, and $P_2(t)$ and P_2^0 are the pressures in the receiving reservoir at any t and at t=0, respectively. The detailed experimental procedure and the set-up of permeation measurement can be found elsewhere [Bae and Do, 2002; Do et al., 2001].

RESULTS AND DISCUSSION

The total permeabilities of *n*-hexane, benzene and carbon tetrachloride through activated carbon were obtained from Eq. (8) and shown in Fig. 2. At very low pressures a sharp increase in total permeability was observed for all adsorbates studied. The adsorbed concentration of these adsorbates increases drastically over this very low range of pressure [Bae and Do, 2002], indicating that surface diffusion must play a significant role in its contribution to the total permeability since the contribution of gas phase diffusion is expected to be relatively small. Interestingly, it can be clearly seen in Fig. 2 that only *n*-hexane exhibits a minimum in the total permeability at reduced pressure of around 0.02. This phenomenon was consistently observed at three different temperatures. At the pressure where the minimum appears, Knudsen diffusion and surface diffusion are expected to dominate the transport of molecules since gaseous viscous flow is insignificant.

1. Significance of Surface Diffusion at Low Pressure

To elaborate the contribution of surface diffusion to total permeability with our model, several parameters are required. First, tortuosity factors for Knudsen diffusion (τ_k) and viscous flow (τ_v) were found to be 5.66 and 3.10, respectively, by comparing the total permeability of adsorbates with that of inert gases whose flow is governed by Knudsen diffusion and gaseous viscous flow. Second, the collision-reflection factors at the limit of zero pressure (f_0) and at high pressure (f_∞) were found to be 1.79 and 1.06, respectively, for the theoretical Knudsen diffusivity [Eq. (2)] to agree with experimental data. Third, the equilibrium isotherms of the three adsorbates were well described by the dual Langmuir equation. Having known the Knudsen diffusion permeability (B_k) and viscous flow permeability (B_v) with above parameters, we can calculate the surface diffusion permeability (B_μ) from the total permeability (B_T). The behavior of B_μ with respect to pressure is depicted schematically in Fig. 3. It can be seen clearly that the contribution of B_μ to the B_T is significant at low pressures. The surface diffusion permeability increases very fast at very low pressures as adsorbed molecules are built up in small pores, followed by its decrease due to the progressive saturation of the small pores (since the chemical
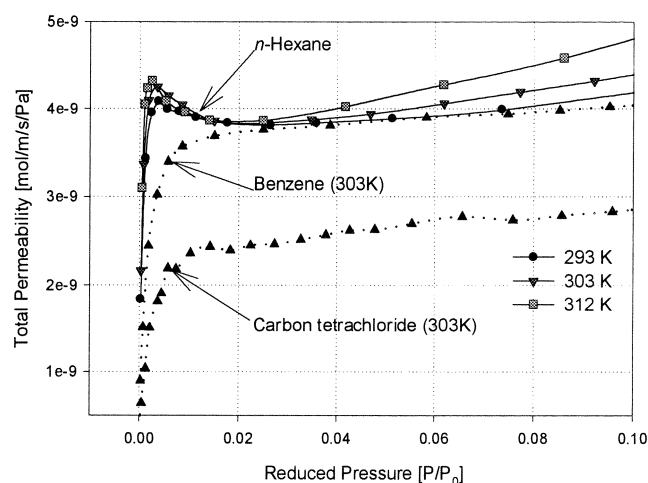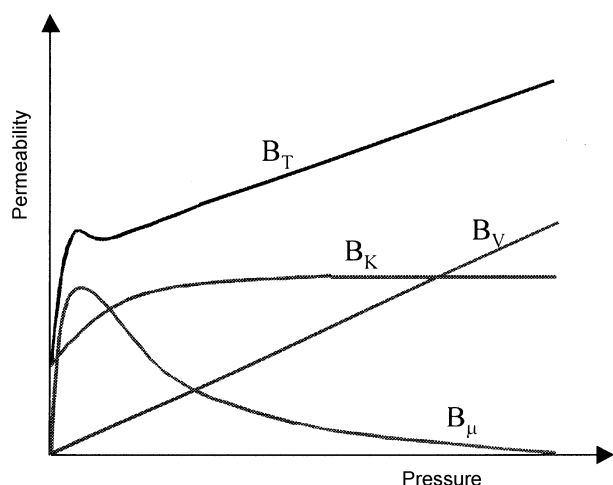
Fig. 3. Schematic illustration of *n*-hexane permeability in activated carbon.

Table 2. Optimal parameters for surface diffusivity of adsorbates studied in activated carbon at 303 K

	n-Hexane	Carbon tetrachloride	Benzene
$D_{\mu 0}^{*}$ [m²/s]	4.432×10^{-10}	1.964×10^{-11}	1.336×10^{-10}
β	2.966×10^{-1}	3.209×10^{-3}	8.095×10^{-3}
E_{μ}^{0} [J/mol]	6.380×10^{3}	9.525×10^{3}	6.198×10^{3}

potential gradient in the small pores is diminished). Another evidence for the significance of surface diffusion at low pressures can be provided by plotting $B_{T}(MT)^{0.5}$ against $(P/\mu)(M/T)^{0.5}$ from Eq. (3) for adsorbing vapors. If there are only Knudsen diffusion and gaseous viscous flow for adsorbing vapors at low pressures, all values should fall on one curve. However, as we have reported [Bae and Do, 2002], the values of $B_{T}(MT)^{0.5}$ at low pressures are dependent on the type of permeating molecule, indicating that considerable surface diffusion takes place.

Optimal parameters for surface diffusivity in Eq. (7) were obtained by matching the simulated results against permeation results and listed in Table 2. The surface diffusivity in the limit of zero loading increases in the order of carbon tetrachloride, benzene and *n*-hexane. We note that the activation energy for surface diffusion of *n*-hexane in the limit of zero loading is similar to that of benzene while there is difference in the value of $D_{\mu 0}^{*}$. The reason for this will be discussed in next section. The parameter β is a measure of how fast the activation energy for surface diffusion decreases with adsorbed concentration. The value of β for *n*-hexane is much higher than that of the others, indicating that the surface diffusivity of *n*-hexane increases much faster with an increase of surface loading.

2. Minimum Appearance in Total Permeability

The permeabilities corresponding to Knudsen diffusion, gaseous viscous flow and surface diffusion calculated for adsorbates in the previous section are plotted in Fig. 4. Only in the case of *n*-hexane a minimum in the total permeability appears at very low pressure. Since the pressure where the minimum appears is very low, the contribution of gaseous viscous flow to the total permeability is insignificant. Thus, the minimum appearance is mainly attributed to the
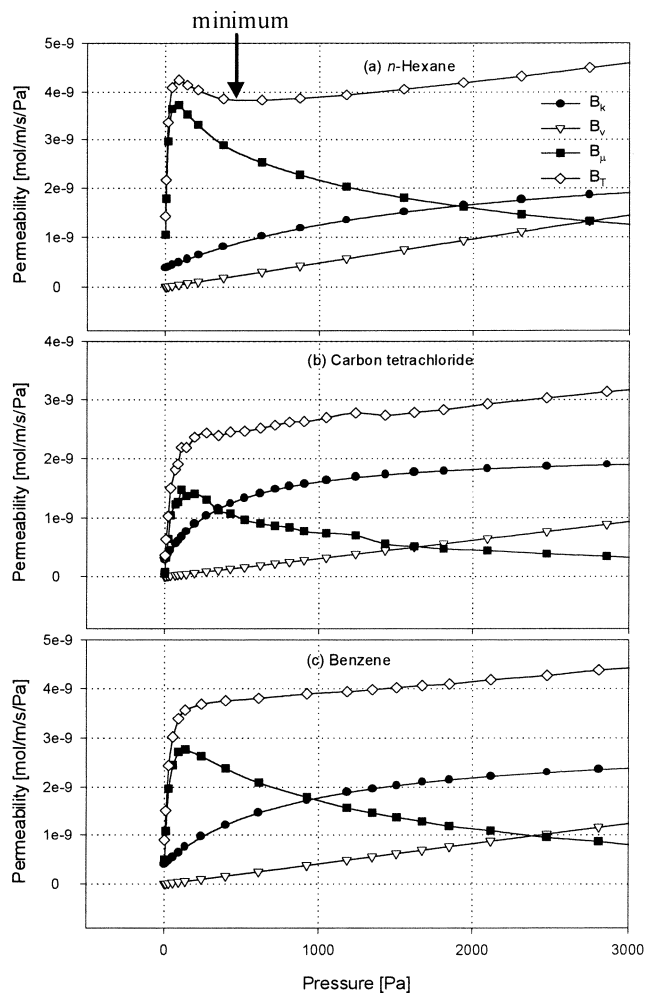
Fig. 4. Plots of permeability for adsorbing vapors in activated carbon 303 K: (a) n-hexane, (b) carbon tetrachloride and (c) benzene.
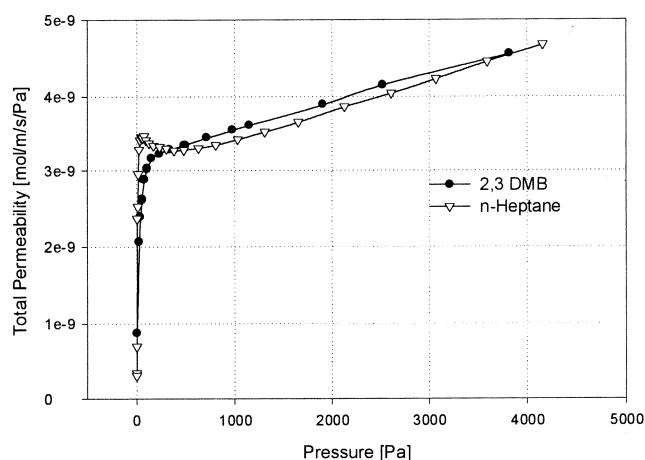

Fig. 5. Total permeability of 2,3-dimethylbutane and *n*-heptane in activated carbon at 312 K.

interplay between Knudsen diffusion and surface diffusion. The Knudsen diffusion permeability (B_{k}) of *n*-hexane increases more slowly while its surface diffusion permeability (B_{μ}) exhibits a sharper
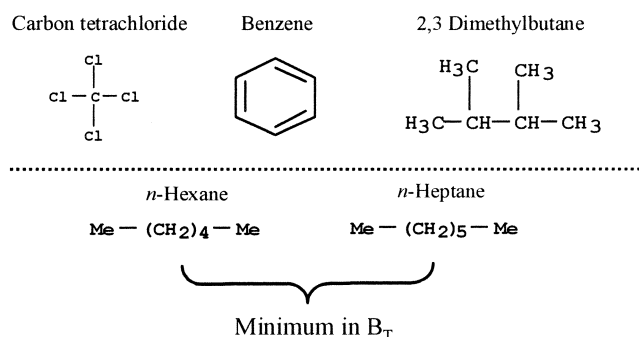
Fig. 6. Molecular structure of adsorbates studied.

increase to a maximum beyond which it decreases faster, compared to those of the other adsorbates. A question is then raised on why n-hexane permeability behaves differently from the others. First, we consider the physical properties of adsorbates. 2,3-dymethylbutane (DMB), which is one of n-hexane isomers, was chosen to explore the possibility for a minimum because DMB has very similar physical properties to n-hexane (as listed in Table 1). Fig. 5 shows the total permeability of DMB versus pressure with no minimum appearance. On the other hand, when we studied the permeability of n-heptane (homology of n-hexane), we observed a minimum like we did for n-hexane (see Fig. 5 for n-heptane). Thus, we may conclude that the molecular structure is the main reason for the minimum existence. To further this investigation, we consider the equilibrium isotherms of n-hexane and DMB, and observe no distinct difference between them. This reinforces the reason of molecular structure as carbon tetrachloride is tetrahedral in structure, benzene has a hexagonal ring and 2,3-DMB has a branched structure while n-hexane and n-heptane, which showed the minimum, are straight chain molecules in structure (Fig. 6). Therefore, the molecular structure of permeating molecules plays a significant role in the minimum appearance. This may point to a possible mechanism for adsorbed phase diffusion in which molecules have 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. Therefore, linear chain molecules such as n-hexane and n-heptane have greater surface diffusion flux than other nonlinear molecules. This substantiates the surface diffusion model proposed by Do [1996].

CONCLUSIONS

The Knudsen diffusion, viscous flow and surface diffusion for sub-critical hydrocarbons are well described at low range of pressures in this paper. The Knudsen diffusivity for strongly adsorbing vapors is found to be a function of loading. The minimum appearance in the total permeability of n-hexane is attributed to the interplay between Knudsen diffusion and surface diffusion. The molecular structure of permeating species is the main reason for the minimum appearance in the cases of n-hexane and n-heptane.

ACKNOWLEDGMENTS

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_μ : adsorbed concentration [mole m^{-3}]
D_k, D_p, D_μ : Knudsen diffusivity, pore diffusivity and surface diffusivity, respectively for adsorbates [m^{2}s^{-1}]
D_k^0, D_p^0 : Knudsen diffusivity and pore diffusivity, respectively for inert gases [m^{2}s^{-1}]
$D_{\mu\infty}^*$, $D_{\mu 0}^*$: corrected surface diffusivities at the infinite temperature and at the reference temperature (T_0) in the limit of zero pressure, respectively [m^{2}s^{-1}]
E_μ : activation energy for surface diffusion [J mol^{-1}]
f : collision reflection factor
P, P_0 : gas phase pressure and vapor pressure, respectively [Pa]
R_g : gas constant [J K^{-1}mol^{-1}]
T : temperature [K]

Greek Letters

β : constant in Eq. (6b)
ε : macropore porosity of the solid
μ : viscosity in gas phase [Pa s]
θ_M : surface coverage in meso/macropores
τ_K, τ_V : tortuosity factor for Knudsen diffusion and viscous flow, respectively

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