



Adsorption and transport of gases in a supported microporous silica membrane

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ABSTRACT

We investigate gas adsorption and transport in a disordered microporous silica membrane having mean pore diameter 1.5 nm, coated on a porous tubular asymmetric support. The adsorption isotherms are found to be Langmuirian, with equilibrium constants that are accurately predicted for nonpolar gases, considering Lennard–Jones (LJ) interactions with a single layer of oxygen atoms on the pore surface. For the polar gas, CO₂, the hydroxyl groups on the pore walls strongly increase the affinity with the pore walls, and a superposition of the LJ potential and an empirically represented electrostatic interaction is found to be adequate in correlating the Langmuirian equilibrium constant. The gas transport in the microporous silica layer is investigated using effective medium theory, with single pore transport represented by combination of pore mouth and internal pore diffusion resistances. Good agreement is observed for all the gases using different coordination numbers, indicating that the essential features of the transport in the silica micropores are captured in the approach. It is found that the overall transport resistance is dominated by the pore mouth barrier; however, the internal diffusion resistance in the relatively smaller pores is significant, especially for weakly adsorbed gases at higher temperature. In addition, the dependence of the pore mouth barrier coefficient on temperature and diffusing species are in good agreement with predictions of transition-state theory, with larger more strongly adsorbed molecules having higher activation energy. The proposed methodology is validated against experiment by comparison of the predicted flux for different gases in the supported membrane at various feed pressures in the low pressure range of 200–400 kPa, using the parameters obtained at 200 kPa.

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1. Introduction

The modeling of fluid transport in narrow pores and confined spaces has attracted considerable interest among scientists and engineers for over a century [1–3], due to its importance to a variety of conventional applications in adsorptive gas separation as well as in heterogeneous catalysis and electrochemical process. Interest in the subject has considerably increased in the last two decades, as a consequence of the development of a vast array of novel disordered and ordered nanoporous materials [4–9], having potential for use in these as well as in emerging applications such as in gas storage [10], molecular sieve membranes [11], drug delivery [12] and biosensors [13], all of which involve the movement of fluids through highly confined spaces. The established and most popular approach to modeling gas transport in narrow pores is that of Knudsen [1], dating back to the first decade of the 20th century, and neglects the effects of dispersive fluid–solid interactions on the diffusion. While this simplification is justified for the

relatively large tubes of 33–145 μm used by Knudsen in his original experimental verification [1], its applicability to nanoscale pores where the density profile is highly nonuniform has been questioned [2,14–16]. However, due to its simplicity and ease of use, the Knudsen model and its analogs have been routinely applied to gas transport in narrow pore materials [17–20].

In actual practice, the intermolecular interaction is non-negligible, and must be considered when the mean free path in the pressure range of interest (generally in the region of a few hundred kilopascals) is not much larger than the pore size. In the case of macropores the effect of intermolecular interactions may be included by means of an additive viscous contribution [21–23]. The most popular method based on this principle is the Dusty Gas Model (DGM) of Mason and coworkers, which arbitrarily divides the total flux vector into a wall-affected diffusive and a hydrodynamic non-segregative contribution [24]. When adsorption is negligible, the pore wall-affected diffusion is often represented by the Knudsen model, which is supplemented by a surface diffusion contribution when adsorption is significant in mesopores [25]. Consequently, the intrinsic characteristics of the Knudsen model are inherited in this approach, and the confirmation of the diffusion model still largely relies on the correlation of diffusion

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data with $\sqrt{T/M}$, where M is molecular weight, as predicted by the Knudsen model [26]. Although it lacks a firm molecular basis, due to its simplicity the DGM approach is commonly employed to explore the diffusion mechanism in newly-synthesized materials; this is generally done by empirically correlating experimental data using a representative pore size, while determining a structure-related parameter such as tortuosity [27]. Use of a single pore size is a key deficiency of this method as the pore size distribution (PSD) has significant influence on the transport, especially for materials with several nanometers. Another weakness inherent to the Knudsen model is the disregard of the dispersive solid–fluid interaction arising from the presence of the wall; the dispersive van der Waals interaction, for example via the Lennard–Jones (LJ) interaction model, dramatically decreases the diffusivity by reducing the travel time between successive collisions [15]. As a result of the dispersive interaction, the fluid density in the pore is non-uniform, and significantly differs from that in the bulk, and is strongly dependent on the pore radius and gas species as well as temperature [2,28].

Traditionally, the tortuosity factor is incorporated as an effective parameter and assumed to be exclusively determined by the properties of the porous medium. However, it has been theoretically and experimentally shown that in nanoscale pores the apparent tortuosity is influenced by operating conditions such as temperature, pressure and gas species [14,15,21–29]. All errors arising from the neglect of such dependence are therefore lumped within the fitted tortuosity, masking errors related to the transport model itself [21]. Consequently, unambiguous confirmation of the validity of the Knudsen diffusion in nanosized pores, to which the Knudsen model is frequently employed, is not possible by simple correlation. Indeed, it has been extensively demonstrated that while the DGM can empirically correlate experimental data, extremely high tortuosities are often obtained for mesoporous materials when the Knudsen model is utilized [17,30–32]. This is mainly due to the omission of adsorption effects and overprediction of the diffusivity by the Knudsen equation, and to a lesser extent due to the disregard of the pore size distribution when a single representative pore size is used [14,15–33].

For small pore sizes, approaching the micropore scale, it is frequently assumed that the gas molecules adsorb on the pore walls, and migrate on the pore surface as an adsorbed species. In this spirit, models comprising surface diffusion and Knudsen flow in parallel have been formulated in order to provide stronger temperature dependence and yield an acceptable tortuosity [18,34]; however, such models often lead to tortuosities that increase greatly for weakly adsorbed gases [18]. Substantial work has been devoted to develop rigorous theories based on molecular principles to account for the effect of dispersive solid–fluid interaction on the transport [35–39], or otherwise indirectly consider the effect of interactions by using measured pure component diffusivities in mixture transport models [25]. However, most interpretations of experimental data largely rely on arbitrary modification of the Knudsen equation by introducing an Arrhenius-type factor to better capture the effect of temperature in micropores [17,19–35]. The most widely used model following this approach, originally used for hydrocarbons and known as the gas translation (GT) theory, is that of Xiao and Wei [35]. Later, the theory was extended to any adsorptive gases by Yoshioka et al. [19] by considering the effective diffusion length instead of the actual pore size. However, the original derivation of the GT theory is semi-empirical, as the estimation of the activation energy based on the difference of LJ potential energy between the pore channel and intersection lacks a firm molecular basis [39]. For instance, in a silica pore of 3 nm, the diffusivity of CH_4 as modeled by the GT approach falls in the Knudsen regime due to the low apparent activation energy for such a small molecule [35], which is contradicted by molecular dynamics (MD) simulations [2,35–40].

Considerable success has been accomplished recently in this laboratory, through the development of a statistical mechanical theory of transport in nanopores, aided by the finding from MD simulations that the nonuniform equilibrium density profile of the fluid is essentially preserved during the transport [41]. The new model, termed as ‘Oscillator model’, considers the dispersive solid–fluid interaction, and the adsorption effect is represented through the canonical energy distribution in the pore [36], overcoming the limitations of the Knudsen approach. In particular, as a result of explicit consideration of the fluid–solid interaction, the Oscillator model diffusion coefficient represents the overall transport coefficient in the pore, overcoming the need to supplement the Knudsen diffusivity with an empirical surface diffusion coefficient, as has been the common practice. Not only has the new theory been extensively validated against MD simulations [36–39], but it has also been successfully used to interpret experimental data [14,16–29]. Indeed, comparison of the Knudsen and Oscillator model diffusivities with those from MD simulations for silica pores shows that the Knudsen equation significantly overpredicts the diffusivity for methane at 450 K by 30% even for a pore diameter of 10 nm, indicating the importance of considering the effect of van der Waals forces on pore diffusion even when the molecule/channel size ratio is less than 5% [39]. However, in disordered materials narrow pore necks may affect the rate of entry of molecules in the pores, although this has little impact on the equilibrium constant, which principally depends on the size of the pore body. This effect may be considered by means of transition-state theory (TST) [37,42–44], and the GT theory of Xiao and Wei [35] may be envisioned in this light. While the pore mouth resistance may be expected to control in materials with very narrow molecularly sized entries, in systems with transitional pores the internal pore diffusion may also have significant resistance. Membrane transport models involving such dual resistances have yet to be formulated, but may be derived by combining the Oscillator model with a TST-based pore mouth resistance model to investigate the transport in such disordered microporous materials.

Another significant impediment in the application of any diffusion theory to microporous or mesoporous materials is the complexity of the pore network, including the pore connectivity, and the presence of a pore size distribution as well as surface roughness. This is particularly challenging for the investigation of supported membranes, in which the system comprises a thin selective top layer and a mesoporous interlayer coated on a macroporous substrate. Not only must the pore size distribution of each layer be considered, but also the aspect ratio and pore shape are of importance. Effective medium theory (EMT) provides the necessary machinery for resolving such issues, and has been used to derive fundamental insights into transport in disordered nanoporous materials [14,16,21–29]. In this method, a nonuniform pore network with a distribution of conductance is replaced by a uniform one in which each conductance is assigned an effective value. This allows explicit modeling of network-related effects, thereby permitting more direct verification of transport models. In our previous work [16] employing this technique we have demonstrated that the transport in a mesoporous silica membrane having pores of mean size 3.7 nm is not well represented by the Knudsen model due to overestimation of the diffusivity and neglect of adsorption effects, and that the Oscillator model, which accounts for these factors provides a more accurate result. Following the line of our previous work [16], here we further develop this approach to include also a pore mouth resistance, and investigate the diffusion for a microporous supported silica membrane, having a mean pore diameter of 1.5 nm, coated on an asymmetric alumina support, while also considering the pore size distribution for each layer. The results permit an understanding of the mechanism of fluid transport in the microporous silica layer, and demonstrate

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