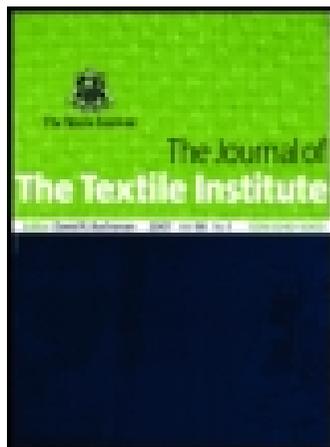


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### A probabilistic model for the permeation of gases through microporous membranes

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## A probabilistic model for the permeation of gases through microporous membranes

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A probabilistic model for the motion of gas molecules through pores of microporous membranes is proposed. The interaction energy between the gas molecules and the surface of membrane pores is investigated using molecular modeling and results are used as input to the probabilistic model. The proposed model was used to evaluate the effect of surface coating on gas permeation of air and ammonia through single- and double-layer microporous membranes. Gas transmission experiments were conducted on uncoated polyethylene terephthalate (PET), nylon and PP/PE, coated PET, and double-layer PET microporous membranes at different pressure levels. Model results were compared with experimental data and a reasonable conclusion was drawn.

**Keywords:** gas transmission; microporous membranes; probabilistic modeling; molecular modeling

### Introduction

Microporous membranes are of high interest in the fields of fuel cells and separation technology. In addition, they are good samples for inclusion in the next generation of garments used to protect first responders against chemical attacks or spills. Some of these membranes are envisioned to be able to block the passage of toxins while providing comfort for the wearer (Schreuder-Gibson et al., 2003; Stull, 1987; Truong, Wilusz, & Rivin, 2004). Selectively permeable systems assembled from a group of microporous membrane layers with tailored degrees of permeability, is an example of such materials (Truong et al., 2004).

Development of these materials can benefit from an understanding of the underlying mechanisms of gas permeation through microporous membranes. The flow of gases through pores is governed by geometric and energetic considerations (Burggraaf, 1999; Shindo, Hakuta, Yoshitome, & Inoue, 1983; Yoshioka, Nakanishi, Tsuru, & Asaeda, 2001). The Knudsen number ( $K_n$ ) is a geometric parameter that is typically used to characterize the type of gas flow (Bird, Stewart, & Lightfoot, 2002; Cunningham & Williams, 1980; Fried, 1995; George & Thomas, 2001).  $K_n = \lambda/D$  where,  $\lambda$  = mean free path of a gas molecule and  $D$  = diameter of a single pore. If the value of  $K_n$  is very small the flow is considered to be a viscous flow, which assumes that molecules move together with an overall average velocity and can be treated similar to a liquid flow inside a tube (Bird et al., 2002). In this case, Maxwell–Stefan and Navier–Stokes equations can be used to model the gas

permeation process. As the value of the Knudsen number increases, the gas no longer has an overall mass velocity behavior and individual molecule-wall collisions become significant (Knudsen flow) (Barber & Emerson, 2002). The exact value of  $K_n$  that differentiates between viscous and Knudsen flow is not known. However, it is acceptable to consider the flow as either Knudsen if  $K_n > 10$  or viscous if  $K_n < 0.01$ . The flow in the intermediate region ( $0.01 < K_n < 10$ ) is called the transition flow. Although in many cases of gas flow in porous media the Knudsen number falls in this intermediate region, there is a lack of analytical or numerical models to describe the flow.

From an energetic perspective, the interaction energy between gas molecules and pore surfaces during the flow of gases through pores can affect the flow rate. A gas molecule can either collide elastically with the pore surface or be trapped in the potential field of the surface and hop on it. If the kinetic energy of the molecule is larger than the interaction energy, the molecule will escape from the surface potential field and rebound elastically without losing energy. Alternatively, if the interaction energy between the surface and the gas molecule is greater than the kinetic energy of the molecule, then the molecule will be trapped in the field, physisorbed on the surface, and may follow a slip-surface flow. The second case means that the molecule will lose some of its kinetic energy and velocity, which can result in a decrease in the gas transmission rate (GTR) (Shindo et al., 1983). Interaction between gas molecules and the membrane surface can be evaluated using theories such as the density functional theory (DFT), and quantities

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like adsorption energies and minimum energy path can be accordingly calculated (Groß, 2003).

Within such geometric and energetic understanding, permeation of gas molecules through a pore of a microporous membrane can be studied either at the level of individual molecules or the level of the molecular population as a whole. At the molecular level, each molecule and its interaction with other molecules and surfaces have to be taken into consideration and may be studied using a probabilistic technique. At the macro-level, the behavior of the molecular population as an average is considered.

In this work, a model is developed to calculate GTR through uncoated and coated microporous membranes based on simulating the random movement of molecules inside the pore and considering the molecule-surface physical interaction. To validate the model, GTR experiments using three different types of membranes were conducted.

### Probabilistic model

A probabilistic model is developed utilizing a Monte Carlo approach to simulate gas transmission through microporous membranes. Gas transmission is assumed to be driven by a pressure difference between the sides of the membrane and is only allowed to pass through the membrane pores ignoring diffusion through the solid material. An alternative approach utilizing concentration as the driving force can be readily implemented within such understanding.

### Modeling parameters and assumptions

Geometric parameters for problem definition included membrane thickness, pore average diameter, and pore diameter distribution. Typically, membrane thickness is uniform and a single value can be used to represent it. On the other hand, pore diameters were assumed to vary randomly between upper and lower bounds observed experimentally and to be perfectly cylindrical. Pores were categorized based on pore size ranges and frequency, and pore size averages were determined for each category using a capillary flow porometer. Molecules were assumed to fill available space with random locations and direction of motion. Due to the large number of pores, a calculation-time barrier on running a full-scale numerical experiment was obvious and a scaling step was necessary. To ensure accuracy, a convergence study was conducted to evaluate proper scaling parameters that will maintain the accuracy level of the analysis. Accordingly, the number of pores, created randomly within pore distribution, was scaled to a smaller value. Calculations were conducted at this scale and then converted to the full-scale based on the scaling ratio.

### Interaction energy between membrane surface and gas molecules

Gaussian<sup>®</sup> molecular modeling software (Frisch et al., 2004) was used to calculate the interaction energy between

ammonia and air molecules and the surface of the microporous membrane. Energy calculations were restricted to the two most dominant components in dry air – nitrogen and oxygen as they represent almost 99% of the air volume. Two surfaces were modeled for the energy calculations – uncoated polyethylene terephthalate (PET) microporous membrane and that coated with a thin layer of an epoxy compound – poly(glycidyl methacrylate). Molecular models were geometrically optimized and the interaction energy calculated using the DFT utilizing B3LYP-method with the base function (6–31 g(d)). The interaction energy was calculated at different distances between the gas molecule and the surface to obtain an interaction energy profile. The pore surface was meshed into regions based on the interaction energy between the surface and the gas molecules. It was assumed that a molecule gets physisorbed onto the surface when it gets into a region where the kinetic energy of gas molecule is less than the interaction energy. Consequently, the physisorbed molecule is removed from the total number of passing molecules. The inner surface area of each pore can be covered with a single layer of physisorbed molecules, which will consequently decrease the pore diameters as well as the membrane porosity. Although for microporous membranes the diameter of the considered molecules is too small compared to the pore diameter, changes in the geometric characteristics of the membrane due to physisorption are considered in the probabilistic model.

### Molecular passage simulation

The molecular trajectory was calculated for molecules that were able to enter the pores and the rest of the molecules were assumed to elastically rebound off the surface. The molecules that entered the pores traveled a distance ( $l_i$ ) in a straight line assumed to be equal to the mean free path ( $\lambda$ ), or less in the case that the molecule hits the pore wall. Once the molecule enters into the pore and after each travel distance ( $l_i$ ) the molecule's coordinate location is checked to explore in which meshed region it falls in. Then the energetic criterion will decide whether the molecule will be physisorbed or continue its passage. The direction of the molecule (angle  $\alpha$ ) after each collision was determined based on its incident angle and a smooth pore surface. The total length of the path of the molecule inside the pore was calculated by following a trajectory similar to that sketched in Figure 1. The total length of the path ( $m_{\text{path}}$ ) is equal to  $\sum_i^n l_i$  where  $n$  is reached as  $z$  reaches the value of  $\delta$  (thickness of the membrane), as shown in Figure 1. The time ( $t$ ) needed for one molecule to pass through the pore is calculated as  $t = \frac{m_{\text{path}}}{v}$ , where  $v$  is the average molecule velocity,  $v = \sqrt{\frac{8RT}{\pi M}}$ , where  $R$  is the gas constant,  $T$  is the temperature, and  $M$  is the molecular weight.

A Matlab<sup>®</sup> code was developed for the probabilistic model presented above and model results were compared

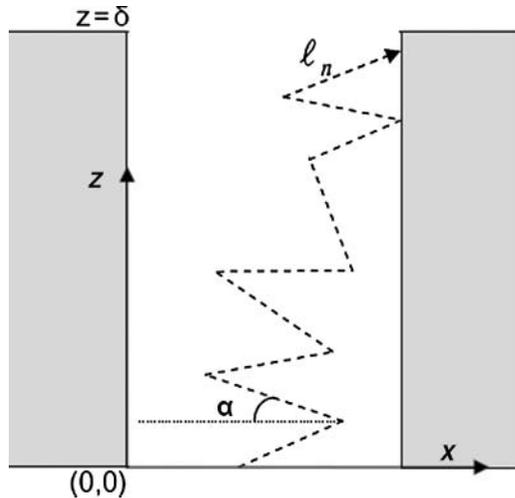


Figure 1. A schematic view of a potential molecular trajectory through pores.

with the average gas flux under a pressure difference ( $\Delta P$ ) calculated for a pure Knudsen ( $J_K$ ) and a pure viscous ( $J_P$ ) flow regimes as possible bounds on the numerical solution (Schofield, Fane, & Fell, 1990):

$$J_K = \frac{2 r \varepsilon}{3 \tau} \left\{ \frac{8 R T}{\pi M} \right\}^{1/2} \frac{M}{R T} \frac{\Delta P}{\delta} \quad (1)$$

$$J_P = \frac{1}{8} \frac{r^2 \varepsilon}{\tau \eta} \frac{M P}{R T} \frac{\Delta P}{\delta} \quad (2)$$

where,  $\varepsilon$  = porosity,  $r$  = average pore radius,  $\tau$  = tortuosity,  $\eta$  = viscosity, and  $P$  = pressure.

### Experimental work for model verification

Three microporous membranes were used in the experiments: a PET, a nylon membrane (both manufactured by GE Osmonics Inc., Minnetonka, MN, USA), and a polypropylene/polyethylene (PP/PE) polymer blend manufactured by BP (London, UK). These membranes were primarily chosen for the large difference in their permeation levels and pore distribution. Scanning electron microscope (SEM) images of these membranes are shown in Figure 2.

### Pore size distribution and porosity calculation

A capillary flow porometer (CFP-1100-AEES, manufactured by Porous Materials, Inc., Ithaca, NY, USA) was used to evaluate the mean value and distribution of pore diameters for these membranes (see Table 1). In this procedure, the pores of the sample are filled with a wetting liquid and air pressure is incrementally applied on one side of the sample (Jena & Gupta, 2002, 2003). At a certain pressure, the

larger pores are emptied of the wetting liquid and airflow starts. On further increase of the pressure, smaller pores are emptied and air pressure and flow through dry and wet samples is measured. Pore diameter is computed from the differential pressures between wet and dry samples.

### Gas transmission rate

GTR was measured using a volumetric measurement instrument (CSI-135 manufactured by Custom Scientific Instruments, Inc., Easton, PA, USA), as defined in the ASTM D 1434 standard, schematically shown in Figure 3. The CSI-135 instrument evaluates gas permeation by measuring the change of volume of a gas that permeates through the membrane from a lower to an upper chamber, at a constant pressure gradient. The change in volume is measured by the displacement of a short slug of an observable liquid in a glass capillary with a diameter of 1 mm. A digital camera was used to record the experiments and the time needed for the slug to move a specific length was obtained by analyzing the product video. Five samples were tested at each pressure difference ( $\Delta P$ ) when evaluating the GTR defined by the ASTM D1434 standard as “the quantity of a given gas passing through a unit of the parallel surfaces of plastic film in a unit time under the conditions of test” and is calculated as follows in mol/(m<sup>2</sup>s):

$$GTR = \frac{10^{-6} p_a V_r}{A R T}$$

where  $A$  = transmitting area of specimen (mm<sup>2</sup>),  $p_a$  = ambient pressure (Pa),  $V_r$  = slope $\times a_c$ , where  $a_c$  = cross-sectional area of capillary (mm<sup>2</sup>) and slope = rate of rise of capillary slug (mm/s).

The PET membrane, having the highest permeation level, was selected for further evaluation and a double-layer PET membrane was manufactured by covering one side with an epoxy compound and depositing unmodified TiO<sub>2</sub> or SiO<sub>2</sub> microparticles (~1 micron) on the coated surface. Microparticles were used as a separator between the two layers in order to prevent blocking of the pores. A second layer, also covered with the same epoxy compound, was pressed under  $39.0 \times 10^5$  Pa pressure at 140°C for 30 min on top of the microparticles. Figure 4 shows SEM cross-sectional images for the assembled layers with incorporated microparticles, which occupied about 20% of the volume between the two layers.

## Results and discussion

### Experimental data for gas transmission

#### Single layer

Permeation through uncoated single-layer membranes was evaluated for air and ammonia. PET microporous

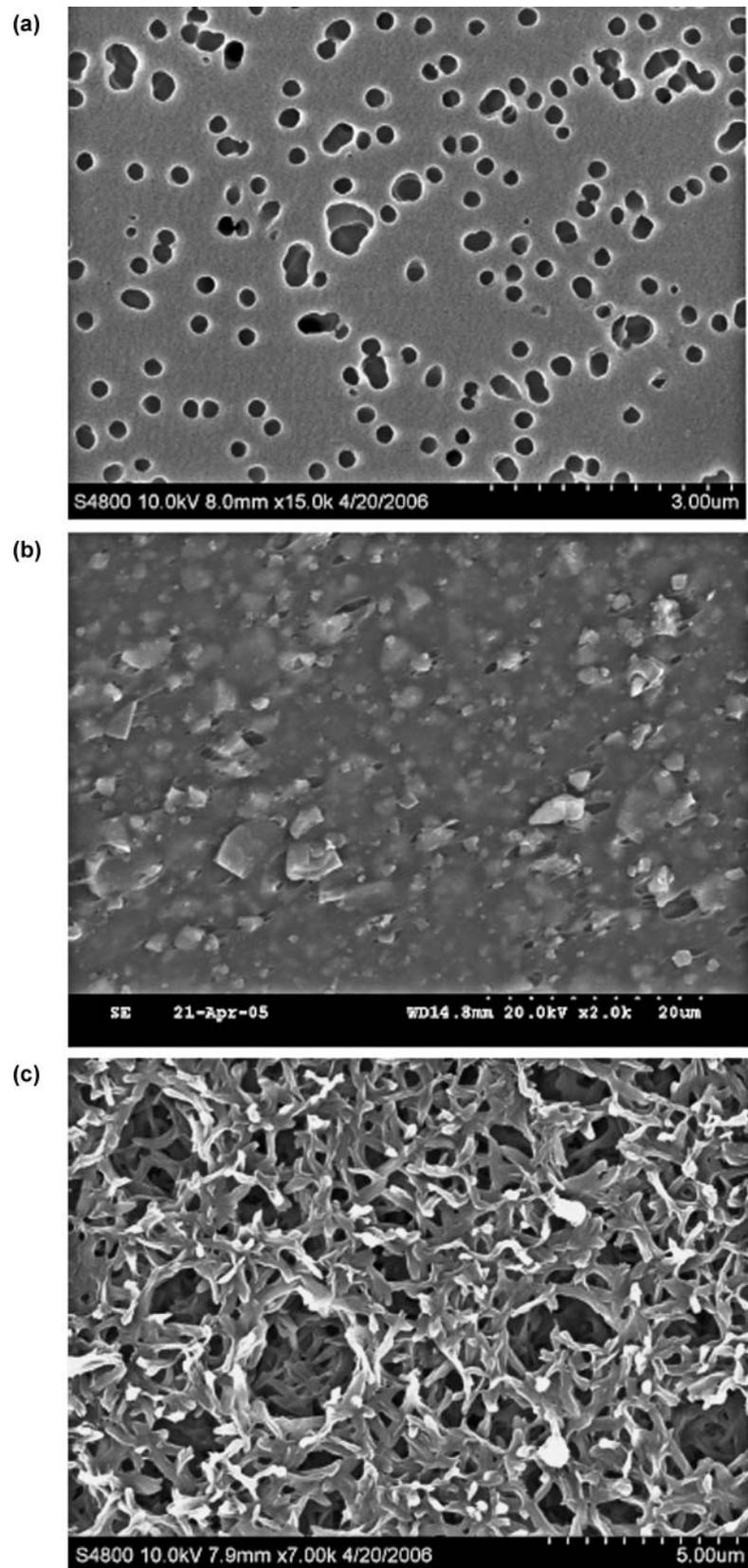


Figure 2. SEM images of microporous membranes: (a) PET (b) PP/PE blend, and (c) nylon.

Table 1. Pore diameter of microporous membranes obtained using a capillary flow meter.

Membrane name	Porosity (%)	Average pore diameter ( $\mu\text{m}$ )	Upper bound on pore diameter ( $\mu\text{m}$ )	Lower bound on pore diameter ( $\mu\text{m}$ )	Thickness ( $\mu\text{m}$ )
PP/PE	0.046	1.28	2.87	0.6439	25
PET	9.40 <sup>a</sup>	0.216	0.53	0.1846	10
Nylon	3.66	0.113	0.234	0.0839	90

Note: <sup>a</sup> Provided by the manufacturer.

membranes exhibited a high level of permeation followed by nylon microporous membrane, while the PP/PE blend resulted in the lowest air transmission rate value as shown in Figure 5. As expected, the permeation was higher for membranes with higher porosity and the increase in pressure caused an increase in the GTR. The error bars illustrate the spread of experimental results at a given pressure, possibly caused by the variability in the porosity of different membrane samples tested. The same behavior can be seen in Figure 6 for the transmission rate of ammonia through the three membranes. However, it was found that the transmission rate of ammonia was higher than that of air, as shown in Figure 7 for PET membrane possibly because of its lower molecular weight. The experimental data for the coated PET showed 14% reduction in the air transmission rate compared to a single layer uncoated PET membrane. The cause of this reduction may be due to a partial blockage of the pore area during the coating process.

#### Double layers

Figure 8 shows permeation results for a two-layer assembly of PET membranes tested for air transmission rate and compared to a single untreated PET membrane. As expected, single-layer PET material exhibited a higher transmission

rate, compared to both two-layer samples. The reduction in air transmission rate using the double-layer membrane was 50% to 70% as compared with the single layer at different pressures. A significant difference was not observed between membranes assembled with  $\text{TiO}_2$  and  $\text{SiO}_2$  spacers at lower pressures; however, as the pressure increased, a slight variation was visible. Membrane separated with  $\text{SiO}_2$  had a comparatively lower permeation rate than that with  $\text{TiO}_2$  at higher pressures. As  $\text{SiO}_2$  was observed to cover more of the open volume between the membranes when compared to  $\text{TiO}_2$  a slightly lower permeation rate than  $\text{TiO}_2$  was expected.

#### Interaction energy evaluation

The interaction energy between the permeates and the membrane surfaces was calculated at different distances between the gas molecule and the surface to obtain an interaction energy profile. The depth of the energy-well was compared with the kinetic energy of the gas molecule calculated at 25°C to be 0.89 kcal/mol. Figure 9 shows interaction energy profiles of the three gases with the surface of uncoated PET as compared to the molecular kinetic energy. It can be seen from the graph that oxygen and nitrogen molecules have enough kinetic energy to rebound from the surface.

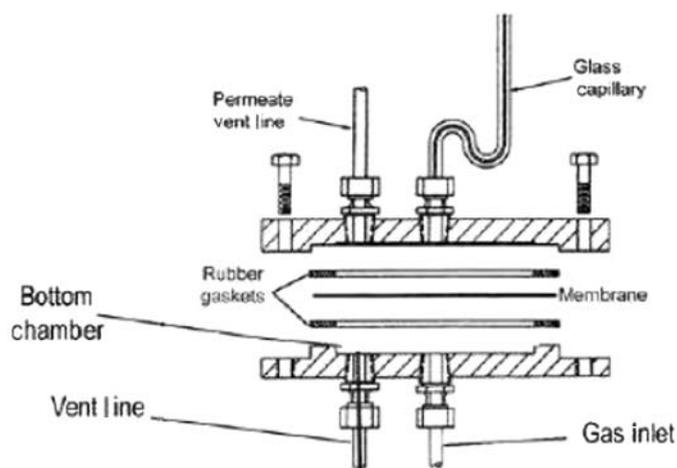


Figure 3. Schematic of CSI-135 volumetric gas permeability instrument (CSI Operating Manual).

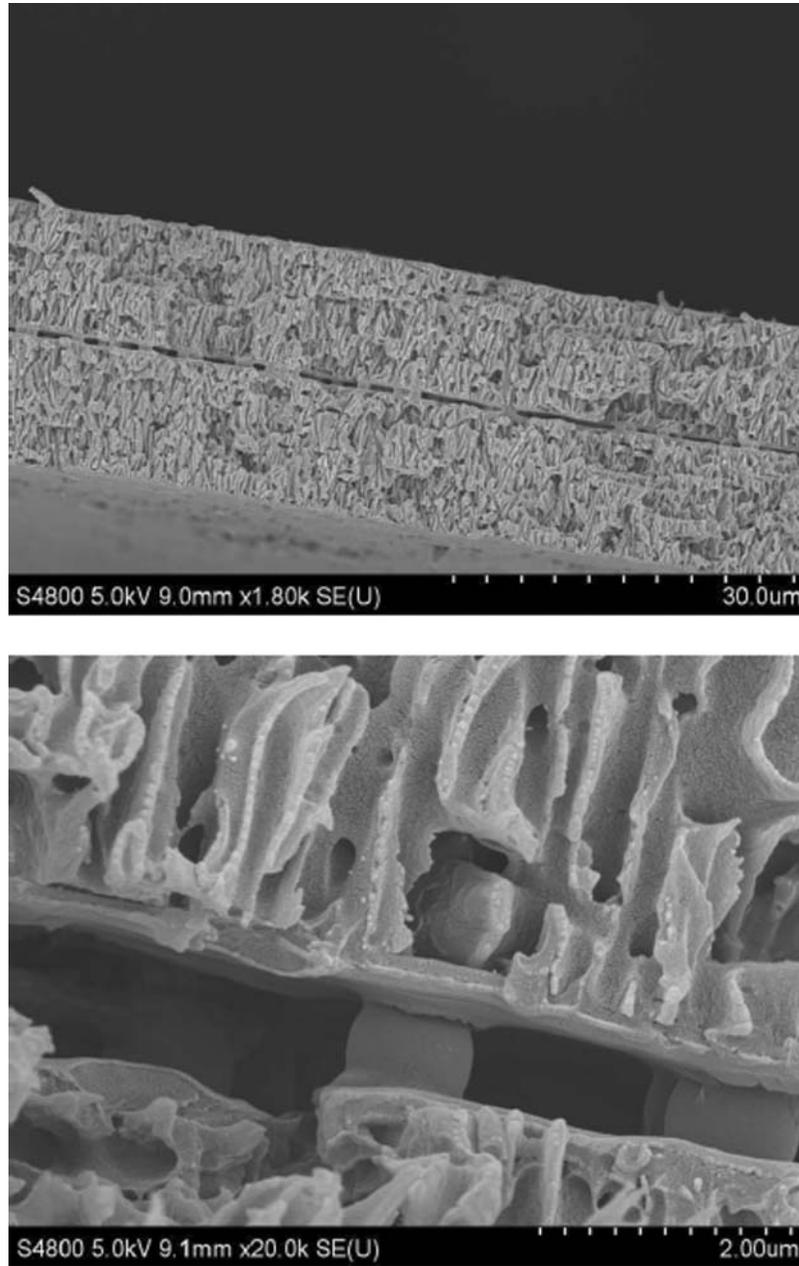


Figure 4. SEM cross-section images of assembled PET membranes with incorporated microparticles.

However, the interaction energy between ammonia and PET surface has a deeper energy-well than the kinetic energy of the molecules. This means that the ammonia molecules will be physisorbed on the PET surface if they pass through the region where the interaction energy becomes greater than the molecule's kinetic energy. The width of this region is the intersection between the interaction energy profile and the kinetic energy ( $\sim 5$  Angstroms from the surface, in this case).

The effect of membrane coated with an epoxy layer on gas permeation was studied utilizing molecular modeling

for air (oxygen and nitrogen) and ammonia to model the interaction between the coat material and the permeate. As shown in Figure 10, nitrogen and ammonia molecules have enough kinetic energy to escape from the surface potential energy and elastically rebound. However, the oxygen energy-well is deeper than the kinetic energy, which means that the molecule will be physisorbed on the surface if it comes 3.5 Angstroms from the surface. It is expected that since the membrane was subjected to air prior to the experiment the physisorption is not playing a major role in transmission reduction. Therefore, the partial blockage of

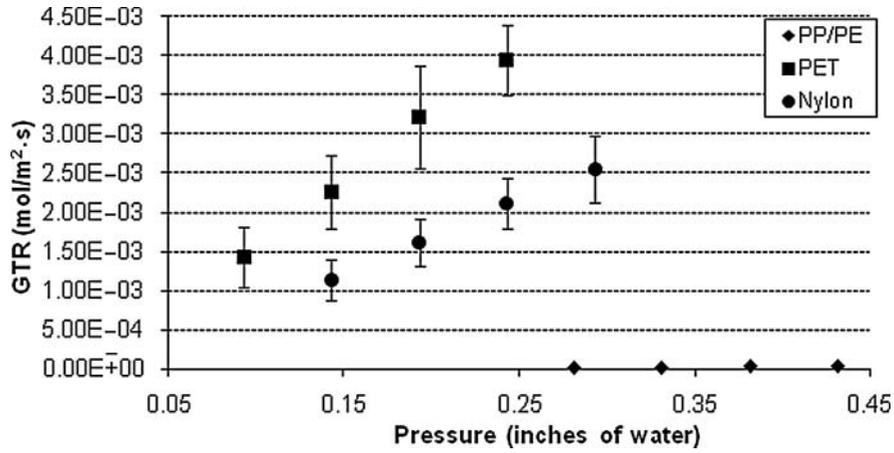


Figure 5. Transmission rate of air at different pressures through microporous membranes.

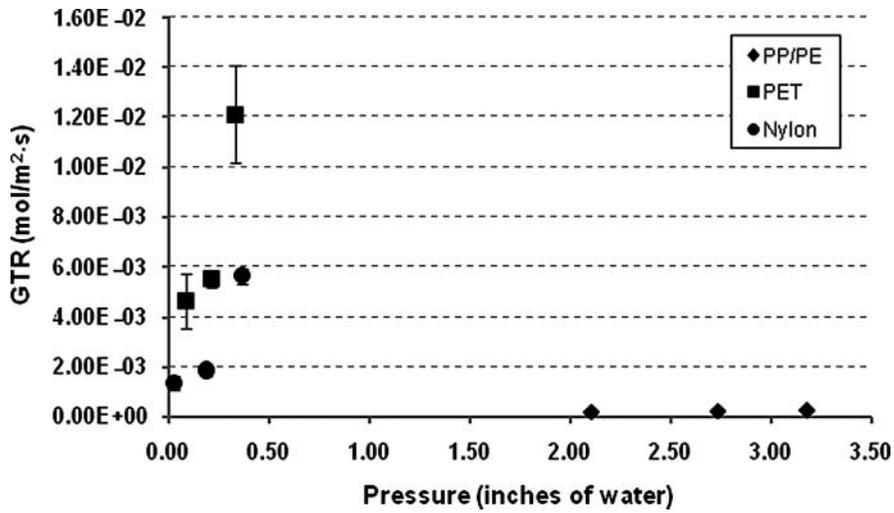


Figure 6. Transmission rate of ammonia at different pressures through microporous membranes.

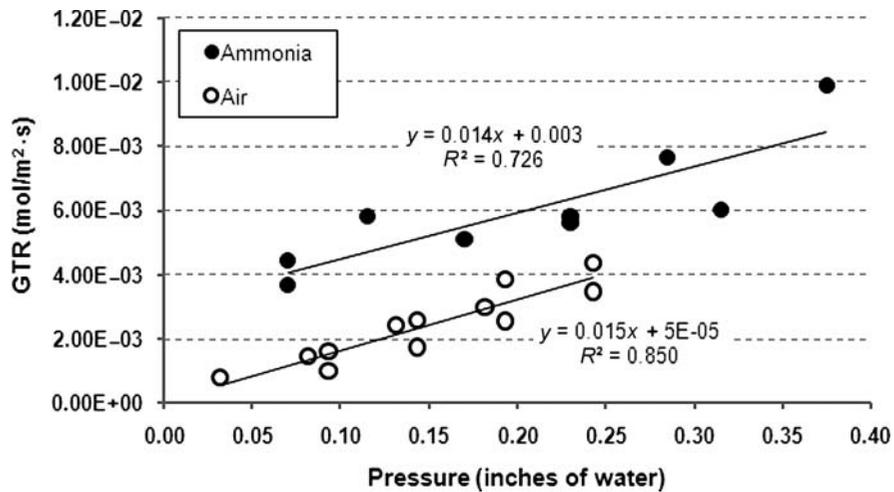


Figure 7. Comparison of transmission rate of air and ammonia at different pressures through PET microporous membrane.

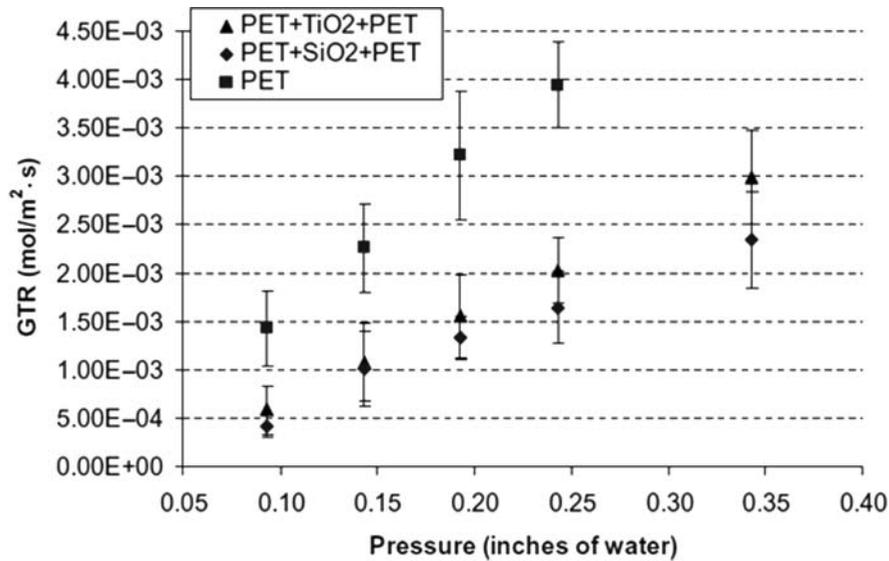


Figure 8. Comparison of permeation of air through PET membrane in single layer and double layers with  $\text{TiO}_2$  and double layers with  $\text{SiO}_2$  as binder.

the pores' area resulted from coating seems to be the main parameter responsible for the gas transmission reduction observed in the experiments.

### Model validation

#### Single layer

The probabilistic mode, including the data of the interaction energy, was used to calculate the GTR through the three membranes for air and ammonia and compared to experimental data. Figures 11–13 show comparison of the

experimental data of air transmission rate, to probabilistic model results and the Knudsen and viscous flow equations (Equations (1) and (2)), for the PET, nylon and PP/PE microporous membranes, respectively.

*PET membrane.* The average pore diameter ( $0.24 \mu\text{m}$ ) was much greater than the mean free path ( $0.0658 \mu\text{m}$ ). The Knudsen number was calculated to be 0.27 and results of the probabilistic model were within the Knudsen and viscous flow boundaries confirming the assumption of a transition regime. The probabilistic model showed acceptable

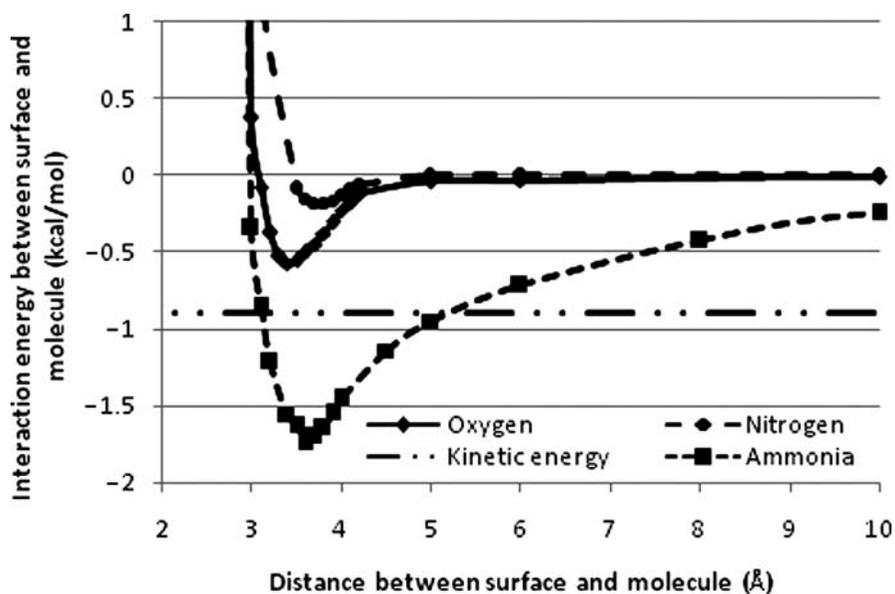


Figure 9. Interaction energy between air and ammonia molecules and uncoated PET microporous membrane.

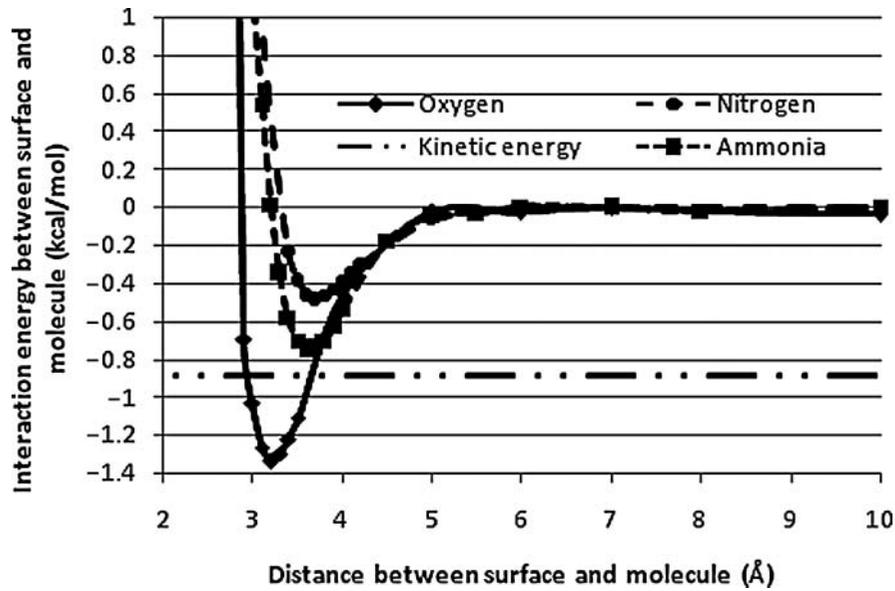


Figure 10. Interaction energy between air and ammonia molecules and PET surface covered with a thin layer of epoxy.

correlation with experimental values and was closer to a Knudsen flow.

*Nylon membrane.* Although the probabilistic model results were slightly higher than the experimental values, they were within acceptable limits. The correlation with experimental data was much better at lower pressures. As the pressure increased, deviation increased slightly. Knudsen and viscous flow equations gave much lower estimations at the given pressures. This large difference between the experiments and Knudsen and viscous flow equations might be a result of several approximations and assumptions introduced in

Equations (1) and (2), which oversimplify the structure of the membranes. Pore diameter of nylon is comparable to the average mean free path of air and  $K_n$  is calculated as 0.66. This membrane contains a large range of pore diameters and the calculated average pore diameter did not represent the real pore distribution. For the probabilistic results, pores were categorized based on pore diameter distribution and averages were calculated separately for each category during calculations. In Knudsen and viscous flow equations, the average pore diameter was calculated for the overall structure, which caused further oversimplification of experimental conditions. Therefore, the probabilistic model

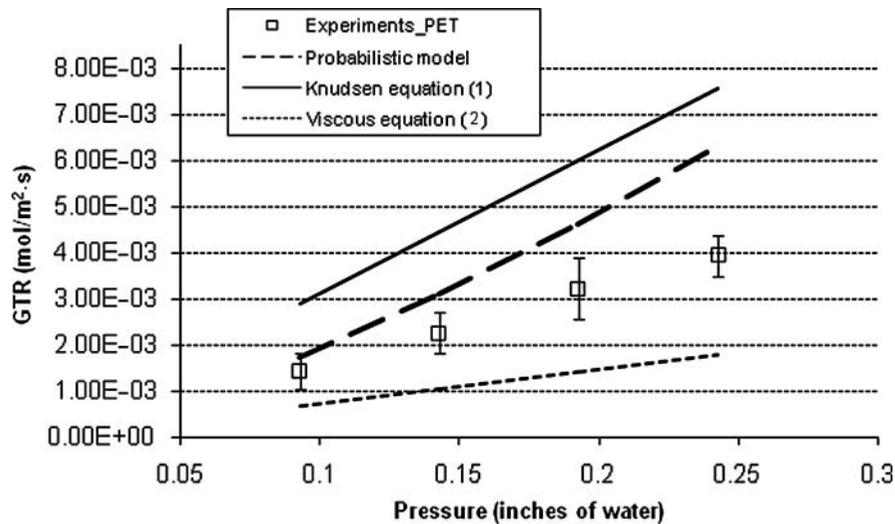


Figure 11. Comparison of experimental data and numerical models for the permeation of air through PET microporous membrane.

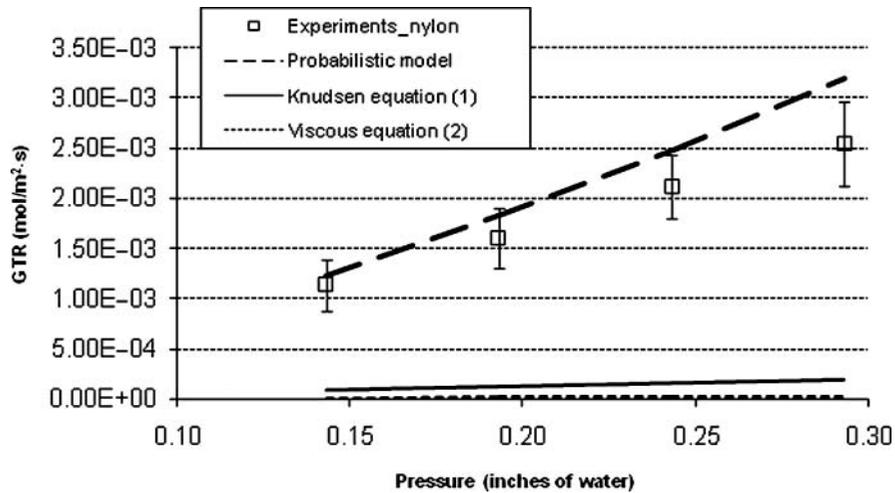


Figure 12. Comparison of experimental data and numerical models for the permeation of air through nylon microporous membranes.

enabled a more realistic estimation of the permeation rate, while Knudsen and viscous flow equations result drastically deviated from the experimental values.

*PP/PE membrane.* The transmission estimations based on probabilistic model were slightly higher than experimental values; moreover, Knudsen and viscous flow equations estimated a higher permeation rate than the experimental results. While PET had a pore diameter population within a small range, PP/PE and nylon membranes had a much wider range of pore diameters. PP/PE is expected to display a comparatively higher viscous tendency based on  $K_n$  calculated as 0.05, which is the lowest  $K_n$  number compared to the other two membranes, and therefore it is expected to be somewhat closer to a viscous type flow. However, with

its low porosity value, PP/PE has a non-negligible amount of pores that are very close to the average mean free path of air; hence a Knudsen-like tendency is not completely unexpected. In addition, the assumption of a cylindrical pore shape for PP/PE membrane seems not realistic enough for this membrane and the pore tortuosity should be involved.

*Effect of the interaction energy.* The kinetic energy of the air molecules was greater than the interaction energy between the molecules and the surface allowing the molecules to escape from the potential field of the surface. In this case there is no energetic effect on the air transmission rate. To investigate the effect of the interaction energy, ammonia was chosen due to its interaction with the PET membrane

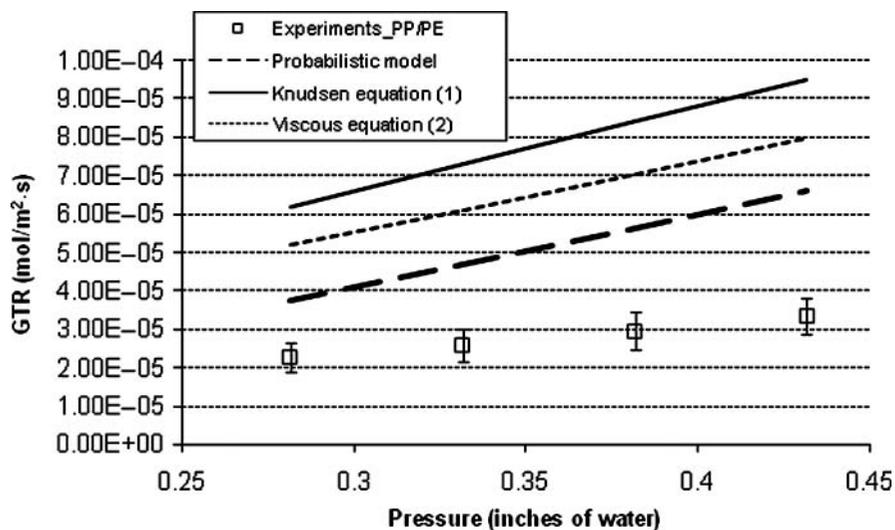


Figure 13. Comparison of experimental data and numerical models for the permeation of air through PP/PE blend microporous membrane.

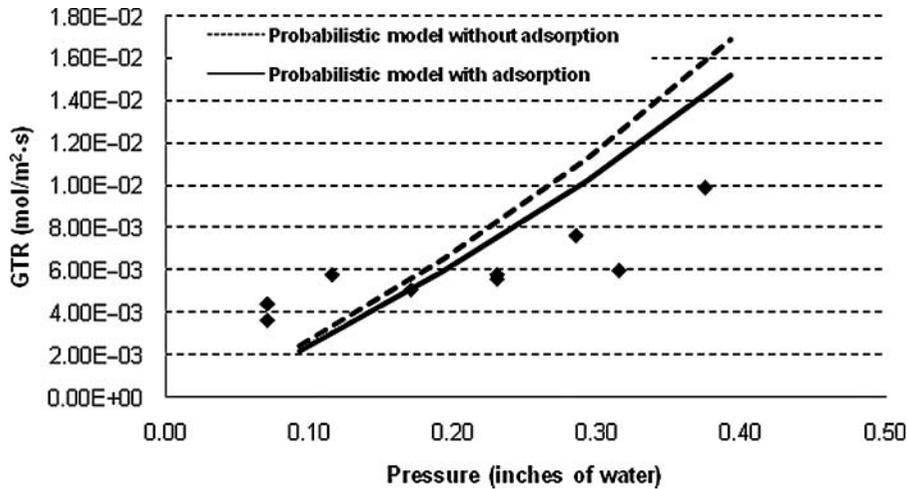


Figure 14. Comparison of experimental data for permeation of ammonia and the probabilistic model for uncoated PET microporous membrane, with and without the interaction energy between molecules and the surface.

as shown in Figure 9. The probabilistic model calculated the transmission rate of ammonia through the PET membrane at different pressure values with and without considering the interaction energy to examine its effect. Both results along with the experimental data are shown in Figure 14. Assuming that only one layer of ammonia molecules can be physisorbed on the pore surface, the results showed a 9.4% reduction in the transmission rate when the interaction energy is considered.

#### Double layers

The probabilistic model was used to calculate the air transmission rate through double-layer samples by dividing the

total molecular passage into three passages: one for each layer and an intermediate one for the space between the two layers. The volume space between the two layers was calculated after considering the particles between layers that occupied 20% of the volume space. The pressure drop along the sample layers between the top and bottom chambers were assumed to be linearly decreasing. Hence, the molecular separation distances and number of molecules are calculated based on the pressure drop in the volume space between layers. Figure 15 shows how the probabilistic model results are close to the experimental data at the low-pressure values. However, as the pressure increases the deviation increases. This can be attributed to a possible collapse of part of the layers under higher pressure.

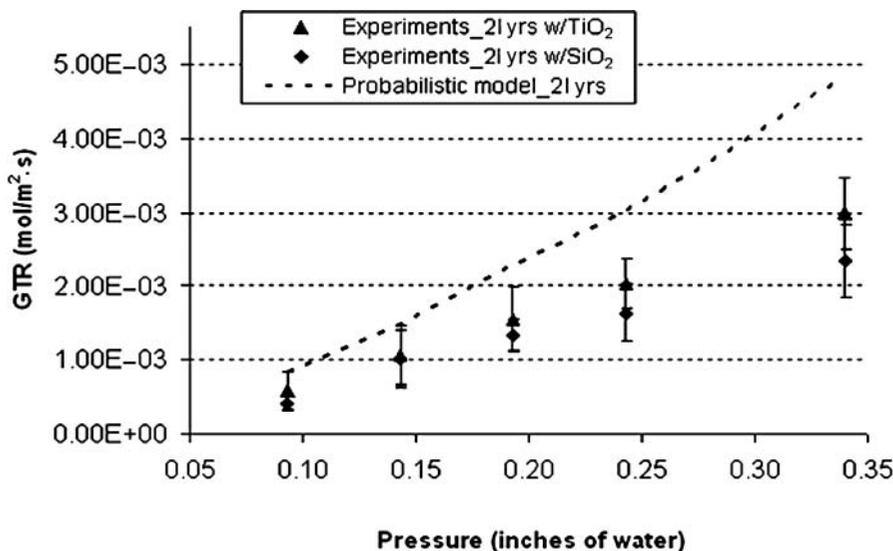


Figure 15. Comparison of permeation of air molecules through double layers of PET with probabilistic results.

## Conclusions

A probabilistic model is developed to calculate the GTR through a single layer of microporous membranes and a double-layer assembly. The interaction energy between the gas molecules and the membrane surface was calculated, using molecular modeling, to assign the effective potential field of the surface in which the molecule is physically adsorbed. Motion of individual molecules through pores was modeled based on their molecular free path and the propensity of molecules to be adsorbed on the surface. The model uses categorized pore ranges based on the pore diameter distribution obtained experimentally instead of using a single value to represent the membrane porosity. Transmission rate of air and ammonia through three microporous membranes with different pore size distributions and porosity was experimentally evaluated for a single and a double-layer assembly and the data was compared to model results. A reasonable correlation between the probabilistic model results and experimental data was observed, while a similar correlation was not evident with average Knudsen and viscous estimations available in the literature. The developed model was able to overcome some of these models' drawbacks such as: using average values for the geometric parameters and the lack of accuracy when applying these models at the transition regime. One more advantage of the developed model is considering the effect of the interaction energy between the molecules and the surfaces on the GTR. This opens a wide area of applications for this model, for example, modeling of efficiency and permeation rate through fuel cells as well as in other technologies that utilize microporous membranes for separation and purification.

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