Carbon molecular sieve membranes
Sorption, kinetic and structural characterization
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Abstract
Carbon molecular sieve membranes (CMSM) from Carbon Membranes Ltd. (Israel) were characterized. These membranes possess a very narrow pore system, in the range of 0.3–0.5 nm, and a sharp pore size distribution, allowing for high selectivities and permeabilities in gas separations. Penetrants O₂, N₂, CO₂, SF₆, Xe and He were used in monocomponent adsorption, permeability and uptake experiments for obtaining adsorption and diffusion data, leading to new insights on the internal pore structure of CMSM. A number of complementary morphological characterizations were also performed.

The permeability and adsorption data were obtained over a temperature range from 273 to 323 K and over a pressure up to 5 bar. A relation between the adsorption and permeability data was used, allowing for the estimation of the diffusivity coefficients, which were further compared with those directly obtained from the uptake experiments. Permeation and uptake experiments showed a similar strong dependence of CO₂ diffusivity on concentration.

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Keywords: Carbon molecular sieve membrane (CMSM); Adsorption; Permeation; Gas transport

1. Introduction
Nowadays, in the area of membrane research, concentrated efforts are focused on the development of novel membranes able to overtake the productivity/selectivity trade-off limit attained with the commercially available polymeric membranes for gas separation. Ultramicroporous (in the 0.3–0.5 nm range) membranes have shown to be promising in this context. Because these have pores with dimensions close to those of the diffusing species, small variations (0.02–0.03 nm) in the molecular or atomic dimensions may imply a variation of several orders of magnitude in diffusion rates [1]. These materials are therefore described as having molecular sieving capabilities. That’s the case of zeolite and carbon molecular sieve membranes.

Carbon molecular sieve membranes (CMSM) are brittle and difficult to handle, however they still offer advantages over zeolite membranes. Indeed, although good progress is being made, the latter are difficult to obtain in large dimensions and in a crack-free, continuous form [2]. CMSM, on the other hand, have been successfully manufactured in different configurations, showing good performances in terms of having higher permeabilities than zeolite membranes, for the same selectivity values [3].

Soffer and Koresh were the first to successfully prepare carbon molecular sieve membranes by pyrolysis of organic precursors (cellulosic and phenolic resins) [4,5]. They studied how high temperature treatments influence the development of the pore structure. High temperature (up to 700°C) evacuation and mild temperature (up to 450°C) air oxidation treatments lead to the opening of the pore structure. A further increase in temperature, under vacuum or inert atmosphere, results in a gradual pore closure due to sintering. This way, by appropriately choosing a sequence of thermal treatments, the membrane’s pore aperture can be nearly continuously tuned. The application of these carbon membranes to gas separation processes was patented in 1987 [6] by the same authors. A few years later, Soffer co-authored...
some other related patents: in 1995, a full description of the process of production of hollow fiber membranes from thermosetting polymers such as cellulose [7]; in 1996, a method for repairing defective hollow fiber membrane modules, by selectively clogging, with a sealant, the cracked fibers [8]; in 1997, a method of improving membrane selectivity using chemical carbon vapor deposition [9]. These patents ended up being bought by an Israeli company named Carbon Membranes Ltd. This was the first and, so far, the only company worldwide to produce, at an industrial scale, high-quality hollow fiber membranes. Commercialization started by the end of the 1990s, but the company closed in 2001.

Since 1987 that many other researchers have been synthesizing microporous carbon membranes, from several precursors such as polyimides [10–16], coal tar pitch [17], condensed polynuclear aromatic resins [18] and, recently, from ultra-filtration fiber membranes [19]. There have also been reports of supported carbon membranes [20–25] (to improve mechanical stability), composite carbon membranes (to reduce adverse humidity effects) [26] and, more recently, mixed matrix membranes (using CMS to counter diffusion data for several gaseous species. The CMSM characterization and tested in this study were supplied by Carbon Membranes Ltd. These industrially produced membranes consisted of 1 m long hollow fibers, which were adapted for assembly in a lab-scale membrane module.

2. Carbon molecular sieve membranes

Carbon Membranes Ltd. has successfully prepared crack-free CMSM hollow fibers having narrow pore size distributions. The production process consists in the pyrolysis of a large bundle of thermosetting polymeric precursor fibers, such as dense cellulose hollow fibers, from which all plasticizers and absorbed water have been previously removed. This thermal decomposition takes place in a controlled atmosphere and involves a rigorous temperature history. Fig. 1 shows an idealized CMSM pore structure. During pyrolysis, heteroatoms are progressively removed leaving a porous carbon skeleton (Fig. 1a). This carbon skeleton is responsible for the membrane’s mechanical properties and, if a selective layer is not added subsequently, will also determine the separation performance. Koresh and Soffer proposed that the pore structure is made of a series of very narrow constric-
tions (<0.5 nm) linking larger pore sections in the micro-


diagram
the “primary” pores at the bore side with a so-called “CVD layer” (Fig. 1b). The deposition occurs on the bore side of the hollow fiber, both within the existing pore structure and as an additional layer on top of the membrane surface. Depending on the size of the molecule used as the carbon source, each of these distinct forms of deposition will prevail [9]. The next stage, called “activation”, consists in applying a high-temperature oxidation treatment in order to create a pore structure of tailored dimensions within the CVD layer (Fig. 1c). A very narrow distribution of “selective” ultramicropores is obtained. Duration and intensity of this treatment determines the diameter of the “selective” pores and therefore allows for the tuning of the membrane performance towards the intended gas separation. Since the CVD is applied to one side of the fiber, this process results in an asymmetric membrane. The “primary” porosity is also affected in this step, as described below.

The structure of these porous inorganic membranes is not as regular as that of zeolite membranes, since they have an amorphous nature. A schematic picture of the carbon porous structure is shown in Fig. 1d. The evolution of the pore structure along the different treatments can be viewed as described next. This is an idealized model, which will be used later in the discussion of the experimental data. Pyrolysis creates the “primary” microporosity. These pores are narrow and the number of those that actually connect both faces of the membrane is small, so that permeability is very low for all gases. It has been suggested that these pores are slit shaped [1]. The posterior activation treatment, applied after the carbon vapor deposition, creates ultramicropores, here designated as “selective” pores (with a characteristic diameter \(d_s\) – see Fig. 1d). These contribute decisively to improve the membrane’s selectivity performance. They are formed in different regions of the membrane: (a) across the CVD layer, (b) connecting “primary” pores and (c) as dead-end pores. The activation treatment additionally contributes to widen the “primary” porosity, which is idealized as consisting of cavities (\(d_h\)) and constrictions (\(d_c\)).

Representative permeabilities for SF\(_6\) and \(N_2\) measured on CMSM samples on two conditions, (1) right after pyrolysis and (2) after three different CVD/activation treatments (designated by samples CMSM1, CMSM2 and CMSM3), are listed in Table 1. The data for \(N_2\) evidences how different permeabilities associated with the original “primary” porosity are quite low and therefore the final activation treatment also plays a role in widening these pores. The fact that SF\(_6\) does not permeate through any of the samples insures that these are crack-free. Carbon Membranes Ltd. did not supply details on the thermochemical treatment history associated to each of the three CMSM samples. These samples (CMSM1, CMSM2 and CMSM3) are used along this study.

In the ultramicropore structure, the pore sizes are comparable to the molecular sizes and therefore molecules may never completely escape the potential field of the pore walls. Gas transport occurs according to an activated diffusion mechanism. Two alternative mechanisms may be responsible for the separation of a gas mixture, depending on the pore size/effective molecular diameter ratio:

1. Molecular sieving will be the preponderant mechanism for diffusing species having approximately the same diameter as the pores. The diffusivity of a species through the membrane depends strongly on the molecular size and shape.
2. The so-called selective adsorption mechanism [35] occurs when a diffusing species is preferentially adsorbed and, due to its size, hinders the passage of less adsorbed species through the pores. This may occur when the pore diameter is up to three or four times larger than the diameter of the more strongly adsorbed species [36].

### Table 1

<table>
<thead>
<tr>
<th>Permeability (10^{-8} \text{ m}^3/\text{STP m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}) of CMSM samples before and after different CVD/activation treatments</th>
<th>Pyrolyzed CMSM samples before CVD/activation</th>
<th>Pyrolyzed CMSM samples after different CVD/activation treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CMSM1</td>
<td>CMSM2</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(N_2)</td>
<td>2.2-6.8</td>
<td>223</td>
</tr>
</tbody>
</table>

\(\beta^2=1\) bar

\(a\) Data supplied by Carbon Membranes Ltd.

#### 3. Experimental

Different gases were selected: He, \(CO_2\), \(O_2\), \(N_2\), \(Xe\) and SF\(_6\) in order to analyze the sorption and transport properties of the CMSM. Three different samples, designated as CMSM1, CMSM2 and CMSM3 (see Table 1) were used. These correspond to different activation treatments applied by the manufacturer (CML).

Several techniques were used in this study to provide insight onto the morphology of the carbon material. These included SEM pictures, wide-angle X-ray diffraction, X-ray microanalysis, helium pycnometry and \(CO_2\) adsorption data.

A volumetric-type apparatus was used to measure pure component isothermal equilibrium data. The internal volumes of the various parts of the system were initially accurately measured. In the experimental runs, a high-accuracy Druck pressure transducer measured the gas-phase pressure and the temperature of the sample was monitored with a thermocouple. Each sample consisted of about 5 g of broken-up fibers. Equilibrium adsorption data for \(N_2\), \(O_2\), \(CO_2\), \(Xe\) and SF\(_6\) at three temperatures and up to 5 bar were determined for sample CMSM2.

Sorption rates of \(CO_2\) and \(N_2\) on CMSM2 and CMSM3 were measured gravimetrically on a Rubotherm suspension magnetic balance having a 0.01 mg weighing resolution and a 0.02 mg reproducibility. The entire system is fully thermostated. Each uptake measurement was performed over...
successive appropriately small increments in adsorbate pressure, so that the sorption equilibrium may be assumed linear in each interval. This allowed for the determination of diffusivities as a function of loading.

Single gas permeation was measured in a dead-end permeation module, in a temperature-controlled system. The feed was applied to the bore side of the membranes. The pressure gradient was generated both by pressurizing the feed and by evacuating the permeate side. The feed was high-purity gas supplied directly from compressed gas cylinders. Its pressure was controlled with a pressure regulator installed after the two-stage regulator on the cylinder. The feed and permeate pressures were read on Druck absolute pressure transducers. The volumetric flow rate of the permeating species was measured using Bronkhorst HI-TEC flowmeters, chosen in accordance to the flow rate range. Two membrane modules, designated as M1 and M2, containing a bundle of CMSM2 fibers, were constructed with 1/4 in. stainless steel tubing of 30 cm length and two Swagelok 1/4 tees (see Fig. 2). Epoxy glue was used to plug the ends of the modules. The characteristics of the in-house-assembled membrane modules are listed in Table 2. A bulky molecule (SF6) has been used as a probe molecule to test the integrity of each module.

4. Results and discussion

4.1. Structural characterization

Several techniques were used in this study for a preliminary characterization of the CMSM structure. Scanning electron microscopy techniques are useful for evaluating the overall quality of the membrane, detecting the presence of any mesoscopic cracks and determining the overall thickness of the hollow fiber wall. The results indicated a uniform wall thickness of 9 μm and an external diameter of 170 μm.

The SEM pictures, illustrated in Fig. 3, also showed a radially symmetric, dense and crack-free structure.

The skeletal density, ρs, was measured by helium pycnometry. The densities obtained for CMSM1 and CMSM2 were 1.7 and 1.6 g cm$^{-3}$, respectively, against 2.3 g cm$^{-3}$ for non-porous crystalline graphite density. As expected, CMSM is a highly disordered material with low density.

![Fig. 2. Sketch of the membrane module.](image1)

![Fig. 3. SEM pictures of a CMSM.](image2)
X-ray microanalysis (0.5% weight detection limit) did not detect the existence of other atoms in addition to carbon. Wide-angle X-ray diffraction indicated an average pore size of 0.4 nm and a highly amorphous structure. This is coherent with the densities obtained by helium pycnometry, which were 20–30% lower than that of crystalline graphite.

To characterize the micropore volume of two different samples, CMSM1 and CMSM2, subcritical carbon dioxide adsorption was employed together with the Dubinin–Radushkevich (DR) equation (Eq. (1)):

\[ q = q_\infty \exp \left( \frac{-1}{\beta E_0} \left( \frac{RT \ln \beta}{p_v} \right)^2 \right) \]  

where \( q \) represents the amount of solute adsorbed at a relative pressure \( p/p_v \), \( q_\infty \) the limiting amount of solute filling the micropores, \( E_0 \) the characteristic energy dependent on the pore structure and \( \beta \) the affinity coefficient which is characteristic of the adsorbate. The value of the affinity coefficient, \( \beta \), for carbon dioxide is around 0.35 [37]. This equation has been used to characterize the micropore volume of many carbon-based microporous materials [38]. It has been shown that CO\(_2\) adsorption at 273 or 298 K is sensitive to the presence of narrow micropores (pore size smaller than 0.6 nm), which are not accessible to N\(_2\) at 77 K, due to diffusional limitations [37,39].

The limiting micropore volume is given by

\[ V_p = \frac{q_\infty M_r}{d_{CO_2} \rho_s} \times 10^6 \]  

where \( d_{CO_2} \) is the density of CO\(_2\) in the adsorbed state.

There is uncertainty as to the true density of the adsorbed phase, and it is likely that the adsorbate is denser than the liquid phase at the same temperature due to the overlap of the potential energy surfaces in the micropores. The approach followed here was suggested by Cazorla-Amarós et al. [37]. The values of density that can be used fall between the density of liquid CO\(_2\) and the value obtained from Dubinin’s approach. The density values proposed for adsorbed CO\(_2\) are 0.85 g cm\(^{-3}\) at 298 K and 0.97 g cm\(^{-3}\) at 273 K.

The characteristic curves obtained from the CO\(_2\) adsorption isotherms on CMSM1 and CMSM2 are quite linear, indicating that the DR equation (Eq. (1)) provides a reasonable description. A characteristic curve for CMSM2 at 273 K is shown in Fig. 4.

The slope of this plot is related to the characteristic energy of the micropore (\( E_0 \)) and the affinity coefficient (\( \beta \)). The intercept is related to the saturation capacity (\( q_\infty \)). The micropore volume, \( V_p \), was estimated and compared with data published in the literature, as shown in Table 3.

Also shown in Table 3, are the average micropore widths, \( L_0 \), estimated from Stoeckli equation which can be used when the DR equation applies [40]:

\[ L_0 (\text{nm}) = \frac{10 800 (\text{nm} \cdot \text{mol}^{-1})}{E_0 - 11 400 \text{ (J mol}^{-1})} \]  

This simple approach provides only a rough estimation, but, as it will be seen in the next section, it is in agreement with equilibrium adsorption experiments involving spherical solutes with different kinetic diameters.

The analysis methods of CO\(_2\) adsorption and helium pycnometry were combined and used to calculate the bulk density of the material, according to the following equation:

\[ 1/\rho_b = 1/\rho_s + V_p. \]  

This is shown in Table 3, together with the estimated porosities. Note that the previous equation does not account for the presence of isolated cavities. It is interesting to note that CMSM1, which is 10 times more permeable toward N\(_2\) than CMSM2 (see Table 1),

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micropore volume, ( V_p ) (cm(^3) g(^{-1}))</th>
<th>( L_0 ) (nm)</th>
<th>( E_0 ) (kJ mol(^{-1}))</th>
<th>( \rho_s ) (g cm(^{-3}))</th>
<th>( \rho_b ) (g cm(^{-3}))</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSM1</td>
<td>0.28(^a)</td>
<td>0.55</td>
<td>51.6</td>
<td>1.6</td>
<td>1.4</td>
<td>0.35</td>
</tr>
<tr>
<td>CMSM2</td>
<td>0.16(^b)</td>
<td>0.45</td>
<td>35.6</td>
<td>1.7</td>
<td>1.3</td>
<td>0.21</td>
</tr>
<tr>
<td>Published data(^c)</td>
<td>CMS, T3A</td>
<td>0.20(^d)</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMS, T3A</td>
<td>0.30(^e)</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) CO\(_2\) adsorption at 283 and 293 K; CO\(_2\) density obtained by interpolation.

\(^{b}\) CO\(_2\) adsorption at 273 K.

\(^{c}\) Ref. [39]
presents higher micropore volume and higher mean pore width. This is in agreement with a larger activation step of the membrane, leading to an additional enlargement of the “primary” micropore system and to wider “selective” pores.

4.2. Adsorption equilibrium experiments

The equilibrium adsorption isotherms for N₂, O₂ and CO₂ up to 5 bar on CMSM2 are represented graphically in Figs. 5 and 6. These are of type I. The Langmuir equation was used to fit the data for CO₂, O₂ and N₂. The Langmuir-Freundlich equation was additionally used for CO₂, giving slightly better results. The isotherm parameters are summarized in Table 4. The adsorption capacity decreases strongly with temperature. Nitrogen and oxygen are both weakly adsorbed in relation to carbon dioxide and the respective isotherms are essentially coincident. No hysteresis is observed, as would be expected for a system with no mesopore condensation.

The analysis of adsorption isotherms is still the most sensitive method for gathering useful information concerning the CMSM structure at the ultra-microporous level. The samples were probed using gas species of varying dimensions, in order to estimate the critical pore widths. Adsorption data for Xe and SF₆ were experimentally obtained on CMSM1 and CMSM2. No measurable uptake was detected for SF₆ up to 5 bar on both samples. The exclusion of this species indicates that the critical pores in this material have a dimension that is somewhere below 0.502 nm (SF₆ molecular dimension based on liquid molar volume [41]). On the other hand, xenon adsorption shows distinct behaviours on each CMSM sample. On CMSM1, xenon was strongly adsorbed and the uptake was relatively fast (1 h). In contrast, on CMSM2, xenon uptake was very slow at the same temperature, so that equilibrium was not yet attained after 8 days. From these observations one concludes that at least a fraction of the pores in CMSM1 are larger than

Table 4

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Langmuir</th>
<th>Q_{Langmuir} (kJ mol⁻¹)</th>
<th>Langmuir-Freundlich</th>
<th>Q_{Langmuir-Freundlich} (kJ mol⁻¹)</th>
<th>−ΔH_{ads} (kJ mol⁻¹)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>p (bar)</td>
<td>q_m (mol m⁻³)</td>
<td>p (bar)</td>
<td>q_m (mol m⁻³)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>288</td>
<td>1.51</td>
<td>4976</td>
<td>1.49</td>
<td>5537</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.93</td>
<td>4208</td>
<td>0.93</td>
<td>5928</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.48</td>
<td>4492</td>
<td>0.48</td>
<td>5738</td>
</tr>
<tr>
<td>O₂</td>
<td>288</td>
<td>0.23</td>
<td>3249</td>
<td>0.23</td>
<td>18.7</td>
</tr>
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<td></td>
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<td>2899</td>
<td>0.19</td>
<td>20.2</td>
</tr>
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<td></td>
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<td>0.09</td>
<td>3044</td>
<td>0.09</td>
<td>20.8</td>
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<tr>
<td>N₂</td>
<td>288</td>
<td>0.24</td>
<td>2888</td>
<td>0.24</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.19</td>
<td>2719</td>
<td>0.19</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.15</td>
<td>2147</td>
<td>0.15</td>
<td>20.8</td>
</tr>
</tbody>
</table>
Fig. 7. Carbon dioxide adsorption isosteres at different coverage on CMSM2 sample.

0.394 nm (Xe molecular dimension based on liquid molar volume [41]) and that on CMSM2 the critical micropore size is close to 0.394 nm.

The isosteric heat of adsorption was determined at different coverages on CMSM2 using the thermodynamic van’t Hoff equation:

\[ \frac{\Delta H}{RT^2} = -\left(\frac{\partial \ln p}{\partial T}\right)_q \]

Table 4 summarizes these results. For N\textsubscript{2} and O\textsubscript{2}, the computed values of \(-\Delta H_{\text{ads}}\) are independent of the amount adsorbed. For CO\textsubscript{2}, on the other hand, the isosteric heat decreases with increasing surface coverage, as shown in Fig. 7. This may be a consequence of surface heterogeneity or repulsive sorbate interactions.

4.3. Permeation experiments

Fig. 8 shows results for bore side feed permeation on membrane (CMSM2) modules M1 and M2 (see Table 2), measured at 303 and 323 K. Permeate pressure was kept at 0.060 bar while feed pressure varied from about 0.400 bar up to 4 bar.

The “permeability”, \( P \), of the CMSM towards a species was determined as described by the following equation:

\[ P = \frac{\text{Flux}}{\Delta p/\ell} \quad (4.1) \]

where \( \Delta p \) is the partial pressure difference of the species across the membrane and \( \ell \) is the thickness of the membrane. For convenience, in this work we also use the mass transfer coefficient or permeance, \( k_p \), defined as

\[ k_p = \frac{P}{\ell} = \frac{\text{Flux}}{\Delta p} \quad (4.2) \]

As seen from Fig. 8, the permeance and hence the permeability of all adsorbing species decreases with increasing feed pressure. This tendency seems to become more evident as the intensity of adsorbate/adsorbent interactions increases. The strongly adsorbed CO\textsubscript{2} shows a pronounced decrease of permeability with pressure, reflecting a strong concentration dependence of the diffusion coefficient. For O\textsubscript{2} and N\textsubscript{2}, adsorption interactions are weaker and the permeabilities are less pressure dependent. Helium permeability, on the other hand, is independent of pressure. Gas molecules having a diameter larger than 0.39 nm, like Xe and SF\textsubscript{6}, do not exhibit measurable permeation up to 5 bar. The permeability of all species increases with temperature.

Effective diffusivity coefficients were evaluated combining experimental data from equilibrium adsorption and steady-state permeation experiments. The flux of a sorbed species is given by [42]

\[ J = -D(q) \Gamma \frac{\partial q}{\partial z} \quad (5) \]

where \( D(q) \) is the corrected diffusivity and \( \Gamma = \partial \ln p/\partial q \) is the thermodynamic correction factor. The Fickian diffusivity, \( D \), also called transport diffusivity, is therefore related to the corrected diffusivity, \( D(q) \), by

\[ D(q) = D(q) \Gamma \]

Eq. (6) is sometimes referred to as the Darken equation [42]. The corrected diffusivity may itself be dependent on coverage [42]. The thermodynamic correction factor can be determined from the equilibrium isotherm equation. For strongly adsorbed species, the transport diffusivity is highly dependent on concentration via the thermodynamic correction factor. If the corrected diffusivity is considered constant, substitution of the Langmuir isotherm equation into Eq. (6) leads to:

\[ D = D_0 \frac{1}{1 - \theta} \quad (7) \]
In this work, the corrected diffusivity was allowed to vary with coverage, according to:

$$D_c(\theta) = \frac{D^0_c}{(1-\theta)^n} \tag{8}$$

$D^0_c$ is the corrected diffusivity at zero loading.

Under steady-state flow, the expression for the flux of the adsorbed species can be obtained by solving Eq. (5) subject to constant boundary conditions, corresponding to the two sides of the membrane. Assuming that sorption is described by the Langmuir equation and using Eq. (8) for describing the dependency of $D_c$ on the coverage, one obtains

$$J = \frac{D^0_c \ell q_m}{T} \ln \left[ \frac{1 + \frac{p_h}{1 + p_p}}{1 + \frac{p_l}{1 + p_p}} \right], \quad n \neq 1 \tag{9}$$

$$J = \frac{D_c \ell q_m \ln \left( \frac{1 + p_h}{1 + p_l} \right)}{T}, \quad n = 1 \tag{10}$$

where $p_h$ and $p_l$ are the pressures on the feed and permeate side of the membrane, respectively.

For non-adsorbing species, the flux through CMSM is simply described by

$$J = \frac{D_c \ell q_m}{T} \left( p_h - p_l \right) \tag{11}$$

The curve fits, using Eq. (10) for $N_2$ and $O_2$, Eq. (9) for $CO_2$ and Eq. (11) for He, are shown in Fig. 8. These agree quite well with the experimental data. The calculated corrected diffusivities at zero loading, $D^0_c$ and $D_c$, are shown in Table 5. In all cases, the effective diffusivities increase with increasing surface coverage. For $O_2$ and $N_2$, this dependence can be described using a constant corrected diffusivity, i.e. using the so-called “Darken-like” dependency.

On the other hand, the data for $CO_2$ cannot be described by a “Darken-like” relation, as shown in Fig. 9. It is important to note that the use of another isotherm equation (like Langmuir-Freundlich), which fits the $CO_2$ equilibrium data somehow better than the Langmuir equation, also does not provide a good fit of the permeance data. A loading-dependent corrected diffusivity (Eq. (8)) had therefore to be used, with a parameter $n = 1.52$ (at 303 K).

The corrected diffusivities $D^0_c$ and $D_c$ were correlated, at three different temperatures, by the Arrhenius equation (see Fig. 10). The corresponding computed values of the activation energies ($E_a$) are given in Table 5. For all gases, transport is well described as being an activated process, as expected for a molecular sieving mechanism.

### 4.4. Uptake experiments

Gravimetric uptake measurements were carried out for $CO_2$ and $N_2$ on CMSM2 to determine the effective diffusivity coefficients and further compare them with the results evaluated from the combination of permeation and adsorption equilibrium data. Since the $CO_2$ diffusivity is strongly concentration dependent, uptake experiments were

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Sample CMSM2</th>
<th>$D^0_c$ or $D_c$ ($\times 10^{-12}$ m$^2$ s$^{-1}$)</th>
<th>Fitted equation</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$</td>
<td>288</td>
<td>0.68</td>
<td>1.47</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>303</td>
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<tr>
<td>$O_2$</td>
<td>288</td>
<td>1.36</td>
<td>1</td>
<td>1</td>
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<td></td>
<td>303</td>
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![Fig. 9. Carbon dioxide permeance concentration dependence at 303 K. The solid line corresponds to the Eq. (9) fitting and the dashed line corresponds to the Eq. (10) fitting.](image)

![Fig. 10. Arrhenius plots for diffusivity (at zero loading) in CMSM2 sample for: (□) CO$_2$; (○) N$_2$; (△) O$_2$; (●) He.](image)
performed only at very low concentration. At higher concentrations, the combination of fast uptake rates with thermal effects made it impossible to accurately extract the diffusivity.

Representative uptake curves, obtained for CO\(_2\) and N\(_2\) at 303 K, are shown in Fig. 11. The gaps in the CO\(_2\) experimental points are related to the automatic baseline correction procedure of the microbalance used. The observed transient behaviour seems to be consistent with micropore diffusion control. Since membrane thickness is less than 6% of the fiber’s external diameter, one can assume a slab geometry model. The fractional uptake, \(F\) (ratio between the total amount of solute adsorbed, at instant \(t\), and the total amount of solute adsorbed in equilibrium at \(t \rightarrow \infty\)), is given by [42]

\[
F = 1 - \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \exp\left(-\frac{D(2k+1)^2\pi^2t}{\ell^2}\right)
\]  

(12)

From uptake measurements, one obtains a diffusivity of 0.76 \(\times 10^{-14} \text{ m}^2 \text{s}^{-1}\) for nitrogen. For carbon dioxide one obtains a diffusivity of 3.51 \(\times 10^{-14} \text{ m}^2 \text{s}^{-1}\), for a feed pressure of 0.048 bar. The corresponding values obtained from permeation data are 50.7 \(\times 10^{-14} \text{ m}^2 \text{s}^{-1}\) for nitrogen and 120 \(\times 10^{-14} \text{ m}^2 \text{s}^{-1}\) for carbon dioxide. This large discrepancy may be associated to the CMSM pore structure, taking into account that the two methods refer to transient and steady-state measurements, respectively. Each method involves transport through different pore systems. In a transient experiment, the entire pore structure is being filled, including a fraction of dead-end pores (see Fig. 12). These pores, in accordance to the structural model described earlier, are mostly composed by “selective” pores, having diameters close to the size of the diffusing species. Therefore, transport through the dead-end pores represents an additional significant resistance. On the other hand, in a steady-state method, as is the permeation measurements, only the fraction of pores whose pass crosses the membrane (wall to wall) contributes to the observed transport performance, which excludes the dead-end pores. Note that molecular probing experiments performed with SF\(_6\) exclude the hypothesis of higher permeabilities being due to the presence of cracks on the membrane. It is interesting to remark that a similar disagreement was also reported by Wang et al. [11], for CMS membranes. These authors observed that CO\(_2\) diffusivities, measured by time lag and steady-state permeation, differed over an order of magnitude.

One might question whether the micropore diffusion model (Fickian diffusion) is actually adequate to describe the transport process observed. Indeed, a surface resistance effect, in the form of a “pore mouth” barrier has been observed in some systems [43,44], which would be better described by a linear driving force (LDF) type model. Fig. 13 shows a plot of \(\ln(1 - F)\) as a function of time for nitrogen, together with the solutions of the LDF model [42] and, using one hundred terms in the rapidly converging se-
The micropore diffusion model provides indeed the best description of the data.

In order to study the concentration dependence of the diffusion coefficient by uptake measurements, another carbon molecular sieve sample, CMSM3, had to be used. This membrane exhibits lower diffusivities, therefore preventing the intrusion of heat effects. Some experimental uptake curves for N₂ and CO₂ are shown in Figs. 14 and 15, respectively. These curves were fitted according to Eq. (12). Experimental data obtained for N₂ show a higher scattering than for CO₂ due to the first gas being less adsorbed. This causes a higher relative weighing error. The experimental diffusivities of N₂ and CO₂ from uptake experiments and the CO₂ diffusivity concentration dependence parameters are given in Table 6. As already concluded from permeation experiments, N₂ diffusivity is weakly dependent on pressure. This is no longer true for CO₂. The variation of the diffusivity with coverage is shown in Fig. 16, together with the best-fit curve according to the Darken relation with a constant corre-

<table>
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<th>Uptake results for sample CMSM3</th>
<th>Fitting curve</th>
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<td></td>
<td>Darken-like relation, $D_c (\times 10^{15} \text{ m}^2 \text{ s}^{-1})$</td>
</tr>
<tr>
<td></td>
<td>$D_0 (\times 10^{15} \text{ m}^2 \text{ s}^{-1})$</td>
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<td><strong>CO₂</strong></td>
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<td>0.28 3.48</td>
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<td>0.07 0.38</td>
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**Table 6** Carbon dioxide and nitrogen diffusivities from uptake experiments with CMSM3 sample. Carbon dioxide diffusivity concentration dependence parameters
ected diffusivity and to Eq. (8). The trend, for the diffusivity dependence on coverage, obtained from these uptake experiments (n = 1.45) agrees quite well with the one observed on the permeation experiments (n = 1.52). The optimal values of the fitting parameters are listed in Table 6.

Researchers have attempted to justify a loading dependence of the corrected diffusivity based on the system heterogeneity [45]. On the other hand, Do et al. [46] argued that this cannot account for the increase of permeability with loading, implying that the so-called corrected diffusivity is a function of loading. This was interpreted by the authors in terms of species sorbed on successive layers having different mobilities. This study referred to microporous activated carbon. In CMSM, however, it is not clear whether multilayer adsorption can occur. Xiao and Wei [47], in the context of zeolite systems, suggested that repulsive interactions among neighboring species at high loadings may also contribute for a concentration dependence of the transport diffusivity. Further studies are necessary for clarifying this topic.

5. Conclusions

Carbon molecular sieve hollow fiber membranes (CMSM), from Carbon Membranes Ltd. (Israel), were characterized. These CMSM are made from a hollow fiber precursor of a thermosetting polymer such as cellulose. The production steps involve pyrolysis followed by carbon vapor deposition (CVD) and an activation step, which consists on a high-temperature oxygen treatment. Adsorption, permeability and diffusion data were collected and analyzed, bringing some insights on the pore structure of these materials.

The porous structure of the asymmetric CMSM is here schematically modeled as involving two main features: cavities linked by constrictions (designated here as "primary" pores), which are associated with the initial pyrolysis procedure, and ultramicropores (<0.5 nm) (designated here as "selective" pores), formed during the activation step, which exist across the CVD layer and as dead-end pores throughout the membrane.

Equilibrium adsorption isotherms and uptake curves were obtained for N₂, O₂ and CO₂. Langmuir (N₂, O₂ and CO₂) and Langmuir–Freundlich (CO₂) equations were fitted to the equilibrium data. Despite equilibrium adsorption information for CMSM being rarely taken into account in the literature, it can be very useful in qualitatively predicting competitive adsorption effects in multicomponent gas separations. In addition, adsorption experiments are a simple method for estimating critical ultramicropore size. Adsorption experiments were complemented with wide-angle X-ray diffraction, used to characterize the CMSM microporous structure. An average pore size of 0.45 nm, with a critical pore size of 0.39 nm, was found.

Single gas permeabilities of He, N₂, O₂ and CO₂ were obtained as a function of feed pressure for two different temperatures. It was observed that permeability decreases with feed pressure. This trend seems to follow the increase on adsorbate/adsorbent interactions. The permeabilities also increase with temperature. The transport of all gases was found to be an activated process, as expected for a molecular sieving mechanism.

Effective diffusivities obtained from steady-state permeation (permeation method) experiments were found to be one order of magnitude higher than the ones obtained from transient experiments (gravimetric/uptake method). This discrepancy is consistent with the idealized pore system presented here. Transport through dead-end pores does not play a role in steady-state experiments. However, these pores are present and are expected to have a measurable contribution to the adsorption capacity of the CMSM. Additionally, they are associated to a significant mass transport resistance, since they are "selective" pores (ultramicroporous). Therefore, since transient uptake experiments involve diffusion through the dead-end pores, those measurements will yield lower average diffusivities.

The increase of the transport diffusivity with loading was also studied. For weakly adsorbed species, this dependence is quite well described by a "Darken-type" relation. However, the transport diffusivity of CO₂ shows strong concentration dependence. A mathematical relation was proposed to describe this dependence. The corresponding fittings to data from permeation or uptake experiments yielded very close results.

Acknowledgements

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Nomenclature

- \( b \): parameter of isotherm equation (bar\(^{-1}\))
- \( d_{\text{CO}_2} \): carbon dioxide density (g cm\(^{-3}\))
- \( D \): transport diffusivity (m\(^2\) s\(^{-1}\))
- \( D_c \): corrected diffusivity (m\(^2\) s\(^{-1}\))
- \( D_{\text{ext}} \): hollow fiber external diameter (m)
- \( D_{0} \): corrected diffusivity at zero loading (m\(^2\) s\(^{-1}\))
- \( E_a \): activation energy (J mol\(^{-1}\))
- \( E_0 \): characteristic energy (J mol\(^{-1}\))
- \( F \): fractional uptake
- \( \Delta H_{\text{ads}} \): isosteric heat of adsorption (J mol\(^{-1}\))
- \( J \): diffusion flux (mol m\(^{-2}\) s\(^{-1}\))
References


