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Peculiarities of Gas Transfer in Track Membranes with Asymmetric Pores

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Abstract

The asymmetry of the transport (permeation) of gases through track membranes with asymmetric pores has been experimentally investigated. Samples with different porosities and diameters of pores have been studied. The difference between the direct and reverse flows (asymmetry of transport) of helium, nitrogen, and carbon dioxide through membranes has been revealed. The flow from the narrow part of a pore (direct flow) is about 15\% larger than the reverse flow. The interaction parameters characterizing the effect of the roughness of the inner surface of pores on the gas flow through a membrane have been determined. The surface flow effect has been demonstrated using the data obtained. Necessary conditions for the appearance of the asymmetric transport effect have been formulated.

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1. Introduction

The asymmetry of the transport of gases in porous membranes, i.e., the dependence of the permeability on the direction of a driven force (pressure drop), was previously observed for asymmetric polymer ceramic and metal—
ceramic composite membranes [1–4]. The asymmetry of the transport of gases in track membranes fabricated by the method presented in [5] was revealed for the first time in [4]. The dependence of gas permeation asymmetry on the etching time was examined in that experimental work, where etching conditions were different for two sides of a membrane; as a result, the diameters of pores were different on different sides; i.e., track membranes with asymmetric pores were obtained. The results reported in [4] confirm that the asymmetry of transport is observed in membranes where the diameter of pores is variable over the thickness. However, the amount of experimental data on the asymmetry of gas transport is insufficient. In particular, there are no data on the effect of the physicochemical properties of the gas on transport in gradient-porous membranes. Furthermore, the effects of the gas flow regime and the structure of the surface of pores are incompletely studied.

The aim of this work is to experimentally study the transport properties of gases through asymmetric track membranes with certain geometric characteristics. The effect of the gas pressure in the range of 0.5–2.5 atm on the asymmetry of transport is studied for three gases with different physical properties.

Track membranes with conical pores are experimentally studied. In our opinion, such membranes are convenient model systems for the investigation of the asymmetry of the transport of gases because pores have a simple geometry.

2. Experiment

We studied track membranes made from polyethylene terephthalate (PET) films. The typical image of the cross section of membranes with asymmetric pores (MA membranes) is shown in Fig. 1. It can be seen that each individual pore penetrates the entire thickness of membranes and has the form of a cylinder transformed to a conical frustum at a certain length. The base of the cylindrical part of a pore is on one side of a membrane and the narrow part of the conical frustum is on the other side. Such a shape of asymmetric pores is obtained by one-sided etching of pores by the method described in [5]. As can be seen in Fig. 1, pores are almost parallel to each other and are perpendicular to the surface of the membrane.

![Fig. 1. Cross section of a track membrane with asymmetric pores.](image)

We studied track membranes with different numbers of pores per unit surface and different input/output diameters of pores. In addition, a track membrane with symmetric (cylindrical) pores (MC membrane) was also studied for comparison. The characteristics of the membranes under study are presented in Table 1. For example, the MA-30/50-2·10⁵ membrane is a track membrane with asymmetric pores 30 and 50 nm in diameter on the first and second sides of the membrane, respectively, where the number of pores per centimeter squared of the surface is 2·10⁵.
Table 1. Characteristics of membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Number of pores per 1 cm²</th>
<th>Thickness of membrane, μm</th>
<th>Diameter on the first side, nm</th>
<th>Diameter on the second side, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-30/50-2·10⁰</td>
<td>2·10⁰</td>
<td>12</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>MA-30/50-3·10⁰</td>
<td>3·10⁰</td>
<td>12</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>MC-50/50-9·10⁰</td>
<td>9·10⁰</td>
<td>12</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>MA-20/50-2·10⁰</td>
<td>2·10⁰</td>
<td>12</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 2 shows photographs of the surfaces of track membranes with high and low porosities.

In order to determine the permeabilities of gases through a membrane, we used the Dines–Barrer volumetric method.

3. Results and discussion

Figure 3 shows the experimental dependences of the permeabilities of various gases through the MA-30/50-2·10⁰ track membrane. The results presented in Fig. 4 were obtained as follows. First, the pressure dependences of the permeability were measured when the gas leaks to the side of the membrane with the smaller diameter of pores (direct flow). Then, the permeabilities were measured when the gas leaks to the side with the larger diameter of pores (reverse flow). The results of the measurements performed with the inverse sequence of gas supply coincide within the errors with the results presented in Fig. 3.
As can be seen in Fig. 3, the direct flow through the membrane exceeds the reverse flow by about 14% for all gases under study. Furthermore, the permeability remains almost unchanged in the pressure drop range from 0.5 to 2.5 atm. The results of study of the asymmetry of transport through other track membranes with conical pores are summarized in Table 2, where the average transport asymmetries in the pressure drop range under study are presented. The error of the determination of the experimental values of the asymmetry of transport in Table 2 is no more than 15%.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Experimental asymmetry of transport, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MA-30/50-2·10⁸</td>
</tr>
<tr>
<td>He</td>
<td>14±2</td>
</tr>
<tr>
<td>N₂</td>
<td>13±2</td>
</tr>
<tr>
<td>CO₂</td>
<td>14±2</td>
</tr>
</tbody>
</table>

Experimental dependences of the permeability of the MC-50/50-9·10⁸ track membrane with symmetric (cylindrical) pores showed no asymmetry of the permeability of the track membrane with symmetric pores is observed.

Table 3 presents the ideal selectivity of membranes with respect to pairs of gases He/N₂ and He/CO₂. As can be seen in the table, these values are close to the theoretical value in a free molecular flow (inverse ratio of the square root of molecular masses).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>P₁₂/P₁₃</th>
<th>P₁₃/P₂₃</th>
<th>P₁₃/P₁₄</th>
<th>P₁₄/P₁₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>Theory</td>
<td>Experiment</td>
<td>Theory</td>
<td>Experiment</td>
</tr>
<tr>
<td>MA-30/50-2·10⁸</td>
<td>2.54</td>
<td>2.65</td>
<td>3.33</td>
<td>3.32</td>
</tr>
<tr>
<td>MA-30/50-3·10⁹</td>
<td>2.56</td>
<td></td>
<td>3.38</td>
<td></td>
</tr>
<tr>
<td>MA-50/50-9·10⁸</td>
<td>2.60</td>
<td></td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>MA-20/50-2·10⁸</td>
<td>2.26</td>
<td></td>
<td>2.94</td>
<td></td>
</tr>
</tbody>
</table>

The comparison of the experimental values of the permeability of the MA-50/50-9·10⁸ membrane with the values calculated under the assumption of a free molecular flow within the diffusion model of the interactions of molecules of the gas with the surface of pores shows that the experimental flows are lower than the calculated values; according to [6], this relation can be explained by the rough structure of the surface of pores.
In [2], the following distribution in direction of motion of molecules in a channel was obtained with the use of stochastic dynamic methods:

\[ w(\theta) = \frac{A}{\pi} \exp(-A \theta^2) \text{erf}\left(\frac{\pi}{2\sqrt{A}}\right) \]

where \( \theta \) is the angle of emission of a molecule from the surface with respect to the normal to the surface and \( A \) is the interaction parameter determining the distribution in direction of emission of molecules from the surface; this parameter depends on the velocity of molecules and on the roughness of the surface. In other words, this parameter characterizes the degree of anisotropy of the scattering of molecules of the gas on the rough surface. It can be shown that the distribution in direction is isotropic when the interaction parameter is small \( A \ll 1 \), whereas this distribution becomes anisotropic with an increase in the interaction parameter and the angles of emission from the surface close to normal are most probable.

Comparing the experimental and theoretical values of the permeability presented in Table 4 with the use of distribution (1), we determined the parameters of the interaction of molecules with the rough inner surface of a pore in the track membrane for the gases under study. For helium, nitrogen, and carbon dioxide, we obtained \( A_{\text{He}} = 3.85 \), \( A_{\text{N}_2} = 3.48 \), and \( A_{\text{CO}_2} = 3.35 \), respectively.

Using the found interaction parameters, we estimated the degree of anisotropy within the model proposed in [2]. According to this model, the asymmetry of transport of 15% can be reached with the 0.3-\( \mu \)m-long conical part of the pore. The authors of [7] attempted to develop the theory of asymmetric gas transport in bilayer membranes under the assumption that the surface flow makes an asymmetric contribution. This assumption is undoubtedly an important step to the development of the theory of asymmetric transport, but the model proposed in [7] cannot describe the known experimental data [1–4].

Figure 4 shows the experimental pressure dependences of the permeability of pure gases multiplied by the square root of the molar mass of the gas (reduced permeability) through the MC-50/50-8-10^8 polyethylene terephthalate track membrane with cylindrical pores. The dependences that are almost parallel to the abscissa axis indicate that the contribution of the viscous flow to the total flow is insignificant.

![Fig. 4. Pressure dependences of the reduced permeability of gases (O) He, (A) N_2, and (c) CO_2 through the MC-50/50-8-10^8 membrane per pore.](image)

Plots in these coordinates usually make it possible to estimate the effect of various factors on the permeability (e.g., the surface flow).

No anisotropy of the permeability for the symmetric sample was revealed, but the dependences of the reduced permeability for nitrogen and carbon dioxide pass much higher than the dependence for helium. These differences in the positions of the curves are attributed to the surface flow, but the surface flow cannot explain a 60% increase in the total flow through 50-nm pores in the chosen pressure range [8].

It can be seen that, as the pressure increases, the anisotropy of the permeability decreases for nitrogen and helium and increases for carbon dioxide. The anisotropy of the permeability is larger than unity throughout the entire
pressure range; i.e., the permeability at gas supply to the side of the membrane with smaller diameters of pores is higher than that in the reverse direction. The data obtained for other track membranes are in complete agreement with the results presented above. The general result completely agrees with the results obtained for bilayer ceramic and metal–ceramic membranes in [2, 3].

A model for the description of asymmetric gas transport through bilayer membranes was proposed in [9] on the basis of an asymmetric surface flow, which is significantly enhanced because of an anisotropic distribution of molecules of a gas inside a porous medium. In particular, it was shown that the asymmetry of gas transport in the case of an anisotropic distribution in direction of motion of molecules \((A > 0)\) qualitatively coincides with the experimental value. Indeed, at the anisotropic distribution in direction of motion of molecules, the number of collisions of molecules with the surface and, consequently, the number of molecules adsorbed on the surface are larger. Since the distributions in direction of motion of molecules are different in different layers of the membrane, a gradient of the surface concentration appears at the interface of a change in the diameter of a pore and, as a result, the flow of adsorbed molecules toward lower surface concentrations is observed; the direction of this flow is independent of the pressure gradient because the surface concentration is higher in the layer with the smaller diameter of pores. Therefore, the total flow increases at supply from the layer where the distribution in direction of motion of molecules is anisotropic and decreases at reverse supply.

Conclusions

To summarize, it has been shown that asymmetric transport is possible in track membranes with asymmetric pores in the free molecular gas flow regime. The gas flow from the narrow side of a pore is higher than the reverse flow. It has also been shown that the asymmetry of transport is due to asymmetric geometry, because the asymmetry of transport is absent in samples with a constant diameter of pores over the thickness of the membrane (cylindrical pores). It has been shown that the surface flow should be taken into account to describe the asymmetry of gas transport. Necessary conditions for the appearance of asymmetric transport, as well as the main concepts of the physical model of the effect, have been formulated.

Acknowledgements

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References