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Article

Modeling of Gas Permeation through Mixed-Matrix Membranes Using Novel Computer Application MOT

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Abstract: The following article proposes a modern computer application MOT (Membrane Optimization Tool) for modeling of gas transport processes through mixed-matrix membranes (MMMs). The current version of the application is based on the Maxwell model, which can be successfully used to model gas transport through the simplest types of hybrid membranes without any defects. The application has been verified on the example of four types of hybrid membranes, consisting of various types of polymer matrix, such as: poly (vinyl acetate), 2, 2′-BAPB + BPADA, Ultem, hyperbranched polyimide (ODPA-MTA) and zeolite 4A. The average absolute relative error (AARE) and root-mean-square error (RMSE) were calculated in order to compare the theoretical MOT-predicted results with the experimental results. It was found that the AARE ranges from 29% to 36%, while the RMSE is in the range of 10% to 29%. The article presents also the comparison of MOT-predicted data obtained with Maxwell and Bruggeman models. To obtain more accurate reproduction of experimental results, further versions of the proposed application will be extended with next-generation permeation models (Lewis–Nielsen, Pal, modified Maxwell or Felske models), allowing for the description of transport in more complex systems with the possibility of taking into account possible defects.

Keywords: polymers; mixed-matrix membranes; gas separation; computer application; Maxwell model; Bruggeman model

1. Introduction

Poland has very minimal oil reserves, and the available natural-gas deposits are not able to cover the demand for natural gas even at the present time. The renewable-energy sources are in our country at an early stage of development, and Polish natural conditions do not favor the development of this type of energy source. That is why the primary energy sources in Poland are coal and lignite, and the acquisition of energy from coal is much more cost effective. However, Poland must meet the European Union's greenhouse-gas emissions requirements, and it is necessary to use clean coal technologies.

During the coal combustion process, besides the energy, undesirable substances are also produced. This phenomenon is unavoidable due to the chemical composition of the combusted fuel and the combustion itself. Substances produced during combustion include primarily sulphur oxides, nitrogen, hydrocarbons, carbon monoxide, solids, and so on [1,2].

Currently, the main goal of the researchers is to create methods that limit the emission of harmful products of hard coal combustion. In recent years, the application of membrane techniques has become

very promising. It is related to their many advantages, such as: the low capital costs; high energy efficiency and thermal, mechanical and chemical stability; good separation properties; and lack of necessity of membrane regeneration [3,4]. That is why the main objective of current membrane research is to obtain stable membranes with appropriate permeability and selectivity. Considering the limitations of both inorganic and polymeric membranes, a new type of hybrid membrane, also called MMM, has been proposed. Mixed-matrix membranes (MMMs) are inorganic fillers in solid, liquid, or both solid and liquid forms (e.g., carbon molecular sieves, zeolites, metals, ceramics, silica, metal organic frameworks, graphene, carbon nanotubes (CNTs), etc.) dispersed in a polymer matrix. These membranes offer the potential to combine the easy processability of polymers with the outstanding gas separation properties of inorganic materials [3–8]. They could be classified into three main groups: the polymer–solid, the polymer–liquid, and the polymer–liquid–solid membranes. However, the polymer–solid MMMs have aroused the greatest interest. For this type of MMM, both zeolitic and nonzeolitic inorganic materials are used as fillers. The zeolites were used as fillers because of their specific adsorption properties, the appropriate thermal stability, and shape selectivity [9].

As a polymer matrix for the preparation of zeolitic or nonzeolitic hybrid membranes, both glassy and rubber polymers are used. In the case of rubbery polymers, the interfacial interaction between them and zeolitic fillers is probably better due to the greater mobility of polymer chains [9]. On the other hand, glassy polymers are characterized by greater mechanical stability and gas transport properties. However, mixed-matrix membranes based on this type of polymer matrix show the presence of interfacial void defects. In order to solve this problem, many types of modifications have been made, such as: application of silane and amine coupling agents to improve interfacial adhesion and gas selectivity (changing the surface properties of fillers from hydrophilic to hydrophobic), coating of nonselective slots with a silicone rubber, and addition of a plasticizer to reduce the intrinsic gas separation performance of polymers [9–18].

Gas transport through a mixed-matrix membrane is a complicated problem (Figure 1). In order to predict the gas permeability through these matrices, many theoretical models were proposed [1,19], as well as the model created by James Clerk Maxwell.

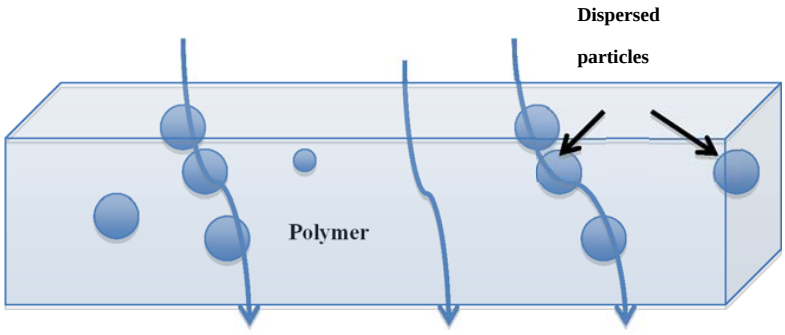


Figure 1. Gas permeation through mixed-matrix membranes.

Our research group has been conducting research on the application of inorganic–organic hybrid membranes in the separation of gas mixtures. Earlier research concerned membranes based on various polymer matrices such as ethylcellulose (EC), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO), linear and hyperbranched polyimides (LPI and HBPI) as well as magnetic powders and iron-encapsulated multi-wall carbon nanotubes (Fe@MWCNT) as inorganic fillers [20–27]. During this research, it was found necessary to have a suitable tool that would allow for the optimal selection of hybrid membrane components. At the same time, this tool should ensure appropriate separation properties of the proposed membranes, which is the subject of the following article.

The following article proposes a modern computer application MOT (membrane optimization tool) for modeling of gas transport processes through mixed-matrix membranes (MMMs). The current

version of the application was based on the simplest Maxwell model, used to model the gas transport through the simplest types of hybrid membranes without any defects. The application has been verified on the example of four types of hybrid membranes, consisting of various types of polymer matrix, such as: poly(vinyl acetate), 2, 2′-BAPB + BPADA, Ultem, hyperbranched polyimide (ODPA-MTA) and zeolite 4A. The AARE (average absolute relative error) and RMSE (average absolute relative error) errors were calculated in order to compare the theoretical results obtained from the application MOT with experimental results obtained from the literature and the authors' own tests. The article presents also the comparison of MOT-predicted data obtained with Maxwell and Bruggeman models.

2. Materials and Methods

2.1. Maxwell Model

The first mathematical studies of gas transport description through the MMMs concerned the ideal structure of these hybrid membranes, both their polymer matrix and the dispersed phase. The contact between these two phases at the polymer−particle interface is assumed to be defect free. This theoretical two-phase morphology typically corresponds to the ideal Maxwell model, which was created to describe thermal or electrical conductivity in composite media. A defect-free polymer−particle contact during the introduction of dispersed fillers in a polymer matrix is, however, difficult to achieve. The incorporation of filler particles can modify the properties of the neighbouring polymer phase, which affects the hybrid membrane separation performance [28–30].

Considering the different types of effects associated with the interaction of the inorganic and organic phase, five various morphologies could be distinguished, that is: the ideal, void, rigidified, with pore blocking, and agglomeration combined with pore blocking.

Taking into account the influence of various morphologies on gas transport properties, different effects could be observed. In the case of the voids' formation between the filler particles and the polymer matrix, an increase in gas permeability can be observed at low filler loading. However, no significant changes in selectivity are observed for such membranes. In turn, in membranes with a high filler loading and poor spatial distribution of particles, the void surrounding clusters of aggregated particles could be created, and their selectivity may drastically decrease. Rigidification can usually increase the selectivity coefficient, while the permeability coefficient decreases. In turn, when the pore blocking increases, the permeability coefficient tends to decrease, while the selectivity coefficient may be higher than that in the pure polymer matrix. Mixed-matrix membranes having both large and small pore fillers represent a case that is a combination of channel defects and pore blocking [9].

Maxwell's equation came from estimating the dielectric properties of the composite materials. Initially, it was considered as a simple and effective tool for predicting mixed-matrix membranes' gas transport properties [1,31].

The theoretical two-phase morphology created as a first one is used here to predict the gas permeation through hybrid membranes and allows us to obtain approximate process parameters, such as the permeation coefficient P and the selectivity coefficient α.

This model was developed to predict the effective permeability of the gas penetrant P through these hybrid membranes as a function of λ_{dm}, which is a ratio of continuous phase P_m (polymer matrix) permeability and dispersed phase P_d (filler particles) permeability, as well as a volume fraction of the dispersed filler phase Φ.

For a given penetrant (1), the permeability coefficient (P_1) can be estimated as the product of diffusivity coefficient (D_1) and solubility coefficient (S_1) [9]:

$$P_1 = D_1 S_1, \quad (1)$$

where:

D_1—a diffusion coefficient of gas penetrant no. 1 (cm^2/s), and
S_1—a sorption coefficient of gas penetrant no. 1 ($cm^3_{STP}/\ cm^3 cmHg$).

The sorption coefficient S_1 is a measure of the size of the gas sorption in a material of membrane. It is characterized by division of the penetrant between the membrane and the outer phase in equilibrium.

The ideal selectivity coefficient, $\alpha_{1/2}$, is the ratio of the permeability coefficient of the gas penetrant no. 1 to the permeability coefficient of gas no. 2:

$$\alpha_{1/2} = \frac{P_1}{P_2} = \frac{D_1 S_1}{D_2 S_2}. \quad (2)$$

The Maxwell equation is as follows [32]:

$$P_r = \frac{P}{P_m} = \left[\frac{2(1-\Phi) + (1+2\Phi)\lambda_{dm}}{(2+\Phi) + (1-\Phi)\lambda_{dm}}\right], \quad (3)$$

where:

P_r—relative permeability of gas components,

P—effective permeability of gas components in MMM (Barrer), $1 Barrer = \frac{cm^3_{STP} \cdot cm}{cm^2 \cdot s \cdot cmHg} \cdot 10^{-10}$,

P_m—permeability of gas components in a polymer matrix (continuous phase) (Barrer),

Φ—volume fraction of filler particles,

λ_{dm}—P_d/P_m permeability ratio, and

P_d—permeability of components in the dispersed phase.

This Maxwell model is one of the most often-used models by scientists during the pre-selection process of membranes. It is suitable for a diluted suspension of spherical particles with low filler concentration values, where the value of a volume fraction of the filler particles is less than 0.2 ($0 < \Phi < 0.2$) and does not take into account the particle size limit (Φ_m). This is because of the assumption that the streamlines around particles are not affected by the presence of nearby particles. For higher values of volume fraction Φ, the Maxwell model cannot predict the gas permeability through the MMMs. Furthermore, the effect of particle size distribution, and the shape and aggregation of particles, are not taken into account. Nevertheless, this model is easy to solve for P_r.

Essentially, the Maxwell model is suitable for describing of the gas permeation process through mixed-matrix membranes, characterized by perfect morphology (no defects). However, this expression could be modified to take into account the nonideal morphology of these membranes exhibiting various types of interfacial defects, such as pore blocking, interfacial voids and polymer chain stiffening [33–41].

Another model used to describe the transport of gases through mixed-matrix membranes is the Bruggeman model, given by the following formula:

$$(P_r)^{\frac{1}{3}}\left[\frac{\lambda_{dm} - 1}{\lambda_{dm} - P_r}\right] = (1-\Phi)^{-1}. \quad (4)$$

This model does not take into account the effects of particles shape and their size distribution, aggregation of particles and the particle size limit (Φ_m). However, it covers a broader range of volume fraction Φ compared to the Maxwell model. As it could be seen from Equation (4), it should be solved numerically for permeability.

2.2. Materials

The 4,4′-oxydiphthalic anhydride (ODPA) was acquired from CHRISKEV (Overland Park, Kansas, USA), 4,4′,4″-triaminotriphenylmethane (MTA) from Dayang Chemicals (Hangzhou, China) and *N*-methylpyrrolidone (NMP) from Acros Organics (Geel, Antwerp, Belgium). The zeolite 4A by Acros Organics (Geel, Antwerp, Belgium) was used as inorganic filler. Compressed gases, such as oxygen (5.6), nitrogen (5.0), helium (6.0) and synthetic air (5.0) have been provided by AirLiquide (Krakow, Lesser Poland, Poland).

2.3. Synthesis of HBPI and Zeolite 4A-HBPI Mixed-Matrix Membranes

The studies included analysis of the polymer and hybrid HBPI (hyperbranched polyimide) membranes with zeolite 4A as a filler. The 4 wt % solution of hyperbranched polyamic acid (HBPAA) in *N*-methylpyrrolidone (NMP) was synthesized from molar ratios (1:1) of 4,4′-oxydiphthalic anhydride (ODPA) and 4,4′,4″-triaminotriphenylmethane (MTA). (NMP was synthesized from molar ratios (1:1) of ODPA and MTA.) Next, this solution was cast into the Teflon dish and subjected to a gradually increasing temperature up to 230 °C. For hybrid membrane formation, as-received zeolite 4A was dried in an oven at 80 °C over 24 h before being dispersed in NMP using sonication. This was followed by the addition of a small amount of dilute solution of the polymer precursor (priming) to promote adsorption of the polymer onto the sieve surface. After that step, the rest of the HBPAA solution was added and sonicated. Such dispersion was cast on the leveled Teflon dish and subjected to a gradually increasing temperature up to 230 °C. Membranes were removed from the dish, submerged in warm deionized water, and then dried for at least 72 h at 40 °C. Membranes were stored in a desiccator under a pressure of 400 Pa. By means of this method, a series of HBPI membranes with a zeolite 4A addition in the range of 15–40% was made.

2.4. Characterization of Mixed-Matrix Membranes

Measurements of oxygen, nitrogen and synthetic air (21% O_2 and 79% N_2) permeability were carried out using the low-pressure IDP-2 gas permeation analyzer, coupled with the PerkinElmer/GC Clarus 580, Arnel Model 4018 gas chromatograph. That enabled the simultaneous determination of transport coefficients and permeate composition. The analyzed gases were fed to the apparatus from compressed gas cylinders. The measurements were performed at 25 °C. The flow-rate and percentage-of-the-air enrichment data were used to evaluate the mass transport coefficients (P and α) [20–27].

3. Results and Discussion

In the initial stage of research, the authors created a computer program MOT (membrane optimization tool) in the Java programming language. In this programme, the user will be able to choose the optimal gas permeation model for the MMMs, such as Maxwell's, Bruggeman's, Lewis–Nielsen's, Pal's, Maxwell's modified model or the Felske model.

Within a chosen model, there will be a possibility to simulate the efficiency of the designed membranes and select the suitable components (organic, such as polyimides, polyphenylene oxide; and inorganic, such as modified carbon nanotubes, zeolites, etc.). In order to verify the correct functioning of the designed tool, the appropriate laboratory tests would be performed, and the experimental results will be compared with the predicted ones.

Within the study, membranes identified as optimal for reducing emissions of undesirable substances or enrichment of gaseous mixtures in a desirable component will be created. The programme will allow us to verify the behavior and efficiency of innovative membranes before they are performed, to determine their performance and the properties of alternative membranes, and to reduce costs of research and their time. It will be an excellent tool for research scientists to study the separation of various gas mixtures using inorganic–organic hybrid membranes. As a result, the proposed method will allow the reduction of gaseous emissions in line with EU standards, which will allow further use of coal—Poland's strategic energy source.

In this article, the experimental results obtained by the authors and the results found throughout the literature [39,41] were compared with the theoretical data predicted by means of the most popular model (Maxwell) used by many researchers to predict membrane permeability.

The users will also have the possibility to model the gas permeation through various hybrid membranes applying other models such as Bruggeman, Lewis−Nielsen, Pal, modified Maxwell's model or Felske model [9,19,28,29,34–36,42–47].

The programme consists of the following windows:

- main window for model selection (Figure 2). Individual models are selected from the combo box.

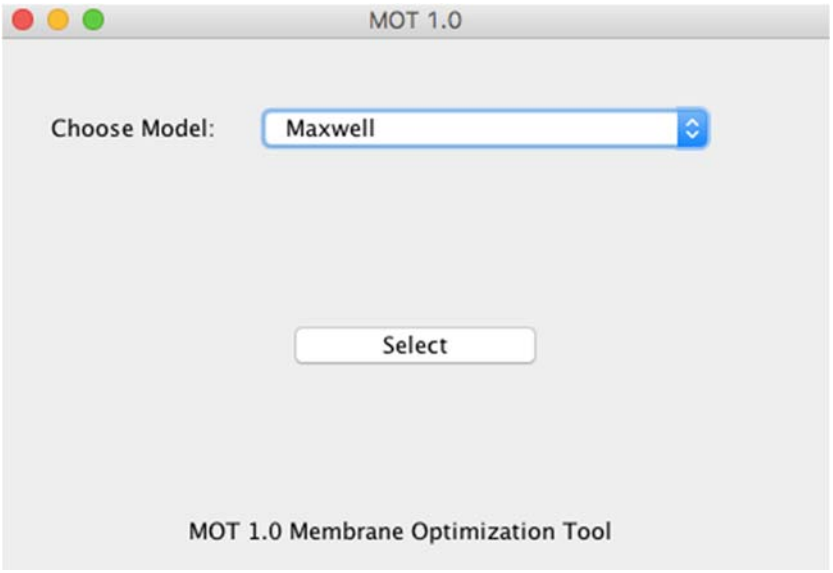


Figure 2. The main window for model selection.

The user could enter the membrane parameters, such as volume fraction of filler particles, phi Φ, P_d/P_m permeability ratio, lambda λ_{dm} and polymer permeation P_m for two gases, in Maxwell's model window (Figure 3). The programme calculates the value of P_1 and P_2, and the value of alpha $\alpha_{1/2}$. The user has the possibility to select the Robeson upper bound for such combinations of gases as O_2/N_2, CO_2/CH_4, H_2/N_2, H_2/CH_4, He/N_2, He/H_2, He/CH_4, CO_2/N_2, N_2/CH_4, H_2/CO_2, He/CO_2.

- the additional tools, such as the diffusion and sorption coefficient calculator, as well as the ability to add the user's experimental data, are located in the More options menu (Figure 4).

The average absolute relative error (AARE) and root-mean-square error (RMSE) were calculated in order to compare the theoretical MOT-predicted results with the experimental data, derived from the literature and our own research.

Average absolute relative error was calculated as follows [48]:

$$\%AARE = \frac{100}{NDP}\sum_{i=1}^{NDP}\left|\frac{P_i^{estim} - P_i^{exp}}{P_i^{exp}}\right|, \quad (5)$$

where:

NDP—number of data points,
P_i^{estim}—estimated value, and
P_i^{exp}—experimental value.

The root-mean-square error [49]:

$$RMSE = \sqrt{\frac{1}{NDP}\sum_{i=1}^{NDP}\left(P_i^{estim} - P_i^{exp}\right)^2}. \quad (6)$$

So, the application will have an additional option of the average absolute relative error and the root-mean-square error calculation.

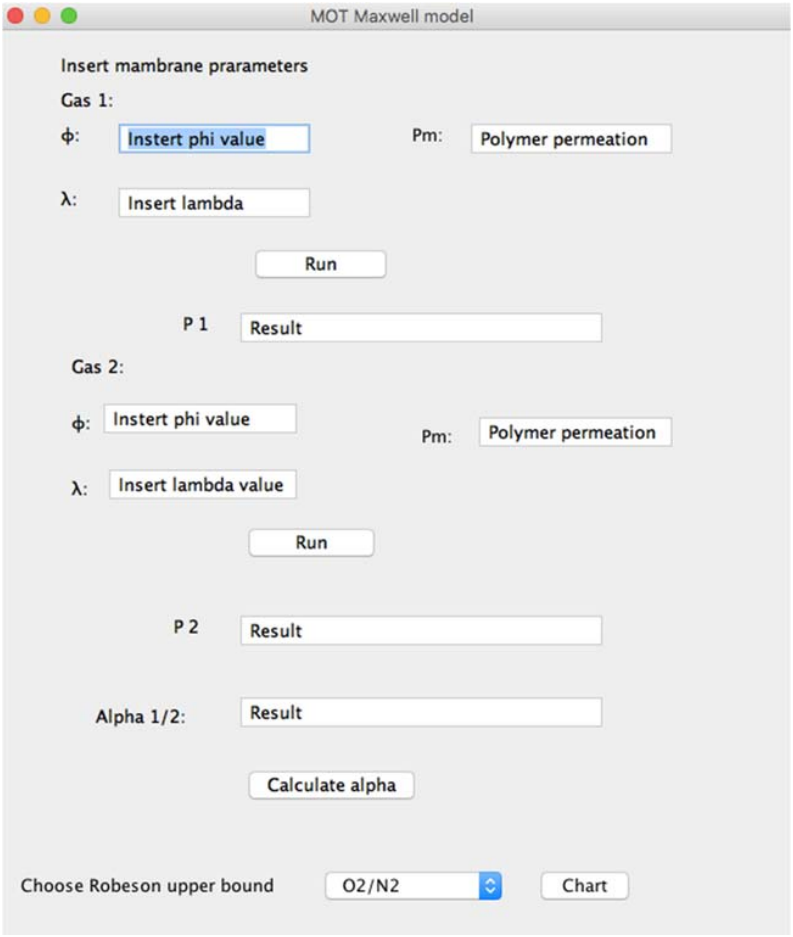


Figure 3. Maxwell's model window.

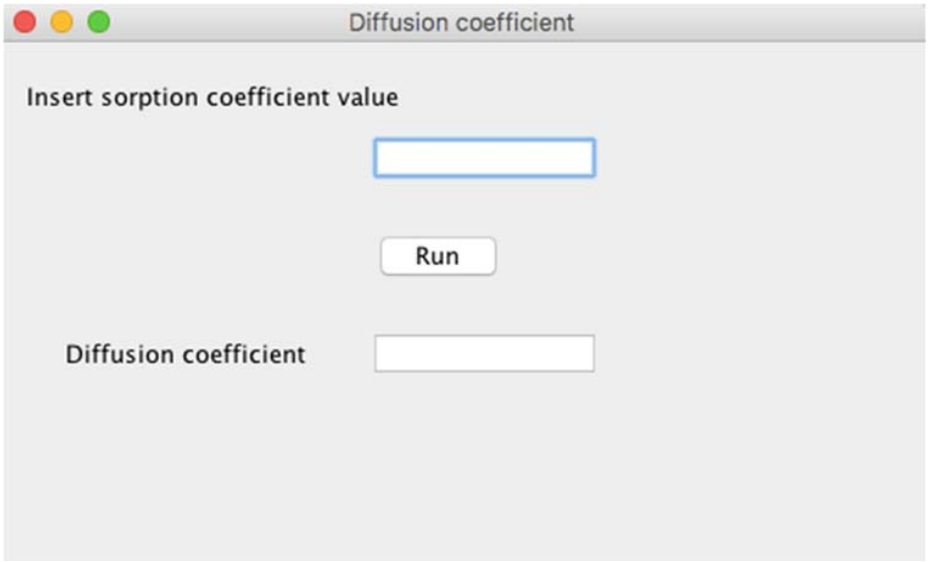


Figure 4. Menu window: More options.

Simulation results obtained from the MOT application based on Maxwell's model are presented on $\alpha_{O2/N2}$ = f(PO_2) dependency graphs (Figures 5–8). The above charts also take into account Robeson's line.

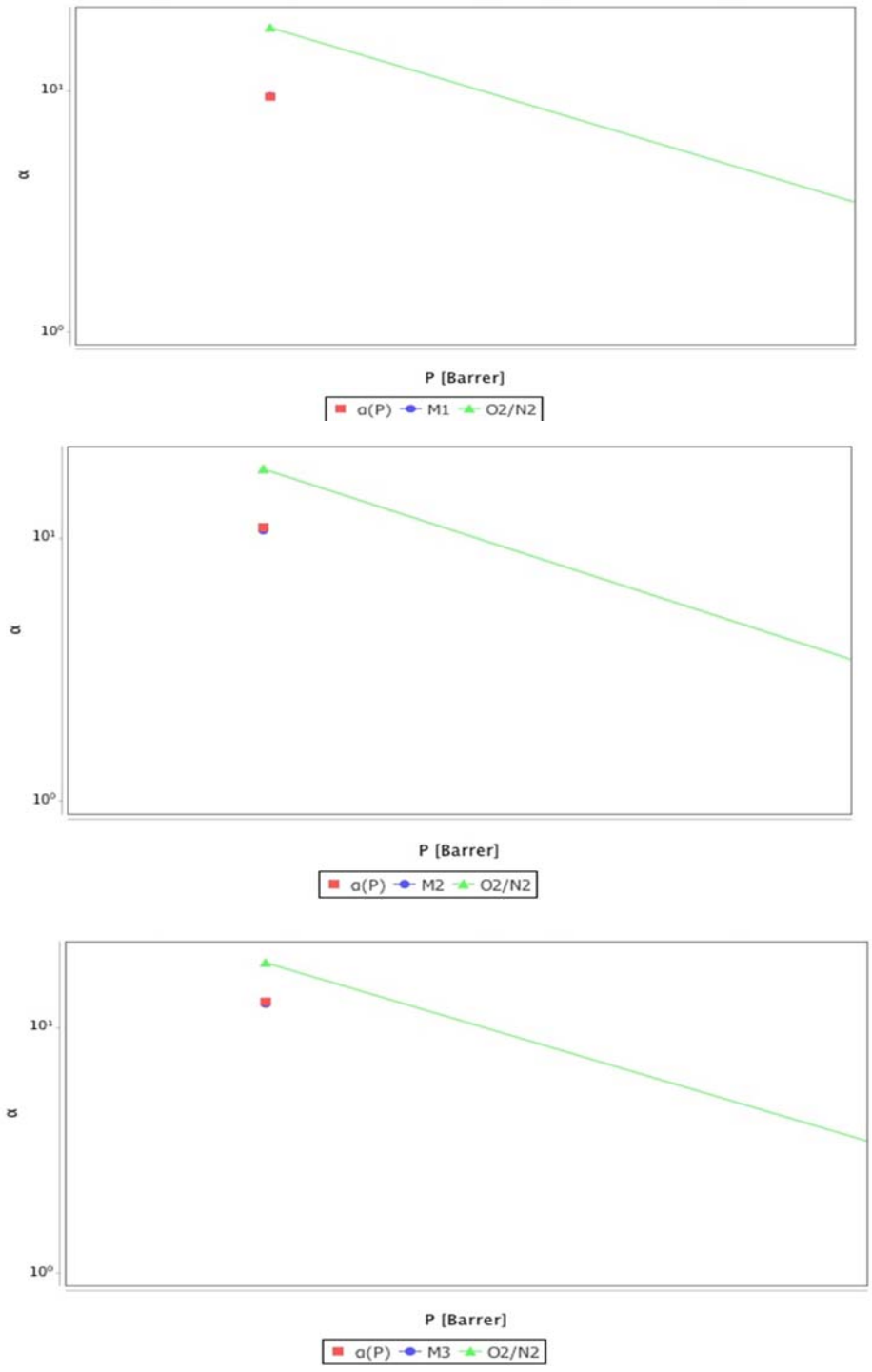


Figure 5. Comparison of experimental results (navy blue point) for the zeolite 4A-2, 2′-BAPB + BPADA mixed-matrix membranes with 3 different filler additions (M1, M2 and M3) with Maxwell theoretical results (red point) and their position relative to the Robeson upper bound line (green line).

This Robeson's upper bound line represents the limits on the selectivity–permeability trade-off behavior achievable with polymer membranes. Nowadays, the main research objective is to find polymeric structures that exceed the empirical upper bound limits. The main parameters for gas separation are the permeability P of a specific component of the gas mixture and the selectivity coefficient α. They are trade-off parameters, because usually, the selectivity coefficient α decreases with increasing permeability P of the more permeable gas component. This trade-off relationship was

shown to be related to an upper bound relationship where the *log α* versus the log *P* determined a limit for achieving the desired result of a high separation factor combined with a large permeability for polymeric membranes. The upper bound relationship was shown to be valid for many of the gas pairs, including O_2/N_2, CO_2/CH_4, H_2/N_2, He/N_2, H_2/CH_4, He/CH_4, He/H_2, H_2/CO_2 and He/CO_2 [50].

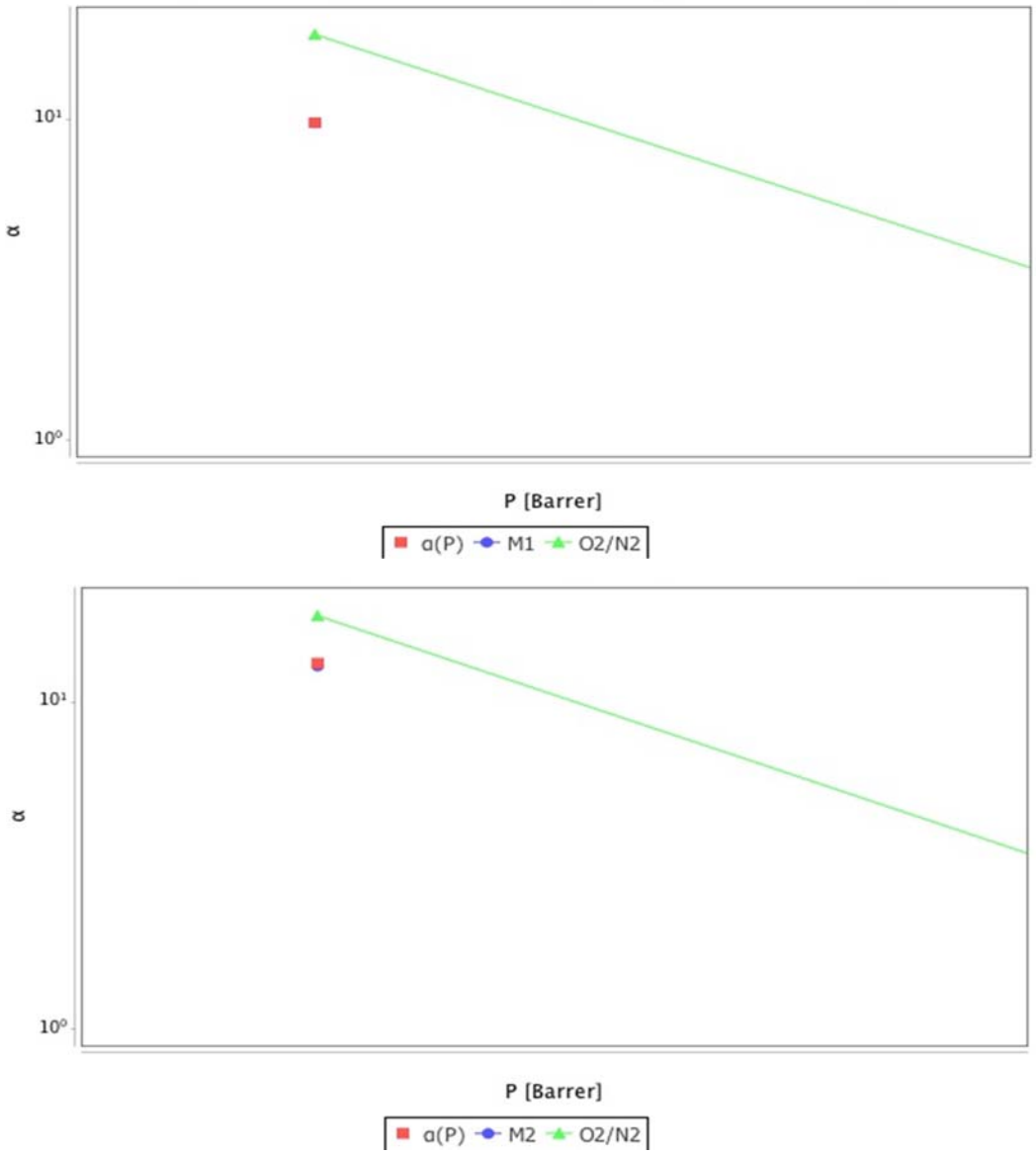


Figure 6. Comparison of experimental results (navy blue point) for the zeolite 4A-Ultem mixed-matrix membranes with 2 different filler additions (M1 and M2) with Maxwell theoretical results (red point) and their position relative to the Robeson upper bound line (green line).

The upper bound relationship could be expressed by the following equation [50]:

$$Pi = k\alpha_{ij}^{n}, \tag{7}$$

where:

Pi—the permeability of the more permeable gas,
α—the selectivity coefficient (*Pi*/*Pj*), and
n—the slope of the log–log limit.

The presented simulation and experimental results concerned hybrid membranes based on polymer matrices, such as 2, 2′-BAPB + BPADA, Ultem and poly (vinyl acetate), and an inorganic additive in the form of zeolite 4A.

The experimental results (Tables 1 and 2) concerning mixed-matrix membranes based on rigid polyimide matrices have shown improvements in the transport parameters [39]. It was stated that the selectivity values were similar to the predicted ones. In contrast, the permeabilities decreased significantly, especially for larger filler addition (Figures 5 and 6). This could be caused by polymer adsorption onto the surface of the sieve and its chain inhibition. In order to explain this phenomenon, a theoretical model of a hybrid membrane was created, which included the existence of three phases: polymeric, inorganic and interphase. In the last one, the permeability is lower than in the bulk polymeric phase [28,29,39]. In this case could be used the modified Maxwell model, where gas-penetrant permeability can be predicted using a two-step approach. In the first step (Equation (8)) is determined the gas permeability in a single core-shell particle P_{eff} (filler is a core and interfacial layer, the matrix treated as a shell) [28]:

$$P_{eff} = P_I \left[\frac{2(1-\Phi_s) + (1+2\Phi_s)\left(\frac{P_d}{P_I}\right)}{(2+\Phi_s) + (1-\Phi_s)\left(\frac{P_d}{P_I}\right)} \right], \quad (8)$$

where:

Φ_s—the volume fraction of filler core particle in the combined volume of core and interfacial shell (in a single core–shell particle),
P_I—the permeability of the gas penetrant in the interfacial shell, and
Peff—the effective permeability of a gas penetrant in a single core–shell particle.

Table 1. Experimental [39] and theoretical (membrane optimization tool) MOT-predicted data for the zeolite 4A-2, 2′-BAPB + BPADA mixed-matrix membranes.

Membrane	Φ	Experimental Data		Theoretical Data		AARE (%)	RMSE (%)
		$\alpha_{O2/N2}$	PO_2 (Barrer)	$\alpha_{O2/N2}$	PO_2 (Barrer)		
M1	0.20	9.50	0.47	9.40	0.55	30	15
M2	0.30	10.70	0.40	10.87	0.57		
M3	0.40	12.45	0.37	12.63	0.60		

Table 2. Experimental [39] and theoretical MOT-predicted data for the zeolite 4A-Ultem mixed-matrix membranes.

Membrane	Φ	Experimental Data		Theoretical Data		AARE (%)	RMSE (%)
		$\alpha_{O2/N2}$	PO_2 (Barrer)	$\alpha_{O2/N2}$	PO_2 (Barrer)		
M1	0.15	9.70	0.38	9.73	0.43	29	10
M2	0.35	12.85	0.28	13.09	0.49		

In the second step (Equation (9)), the Maxwell model is applied again to obtain the permeability of three-phase MMM P_r (taking the permeability P_{eff} from the first step as a gas permeability through filler particles) [28]:

$$P_r = \frac{P}{P_m} = \left[\frac{2(1-\Phi) + (1+2\Phi)\left(\frac{P_{eff}}{P_m}\right)}{(2+\Phi) + (1-\Phi)\left(\frac{P_{eff}}{P_m}\right)} \right], \quad (9)$$

where:

Φ—the volume fraction of total dispersed phase (core–shell particles) in the whole membrane, and

P_m—the permeability of gas components in a polymer matrix (Barrer).

In order to form successful MMMs, one must maintain flexibility during membrane formation (the use of high temperatures) and interaction between polymer and sieve phase (chemical coupling) [39,51,52].

In order to ensure flexibility, R. Mahajan and W.J. Koros proposed a different polymer matrix, PVAc, which is an extremely flexible material with a low glass transition temperature (35 °C), an affinity for alumina (expected better contact between PVAc and the aluminosilicate-type 4A zeolite) and reasonable gas transport properties [41]. In fact, for 15% loading was noted an improvement in O_2/N_2 selectivity and a slight decline in permeability (Table 3). However, for higher loading (25% and 40%), most of the membranes were full of defects, which negatively affected their transport properties (Figure 7). It was caused by poor adhesion and dispersion at higher filler loading, which led to formation of nonselective nanochannels. Compliance between experimental and theoretical results has been observed to a certain extent. However, the deviation between the results became more significant with increasing filler loading.

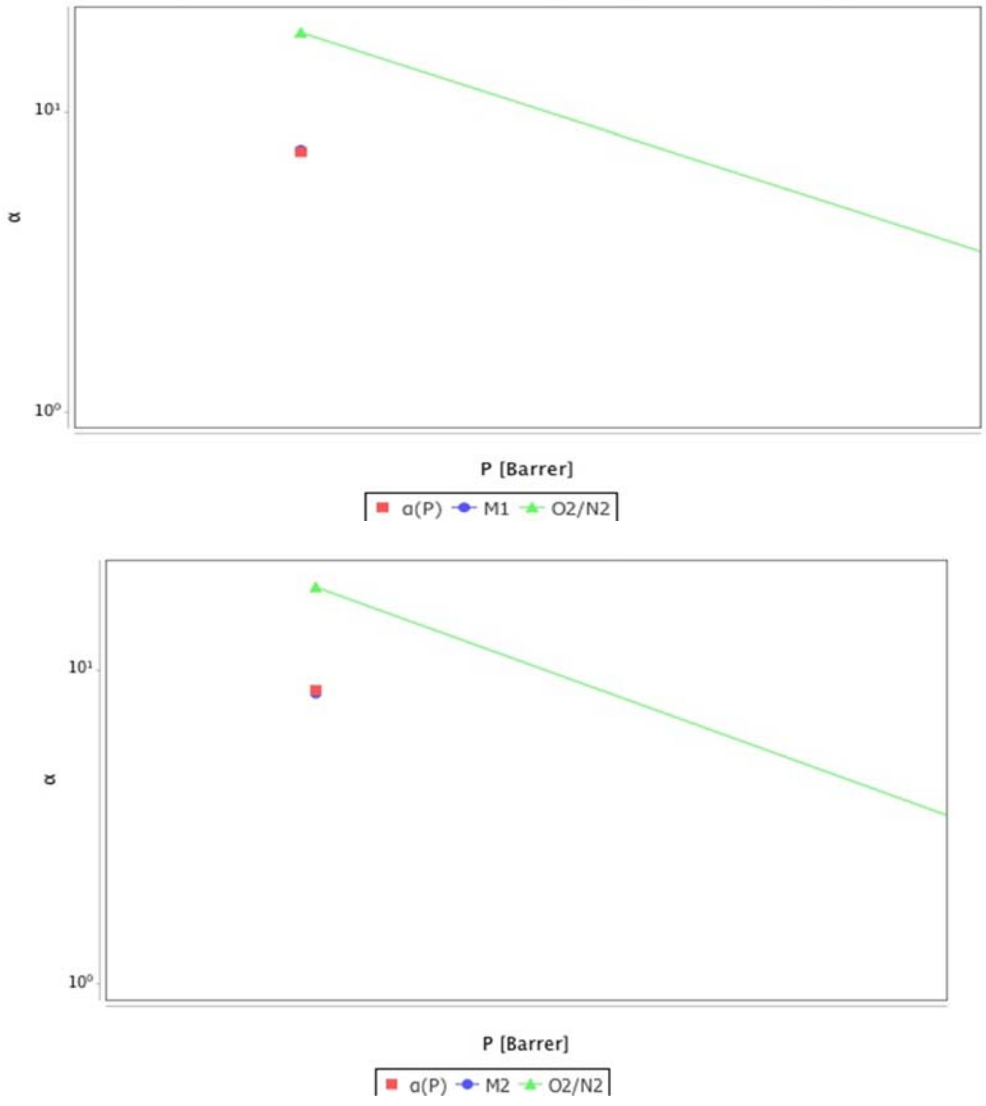


Figure 7. *Cont.*

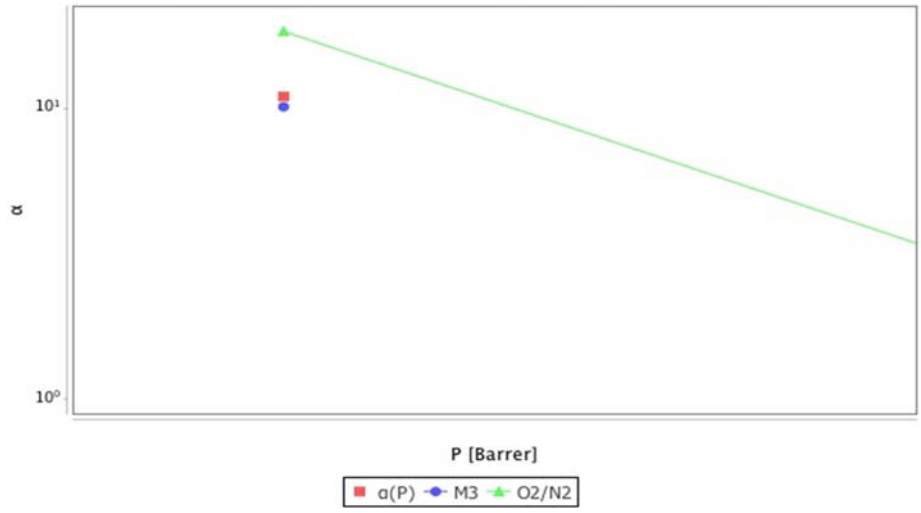


Figure 7. Comparison of experimental results (navy blue point) for the zeolite 4A-poly (vinyl acetate) mixed-matrix membranes with 3 different filler additions (M1, M2 and M3) with Maxwell theoretical results (red point) and their position relative to the Robeson upper bound line (green line).

Table 3. Experimental [41] and theoretical MOT-predicted data for the zeolite 4A-poly (vinyl acetate) mixed-matrix membranes.

Membrane	Φ	Experimental data		Theoretical data		AARE (%)	RMSE (%)
		$\alpha_{O2/N2}$	PO_2 (Barrer)	$\alpha_{O2/N2}$	PO_2 (Barrer)		
M1	0.15	7.50	0.45	7.40	0.54	36	29
M2	0.25	8.40	0.40	8.65	0.56		
M3	0.40	10.10	0.32	11.03	0.60		

The used Maxwell model assumes uniform gas permeability throughout the polymer matrix. That is why the observed polymer chains' mobility inhibition near the interface would be more significant as the sieve loading rises and leads to permeability reduction. The ideal system (the basic assumption of the proposed Maxwell model) would be one where the sieve has a stronger affinity for the polymer than the solvent, while the polymer has a stronger affinity for the zeolite surface than the solvent. The main keys to the success of the mixed-matrix materials are the choice of proper molecular sieve and polymer matrix for the given separation, promotion of the adsorption of the polymer on the sieve surface, and polymer flexibility during membrane formation. One of the proposed solutions could be a priming of the zeolites with a thin polymer layer, the annealing at higher temperatures or application of suitable plasticizing mechanisms [41].

An analogous analysis was carried out for the experimental data obtained by the authors. They concerned hybrid membranes consisting of the hyperbranched polyimide matrix (ODPA-MTA) and zeolite 4A.

It was observed (experimental data in Table 4) that with the increasing filler addition, the zeolite 4A-HBPI hybrid membranes were characterized by the rise of the selectivity coefficient and decrease of the permeability coefficient, as in the case of Koros and Mahajan's research [39,41].

In spite of this, it was found that the measurement points were approaching Robeson's line (Figures 8 and 9) along with the increase in filler content. That indicates that after earlier proposed modifications, it will be possible to obtain more productive membranes. It was also found that for the value of a volume fraction of filler particles Φ bigger than 0.2, the observed difference between experimental results and theoretical data is large. This is directly related to higher values of calculated

errors. That is why this method is not the appropriate gas transport description through MMMs with large filler loading.

Table 4. Experimental and theoretical MOT-predicted data for the zeolite 4A-HBPI mixed-matrix membranes.

Membrane	Φ	Experimental Data		Theoretical Data		AARE (%)	RMSE (%)
		$\alpha_{O2/N2}$	PO_2 (Barrer)	$\alpha_{O2/N2}$	PO_2 (Barrer)		
M1	0.15	7.35	0.56	7.11	0.66	31	18
M2	0.20	7.87	0.53	7.62	0.67		
M3	0.25	8.38	0.51	8.18	0.67		
M4	0.30	8.89	0.48	8.80	0.67		
M5	0.35	9.41	0.45	9.48	0.68		
M6	0.40	9.92	0.42	10.23	0.69		

It was observed that for all chosen examples, the mean absolute relative error percentage ranges from 29% to 36%, while the root-mean-square error was in the range of 10% to 29%.

The proposed MOT application also gives the possibility of simulation for further models of gas permeation through mixed-matrix membranes. The above article presents preliminary results from the comparison of gas transport data through zeolite 4A-HBPI membranes obtained with two models, namely Maxwell and Bruggeman (Figure 10).

It was found that the theoretical data obtained from the Bruggeman model regarding the selectivity coefficient was worse than those obtained based on the Maxwell model, while the MOT-predicted data regarding the permeability coefficient were slightly better. Finally, the errors calculated within the Bruggeman model are comparable with errors obtained based on the Maxwell model proposed earlier; namely, AARE was 33% and RMSE was 18%.

Because the calculated errors show that both the Maxwell and Bruggeman models are not accurate enough for description of proposed membranes, further research will focus on two solutions. The first one will be the application of next-generation permeation models for the description of transport in more complex systems. And the second one will be the appropriate modification of analysed mixed-matrix membranes, leading to an ideal system.

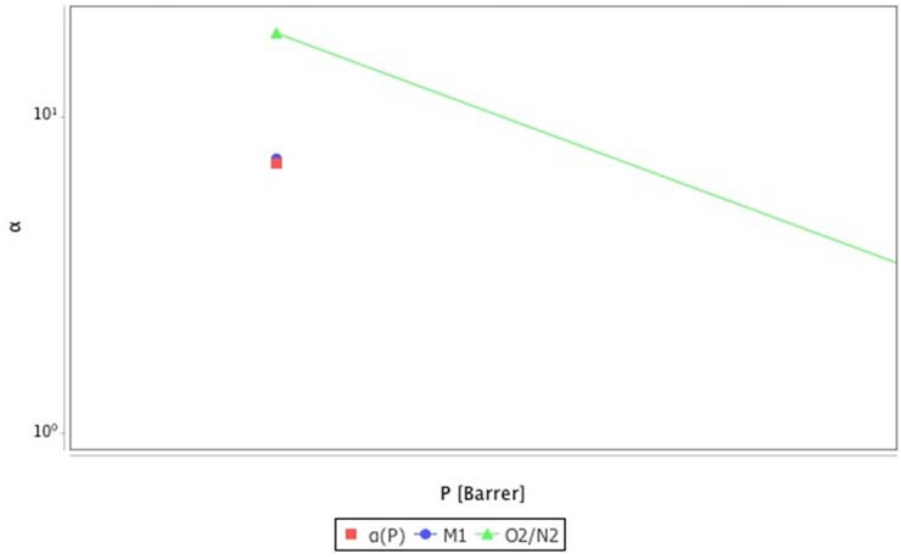
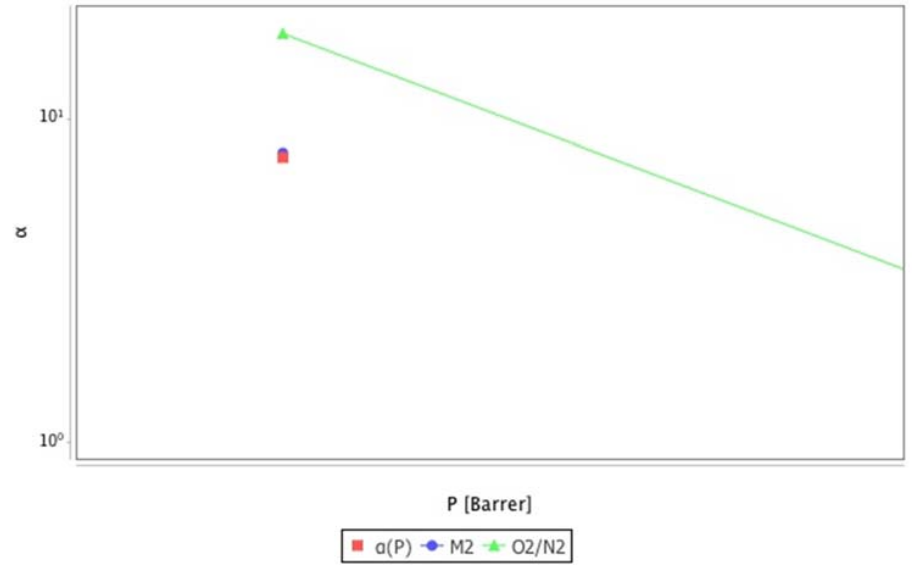
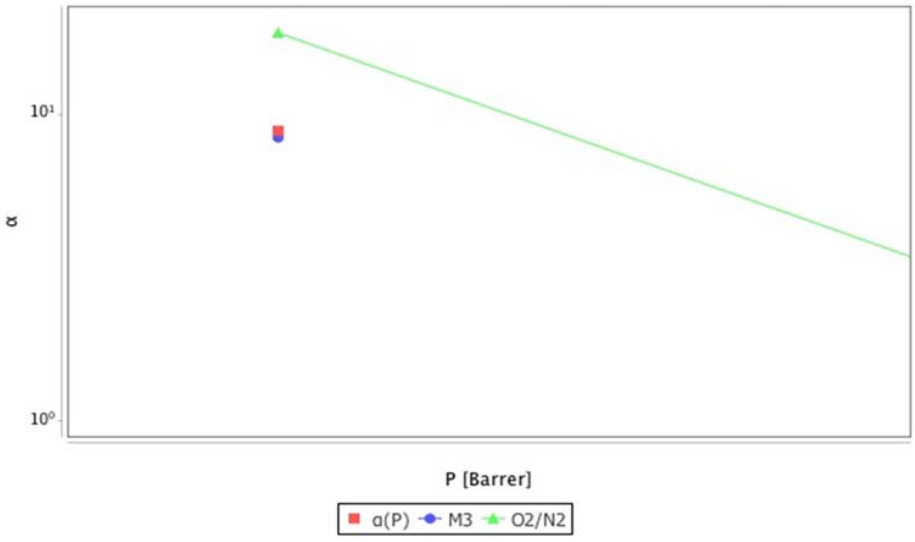


Figure 8. *Cont.*





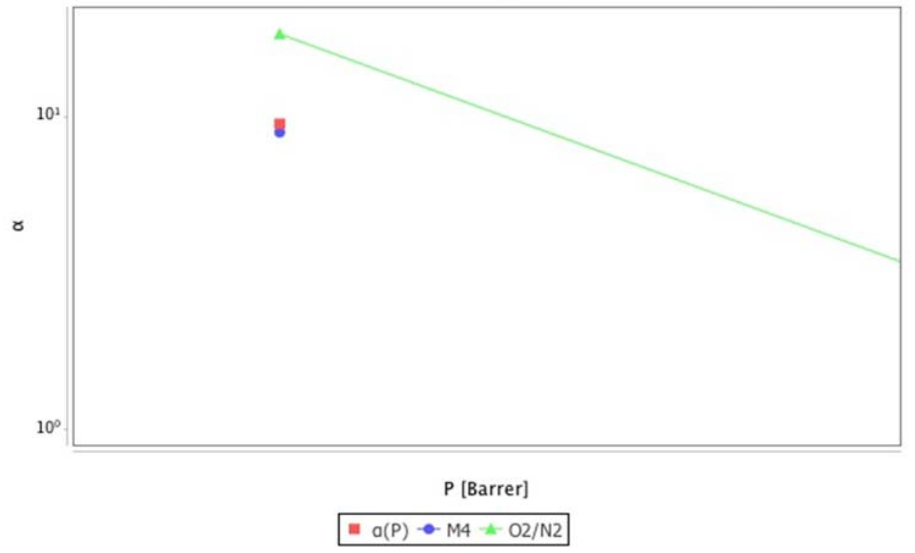


Figure 8. *Cont*.

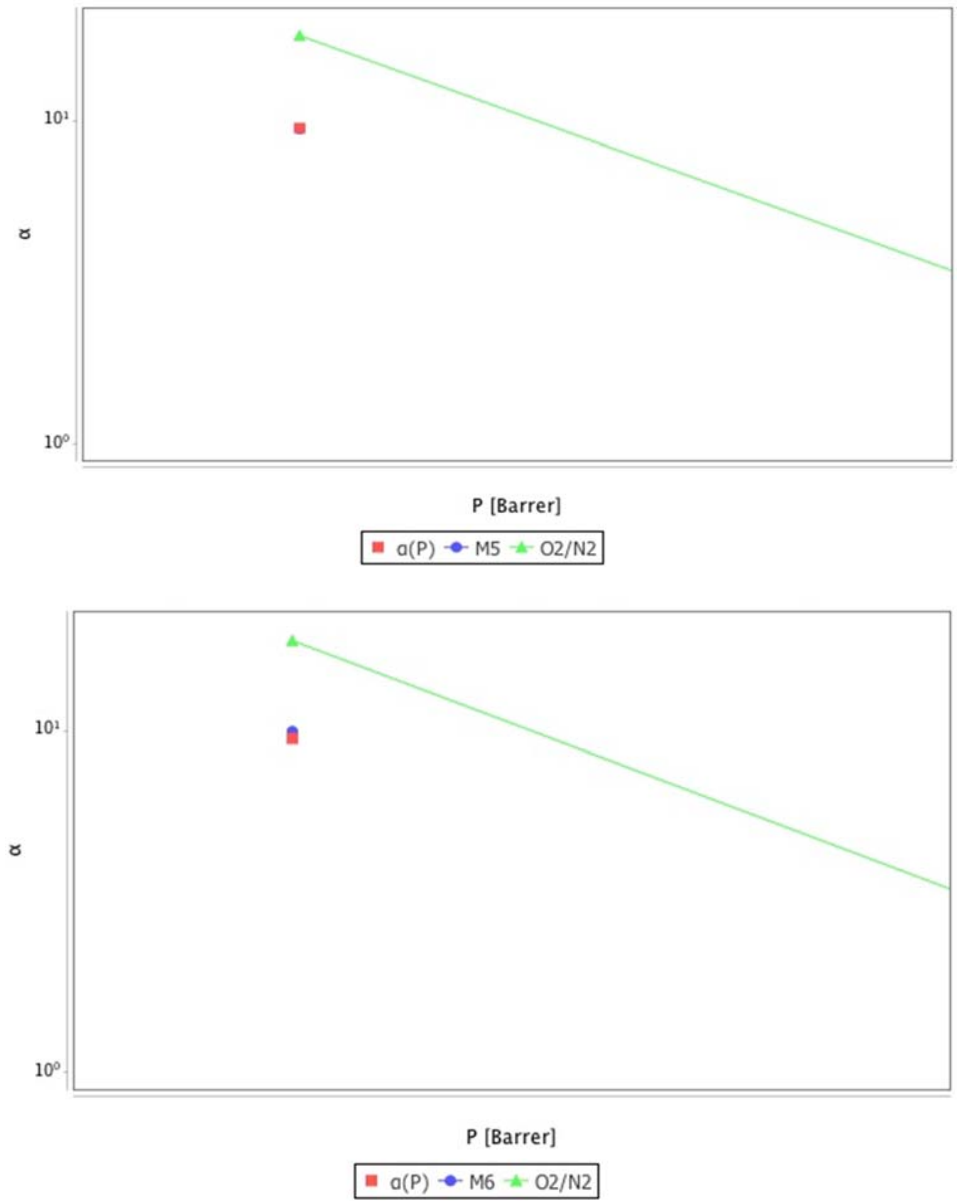


Figure 8. Comparison of experimental results (navy blue point) for the zeolite 4A-HBPI mixed-matrix membranes with 6 different filler additions (M1–M6) with Maxwell theoretical results (red point) and their position relative to the Robeson upper bound line (green line).

So we can see that thanks to the tools gathered in one place (application MOT), the researchers will be able to quickly and comprehensively evaluate potential membranes.

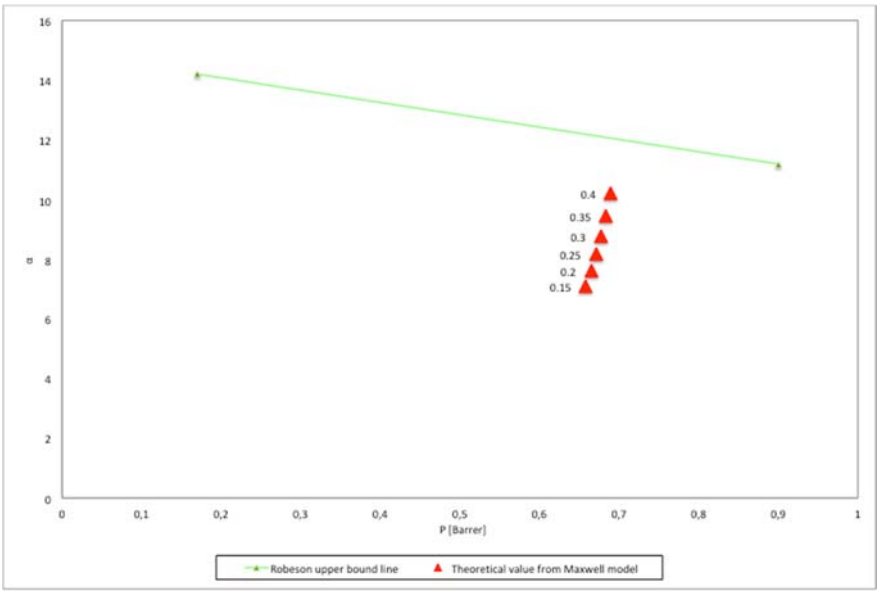
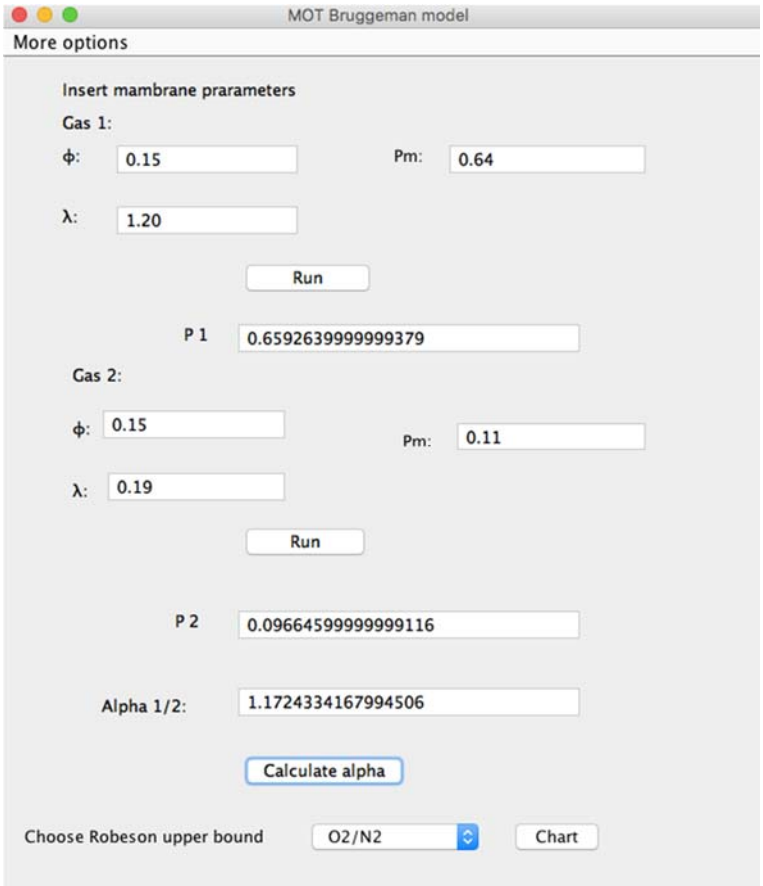
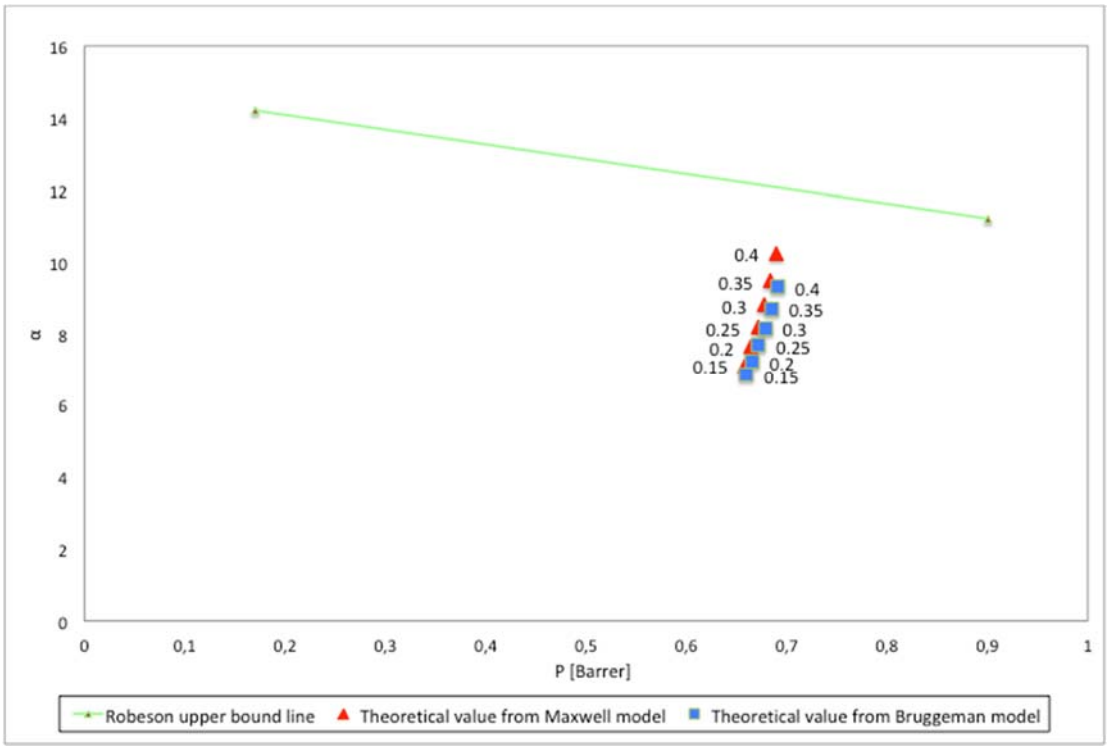


Figure 9. Dependence of the MOT predicted selectivity coefficient $\alpha_{O2/N2}$ on the oxygen permeability coefficient P for various volume fractions of zeolite 4A particles Φ in the HBPI mixed-matrix membrane relative to the Robeson upper bound line (green line).



(**a**)

Figure 10. *Cont.*



(**b**)

Figure 10. (**a**) Bruggeman's model MOT window and (**b**) comparison of the theoretical MOT-predicted data for two different models: Maxwell (red points) and Bruggeman (blue points) on HBPI mixed-matrix membranes with various volume fractions of zeolite 4A particles relative to the Robeson upper bound line (green line).

4. Conclusions

In this paper, the authors proposed a modern computer application MOT (Membrane Optimization Tool) to model the gas transport processes through mixed-matrix membranes MMMs.

The current version of application was based on the Maxwell model, which, can be successfully used to model the gas transport through the simplest types of hybrid membranes without any defects, consisting of two phases, organic and inorganic. The operation of the computer application has been verified on the basis of experimental results of O_2/N_2 separation for four types of hybrid membranes, consisting of various types of the polymer matrix, such as poly (vinyl acetate), 2, 2′-BAPB + BPADA, Ultem, hyperbranched (ODPA-MTA) and zeolite 4A.

Two errors (the average absolute relative error and the root-mean-square error) were calculated in order to compare the theoretical MOT-predicted results with the experimental data obtained from the literature and the authors' own research.

It was found that the mean absolute relative percentage ranges from 29% to 36%, while the root-mean-square error was in the range of 10% to 29%. The article presents also the preliminary comparison of MOT predicted gas transport data through zeolite 4A-HBPI membranes, obtained with two models, namely Maxwell and Bruggeman. It was found that the errors calculated from the Bruggeman model were comparable with errors obtained based on the Maxwell model proposed earlier, namely AARE was 33% and RMSE was 18%.

To obtain more accurate reproduction of experimental results, further versions of the proposed application will be extended with next-generation permeation models, allowing for the description of transport in more complex systems with the possibility of taking into account possible membrane defects.

The created application will allow us to verify the behavior and effectiveness of innovative membranes before they are made. In addition, it will allow us to determine their performance, verify the properties of alternative membranes and reduce capital-intensive research and time.

It will be an excellent tool for scientists studying the separation of various gas mixtures using the inorganic–organic hybrid membranes.

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