

VERENA KRAMER, DENIZ HÜLAGÜ, MATHIAS KRAUME\*

## DEVELOPMENT OF A MECHANISTIC MODEL FOR SORPTION SELECTIVE MIXED-MATRIX MEMBRANES FOR GAS SEPARATION

---

### OPRACOWANIE MODELU MECHANICZNEGO DLA WIELOMATRYCOWYCH SELEKTYWNYCH MEMBRAN SORPCYJNYCH SŁUŻĄCYCH DO ODDZIELANIA GAZU

#### Abstract

In this article a new, mechanistic model for mass transport in mixed-matrix membranes (MMM) is introduced. It was developed for sorption selective MMMs taking into account sorption characteristics, morphological parameters and operation conditions. Model structure, equations and input parameters are discussed. Investigations of different determining factors on permeability are shown for permeation of n-butane through mixed-matrix membranes made of PDMS and activated carbon. The results are compared with the Maxwell model to prove plausibility of the new concept.

*Keywords: gas permeation, mixed-matrix membranes, modeling, n-butane*

#### Streszczenie

W artykule niniejszym wprowadzono nowy, mechaniczny model przenoszenia masy w membranach wielomatrixowych (MMM). Został on opracowany dla selektywnych MMM sorpcyjnych z uwzględnieniem charakterystyki sorpcji, parametrów morfologicznych oraz warunków pracy. W artykule omówiono strukturę modelu, równania i parametry wejściowe, a także przedstawiono badanie różnego rodzaju czynników decydujących o przenikalności w zakresie przenikania n-butanu przez membrany wielomatrixowe wykonane z PDMS i węgla aktywowanego. Aby udowodnić wykonalność nowej koncepcji, wyniki porównano z modelem Maxwella.

*Słowa kluczowe: przenikanie gazu, membrany wielomatrixowe, model, n-butan*

---

\* Verena Kamer, Deniz Hülagü, Prof. PhD. Eng. Matthias Kraume, Chair of Chemical and Process Engineering, TU Berlin.

## 1. Motivation

Gas permeation is an innovative technique for gas separation that has attracted a lot of interest during last decades. But in some industrial applications the cost-effectiveness in comparison to conventional separation techniques like pressure swing adsorption or gas scrubbing is not sufficient. Advancement in membrane material in terms of selectivity and permeability will reduce energy demand of gas permeation plants and help to bring gas permeation better on the market. A new promising concept for membrane material is the so called mixed-matrix membrane (MMM).

Separation of higher hydrocarbons from permanent gases is an important field of gas separation. For these application a sorption selective membrane is needed, that transports higher hydrocarbons and restrains the permanent gas. State of the art are rubbery polymeric membranes. This work is part of a BMBF (Bundesministerium für Bildung und Forschung) project, where rubbery polymers PDMS and POMS are combined with activated carbon in mixed-matrix-membranes in order to improve selectivity and permeability compared to the pure polymer for separation of n-butane and methane. The challenges are to find suitable carbons for the polymers, to develop a membrane preparation procedure and to choose the right operation conditions for maximal improvement in selectivity and permeability. A mechanistic model is expected to be of great advantage, because the influence of different factors could be simulated and improper material combinations or operating conditions could be ruled out to decrease experimental effort. Therefore this work concentrates on the development of a mechanistic model for sorption selective mixed-matrix membranes.

## 2. State of the art

### 2.1. Membrane materials

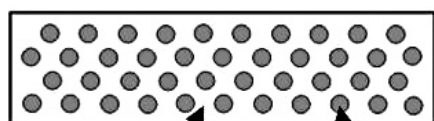
Nowadays most gas permeation membranes are polymeric. They can be easily produced in flat sheets or hollow fibers and are mechanically robust. Mass transport is always based on solution and diffusion in the polymer. Therefore polymers can have quiet good separation properties for certain gas mixtures. But there is a rather general trade off curve between membrane selectivity and permeability found by L. M. Robeson [1, 2]. High permeable polymers (rubbers) tend to have comparably low selectivity, while high selective polymers (glassy polymers) use to have low permeability. The most attractive region of high permeability and high selectivity cannot be reached.

Inorganic membranes like zeolitic and carbon membranes have proven themselves to be able to overcome the Robeson trade off line. These materials have very special pore structures, where molecular sieving, pore diffusion and surface diffusion can take place. But inorganic membranes underlie disadvantages in terms of stability and producibility, because they are brittle. As we know, there is no industrial gas permeation application with inorganic membranes so far.

Mixed-matrix membranes (MMM) are supposed to combine the advantages of polymeric and inorganic membranes. The separation layer consists of a polymeric matrix em-

bedding inorganic material as dispersed phase, see Fig. 1. The overall separation performance basically depends on separation properties in both phases and phase fraction. Therefore separation performance of mixed-matrix membranes can lie over the Robeson upper bound. This is illustrated in Fig. 2 showing results of Vu et al. [3]. They combined two glassy polymers with carbon molecular sieves (CMS) for separation of air and proved the concept of MMM. More combinations of glassy polymers and mole sieves like zeolites or CMS were examined in several publications that were reviewed lately [4]. To our knowledge sorption selective mixed-matrix membranes were not developed yet.

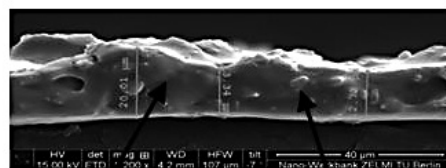
### Idealised MMM structure



polymer

particle

### Real MMM structure:



polymer

particle

Fig. 1. Idealised and real structure of a mixed-matrix membrane; real structure: SEM image (ZELMI, TU Berlin)

Rys. 1. Idealna i realna struktura membrany wielomatrixowej; struktura realna: obraz SEM (ZELMI, Uniwersytet Techniczny w Berlinie)

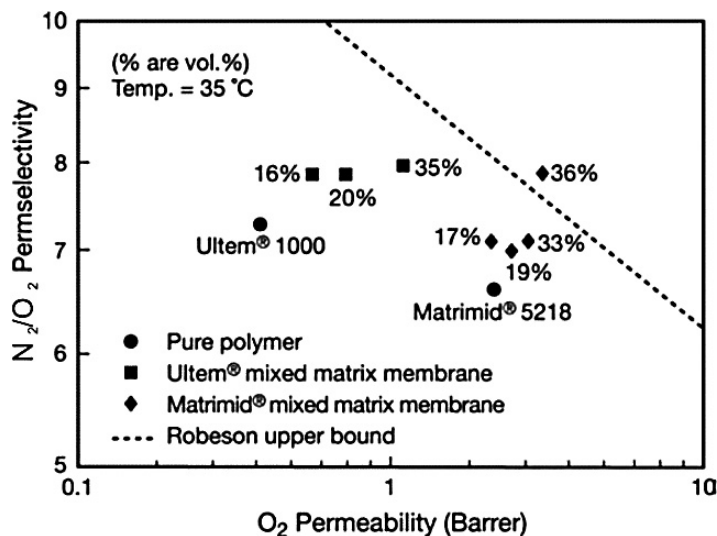


Fig. 2. Performance of mixed-matrix membranes made of two different glassy polymers and carbon molecular sieves, for N<sub>2</sub>/O<sub>2</sub> separation, (data:[3], figure:[5])

Rys. 2. Wydajność membran wielomatrixowych wykonanych z dwóch różnych polimerów szklanych i sitowych cząsteczek węgla dla oddzielania N<sub>2</sub>/O<sub>2</sub> (dane:[3], rysunek:[5])

2.1.1. Models for mass transfer in MMM

The existing models for mass transfer in mixed-matrix membranes [6, 7] are adaptations of thermal or electrical conductivity models in composite materials. Because of the close analogy between thermal or electrical conduction and diffusion, these models can be adapted for permeation through mixed-matrix membranes [7].

All models have a similar structure, where total permeability of a component  $A$  basically depends on permeability in dispersed phase  $P_{A,d}$ , permeability in continuous phase  $P_{A,c}$  and phase fraction  $\phi_d$ :  $P_{A,tot} = f(P_{A,d}, P_{A,c}, \phi_d)$ . Permeability itself is defined as mass flow divided by membrane area and pressure difference, multiplied with membrane thickness:

$$P_A = \frac{N_A}{A} \frac{\delta_M}{(p_{A,feed} - p_{A,perm})} \tag{1}$$

Selectivity of two components A and B is the ratio of their permeabilities:  $S_{AB} = P_A/P_B$ .

The most common and mostly applied model for mixed-matrix membranes is the Maxwell model, which was originally developed for electrical conductivity in dielectric media 1873 [6]. The Maxwell equation for total permeability is:

$$P_{A,tot} = P_{A,c} \frac{2(1 - \phi_d) + (1 + 2\phi_d)\lambda}{(2 + \phi_d) + (1 - \phi_d)\lambda} \tag{2}$$

with  $\lambda = P_{A,d}/P_{A,c}$ . It assumes well distributed, homogeneous and non-interacting solid spheres as dispersed phase and describes permeability well up to a phase fraction of  $\phi_d \leq 0,2$ .

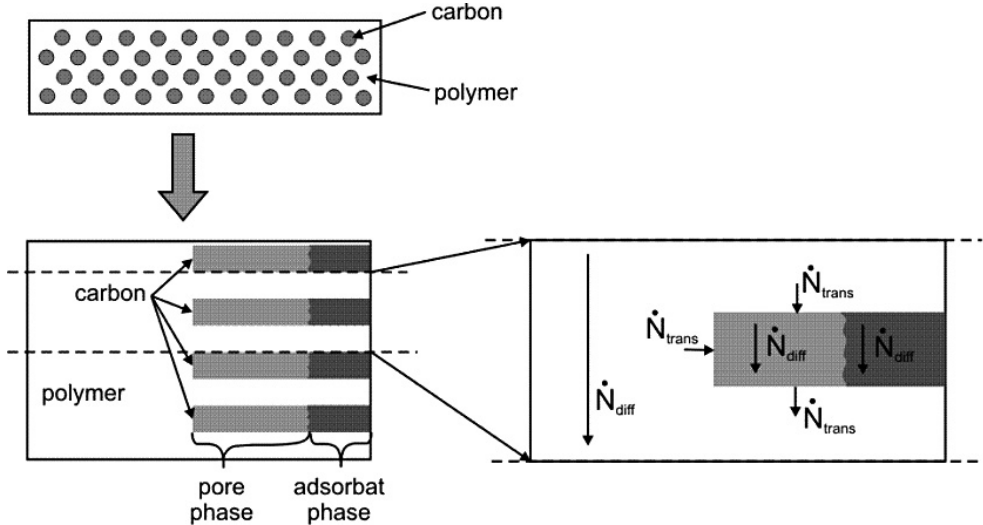


Fig. 3. Structure of the new model

Rys. 3. Struktura nowego modelu

Well known enhancements of the Maxwell equation for example the Bruggemann model or the Lewis-Nielsen model are recently discussed by Pal [7].

### 2.1.2. Limitations of these models

Hypothetically these models can be used to predict total permeability for a certain material combination, which is of interest for this project. But therefore all input parameters need to be known. Phase fraction  $\phi_d$  can be calculated from mass fraction and densities known from membrane preparation. Permeability  $P_c$  can be measured by permeation tests with a pure polymer membrane. But unfortunately it is not possible to measure permeability of the dispersed phase  $P_d$ , because the carbon particles are in powder form. Further the classical MMM models do not take into account parameters like particle size, sorption characteristics, mass transfer coefficient and operation conditions that are decisive for separation performance of a sorption selective MMM. Therefore a mechanistic model is needed.

## 3. Development of a mechanistic model

### 3.1. Structure

The new MMM model is based on a classical model for two-phase systems with axial mass transport, such as bubble columns or packed beds. It assumes that there is only mass transport normal to membrane surface in both phases and a mass transfer between them. Leaving out transport in radial direction, the dispersed phase within one layer can be combined into a block with same phase fraction. Those two-phase layers alternate with layers of pure polymer, so that the continuous phase encloses the dispersed phase completely, see Fig. 3. Pure polymer layers are of the same thickness as the two-phase layers. Therefore, the maximum possible dispersed phase fraction of spherical filler particles within a mixed-matrix-membrane of this structure is  $\phi_{d,max} = 0.37$  instead of 0.74.

The dispersed carbon phase itself is divided into two parts: pore volume and volume of adsorbed phase. Accordingly the new model is actually a three-phase model taking into account polymer phase, pore phase and adsorbate phase. This is necessary, because the crucial mass transfer mechanism inside the dispersed phase of a sorption selective MMM has to be a selective surface flow (SSF) in the adsorbed phase.

### 3.2. Model equations

The membrane is discretized in axial direction and differential balance equations are formed. Balances for polymer phase and carbon phase are set up within two-phase layers, while only polymer balances are formed within single phase layers. The carbon balances include pore phase and adsorbate phase, because these are assumed to be in equilibrium.

Diffusive mass transport normal to membrane surface is considered in all phases (polymer, pore and adsorbate). Further mass transfer between polymer and carbon is taken into account. In Table 1 mass transport equations used to set up the differential balances are summarized.

**Summary of the equations used to set up the balances in the mechanistic model**

Diffusion in Polymer	Diffusion in carbon
<p><i>Single phase layer:</i></p> $\dot{N}_{\text{diff},p} = D_p A \frac{dc}{dx}$ <p><i>Two phase layer:</i></p> $\dot{N}_{\text{diff},p} = D_p A (1 - \varphi_d) \frac{dc}{dx}$	<p><i>Pore diffusion:</i></p> $\dot{N}_{\text{diff},\text{pore}} = D_K A \varphi_d (1 - \psi) \frac{dz}{dx}$ <p><i>Surface diffusion:</i></p> $\dot{N}_{\text{diff},\text{surf}} = D_S A \varphi_d \psi \frac{dq}{dx}$
Mass transfer	Adsorption equilibrium
$\dot{N}_{\text{trans}} = \beta A_1 (c - c^*(z))$ <p>with <math>Sh = \frac{\beta d_p}{D_p} = 2, \quad A_1 = \frac{6}{d_p} \varphi_d</math></p>	<p><i>Polymer absorption</i> <math>c^* = f(z)</math></p> <p><i>Carbon adsorption</i> <math>q^* = f(z)</math></p>

### 3.3. Input parameters

#### Diffusion coefficients

- Diffusion coefficient of n-butane in PDMS was taken from literature [8]. So far concentration dependency due to polymer plasticization is neglected and the value is assumed to be constant:  $D_p = 10^{-10}$  m<sup>2</sup>/s.
- In pore phase the dominant diffusion mechanism is Knudsen diffusion. Pore diffusion coefficient for n-butane lies therefore between  $D_K = 10^{-7}$  m<sup>2</sup>/s and  $D_K = 10^{-8}$  m<sup>2</sup>/s.
- Surface diffusion coefficient was calculated according to the model of Okazaki (1981) as described by D. D. Do [9]. The necessary data was taken partially from literature [10] and partially from own adsorption experiments. This theoretical approach underlies some uncertainties, but the range of  $D_S$  can be reasonably limited to:  $10^{-8}$  m<sup>2</sup>/s <  $D_S$  <  $10^{-9}$  m<sup>2</sup>/s.

#### Membrane morphology

- Membrane thickness was orientated on the thickness of experimentally produced MMMs of PDMS and carbon :  $\delta_M = 20$   $\mu$ m.
- Mean particle size was assumed to be  $d_p = 3.3$   $\mu$ m. That results in three two-phase and three single phase layers within the model.
- Total phase fraction of carbon  $\varphi_d$  was varied between 5% and 30%.

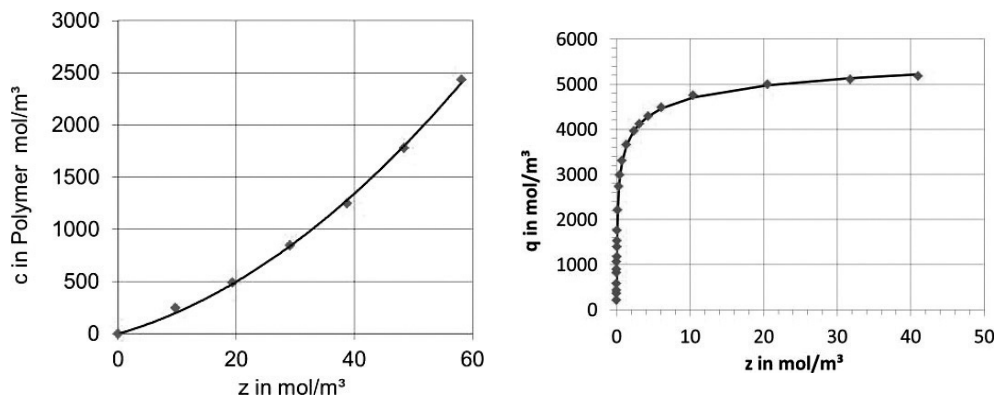


Fig. 4. Sorption isotherms of n-butane at 25°C: a) in PDMS [11], b) on activated carbon

Rys. 4. Izotermia sorpcji n-butanu w temperaturze 25°C: a) w PDMS [11], b) na węglu aktywowanym

#### Adsorption isotherms

- The sorption isotherm of n-butane in PDMS is convex [11] and can be well described with a quadratic function:  $c = Ap^2 + Bp$ , see Fig. 4 a)
- Adsorption isotherm of n-butane on carbon is concave and follows the Tóth isotherm:  $q = q_{max} bp[1 + (bp)^t]^{-1/t}$ , see Fig. 4 b)

#### Operating conditions

- Single component permeation of n-butane was simulated.
- Feed pressure and permeate pressure were:  $p_{feed} = 1$  bar,  $p_{perm} = 0.01$  bar.
- Temperature was constant at  $T = 25^\circ\text{C}$ .

### 3.4. Solving

Steady state differential balance equations are rewritten with first and second order difference quotients resulting in a system of nonlinear equations. The system is solved simultaneously in MATLAB with the Levenberg-Marquardt algorithm implemented in MATLAB optimization toolbox. In this way concentration profiles in all three phases are calculated which can be used to determine mass flows and permeabilities as described below.

## 4. Results

### 4.1. Calculation of permeabilities

Calculations are in accordance to equation (1) and shown in Table 2.

- For total permeability  $P_{tot}$  mass flow  $\dot{N}$  is the total mass flow given as sum of all three diffusive flows within a two phase layer. The product  $\dot{N} \delta_M$  can be described as integral of total diffusive mass flow over thickness within a two phase layer.

- Permeability of the dispersed phase  $P_d$  is calculated similarly. Here  $\dot{N}$  is the diffusive mass flow through carbon phase, which is not constant over membrane thickness because of adsorption isotherm. Therefore a mean value over all membrane layers is set into equation (1).
- Permeability of the polymer  $P_c$  can be calculated for a pure polymer membrane with same trans-membrane pressure difference.

Table 2

**Summary of equations for calculation of permeabilities with the new model**

Total Permeability	$P_{\text{tot}} = \frac{1}{(p_{\text{feed}} - p_{\text{perm}})} \int_0^X \left[ \left( D_s \frac{dq}{dx} \psi + D_{\text{pore}} \frac{dz}{dx} (1 - \psi) \right) \varphi_d + D_p \frac{dc}{dx} (1 - \varphi_d) \right] dx$ <p align="center">X: thickness of two phase layer</p>
Permeability of dispersed phase	$P_d = \frac{1}{(p_{\text{feed}} - p_{\text{perm}})} \frac{1}{s} \sum_{i=1}^s \left[ \int_0^X \left( D_s \frac{dq}{dx} \psi + D_{\text{pore}} \frac{dz}{dx} (1 - \psi) \right) dx \right]_i$ <p align="center">s: number of Layers</p>
Permeability of continuous phase	$P_c = \frac{1}{P_{\text{feed}} - P_{\text{perm}}} D_p (c^*(p_{\text{feed}}) - c^*(p_{\text{perm}}))$

#### 4.2. Case studies and comparison with maxwell model

The new model was used to calculate permeation of n-butane as a function of dispersed phase fraction  $\varphi_d$ . Surface diffusion coefficient  $D_s$  was varied between  $10^{-9}$  m<sup>2</sup>/s and  $10^{-7}$  m<sup>2</sup>/s and adsorbate phase fraction  $\psi$  was modified between 10% and 30%. In Fig. 5 and Fig. 6 results are shown and compared with the Maxwell model.

For all three surface diffusion coefficients the addition of carbon results in an increase of total permeability  $P_{\text{tot}}$  compared to pure polymer  $P_c$ . This effect increases with increasing dispersed phase fraction and with increasing surface diffusion coefficient. The correlation of total permeability and phase fraction is convex. That means the influence of the dispersed phase on permeability is higher for lower phase fraction than for higher ones.

Further an increase in adsorbate phase fraction  $\psi$  from 10% to 30% results in higher permeabilities in case of  $D_s = 10^{-8}$  m<sup>2</sup>/s and  $D_s = 10^{-7}$  m<sup>2</sup>/s. But for  $D_s = 10^{-9}$  m<sup>2</sup>/s total permeability decreases with increasing  $\psi$ . This is because for  $D_s = 10^{-9}$  m<sup>2</sup>/s pore diffusion is faster than surface diffusion. A small value of  $\psi$  results in a higher cross section area for pore diffusion.



In case of  $D_s = 10^{-8} \text{ m}^2/\text{s}$  surface diffusion is already faster than pore diffusion although pore diffusion coefficient is  $D_k = 2 \cdot 10^{-7} \text{ m}^2/\text{s} > D_s$ . This is due to the shapes of sorption isotherms, which cause a higher concentration gradient within adsorbate phase than in pore phase.

The Maxwell model shows an almost linear correlation for  $P_{\text{tot}}(\phi_d)$ . In Fig. 5 it is shown, that both models fit quiet well together up to a phase fraction of  $\phi_d = 0.2$ , which is known to be the scope of validity of the Maxwell model. This comparison backs up the plausibility of the new model within this range.

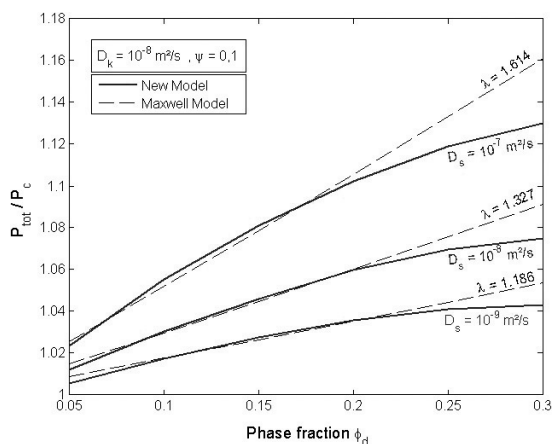


Fig. 5. Total permeability as a function of dispersed phase fraction and surface diffusion coefficient – comparison between new model and Maxwell model

Rys. 5. Przenikalność całkowita jako funkcja frakcji fazy rozproszonej i współczynnik dyfuzji powierzchniowej – porównanie nowego modelu z modelem Maxwella

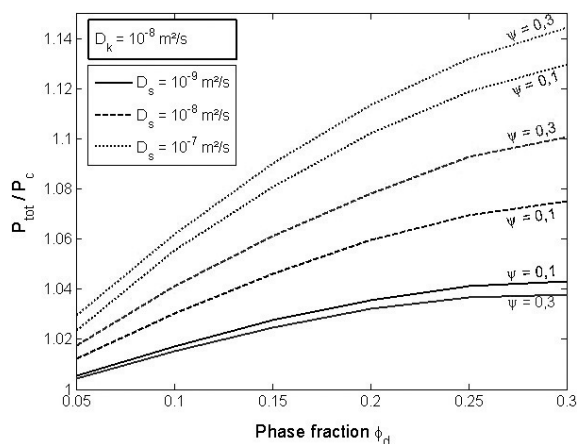


Fig. 6. Total permeability as function of dispersed phase fraction, surface diffusion coefficient and adsorbate phase fraction  $\psi$

Rys. 6. Przenikalność całkowita jako funkcja frakcji fazy rozproszonej, współczynnik dyfuzji powierzchniowej i frakcja fazy adsorbentu  $\psi$

The best fitting value of  $\lambda$  according to equation (2) was calculated with least square and is given in Fig. 5 and Table 3. As described in section 2.2,  $\lambda$  represents the ratio  $P_d/P_c$ , which can also be calculated for the new model according to equations given in Table 3. According to the new model,  $\lambda$  is not constant but decreases with dispersed phase fraction. The mean value agrees with the best fitted value of the Maxwell model.

Nevertheless the convex shape of  $P_{\text{tot}}(\phi_d)$  is unusual compared to the Bruggemann model or the Lewis Nielsen model, which are known to be valid for higher phase fractions than the Maxwell model, and show concave dependency. It has to be investigated closer, whether this is due to the structure of the new model or any adsorption effects.

Table 3

**Parameter  $\lambda$  calculated for the new model and comparison with the least square fitted values for Maxwell model**

	$\phi_d$ 0.05	$\phi_d$ 0.1	$\phi_d$ 0.15	$\phi_d$ 0.2	$\phi_d$ 0.25	$\phi_d$ 0.3	mean value 0.05 to 0.2	Maxwell best fit 0.05 to 0.2
$D_S = 10^{-7} \text{ m}^2/\text{s}$	1.59	1.54	1.48	1.42	1.37	1.32	1.51	1.61
$D_S = 10^{-8} \text{ m}^2/\text{s}$	1.39	1.35	1.31	1.27	1.24	1.20	1.33	1.33
$D_S = 10^{-9} \text{ m}^2/\text{s}$	1.26	1.24	1.21	1.18	1.15	1.13	1.20	1.19

## 5. Conclusion

The new mechanistic model has proven itself plausible by comparison with the Maxwell model, which is commonly accepted as model for mass transfer in mixed-matrix membranes. With the new model it is possible to investigate the influence of different parameters and different carbons on mass transfer properties of the MMM to find promising combinations that are going to be realized experimentally.

## 6. Outlook

The model is going to be extended for single component methane permeation and binary gas mixtures of n-butane and methane to enable calculation of selectivity, which can be compared with experimental data. Further concentration dependency for diffusion coefficient in PDMS will be taken into account.

*The authors gratefully acknowledge project funding by the Bundesministerium für Bildung und Forschung (BMBF) and thank their partners Blücher GmbH, Helmholtz-Zentrum Geesthacht and Sterling SIHI for good cooperation.*

## Symbols

$A$	– Membrane area [m <sup>2</sup> ]
$A_I$	– Interfacial area between polymer and carbon [m <sup>2</sup> ]
$c$	– Concentration in polymerphase [mol/m <sup>3</sup> ]
$D_P$	– diffusion coefficient in polymer [m <sup>2</sup> /s]
$D_K$	– diffusion coefficient in carbon pores [m <sup>2</sup> /s]
$D_S$	– surface diffusion coefficient in adsorbate phase [m <sup>2</sup> /s]
$z$	– Concentration in pore phase [mol/m <sup>3</sup> ]
$\dot{N}$	– mass flow [mol/s]
$P$	– Permeability [mol/(s m bar)]
$p$	– Pressure [Pa]
$q$	– Concentration in adsorbate phase [mol/m <sup>3</sup> ]
$S$	– Selectivity [–]
$x$	– Length coordinate [m]
$\beta$	– Mass transfer coefficient [m/s]
$\delta_M$	– thickness [m]
$\lambda$	– Parameter of Maxwell model [–]
$\phi_d$	– Dispersed phase volume fraction [–]
$\psi$	– adsorbate phase fraction inside the pores [–]

## References

- [1] Robeson L.M., Journal of Membrane Science, **62**, (1991), 165-185.
- [2] Robeson L.M., Journal of Membrane Science, **320**, (2008), 390-400.
- [3] Vu D.Q., Koros W.J., Miller S.J., Journal of Membrane Science, **211**, (2003), 335-348.
- [4] Aroon M.A., Ismail A.F., Matsuura T., Montazer-Rahmati M.M., Separation and purification Technology, **75**, (2010), 229-242.
- [5] Ismail A.F., Rana D., Matsuura T., Foley H.C., Carbon based Membranes for Separation processes; 1 ed.; Springer New York, 2011.
- [6] Gonzo E.E., Parentis M.L., Gottifredi J.C., Journal of Membrane Science, **277**, (2006), 46-54.
- [7] Pal R., Journal of Colloid and Interface Science, **317**, (2008), 191-198.
- [8] Raharjo R.D., Freeman B.D., Paul D.R., Sarti G.C., Sanders E.S., Journal of Membrane Science, **306**, (2007), 75-92.
- [9] Do D.D., Adsorption Analysis: Equilibria and Kinetics; Imperial College Press: London, 1998.
- [10] VDI Wärmeatlas; 6. ed.; GVC, V. G. V. u. C., Ed.; VDI Verlag: Düsseldorf, 1991.
- [11] Raharjo R.D., Freeman B.D., Sanders E.S., Journal of Membrane Science, **292**, (2007), 45-61.