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Comparison of Predictive Models for Relative Permeability of CO₂ in Matrimid-Carbon Molecular Sieve Mixed Matrix Membrane

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Abstract: Different well-known gas permeation theoretical models such as Maxwell model, Bruggeman model, Lewis-Nielsen model, Pal model, Felske model and modified Felske model has been discussed for prediction of the relative permeability of CO₂ in Matrimid® 5218-Carbon Molecular Sieve (CMS) Mixed Matrix Membranes (MMMs). For evaluation of the theoretical models, experimental data of relative permeability for CO₂ in Matrimid® 5218-Carbon Molecular Sieve (CMS) mixed matrix membrane were compared with the prediction of the theoretical models for the relative permeability of CO₂ in ideal and rigidified interfacial morphology of the mixed matrix membrane. Comparison of those models was carried out based on the widely used model validation criteria including absolute average relative error percent and standard deviation. For the models evaluated under ideal morphology, the results showed a decrease in the absolute average relative error percent and standard deviation in the following order: Pal model > Lewis-Nielsen model > Maxwell model > Bruggeman model. For other models evaluated considering the presence of rigidified interfacial morphology, the absolute average relative error percent and standard deviation showed a decrease in the order, Felske model > modified Felske model. Hence, the modified Felske model was found to be in a better agreement with experimental data for prediction of relative permeability CO₂ in Matrimid® 5218-CMS mixed matrix membrane.

Key words: Mixed matrix membrane, relative permeability of CO₂, theoretical models of gas permeation

INTRODUCTION

The application of membranes in gas separation process is playing an increasingly important role in reducing the environmental impact and costs of industrial processes as they offer potential advantages in operating energy requirements and environmental standards (Shimekit *et al.*, 2009; World Intellectual Property Organization, 2009; Shekhawat *et al.*, 2003).

Polymeric membranes have the advantages of desirable mechanical properties and economical processing capabilities. However, current polymeric membrane materials have seemingly reached a limit in the tradeoff between permeability and selectivity and thus are inadequate to fully exploit the application opportunities on industrial scale; the improvement in permeability is at the expense of selectivity and vice versa (World Intellectual Property Organization, 2009). For instance in CO₂/CH₄ mixtures, high CO₂ pressures plasticize polymeric membranes and decrease their separation ability. Moreover, some polymeric membranes lose their selectivity and productivities in the presence of condensable heavy hydrocarbons. On the other hand,

inorganic membranes such as zeolite membranes have been used to separate CO₂ from CH₄ because of their superior thermal, mechanical and chemical stability, good erosion resistance and stability at high CO₂ pressures. But the application of inorganic membranes is still seriously affected by the lack of technology to form continuous and defect-free membranes, the extremely high cost for the membrane production and handling issues e.g., inherent brittleness. Therefore, in view of this situation, the development of mixed matrix composite membranes can be considered to be the most practical approach for future applications. It can be considered as alternative cost-effective membrane which combines homogeneously interpenetrating polymeric and inorganic particle matrices for high permeability and selectivity well above the upper-bound limit (Shekhawat *et al.*, 2003).

Mixed Matrix Membranes (MMMs) are hybrid membranes with the latest membrane morphology. They contain inorganic fillers such as rigid molecular sieving materials of superior gas separation properties embedded in an organic polymer matrix for ease of processability and economics (Shekhawat *et al.*, 2003). Mixed matrix composite materials, comprised of molecular sieving

materials embedded in a polymer matrix, have potential to provide economical and high performance gas separation membranes if defects at the molecular sieve/polymer interface can be eliminated. Moreover, careful matching of the intrinsic permeability and selectivity of the support matrix and the molecular sieve domains is necessary for an effective separation by mixed matrix membranes (Shimekit *et al.*, 2009).

The molecular-sieve type fillers used in MMMs such as zeolite and Carbon Molecular Sieve (CMS) are capable of discriminating between different molecules present in the feed mixture, usually on the basis of size and shape of molecules (Shimekit *et al.*, 2009; Pal, 2007). The CMS are basically carbonaceous materials and known for their high surface area, high void volume and a narrow pore size distribution with pores of molecular dimensions. In industrial applications, CMS are used for the separation and purification of gas mixtures. Gas separation process using CMS materials is based on the difference in the adsorption kinetics of different kind of molecular species present in the gaseous feed mixture (Pal, 2007).

Carbon Molecular Sieves (CMS) are also known for their simultaneously high permeabilities and selectivities (Vu *et al.*, 2002; Steel, 2000; Suda and Haraya, 2000; Singh and Koros, 1996). The presence of porous morphology, shape and size-selective pores within their network enables very effective separation of gases compared to polymeric membranes. However, the porous, rigid characteristic of molecular sieving materials that allows for precise discrimination of gas penetrants creates difficulties in forming high surface area modules because of their inherent brittleness. This limitation currently makes pure CMS membranes economically unattractive for industrial-scale implementation. On the other hand, using these CMS as dispersed fillers in a mixed matrix membrane provides a very attractive alternative strategy (Zimmerman, 1998; Zimmerman *et al.*, 1997). Such an approach gives an opportunity for the superior separation properties of carbon membranes while potentially maintaining the superior processability typical of conventional membrane formation technology.

From the domain of the polymer matrix that are typically used as the constituent materials in gas separation mixed matrix membranes system, Matrimid® 5218 was selected for this study. Matrimid® 5218 is a commercially available thermoplastic solid polyimide made from the monomers 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride and diaminophenylindane and is currently used as a gas separation membrane material. Like other polyimides, Matrimid® 5218 has a high glass transition temperature (T_g) with the characteristic rigid polymer chain backbone. Moreover, Matrimid® 5218 has considerably higher permeabilities (Vu *et al.*, 2003a).

In order to make efficient use of the mixed matrix membranes, the variation in penetrants permeability with the kind and concentration of filler materials should be known. Knowledge of the permeabilities of different penetrants is therefore, the basic requirement for the design and operation of a Mixed Matrix Membranes (MMM) separation process (Pal, 2007).

The proper theoretical explanation of the permeability of composite polymeric materials such as Matrimid® 5218-Carbon Molecular Sieve (CMS) MMMs in order to model their permeation properties is of great interest, particularly in view of the growing technological importance of these materials (Hashemifard *et al.*, 2010). The existing models for prediction of permeation through Mixed Matrix Membranes (MMM) have been mostly reported by different researchers as adaptations of thermal/electrical conductivity models. Since there exists a close analogy between thermal/electrical conduction in composite materials and permeation of species through such materials, the conductivity models are readily adapted to permeability of species in Mixed Matrix Membranes (MMM) (Pal, 2008).

Although, there are other models in the study (Agari and Uno, 1986; Cheng and Vachon, 1969; Higuchi and Higuchi, 1960; Bottcher, 1945), this study is confined to the examination of more popular models such as the Maxwell, Bruggeman, Pal Lewis-Nielsen, Felske and modified Felske models (Hashemifard *et al.*, 2010).

The objective of this study is to briefly discuss, compare and evaluate the well-known gas permeation theoretical models for relative permeability of CO₂ in ideal and rigidified interfacial morphology of Matrimid® 5218-carbon molecular sieve mixed matrix membranes. In this study, an ad hoc linear least square computational approach was applied to compute the relative permeability of CO₂ as a function of the volume fraction of the CMS.

THEORY

Mathematically, gas transport through a mixed matrix membrane presents a complex problem. Several theoretical permeation models have been used to predict the permeation properties of mixed matrix (heterogeneous) membranes as functions of the permeabilities of the continuous and dispersed phases (Hashemifard *et al.*, 2010).

The Maxwell (1954) model was originally developed for electrical conductivity of particulate composites and can be adapted to permeability as:

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

where, P_r is the relative permeability of species, P is the effective permeability of species in MMMs, P_m is the permeability of species in the matrix (continuous phase), ϕ is the volume fraction of the filler particles and λ_{dm} is the permeability ratio P_d/P_m (P_d is the permeability of species in dispersed phase) (Hashemifard *et al.*, 2010).

The Bruggeman (1935) model was originally developed for the dielectric constant of particulate composites and can be adapted to permeability as: (Hashemifard *et al.*, 2010).

$$(P_r)^{\frac{1}{3}} \left[\frac{\lambda_{dm} - 1}{\lambda_{dm} - P_r} \right] = (1 - \phi)^{-1} \quad (2)$$

The Lewis and Nielsen (1970) and Nielsen (1973) model was originally proposed for the elastic modulus of particulate composites and can be adapted to permeability as:

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

Where:

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi$$

and ϕ_m is the maximum packing volume fraction of filler particles (ϕ_m is 0.64 for random close packing of uniform spheres) (Hashemifard *et al.*, 2010).

The Pal (2007) model was originally developed for thermal conductivity of particulate composites, can be adapted to permeability as:

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

The modified Maxwell model, Eq. 5 and 6 considered the influence of interfacial layer on the permeability of species in MMMs to determine the permeability of three-phase MMM (Chung *et al.*, 2007; Moore *et al.*, 2004; Mahajan and Koros, 2002). Thus,

$$P_r = \frac{P}{P_m} = \left[\frac{2(1 - \phi) + (1 + 2\phi)(P_{eff}/P_m)}{(2 + \phi) + (1 - \phi)(P_{eff}/P_m)} \right] \quad (5)$$

where, ϕ is the volume fraction of total dispersed phase (core-shell particles) in the whole composite and P_{eff} is the effective permeability of a single core-shell particle given as:

$$P_{eff} = P_1 = \left[\frac{2(1 - \phi_s) + (1 + 2\phi_s)(P_d/P_1)}{(2 + \phi_s) + (1 - \phi_s)(P_d/P_1)} \right] \quad (6)$$

where, ϕ_s is the volume fraction of filler core particle in the combined volume of core and interfacial shell (in a single core-shell particle) and P_1 is the permeability of the interfacial shell.

The Felske (2004) model was recently developed and it described an exact expression for the thermal conductivity of composites of core-shell particles (core particle covered with interfacial layer).

When the Felske thermal conductivity model is adapted to permeability (substituting thermal conductivity by permeability), it can be written as:

$$P_r = \frac{P}{P_m} = \left[\frac{2(1 - \phi) + (1 + 2\phi)(\beta/\gamma)}{(2 + \phi) + (1 - \phi)(\beta/\gamma)} \right] \quad (7)$$

where, β and γ are given as:

$$\beta = \frac{(2 + \delta^3)P_d - 2(1 - \delta^3)P_1}{P_m} \quad (8)$$

$$= (2 + \delta^3)\lambda_{dm} - 2(1 - \delta^3)\lambda_{im}$$

$$\gamma = (1 + 2\delta^3) - (1 - \delta^3)(P_d/P_1) \quad (9)$$

$$= (1 + 2\delta^3) - (1 - \delta^3)\lambda_d$$

where, δ is the ratio of the rigidified outer radius of interfacial shell to core radius, ϕ is the volume fraction of core-shell particles (volume fraction of total dispersed phase, filler core particles with interfacial layers), P_1 is the permeability in the interfacial shell, P_d is the permeability in filler core particle, P_m is the permeability in matrix, λ_{dm} is the permeability ratio P_d/P_m , λ_{im} is the permeability ratio P_1/P_m and λ_{di} is the permeability ratio P_d/P_1 .

The Fleske model was also modified by Pal (2007) to account for the morphology and packing difficulty of particles as shown on Eq. 10.

$$P_r = \frac{P}{P_m} = \left[\frac{1 + 2((\beta - \gamma)/(\beta + 2\gamma))\phi}{1 - ((\beta - \gamma)/(\beta + 2\gamma))\phi\psi} \right] \quad (10)$$

where, β and γ are given by Eq. 8 and 9, respectively and Ψ is given by Eq. 3 in terms of ϕ_m (maximum packing volume fraction of core-shell particles).

MATERIALS AND METHODS

In order to evaluate the performance of the gas permeation theoretical models on Matrimid[®] 5218-CMS mixed matrix membrane, the researchers at first categorized the models based on their parameters incorporating interface morphologies. Ideal morphology (i.e., perfect compatibility between CMS and the Matrimid[®] 5218) was

Table 1: Experimental permeation data of CO₂ in Matrimid®-CMS mixed matrix membrane and their constituent membranes

References	Constituents	P CO ₂ (Barrer)
Vu <i>et al.</i> (2003a)	17 vol. % CMS	10.3
Vu <i>et al.</i> (2003a)	19 vol.% CMS	10.6
Mahajan <i>et al.</i> (2002)	27 vol.% CMS	11.1
Mahajan <i>et al.</i> (2002)	30 vol.% CMS	12.1
Vu <i>et al.</i> (2003a)	33 vol.% CMS	11.5
Vu <i>et al.</i> (2003b)	36 vol.% CMS	12.6
Vu <i>et al.</i> (2003b)	Pure Matrimid® 5218	10.0
Vu <i>et al.</i> (2003b)	Pure CMS 800-2	44.0

considered in the computation of the relative permeability of CO₂ for all the models except Felske and its modified model. For these models non ideal (rigidified interface layer) morphology was taken into consideration. Due to the limitation of availability of large number of published experimental data for relative permeability CO₂ in Matrimid®5218-CMS MMMs, the study was delineated to the cases of ideal morphology for Maxwell, Bruggeman, Lewis-Nelson, Pal models and the case of rigidified interfacial layer for Felske and its modified model. The available CO₂ permeation data were collected for intrinsic Matrimid® 5218 membrane and CMS membrane and Matrimid® 5218-CMS mixed matrix membrane with respect to loading of CMS as shown on Table 1. The numerical analysis was conducted by the aid of MATLAB 7.6.0.324 using the most widely used model validation criteria including standard deviation and percentage of average absolute relative error. Furthermore, linear least square computational ad hoc approach was used for reasonable regression and simplicity of comparison.

RESULTS AND DISCUSSION

For the evaluation of each theoretical models, the mixed matrix membranes consisting of carbon molecular sieves as filler particles and Matrimid® 5218 as matrix were used as reported by Vu *et al.*, (2003b) and Mahajan and Koros (2002) for CO₂/CH₄ separation. Further detail about the system can be found in the original references shown in Table 1. Due to the limited number of experimental data for CO₂ relative permeation in Matrimid® 5218-Carbon Molecular Sieves (CMS) system, the researchers used a linear least square ad hoc approach to improvise more number of experimental data for CO₂ relative permeation behavior with respect to volume fraction of CMS having a correlation coefficient (R²) of larger than 0.98.

Standard deviation and percentage of average absolute relative error were calculated using Eqs. 11-14 (Hashemifard *et al.*, 2010).

$$RE_i (\%) = \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \quad (11)$$

Table 2: Comparison of the standard deviation (σ) and Average Absolute Relative Error percentage (AARE %) of the selected theoretical models from the relative permeation experimental data.

Theoretical models	σ	AARE (%)
Maxwell model	31.74	32.06
Bruggeman model	23.51	23.75
Lewis Nielsen model	33.78	34.13
Pal model	41.12	41.53
Felske model	12.75	12.88
Modified Felske model	5.86	5.92

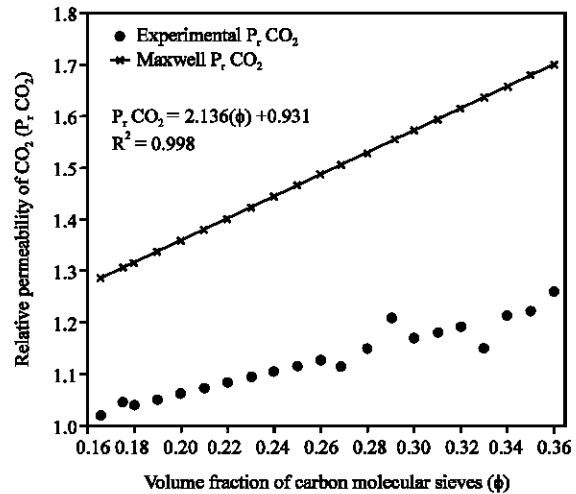


Fig. 1: The comparison of the Maxwell model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid® 5218-Carbon Molecular Sieves (CMS) system

$$ARE_i (\%) = \frac{100}{N} \sum_{i=1}^N RE_i (\%) \quad (12)$$

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (RE_i (\%) - ARE_i (\%))^2} \quad (13)$$

$$AARE_i (\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| \quad (14)$$

The experimental permeation data and the model predictions were plotted as relative permeability P_{CO₂} versus volume fraction of CMS particles φ. The comparison result of the available theoretical models towards their CO₂ relative permeation behavior with respect to volume fraction of CMS are reported (Fig. 1-7). Furthermore, the standard deviation and percentage of average absolute relative error of the models were reported on Table 2.

The comparison of the Maxwell model relative permeability of CO₂ with improvised relative experimental permeation data for Matrimid® 5218-Carbon Molecular Sieves (CMS) system is described (Fig. 1). As can be seen

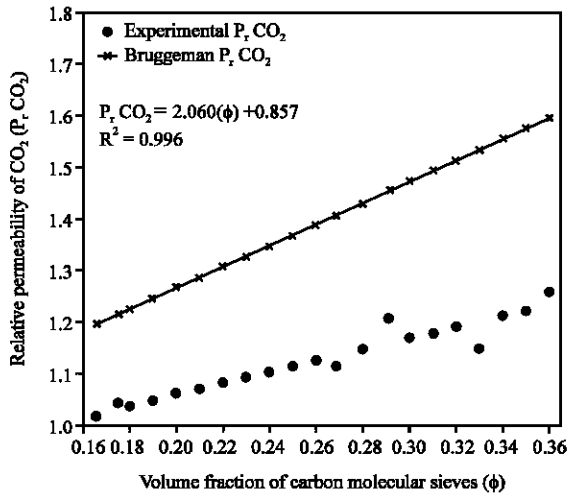


Fig. 2: The comparison of the Bruggeman model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system

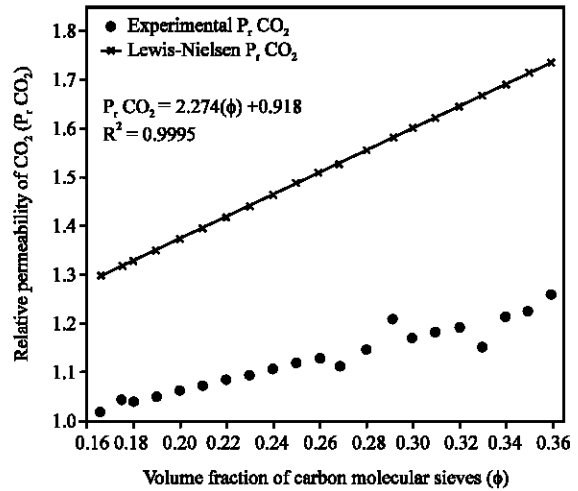


Fig. 3: The comparison of the Lewis-Nielsen model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system

from the Fig. 2 and further from Table 2, there was a deviation between the relative permeation experimental data and the Maxwell model relative permeability prediction with standard deviation (σ) of 31.74 and AARE(%) of 32.06.

Comparison of the Bruggeman model relative permeability prediction of CO₂ with improvised relative experimental permeation data for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system is shown (Fig. 2). As can be seen from the figure and further from Table 2, it was calculated that there was also a deviation between the experimental data and the Bruggeman model prediction with standard deviation (σ) of 23.51 and AARE (%) of 23.75.

Comparison of the Lewis-Nielsen model relative permeability of CO₂ with improvised relative experimental permeation data for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system is shown (Fig. 3). As can be seen from the figure and further from Table 2, a standard deviation (σ) of 33.78 and AARE (%) of 34.13 was obtained between the experimental data and the Lewis Nielsen model prediction.

A standard deviation (σ) of 41.12 and AARE (%) of 41.53 was obtained with regards to comparison of the Pal model relative permeability of CO₂ and improvised relative experimental permeation data for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system (Fig. 4, Table 2).

Comparison of the Fleske model relative permeability prediction of CO₂ with improvised relative experimental permeation data for Matrimid[®] 5218-Carbon Molecular

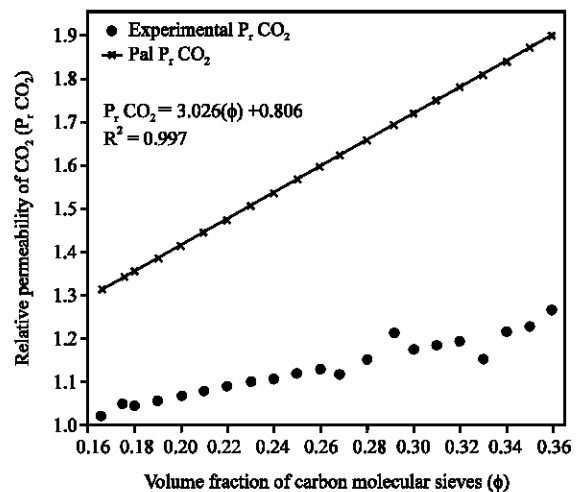


Fig. 4: The comparison of the Pal model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system

Sieves (CMS) system is shown (Fig. 5). As can be seen from the figure and further from Table 2, it was reported that there was a deviation between the experimental data and the Fleske model prediction with standard deviation (σ) of 12.75 and AARE (%) of 12.88.

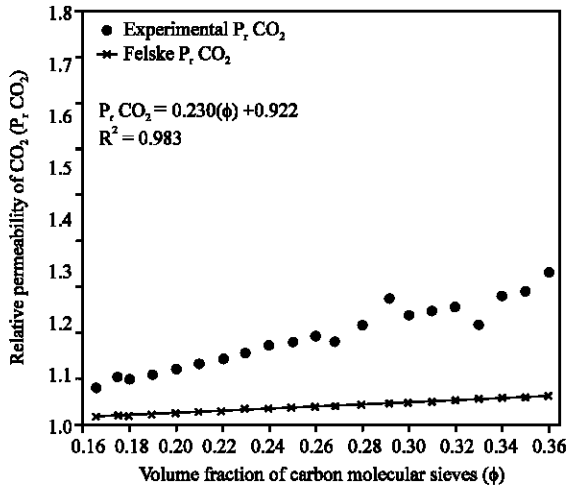


Fig. 5: The comparison of the Felske model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system

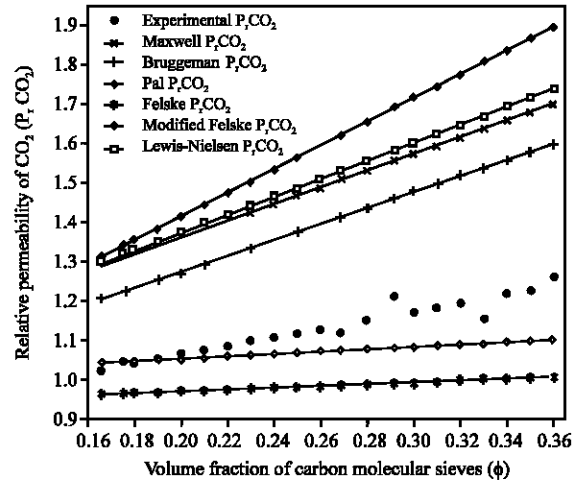


Fig. 7: The overall comparison of the selected theoretical models for relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system

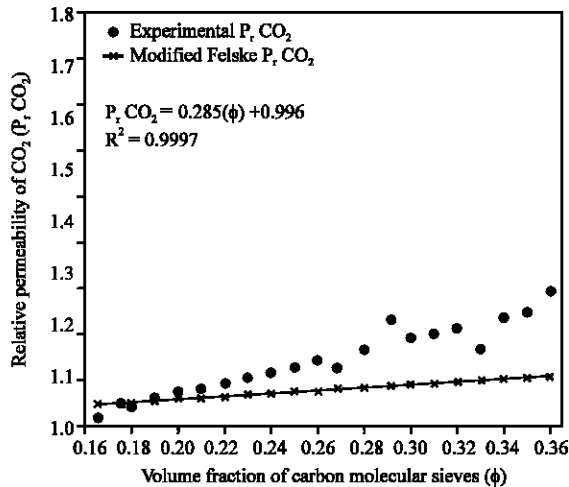


Fig. 6: The comparison of the modified Felske model relative permeability of CO₂ with improvised relative permeation experimental data from Vu *et al.* (2003b) and Mahajan and Koros (2002) for Matrimid[®]5218-Carbon Molecular Sieves (CMS) system

From the results, the lowest standard deviation (σ) of 5.86 and AARE (%) 5.92 was obtained with regards to comparison of the modified Fleske model relative permeability prediction of CO₂ with experimental permeation data for Matrimid[®] 5218-Carbon Molecular Sieves (CMS) system (Fig. 6).

For ease of visualization of the deviations, the overall comparison of the selected theoretical models is summarised (Fig. 7).

Table 2 showed the standard deviation and the average absolute relative error percentage for the evaluated theoretical models from the results, it can be shown that the modified Felske model predicted the most reasonable agreement with experimental data. Moreover, the result of the Felske model and further its modified model asserted that incorporation of parameters that considers the effect of non-ideal morphology (such as rigidified interface layer) contributed for the permeation results to be in a more reasonable agreement with the actual observation than assuming ideal morphology in the computational process.

The results also showed that those theoretical models that were evaluated considering ideal morphology of Matrimid[®]5218-CMS MMM predicted their relative permeation at higher deviation than the experimental observation. Comparatively, for the theoretical models evaluated considering ideal morphology, their standard deviation (σ) and AARE (%) were found out in decreasing order of: Pal model > Lewis-Nielsen model > Maxwell model > Bruggeman model. And for the models evaluated considering rigidified interfacial layer, the standard deviation (σ) and AARE (%) were obtained in decreasing order of: Felske model > modified Felske model.

Although, there was limited number of data for relative permeability of CO₂ in Matrimid[®] 5218-Carbon

Molecular Sieves (CMS) system for evaluation of the theoretical models, the findings of this study were in good agreement with similar researches conducted considering large number of data (Hashemifard *et al.*, 2010; Mahajan and Koros, 2002).

The possible error sources that will explain the higher deviations for the predicted relative permeability of CO₂ apart from the effect of interfacial morphology includes but not limited to the following: errors can be generated during permeation measurements and transferring experimental data, prediction of inorganic permeabilities is not free of errors and although incorporating the effect of interfacial morphology will predict the relative permeability reasonably well, the systematic approach to calculate the interface permeability will also determine the degree of accuracy of the morphology.

CONCLUSIONS

A brief review of the existing well-known gas permeation theoretical models has been discussed. Comparison and evaluation of the theoretical models for prediction of the relative permeability of CO₂ in Matrimid[®] 5218-CMS mixed matrix membranes (MMMs) has also been studied. Comparison of those models based on the widely used model validation criteria including absolute average relative error percent and standard deviation was conducted. For the models evaluated under ideal morphology, the comparison result showed a decrease in the absolute average relative error percent and standard deviation with the order as follows: Pal model > Lewis-Nielsen model > Maxwell model > Bruggeman model. And for the other models evaluated considering interfacial morphologies, the absolute average relative error percent and standard deviation showed a decrease in the order of Felske model > modified Felske model. Hence, the modified Felske model was found to describe the experimental data reasonably well for the prediction of relative permeability of CO₂ in Matrimid[®] 5218-CMS MMMs system. However, continuous work should be done for further evaluation of the theoretical models with experimental data for relative permeability of CO₂ in Matrimid[®] 5218-CMS MMMs.

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REFERENCES

Agari, Y. and T. Uno, 1986. Estimation on thermal conductivities of filled polymers. *J. Applied Polym. Sci.*, 32: 5705-5712.

- Bottcher, C.J.F., 1945. The dielectric constant of crystalline powders. *Recueil des Travaux Chimiques des Pays-Bas.*, 64: 47-51.
- Bruggeman, D.A.G., 1935. Berechnung verschiedener physikalischer Konstanten von heterogenen substanzen. *Annalen der Physik*, 24: 636-679.
- Cheng, S.C. and R.I. Vachon, 1969. The prediction of the thermal conductivity of two and three phase solid heterogeneous mixtures. *Int. J. Heat Mass Transfer*, 12: 249-264.
- Chung, T.S., L.Y. Jiang and S. Kulprathipanja, 2007. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog. Polym. Sci.*, 32: 483-507.
- Felske, J.D., 2004. Effective thermal conductivity of composite spheres in a continuous medium with contact resistance. *Int. J. Heat Mass Transfer*, 47: 3453-3461.
- Hashemifard, S.A., A.F. Ismail and T. Matsuura, 2010. Prediction of gas permeability in mixed matrix membranes using theoretical models. *J. Memb. Sci.*, 347: 53-61.
- Higuchi, W.I. and T. Higuchi, 1960. Theoretical analysis of diffusional movement through heterogeneous barriers. *J. Am. Pharm. Assoc. Sci.*, 49: 598-606.
- Lewis, T. and L. Nielsen, 1970. Dynamic mechanical properties of particulate-filled composites. *J. Applied Polym. Sci.*, 14: 1449-1471.
- Mahajan, R. and W.J. Koros, 2002. Mixed matrix membranes materials with glassy polymers (Part 1). *Polym. Eng. Sci.*, 42: 1420-1431.
- Maxwell, J.C., 1954. *A Treatise on Electricity and Magnetism*. Dover Publications, Mineola, New York.
- Moore, T.T., R. Mahajan, D.Q. Vu and W.J. Koros, 2004. Hybrid membrane materials comprising organic polymers with rigid dispersed phases. *AIChE J.*, 50: 311-321.
- Nielsen, L., 1973. Thermal conductivity of particulate filled polymers. *J. Applied Polym. Sci.*, 17: 3819-3820.
- Pal, R., 2007. New models for thermal conductivity of particulate composites. *J. Reinforced Plastic Compos.*, 26: 643-651.
- Pal, R., 2008. Permeation models for mixed matrix membranes. *J. Colloid Int. Sci.*, 317: 191-198.
- Shekhawat, D., D.R. Luebke and H.W. Pennline, 2003. A review of carbon dioxide selective membranes: A topical report, National Energy Technology Laboratory, United States Department of Energy. http://www.osti.gov/bridge/product.biblio.jsp?query_id=1&page=0&osti_id=819990.
- Shimekit, B., H. Mukhtar and S. Maitra, 2009. Ceramic membranes for the separation of carbon dioxide: A review. *Trans. Ind. Ceram. Soc.*, 68: 115-138.

- Singh, A. and W.J. Koros, 1996. Significance of entropic selectivity for advanced gas separation membranes. *Ind. Eng. Chem. Res.*, 35: 1231-1234.
- Steel, K., 2000. Carbon membranes for challenging gas separations. Ph.D. Dissertation, The University of Texas at Austin.
- Suda, H. and K. Haraya, 2000. Carbon molecular sieve membranes: preparation, characterization and gas permeation properties. *ACS. Symp. Ser.*, 744: 295-313.
- Vu, D.Q., W.J. Koros and S.J. Miller, 2002. High pressure CO₂/CH₄ separation using carbon molecular sieve hollow fiber membranes. *Ind. Eng. Chem. Res.*, 41: 367-380.
- Vu, D.Q., W.J. Koros and S.J. Miller, 2003a. Mixed matrix membranes using carbon molecular sieves I. Preparation and experimental results. *J. Memb. Sci.*, 211: 311-334.
- Vu, D.Q., W.J. Koros and S.J. Miller, 2003b. Mixed matrix membranes using carbon molecular sieves. II. Modeling permeation behavior. *J. Memb. Sci.*, 211: 335-348.
- World Intellectual Property Organization, 2009. High performance mixed matrix membranes incorporating at least two kinds of molecular sieves. <http://www.wipo.int/pctdb/en/wo.jsp?WO=2009061560&IA=US2008077481&DISPLAY=STATUS>.
- Zimmerman, C.M., A. Singh and W.J. Koros, 1997. Tailoring mixed matrix composite membranes for gas separations. *J. Membr. Sci.*, 137: 145-154.
- Zimmerman, C.M., 1998. Advanced gas separation membrane materials: hyper rigid polymers and molecular sieve-polymer mixed matrices, Ph.D. Dissertation, The University of Texas at Austin.