diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusion of Light Gases in 6FDA/BPDA-DAM Carbon Molecular Sieve Membranes by Pulsed Field Gradient NMR

Robert Mueller[1], *Rohit Kanungo*[1], *Mayumi Kiyono-Shimobe*[2], *William J. Koros*[2], *Sergey Vasenkov*[1]

[1] Department of Chemical Engineering, University of Florida, USA
[2] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, USA

Corresponding author: Sergey Vasenkov
University of Florida
Gainesville, FL, USA 32611
Email: svasenkov@che.ufl.edu

Abstract

In this paper, we demonstrate the potential of pulsed field gradient (PFG) NMR spectroscopy to reveal detailed knowledge of self-diffusion of light gases and light gas mixtures in carbon molecular sieve membranes on small length scales. PFG NMR is used to investigate intra-membrane diffusion of carbon dioxide and methane for a broad range of temperatures and mean square displacements in a carbon molecular sieve membrane derived from a 6FDA/BPDA-DAM polyimide film. Diffusion is investigated with single component sorbates as well as with a carbon dioxide / methane mixture. Results obtained from these studies are compared and discussed.

Keywords

Diffusion, CMS membranes, PFG NMR, separations

1. Introduction

The separation of commercially valuable light gases is a promising application of carbon molecular sieve (CMS) membranes, microporous carbon membranes formed by pyrolysis of polymers [1-4]. One attractive separation for CMS membranes is the separation of carbon dioxide / methane mixtures [3,5,6]. This separation is of great importance for natural gas and bio-gas applications where carbon dioxide is an abundant impurity. While there are many reports on macroscopic transport properties of CMS membranes investigated by permeation measurements

[2,4,7-9], there appears to be few reported investigations of microscopic transport. Knowledge of the latter can provide understanding of how light gases and their mixtures diffuse in CMS membranes on small length scales and how microscopic diffusion behaviour compares with macroscopic transport measurements.

2. Experimental

The CMS membrane used in this study was formed by the pyrolysis of 6FDA/BPDA-DAM polyimide thin films. Pyrolysis was conducted under an inert argon atmosphere with < 1 ppm of O_2 at a pyrolysis temperature of 550 °C. Interested readers are referred to refs. 1 and 7 for full synthesis details.

Pulsed field gradient (PFG) NMR measurement of CH_4 and CO_2 diffusion in the CMS membrane were performed using a 17.6 T wide-bore NMR spectrometer located at the University of Florida campus. Both ^{1}H and ^{13}C resonances were used in this work, with the latter used for a majority of the measurements to take advantage of the longer ^{13}C NMR relaxation times afforded for sorbate inside the studied CMS membrane. Magnetic field gradients were produced using a Diff60 gradient probe and Great60 gradient amplifier (Bruker Biospin) which can generate field gradients of up to 30 T/ m.

The stimulated echo with longitudinal eddy current delay (PGSTE LED) pulse sequence and the 13-interval pulse sequence [10] were used to measure PFG NMR attenuation curves *i.e.*, the dependence of the normalized PFG NMR signal intensity on the amplitude of the magnetic field gradient. The former pulse sequence was used for ^{13}C nuclei measurements, while the latter was used for ^{1}H nuclei measurements. The signal intensities were obtained by integrating the area under the NMR lines of the studied sorbates. It was verified that within the experimental uncertainty the line shape does not depend on the gradient amplitude. Diffusivities D were obtained from best fit of the PFG NMR attenuation curves with the following relation [10]

$$\Psi \equiv \frac{S(q)}{S(q=0)} = \exp(-D\,q^2 t_{eff}). \tag{1}$$

In Eq. 1, Ψ is the PFG NMR signal attenuation due to diffusion, S is the signal intensity, D is the self-diffusivity, t_{eff} is the effective diffusion time that corresponds to the time of the diffusion observation in the PFG NMR experiment and q is a convenient measure of the spatial labeling strength of the field gradients. For the PGSTE LED pulse sequence, $q = \gamma g \delta$ where γ is the gyromagnetic ratio, g is the amplitude of the field gradient and δ is the effective duration of a field gradient pulse. For the 13-interval pulse sequence, $q = 2\,\gamma g \delta$.

2. Results and Discussion

The measured PFG NMR attenuation curves were found to be in agreement with Eq. 1, *viz.* the attenuation data for each sorbate is consistent with isotropic diffusion with a single effective diffusion coefficient. It was observed that the attenuation curves measured for methane under identical or similar conditions by ^{1}H and ^{13}C PFG NMR yield the same self-diffusivities within the experimental uncertainty. This indicates that our PFG NMR data were not disturbed by magnetic susceptibility effects and were artefact-free.

PFG NMR studies were performed for a broad range of effective diffusion times between 9 and 319 ms. The corresponding values of the root mean square displacements (RMSDs), which were obtained from the measured attenuation curves using the Einstein relation and Eq. 1, were found to be between ~3 and ~18 µm. For this range of RMSDs the measured diffusivities correspond to intra-membrane diffusion coefficients because the largest value of RMSD is smaller than 1/3rd of the thickness of the membrane (~60 µm). Under these conditions, the measured diffusivities were found to be independent of the effective diffusion time.

Fig. 1 shows sorbate self-diffusivities measured for diffusion inside the membranes with one-component sorbate (CO_2 or CH_4) and two-component CO_2/CH_4 mixture at different temperatures used in this work. It is seen in Fig. 1 that the temperature dependence of self-diffusivity ($D(T)$) in the single component samples can be described using the Arrhenius relation

$$D(T) = D_0 \exp(-E_a/kT), \tag{2}$$

where E_a is the apparent activation energy of diffusion. Fitting the experimental diffusion data by this equation reveals that E_a is about 10 kJ / mol for both carbon dioxide and methane with a large experimental uncertainty of around a factor of two.

The data in Fig.1 show that for the membrane loaded with a single-component sorbate carbon dioxide has a higher self-diffusivity than methane at the same or comparable temperatures. It can also be seen in Fig. 1 that the self-diffusivity of carbon dioxide in the membrane sample with mixture sorbate and in the sample with only carbon-dioxide sorbate are the same within the experimental uncertainty. However, the self-diffusivity of methane in the mixture sample is about a factor of two smaller than that in the sample loaded only with methane. The reduction in the self-diffusivity of methane can be attributed to the hindrance of methane diffusion due to strong adsorption of carbon dioxide. The latter reduces the amount of free volume available for methane molecules to diffuse. Such an effect has been observed for carbon dioxide/methane mixtures in other micropores materials [11].

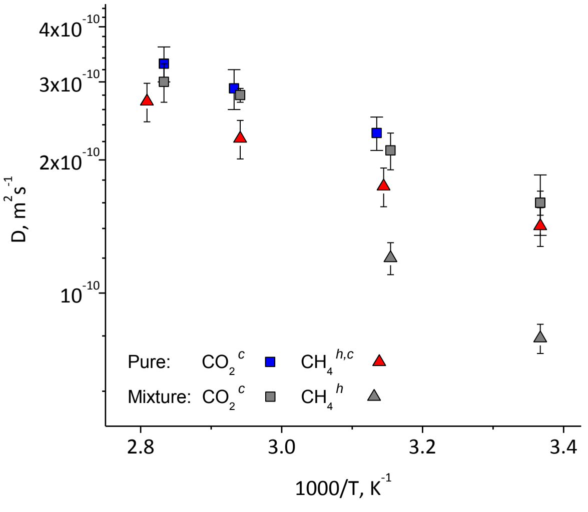

Fig. 1: Temperature dependence of sorbate self-diffusion coefficients in 6FDA/BPDA for: carbon dioxide in the sample loaded only with carbon dioxide at the pressure of 51 kPa (■), methane in the sample loaded only with methane at the pressure of 51 kPa (▲), carbon dioxide (■) and methane (▲) in the sample loaded with the mixture of carbon dioxide and methane at the partial pressures of 48 kPa and 46 kPa, respectively. The diffusivities were obtained by fitting PFG NMR attenuation curves with Eq. 1.

[c] data obtained using ^{13}C PFG NMR, [h] data obtained using ^{1}H PFG NMR

4. Conclusions

In this study, we demonstrated the potential of high field, high gradient PFG NMR to reveal intra-membrane diffusion behaviour of light gases and light gas mixtures in microporous membranes. Intra-membrane diffusion of carbon dioxide and methane was investigated for a broad range of temperatures and RMSDs in a CMS membrane derived from 6FDA/BPDA-DAM. It was observed that under the experimental conditions used the intra-membrane self-diffusion coefficients of sorbate molecules were independent of the values of RMSD. This provides evidence that the membrane has homogenous transport and related structural properties. For a binary carbon dioxide/methane mixture, the self-diffusivity of methane is significantly reduced relative to the membrane loaded only with methane at a similar partial pressure. Such diffusivity reduction is attributed to the decrease in the free volume available for methane diffusion due to co-adsorption of carbon dioxide, which occupies much larger intra-membrane pore volume than methane under the experimental conditions used. No significant differences were observed between the diffusivities of carbon dioxide in the membranes loaded only with carbon dioxide and with methane/carbon dioxide mixture.

Acknowledgements

We are grateful for the financial support of this work by the NSF CAREER award (CBET No. 0951812). NMR data were obtained at the Advanced Magnetic Resonance Imaging and Spectroscopy (AMRIS) facility located in the McKnight Brain Institute at the University of Florida. The NMR measurement time provided in the framework of the external user program of the National High Magnetic Field laboratory, AMRIS, is gratefully acknowledged.

References

[1] M. Kiyono, P.J. Williams, W.J. Koros, J. Membr. Sci. 359 (2010) 2-10.
[2] H. Suda, K. Haraya, J. Phys. Chem. B 101 (1997) 3988-3994.
[3] A.F. Ismail, L.I.B. David, J. Membr. Sci. 193 (2001) 1-18.
[4] P.S. Tin, T.-S. Chung, Y. Liu, R. Wang, Carbon 42 (2004) 3123-3131.
[5] L.M. Robeson, J. Membr. Sci. 320 (2008) 390-400.
[6] R.W. Baker, Ind. Eng. Chem. Res. 41 (2002) 1393-1411.
[7] M. Kiyono, P.J. Williams, W.J. Koros, Carbon 48 (2010) 4432-4441.
[8] K.M. Steel, W.J. Koros, Carbon 41 (2003) 253-266.
[9] H. Suda, K. Haraya, Chem. Commun. (1997) 93-94.
[10] R.M. Cotts, M.J. Hoch, T. Sun, J.T. Markert, J. Magn. Reson. 83 (1989) 252-266.
[11] C. Chmelik, J. van Baten, R. Krishna, J. Membr. Sci. 397–398 (2012) 87-91.