Diffusion of One- and Two-Component Gaseous Sorbates in Carbon Molecular Sieve Membranes by Multinuclear Pulsed Field Gradient NMR

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Introduction

Carbon molecular sieve (CMS) membranes are microporous carbon membranes formed by pyrolysis of polymers. CMS membranes represent a promising class of materials for "difficult" separations of gas mixtures such as carbon dioxide / methane and ethane / ethylene separations. While there are many reports on macroscopic transport properties of CMS membranes investigated by permeation measurements, until now there were no 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 behavior compares with macroscopic transport.

Experimental

The three CMS membrane used in this work were derived from 6FDA/BPDA(1:1)-DAM and Matrimid polymers. Carbon dioxide, methane, ethane and ethylene were used as sorbates. Diffusion studies were performed with one-component gases and also with selected two-component mixtures. Diffusion data were obtained by H-1 and C-13 pulsed field gradient (PFG) NMR using a wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida. Magnetic field gradients with the amplitude up to 30 T/m were generated using diff60 diffusion probe and Great60 gradient amplifier (Bruker BioSpin).

Results and Discussion

Intra-membrane diffusion of the gaseous sorbates in the CMS membranes was investigated for a broad range of temperatures and root mean square displacements (RMSDs). It was observed that the intra-membrane self-diffusion coefficients of sorbate molecules were independent of the values of RMSD [1,2]. This provides evidence that the membranes have homogenous transport and related structural properties. **Figure 1** shows sorbate self-diffusivities measured for diffusion inside a selected membrane 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 that the self-diffusivity of methane in the membrane loaded with CO_2/CH_4 mixture 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 [1,2].

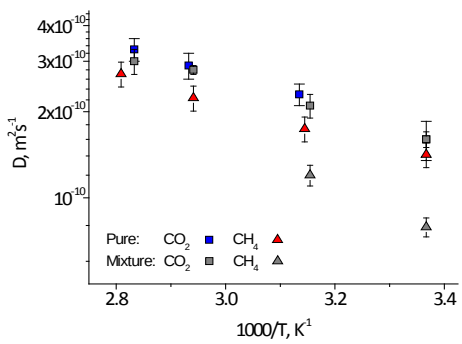

Figure 1. Temperature dependence of sorbate self-diffusion coefficients in 6FDA/BPDA CMS for: CO_2(■) in the sample loaded only with CO_2, CH_4 (▲) in the sample loaded only with CH_4, CO_2(■) and CH_4(▲) in the sample loaded with the CO_2/CH_4 mixture.

Conclusions

Here we demonstrate the potential of high field, high gradient PFG NMR to reveal intra-membrane diffusion behavior of light gases and light gas mixtures in microporous membranes.

Acknowledgements

We are grateful for the financial support of this work by the NSF CAREER award (CBET No. 0951812) and by the external user program of the NHMFL (project No. P01239).

References

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[2] Mueller, R., *et al*., Langmuir **28**, 10296-10303 (2012).