Self-Diffusion of Ethane and Ethylene in Carbon Molecular Sieve Membranes by Pulsed Field Gradient NMR

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Introduction

The separation of commercially valuable light olefins from mixtures containing their paraffin analogs (e.g., ethylene/ethane, propylene/propane) has attracted increased attention of the scientific community over the recent years. Current industrial scale separations of such mixtures are, for the most part, performed via distillation, which is an energy expensive process because of low temperature and high pressure requirements. Separations using carbon molecular sieve (CMS) membranes, microporous membranes formed by pyrolysis of glassy polymers, represent one potential alternative technology with low or zero energy requirements. Despite the importance of mass transport in these materials there have been no reported diffusion studies of C_2 (or larger) hydrocarbons in CMS membranes using microscopic techniques. In this work, a pulsed field gradient (PFG) NMR technique employing high magnetic field and large magnetic field gradients enabled the measurement of microscopic self-diffusion of ethane and ethylene in selected CMS membranes.

Experimental

The following precursor polymers and pyrolysis conditions were used to form the studied CMS membranes: 6FDA/BPDA:DAM polyimide pyrolyzed under inert argon atmosphere with <1 ppm of O_2 (6FDA/BPDA), Matrimid® polyimide pyrolyzed under inert argon atmosphere with <1 ppm of O_2 (Matrimid (Inert)) and Matrimid® polyimide pyrolyzed under vacuum (Matrimid (Vacuum)). 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

Fig. 1 presents intramembrane self-diffusivities of ethane and ethylene in the CMS membranes for temperatures between 297 and 352 K in an Arrhenius plot (i.e., D vs. 1000/T).[1] The data in Fig. 1 demonstrate that the self-diffusivity of ethylene is larger than that of ethane in the same CMS membrane at the same or similar temperature. Owing to the similarities in molecular sizes of ethane and ethylene, the observed diffusivity difference can be mostly related to entropic effects, viz. the difference in the number of available configurations of these two types of molecules in the slit-like ultramicropores that are believed to be responsible for molecular sieving in CMS membranes. It is seen in Fig. 1 that the extrapolated microscopic self-diffusivities are smaller than the corresponding macroscopic transport diffusivities (from permeation) reported in the literature. This difference was attributed to a concentration dependence of diffusivities in the limit of small sorbate concentrations.[1]

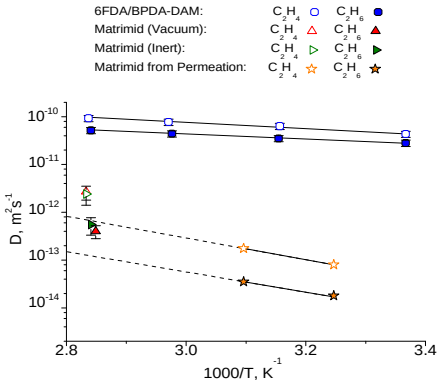

Fig. 1. Temperature dependence of sorbate diffusivities in CMS membranes.

Conclusions

In this work, PFG NMR technique employing high magnetic field and large magnetic field gradients enabled the measurement of microscopic self-diffusion of ethane and ethylene in CMS membranes.

Acknowledgements

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References

[1] Mueller, R., *et al*., Microporous and Mesoporous Materials **181**, 228-232 (2013).