Relationship between Long-Range Diffusion and Diffusion in the ZIF-8 and Polymer Phases of a Mixed-Matrix Membrane by High Field NMR Diffusometry

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Introduction

Mixed matrix membranes (MMMs) are heterogeneous membranes, which typically consist of molecular sieve particles dispersed in a polymeric matrix. These embedded molecular sieve particles commonly consist of zeolites or, increasingly, metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs), a subset of metal-organic frameworks that are topologically isomorphic with zeolites. MMMs are of intense interest in the scientific community owing to their potential for high-performance gas separations. In this work PFG NMR is applied to resolve different modes of ethene self-diffusion inside a mixed-matrix membrane (MMM) consisting of ZIF-8 particles embedded in 6FDA-DAM polymer.

Experimental

Samples of MMM were prepared in the laboratory of Prof. Ryan Lively. Diffusion data were obtained by C-13 PFG NMR using a wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida. Magnetic field gradients with the amplitude of up to 30 T/m were generated using diff60 diffusion probe and Great60 gradient amplifier (Bruker BioSpin).

Results and Discussion

In Fig. 1a the self-diffusivities measured for the ZIF-8 and polymer ensembles of ethane molecules in the MMM are compared with the corresponding diffusivities in the bed of ZIF-8 particles and 6FDA-DAM polymer samples for a broad range of diffusion times between 11 ms and 1.0 s. Fig. 1b presents the measured time dependence of the effective ethene diffusivity, which is expected to be a representative diffusivity for the whole MMM.

Conclusions

The reported studies allowed for the first time the resolution of self-diffusion properties of the ZIF-8 particles and the surrounding polymer in MMMs on different length scales.

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References

[1] Mueller, R. *et al*., J. Membr. Sci., submitted (2014).

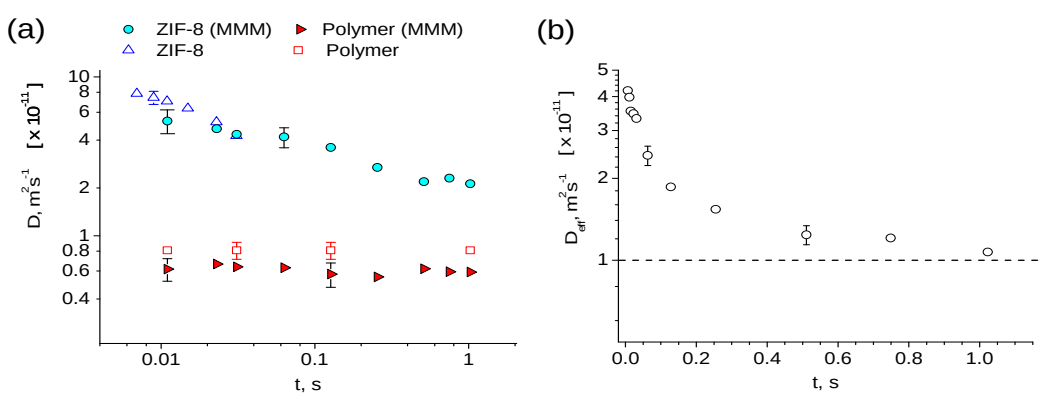

Fig.1 Time dependencies of ethene diffusivities at 298 K. (a) Data obtained using the two-ensemble diffusion in the MMM sample (filled symbols). Also shown are the time dependencies of the corresponding intra-ZIF and intrapolymer diffusivities (unfilled symbols). (b) Effective self-diffusion coefficients obtained from mono-exponential regression of the initial slope of the PFG NMR attenuation curves measured in the MMM sample. The dotted line is the long-range diffusivity obtained by the proposed model [1].