Diffusion of Organic Molecules in Nafion® by Pulsed Field Gradient NMR

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Introduction

Perfluorosulfonic acid (PSA) polymer membranes, such as the commercially available Nafion®, combine high ion permselectivity with chemical durability and are among the most promising candidates for novel applications including optodes for chemical sensing and personal protective clothing. There presently exists a significant gap in scientific knowledge concerning the transport mechanisms of a number of environmentally and industrially significant organic compounds inside Nafion® and other PSA polymer membranes. Such lack of understanding hinders progress in the rational formulation and processing of these materials aiming to optimize permselectivity while retaining chemical durability in the important new applications listed above.

Experimental

^{13}C and ^{1}H pulsed field gradient (PFG) NMR at 14 T was used to study self-diffusion of C-13 labeled vanillic acid and acetone in Nafion® at 296 K. For loading Nafion® membrane with vanillic acid, the membrane was submerged in a saturated vanillic acid in D_2O solution. For loading with acetone, the membrane was exposed to around 120 mbar of acetone vapor in a vacuum system for 3 hours.

Results and Discussion

Figures 1 and 2 show examples of the PFG NMR attenuation curves measured in the Nafion® samples for diffusion of C-13 labeled vanillic acid and acetone, respectively. For both types of guest molecules the attenuation curves show a deviation from a monoexponential behavior. The monoexponential behavior is expected when all molecules of a particular type in a sealed sample diffuse with the same diffusivity. It was observed that the following equation assuming the existence of two molecular ensembles diffusing with different diffusivities can be used to fit the data satisfactorily:

$$\Psi = p_1 \exp(-q^2 D_1 t_{eff}) + p_2 \exp(-q^2 D_2 t_{eff}), \qquad [1]$$

where p_1 and p_2 represent the fractions of the diffusion ensembles, D_1 and D_2 are the corresponding diffusivities of the ensembles, $q=2\gamma g\delta$, γ is the gyromagnetic ratio, δ is the effective gradient pulse length, t_{eff} is the diffusion time, and g is the gradient amplitude. For vanillic acid, the larger diffusivity was assigned to diffusion in the water solution outside the membrane, while the smaller diffusivity (2×10^{-11} m^2s^{-1}) was assigned to intramembrane diffusion. For acetone, both measured diffusivities (2×10^{-11} m^2s^{-1} and 3×10^{-12} m^2s^{-1}) were assigned to diffusion inside the membrane where domains with different transport properties are expected. The nature of these domains is currently under investigation.

Conclusions

PFG NMR was successfully applied to generate first data on microscopic diffusion of vanillic acid and acetone in Nafion®.

Acknowledgements

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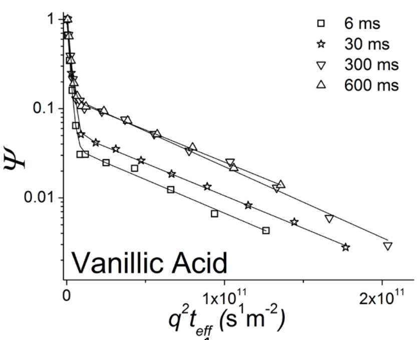

Fig.1 Examples of ^{1}H PFG NMR attenuation curves for diffusion of vanillic acid in a Nafion® membrane at different diffusion times. Solid lines show the best fit results using Eq. 1.

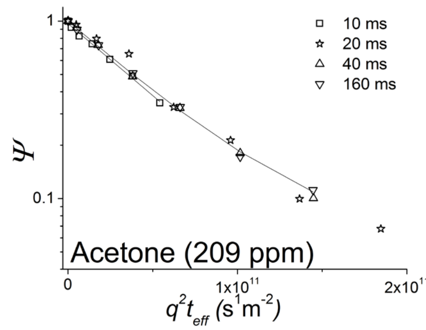

Fig.2 Examples of ^{13}C PFG NMR attenuation curves for acetone diffusion in a Nafion® membrane at different diffusion times. Solid line shows the result of fitting the data using Eq. 1.