Molecular diffusion in membranes and related systems by high field NMR

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Combining advantages of high magnetic field and large magnetic field gradients in diffusion NMR studies can allow elucidating influence of microscopic structural properties of membranes and porous sorbents on gas and liquid diffusion in these materials. In this seminar, I will present most recent examples of such studies performed in my group. The first example is related to metal-organic framework materials (MOFs), which consist of metal centers interconnected by organic linkers. Gas diffusion in MOFs will be discussed as a function of the fraction of a "native" organic linker substituted by a different linker type. Such systematic linker substitution can allow modifying transport properties of these materials and make them more attractive for applications in gas separations. I will also demonstrate that diffusion NMR can be used to detect and quantify transport properties of defects that can form at the interfaces between MOF crystals and a polymer phase in mixed-matrix membranes (MMMs), which are formed by dispersing MOF crystals in a polymer. In such membranes, a completely restricted diffusion of liquid molecules was observed inside microscopic pockets of free volume formed at the interfaces. Finally, diffusion of acetone and water in Nafion will be discussed as a function of molecular displacement on the micrometer and sub-micrometer length scales. Nafion is a commercially available perfluorosulfonic acid (PSA) polymer, which exhibits phase separation. The Nafion structure in the presence of water consists of a hydrophobic crystalline matrix made of backbone of polytetrafluoroethylene and channels available for water diffusion. These channels are formed by the ionic side chains containing sulfonic groups. Our diffusion data demonstrate that at low water concentrations and in the presence of acetone, water experiences a significant stepwise decrease in the self-diffusivity with increasing root mean square displacement in Nafion at around a 5 micrometer length scale. This is in agreement with Percolation Theory that, at some sufficiently small water concentration, the hydrophilic water channels of the membrane form finite clusters and are no longer interconnected into a spanning (infinite) percolation cluster. The knowledge of such anomalous diffusion behavior is required for the development of Nafion applications. In particular, it can be used as a very sensitive acetone sensor.