PFG ^{1}H NMR Studies of Water Diffusion in Zeolite Beds

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Introduction

The diffusion of water in zeolites is important to understanding the material's performance. This laboratory has used pulsed field gradient (PFG) ^{1}H NMR spectroscopy to study diffusion of water in type 3A (pore = 3Å) and type 4A (pore = 4Å) zeolite beds. The water diffusion rates were studied as a function of temperature and loadings. The pore size in type 3A zeolite is reduced due to the substitution of K^+ for the Na^+ of a type 4A zeolite. This reduction in pore size is expected to diminish the observed diffusion rate of water.

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Experimental

Sample Preparation:

- Zeolites 3A and 4A, Aldrich were dried under vacuum at 250°C for 24 hours.
- Based on the desired concentration, approximately 100 mg 3A or 4A was added to 5mm sample tubes containing water.
- The weights of sealed sample tubes were monitored to detect leaks.
- Samples were stored at room temperature.
- Weight % was calculated by: $\frac{H_2O\ weight}{zeolite\ weight + H_2O\ weight}$

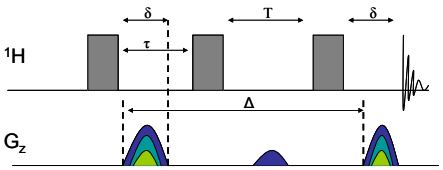
NMR Spectroscopy:

- Experiments were performed on a Bruker DRX400.
- Diffusion measured using stimulated echo (STE).
- Decay of signal monitors a function of gradient strength.
- The root mean square displacement length corresponds to

$$l_{Diff} = \sqrt{\langle z^2(\Delta)\rangle} = \sqrt{2D\Delta}$$

with a single gradient measuring displacement in the z direction.

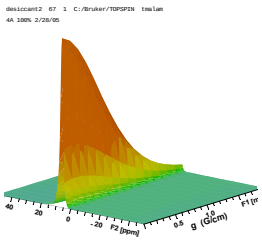
PFG STE



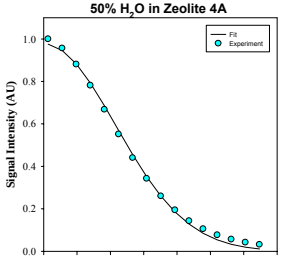
$$S(T+2\tau_1) = \frac{M_0}{2}\exp(-2\tau_1/T_2 - T/T_1)\exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right]$$

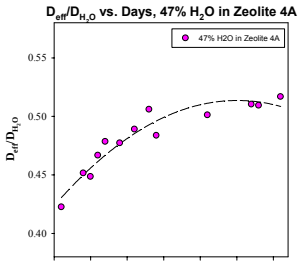
Where:
T_1= spin lattice relaxation time
T_2= spin-spin relaxation time
δ= length of gradient pulse
Δ= inter pulse delay
g= gradient strength
D= diffusion constant
γ= gyromagnetic ratio

Typical PFG Results:



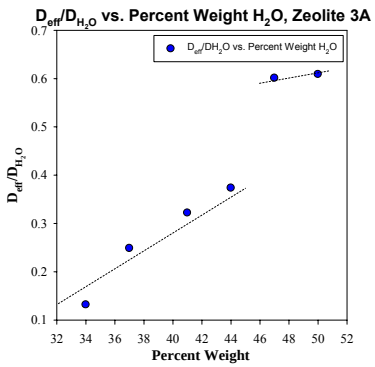
- ^{1}H signal of the H_2O decays as a function of gradient strength

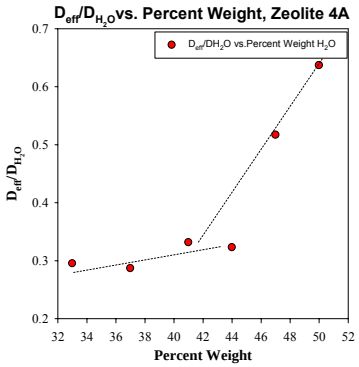


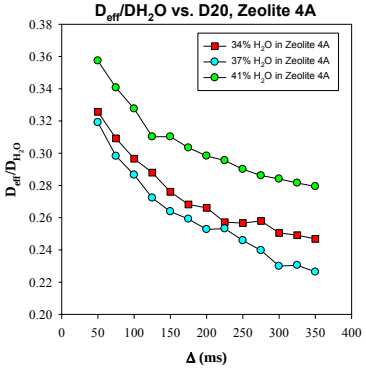


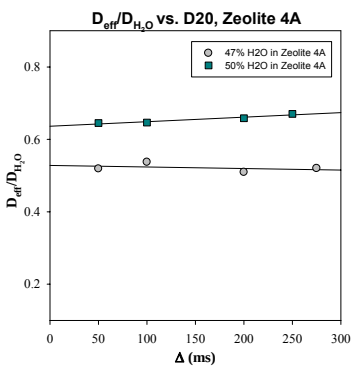
- Samples require long equilibrium times.

Diffusion Studies:

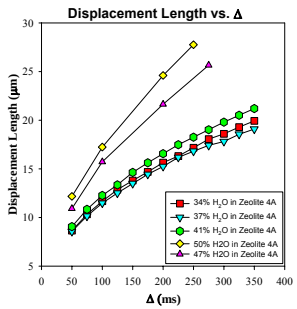




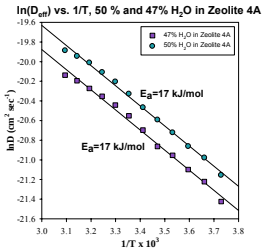


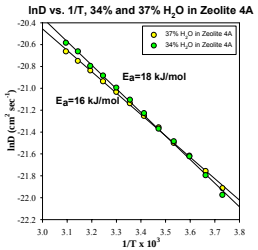


Δ Dependence of D:



Temperature Dependence of D





Conclusions

- PFG NMR can be used to measure the diffusion properties of water in zeolites.
- D_{eff} is a function of loading, and this loading effect differs between 3Å and 4Å.
- Variation in D_{eff} is a function of Δ, i.e. diffusion period.
- D_{eff} decreases with increasing Δ.
- Temperature dependence of D_{eff} with loading small.
- The decrease in D_{eff} with increasing Δ suggests the importance of surface interactions.
- We are in the regime l_{diff} >>> R_{pore}> particle size. Therefore, the effects we see are inter-particle, long-range diffusion.