

## Electronic Supplementary Information

# Influence of vanillic acid immobilization in Nafion membranes on intramembrane diffusion and structural properties

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Table S1: Comparison of  $^1\text{H}$   $T_1$  and  $T_2$  relaxation times for water and acetone between VA functionalized and Non-functionalized Nafion membranes at 2 example concentrations, each measured at 17.6 T and 296 K. The experimental uncertainty of the relaxation times is around 25%.

Membrane Type	Water Concentration (mmol/g)	Acetone Concentration (mmol/g)	$T_{2\text{water}}$ (ms)	$T_{2\text{acetone}}$ (ms)	$T_{1\text{water}}$ (s)	$T_{1\text{acetone}}$ (s)
Non-functionalized Nafion	$1.4 \pm 0.3$	$0.47 \pm 0.09$	16	5.3	0.4	1.3
	$2.0 \pm 0.5$	$0.74 \pm 0.15$	40	53	0.4	1.7
VA Functionalized	$1.4 \pm 0.3$	$0.47 \pm 0.09$	2.6	1.1	0.5	2.8
	$2.0 \pm 0.5$	$0.77 \pm 0.15$	20	13	0.3	1.4

Table S1 offers an example comparison of NMR relaxation times between VA-functionalized and non-functionalized Nafion. The addition of VA to the Nafion membranes results in shorter  $T_2$  relaxation times for both diffusing molecules, which causes problems with acquiring NMR signal at large diffusion times.

Table S2: Water self-diffusion data as a function of diffusion time in VA-functionalized Nafion at 296K obtained from fitting the PFG NMR attenuation data in Fig 1 using Eq. 4. Acetone and water concentrations were 0.47mmol/g and 1.4mmol/g, respectively.

Diffusion time (ms)	$D_1 \times 10^{12}$ ( $\text{m}^2/\text{s}$ )	$D_\infty \times 10^{12}$ ( $\text{m}^2/\text{s}$ )	$p_1^{**}$	$p_\infty^{**}$
8.7	$7.7 \pm 0.8$	n/a <sup>†</sup>	1	0
19	$8.2 \pm 0.8$	n/a <sup>†</sup>	1	0
39	$7.7 \pm 0.8$	n/a <sup>†</sup>	1	0
79	$7.6 \pm 0.8$	n/a <sup>†</sup>	1	0
160	$7.0 \pm 0.7$	n/a <sup>†</sup>	1	0
320	$6.2 \pm 0.9$	$2.2 \pm 0.2^\ddagger$	0.98	0.02
640	$5.8 \pm 0.9$	$2.2 \pm 0.2^\ddagger$	0.87	0.13
1280	$9.1 \pm 0.9$	$2.2 \pm 0.2^\ddagger$	0.65	0.35
2560	n/a <sup>†</sup>	$2.3 \pm 0.2$	0	1
4000	n/a <sup>†</sup>	$2.2 \pm 0.2$	0	1

\*Experimental uncertainty of the self-diffusivity is large because the fraction of molecules corresponding to this self-diffusivity is small. \*\*Uncertainty values for  $p_1$  and  $p_\infty$  are  $\pm 0.05$ . <sup>†</sup> "n/a" indicates that Eq. 1 corresponding to a single diffusing ensemble was used to fit the data. At low diffusion times, the single  $D$  value is labelled  $D_1$ . At large diffusion times, the  $D$  is designated as  $D_\infty$ . <sup>‡</sup>These values were constrained to be equal to the  $D_\infty$  values at high diffusion times (2560 – 4000 ms).

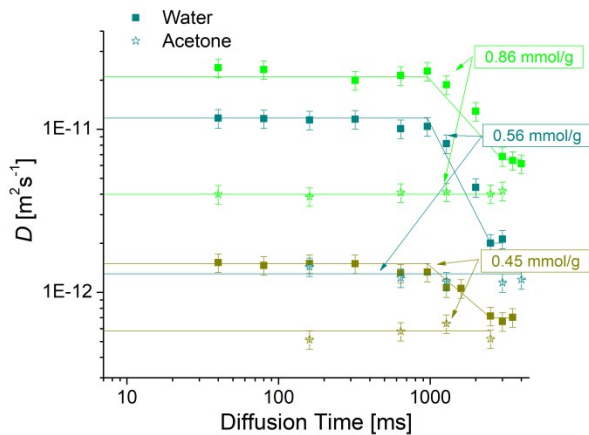


Figure S1. Dependence of the measured self-diffusivities of acetone (stars) and water (squares) on diffusion time in VA functionalized Nafion membranes at 296 K. Water concentration in Nafion was held constant at  $\sim 2$  mmol/g. Solid lines are guidelines shown as visual aids.

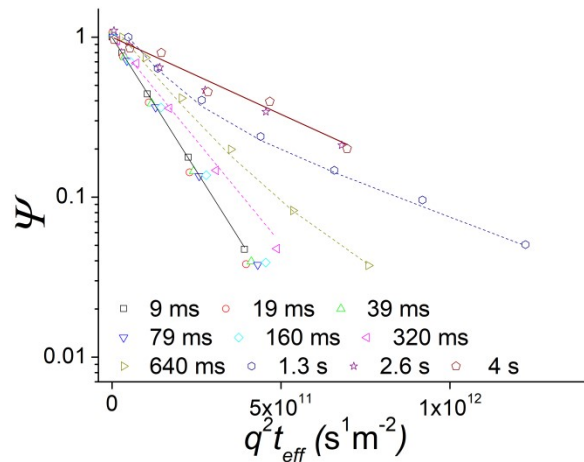


Figure S2. Examples of  $^1\text{H}$  PFG NMR attenuation curves for water in VA-functionalized Nafion membranes at 296 K. The intramembrane concentrations of acetone and water were around 0.47 mmol/g and 1.4 mmol/g, respectively. Solid lines represent the best fit lines using Eq. 1 for the range of the diffusion times showing coinciding data, within uncertainty. Dashed lines represent a biexponential fit using Eq. 3 for the water attenuation curves showing deviations from the monoexponential behavior.

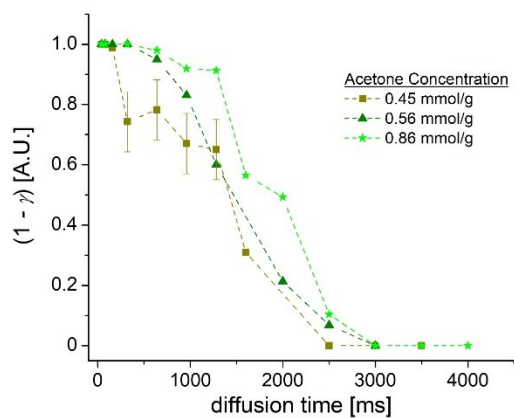


Figure S3. Fraction of water molecules ( $1-\gamma$ ) which remain in the same domain of interconnected water channels after a certain diffusion time plotted as a function of this diffusion time for VA functionalized Nafion membranes loaded with 2.0mmol/g water and varying acetone concentrations

When considering data in Figs. S4, S5, S7-S10, which report SAXS and QENS data, it needs to be taken into account that there is an estimated residual water content in the membranes of around 0.7 mmol/g before any acetone and/or D<sub>2</sub>O were added (see section 2.1 for more details)

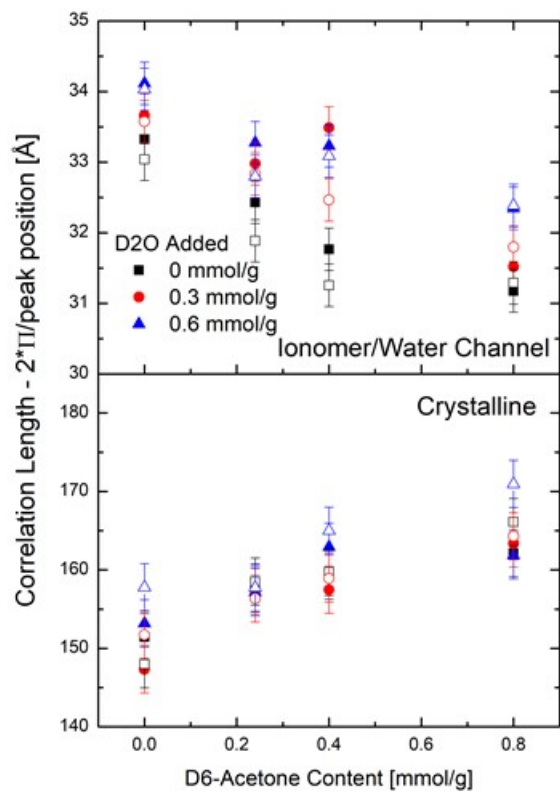


Figure S4. SAXS peak position as a function of acetone concentration in non-functionalized Nafion (filled points) and VA functionalized Nafion (empty points) at 296 K. The data are presented for different added  $D_2O$  concentrations shown in the figure.

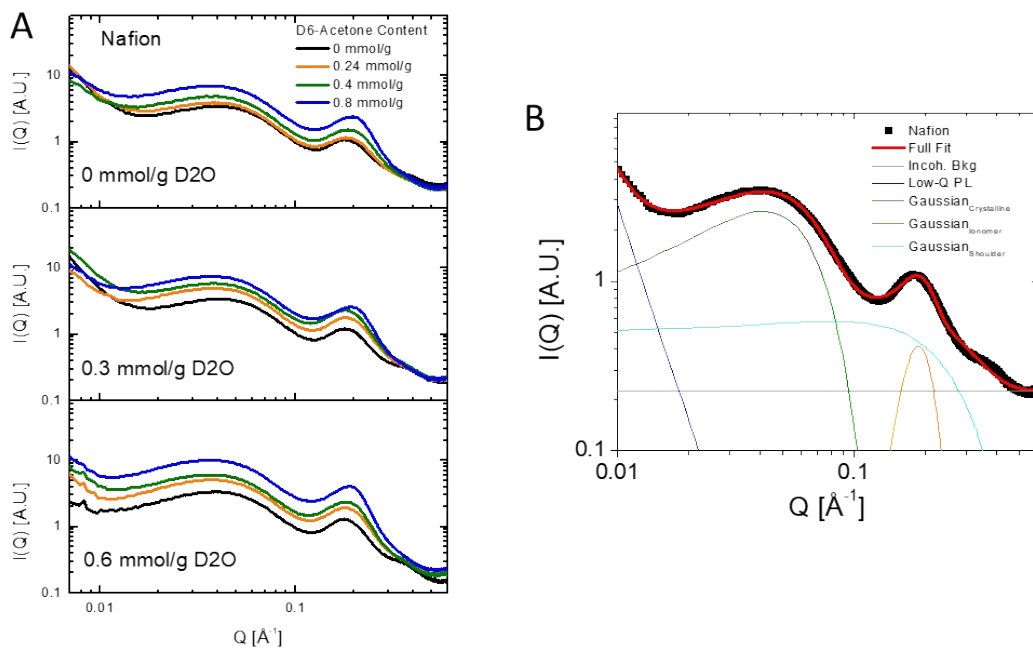


Figure S5. (A) SAXS spectra. (B) Example data fitting for SAXS spectra, shown here for unmodified Nafion. Here,  $Q$  refers to the scattering wave vector. Peak positions are reported as the center of the Gaussian functions used.

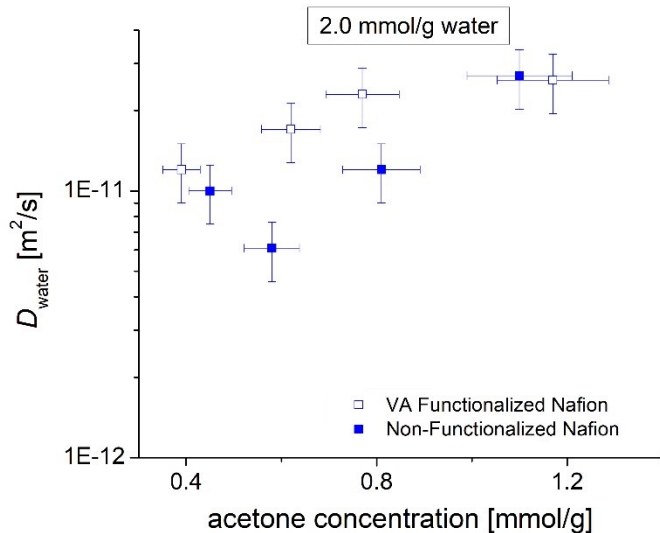


Figure S6. Self-diffusivities measured with PFG NMR at 296 K for water in Nafion in the limit of short diffusion times at a constant, within uncertainty, water concentration of around 2 mmol/g. The data are shown for non-functionalized Nafion (filled points) and Nafion functionalized with VA (empty points).

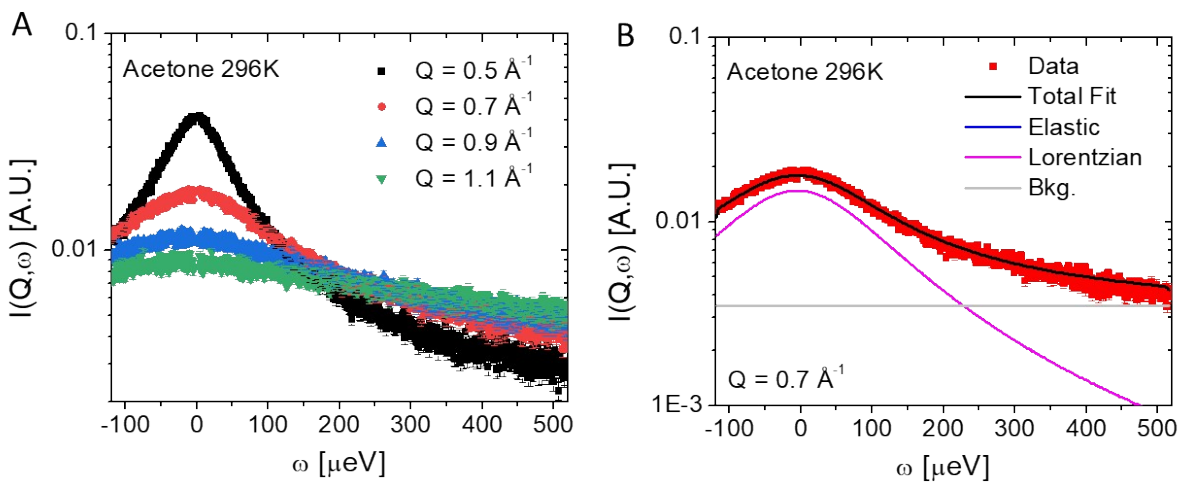


Figure S7. QENS spectra for liquid acetone at 296K as a function of scattering wave vector (A) showing the  $q$ -dependent broadening of the spectra indicating shorter diffusion times at smaller distances. (B) QENS spectra were fitting using an elastic component to represent immobilized molecules, a Lorentzian function to describe diffusing acetone molecules, and a flat background. This was performed at each  $Q$ -value. (Here  $q$  represents the scattering wave vector.)

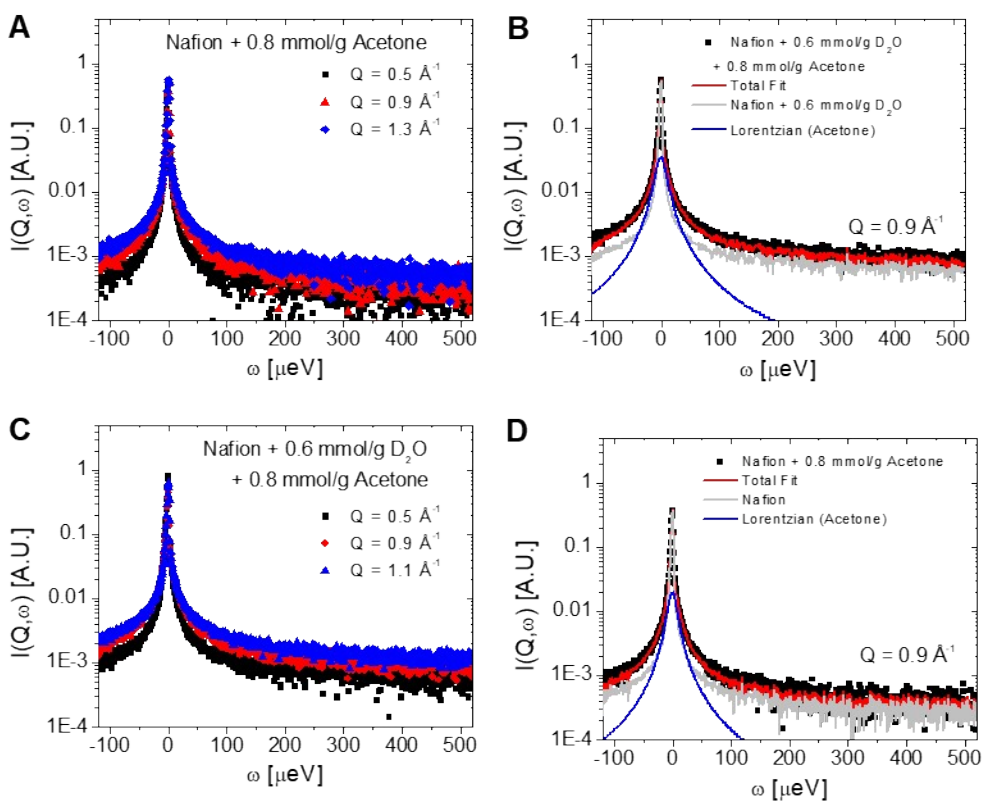


Figure S8. QENS data for acetone loaded in Nafion with and without 0.6 mmol/g  $D_2O$ . (A) QENS spectra for Nafion loaded with acetone; a broadening in the spectra is observed with increasing  $Q$ . (B) Data fitting used an acetone free Nafion measurement to represent the elastic intensity and any polymer motions and a Lorentzian function to represent acetone diffusion, this fitting was applied at all  $Q$ -values. (C) QENS spectra for Nafion loaded with acetone in the presence of  $D_2O$ ; a broadening in the spectra is again observed with increasing  $Q$ . (D) Data fitting used an acetone free Nafion measurement with an equivalent water content added to represent the elastic intensity and any polymer motions and a Lorentzian function to represent acetone diffusion, this fitting was applied at all  $Q$ -values. (Here  $Q$  represents the scattering wave vector.)



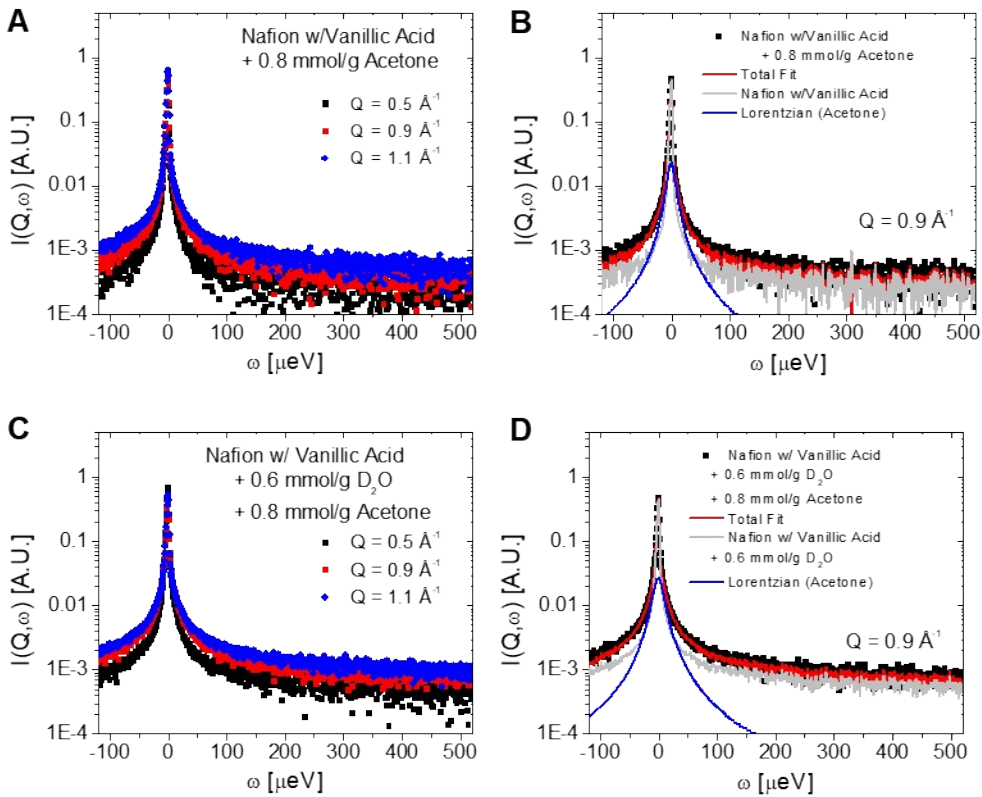


Figure S9. QENS data for acetone loaded in Nafion with VA with and without 0.6 mmol/g  $D_2O$ . (A) QENS spectra for Nafion with VA loaded with acetone; a broadening in the spectra is observed with increasing  $Q$ . (B) Data fitting used an acetone free Nafion with VA measurement to represent the elastic intensity and any polymer motions and a Lorentzian function to represent acetone diffusion, this fitting was applied at all  $Q$ -values. (C) QENS spectra for Nafion with VA loaded with acetone in the presence of  $D_2O$ ; a broadening in the spectra is again observed with increasing  $Q$ . (D) Data fitting used an acetone free Nafion with VA measurement with an equivalent water content added to represent the elastic intensity and any polymer motions and a Lorentzian function to represent acetone diffusion, this fitting was applied at all  $q$ -values.

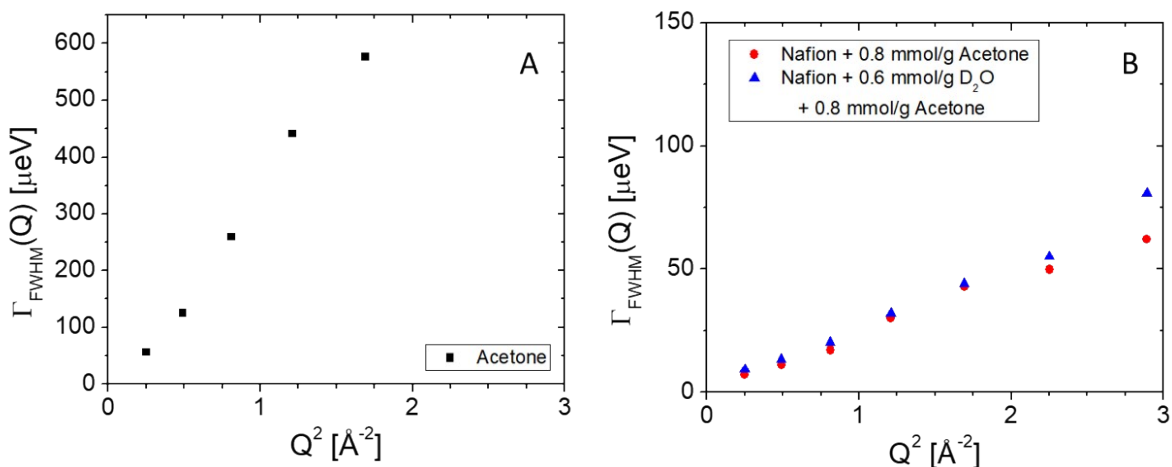


Figure S10. QENS measurements of acetone diffusion are quantified using the full width at half max (FWHM) of the Lorentzian function used in fitting the spectra at each  $Q$ -value. Diffusion is expected to follow a  $Q^2$  dependence; this is illustrated by the linear dependence of the FWHM versus  $Q^2$ . The slope is the diffusion coefficient, showing that acetone diffuses faster in bulk acetone (A) than in the studied Nafion samples loaded with acetone (B).

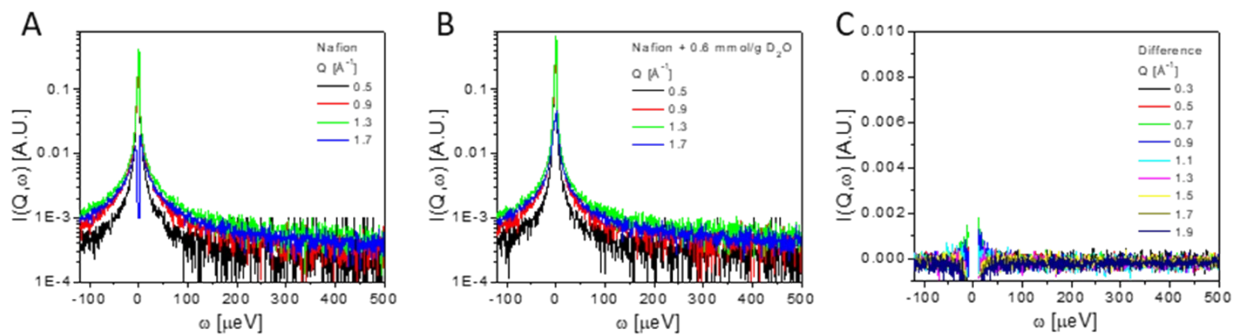


Figure S11. QENS data for activated Nafion (A) and activated Nafion with added 0.6 mmol/g  $D_2O$  (B) as well as the corresponding difference spectra (C) for selected  $Q$ -values. The small differences resulting from the added  $D_2O$ , are comparable with uncertainty. They can be a consequence of the residual  $H_2O$  becoming partially mobile and/or changes in polymer motions due to the increasing hydration.