Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 534–536

Mobility of water molecules in Li^+, Na^+ and Cs^+ ionic forms of Nafion membrane studied by NMR

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Extruded N117 (thickness 183 μm, equivalent weight (*EW*) = 1100, Dupont, Ion Power Inc.) membranes were used for the experimental characterization of Nafion in salt (Li^+, Na^+, Cs^+) ionic form.

High resolution ^{1}H spectra were recorded on the AVANCE-III-500 Bruker NMR spectrometer (proton Larmor frequency is 500 MHz) in the temperature range from –40 ºC to +60 ºC. The ^{1}H chemical shift was calculated relative to the bulk water ^{1}H NMR signal ($\delta_{\mathrm{H2O}} = 4.30$ ppm relative to TMS), chemical shift measurement error was less than 0.05 ppm.

NMR spectra of ^{1}H nuclei belonging to water molecules represent singlet lines, whose width is small even at temperatures below 0 ºC, which indicates the high water mobility at low temperature.

Obtained temperature dependences of water molecules ^{1}H chemical shift enables to calculate the hydration numbers h of Li^+, Na^+ and Cs^+ cations in Nafion 117 membrane using equation (1).[S1]

$$h = \lambda \left[1 - \frac{\frac{d\delta}{dt}}{\frac{d\delta_{H_2O}}{dt}} \right] \qquad (1)$$

where $d\delta/dt$ is the temperature dependence of the chemical shift of ^{1}H nuclei in the membrane; $d\delta_{\mathrm{H2O}}/dt$ is is the temperature dependence of the chemical shift of ^{1}H nuclei in the bulk water.[S1] Chemical shift temperature dependences were linearly approximated; slopes of the lines compised –0.0048, –0.0035, –0.0039 and –0,0106 for Li^+, Na^+, Cs^+ cations and bulk water, respectively. Values λ (amount of water molecules per sulfonate group at *RH* = 75% were 6.4, 5.1, 1.5 and hydration numbers) $h = 3.3 \pm 0.4$, 3.3 ± 0.4 and 0.5 ± 0.2, for Li^+, Na^+ and Cs^+ cations, respectively.

Diffusion coefficients were measured on ^{1}H nuclei by pulsed field gradient technique at the frequency 400.22 MHz on Bruker AVANCE-III-400 NMR spectrometer, equipped with the diff60 gradient unit. The pulsed field gradient ‘stimulated echo’ sequence was used.[S1–S3]

The evolution of spin echo signal (diffusion decay) is described by the following equation:

$$A(g) = A(0)\exp(-\gamma^2 g^2 \delta^2 t_d D_s), \qquad (2)$$

where γ is gyromagnetic ratio, g is gradient pulse amplitude, δ is gradient pulse duration, $t_d = \Delta - \delta/3$ is the diffusion time, Δ is an interval between gradient pulses and D is the diffusion coefficient.

Experimental diffusion decays are well approximated by equation (2) in 2–3 orders of magnitudes, diffusion coefficient measurement error was less than 10%.

Spin–lattice (T_1) and spin–spin (T_2) nuclear relaxation times of ^{1}H nuclei were measured using 180º-τ-90º and Carr-Purcell-Meiboom-Gill (90º-τ-n180º) pulsed sequences, correspondingly. Longitudinal magnetization M_z recovery and transverse magnetization $M_{x.y}$ decays were approximated by exponential dependences; measurement error was less than 10%.

Spin of ^{1}H nuclei is 1/2, therefore spin relaxation occurs due to proton dipole–dipole interaction modulated by water molecule mobility. In the case of exponential correlation function relaxation times described by Bloembergen, Purcell and Pound (BPP) equations.[S1,S2,S4]

$$\frac{1}{T_1} = \frac{2}{3}\gamma^2\langle\Delta H^2\rangle\left(\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{4\tau_c}{1+(\omega\tau_c)^2}\right) \tag{3}$$

$$\frac{1}{T_2} = \frac{1}{3}\gamma^2\langle\Delta H^2\rangle\left(3\tau_c + \frac{5\tau_c}{1+(\omega\tau_c)^2} + \frac{2\tau_c}{1+(2\omega\tau_c)^2}\right) \tag{4}$$

$$\langle\Delta H^2\rangle = \frac{9\gamma^2\hbar^2}{20r^6} \tag{5}$$

$$\tau_c = \tau_{c_0} exp\left[\frac{E_c}{RT}\right] \tag{6}$$

where h is Plank constant, r is the distance between protons, γ is proton gyromagnetic ratio, ω is proton NMR frequency, τ_c is correlation time.

In this instance the dependence of T_1 *vs.* T^{-1} posesses Lorentz shape and shows minimum at condition $\omega\tau_c = 0.62$. At this temperature T_1/T_2 is equal to 1.6.

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