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

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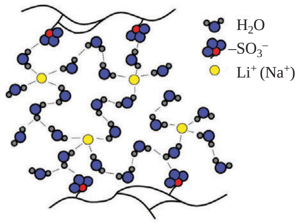
Correlation times and diffusion coefficients of water molecules were measured for the first time by ^1H spin relaxation and pulsed field gradient NMR in Li^+, Na^+ and Cs^+ ionic forms of Nafion 117 membrane. Hydration numbers of Li^+, Na^+ and Cs^+ cations were calculated. It was shown that at high humidity macroscopic transfer is controlled by the local translational motion of water molecules.



Keywords: Nafion membrane, hydration number, water diffusion, ^1H NMR relaxation times, correlation time.

Sulfonic cation-exchange membranes are widely applied in modern ionic separation electrochemical processes.[1,2] Interconnection between transport channels nanostructure, cations hydration as well as ionic and molecular mobilities in different spatial scales should be revealed to establish the transport mechanism. NMR is successfully used to obtain the structural and dynamic characterisctics of the complex molecular systems.[3–5] The preferred methods to determine the molecular and ionic mobility in polymer electrolytes are nuclear spin relaxation and pulsed field gradient NMR (PFG NMR).

The most fundamental results revealing the peculiarities of alkaline ions and water molecule diffusion in perfluorinated sulfonic cation-exchange membranes[6–18] and in membranes on the basis of polyethylene and sulfonated grafted polystyrene have been published earlier.[16,19–21] Nafion[6–17] and MF-4SC[14,16,18] perfluorinated membranes in acid ionic form are especially attractive as they are the main component of low-temperature fuel cell membrane electrode units.

The correlation between membrane humidity, cation hydration numbers and water diffusion coefficients has been established. Water molecule ^1H nuclei and lithium cation ^7Li nuclei spin relaxation study enabled calculation of correlation times of water molecules and Li^+ in the lithium ionic form of MF-4SC membrane. It has been suggested that local molecular and cation mobility in the vicinity of sulfonated groups regulates its macroscopic transport.[14,16,18] To our best knowledge, the information regarding water molecule nanoscale mobility and its comparison with diffusion coefficients in other ionic membrane forms remained scarce. The research of the cations possessing different hydration abilities, *e.g.*, Li^+, Na^+ and Cs^+ is of great interest as it allows one to understand the microscopic ion selectivity transport mechanism.

Herein, the local mobility and diffusion peculiarities of water in Li^+, Na^+, Cs^+ Nafion 117 membrane ionic forms have been revealed by ^1H spin relaxation and PFG NMR .

The temperature dependences of water molecules diffusion coefficients in Li^+ (curves *1* and *1*′), Na^+ (curves *2* and *2*′) and Cs^+ (curve *3*) Nafion 117 ionic forms are shown in Figure 1.

Diffusion coefficient temperature dependences are approximated with the Arrhenius equation (1):

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right), \tag{1}$$

where D_0 is temperature independent pre-exponential factor; R is gas constant; T is absolute temperature; E_a is diffusion activation energy.

Activation energies of water diffusion in Li^+ and Na^+ membrane ionic forms increase in low temperature region below 0 °C (curves *1* and *2* in Figure 1). At $RH = 75\%$ activation energies are 19 ± 1 and 29 ± 1 kJ mol^{-1} for Li^+ and 22 ± 1 and 34 ± 1 kJ mol^{-1} for Na^+ membrane ionic forms in high and low temperature regions, respectively. Activation energies in high

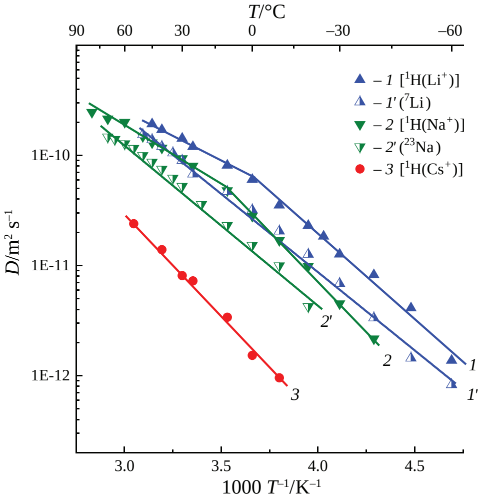


Figure 1 Temperature dependences of water molecules diffusion coefficients in (*1*) Li^+, (*2*) Na^+, (*3*) Cs^+ Nafion 117 ionic forms at $RH = 75\%$ and in (*1*′) Li^+ and (*2*′) Na^+ ionic forms at $RH = 58\%$.

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temperature region are close to the diffusion activation energy of bulk water. Water molecules diffusion activation energy in Cs^+ ionic form is 36 ± 1 kJ mol^{-1} (curve *3*). It should be noted that water molecules retained high mobility below 0 °C in all ionic forms of membranes. Obviously, an increase of water diffusion activation energy in low temperature region at *RH* = = 75% for Li^+ and Na^+ membrane ionic forms (λ = 6.4 and 5.1, respectively) (see Figure 1, curves *1* and *2*) can not be explained by partial freezing of water. It is safe to assume that, whereas water doesn't form the ice phase, the additional hydrogen bonds appear below 0 °C. On the one hand, it is accompanied by appearance of DSC thermo grams peak. On the other hand, the activation energy of the diffusion of these associated molecules is higher.[9,14–18] At lower water content (*RH* = 58% for Li^+ and Na^+ ionic forms and for Cs^+ ionic form λ = 1.5) the water is immobilized *via* interaction with cation and sulfonate group and it is unable to form additional hydrogen bonds at temperature below 0 °C. For this reason, there are no breaks of temperature curves *1'*, *2'*, *3* (Figure 1) and activation energy is higher compared with the bulk water. Water diffusion activation energies are 28 ± 1, 25 ± 1 and 35 ± 1 kJ mol^{-1} in Li^+, Na^+ and Cs^+ Nafion ionic forms, respectively.

Temperature dependences of spin–lattice (T_1) and spin–spin (T_2) relaxation times are shown in Figure 2.

As shown in Figure 2, T_1 *vs.* T^{-1} dependences are not approximated by Lorentz functions in accordance with Bloembergen, Purcell, Pound (BPP) equations and $T_1/T_2 > 1.6$, which indicates the correlation times distribution. Two types of distribution functions, Gaussian and rectangular, were applied. Referring to Figure 2, temperature dependences T_1 *vs.* T^{-1} are satisfactory described by Gaussian functions of the correlation times distribution. Despite the correlation times distribution the condition of T_1 minimum does not depend on the type of distribution $\omega\tau_{av} = 0.62$, where ω is ^{1}H NMR frequency, τ_{av} is an average correlation time.[14,16,18] Correlation time distribution doesn't affect the slope of the curve of spin–spin relaxation temperature dependence T_2 *vs.* T^{-1}. Thus, activation energy of water molecules mobility can be estimated from this curve. The value of average correlation time τ_{av} in the minimum of T_1 *vs.* T^{-1} curve is 2.46×10^{-10} s. Water diffusion coefficient *D* may be calculated by the Einstein relation:

$$D = l^2/6\,\tau_{av}, \tag{2}$$

where *l* is an average jumping distance.

For water molecule $l = 3 \times 10^{-10}$ m (equal to the water molecule diameter) at minimum temperature on T_1 *vs.* T^{-1} curve *D* value about 6×10^{-11} m^2 s^{-1}. At these temperatures water diffusion coefficients measured by PFG ^{1}H NMR for Li^+, Na^+ and Cs^+ ionic forms of Nafion 117 are 3×10^{-11}, 2×10^{-11} and 4×10^{-12} m^2 s^{-1}, respectively, at *RH* = 75% (see Figure 1).

Water diffusion coefficients calculated from local mobility and measured water macroscopic diffusion coefficients differ within a factor of two for Li^+ and Na^+ ionic forms. This can be considered a good agreement, taking into account an approximate evaluation of diffusion coefficients by the Einstein relation (2).

Therefore, it can be concluded that, similar to acid ionic form, macroscopic water diffusion in Li^+ and Na^+ ionic forms is controlled by the local translation jumps of water molecules along the continuous hydrogen bond network that is formed at high enough water content $\lambda > h$. Value of λ strongly depends on the cation type, *e.g.*, λ = 6.4, 5.1 and 1.5 for Li^+, Na^+ and Cs^+ ionic forms, respectively. Li^+ and Na^+ cations located next to the sulfonate groups are adsorption sites of water molecules due to the high hydration energy. Hydration numbers are close to water content λ (*h* = 3.3 ± 0.4 for Li^+ and Na^+ ionic forms). Apparently, the jumps of water molecules between sulfonate groups represent a primary act of macrotransfer. This is supported by the fact that water mobility sharply increases with the increasing of sulfonate groups concentration (*i.e.*, decreasing the distance between groups).

For Cs^+ ionic form the measured diffusion coefficient in water is an order of magnitude smaller than the calculated value; water content λ = 1.5 and hydration number *h* = 0.5 ± 0.2 at *RH* = 75%. Continuous hydrogen bond network is broken and one or two water molecules are fixed upon the ionic pair $Cs^+SO_3^-$. The fast local rotation of water molecules (which causes spin relaxation) does not correlate with its translation jumping; rotation frequency is higher than the translational frequency.

In summary, spin relaxation and pulsed field gradient NMR of ^{1}H nuclei were applied for the first time to reveal water dynamic pecularities in different spatial scales in alkaline metal ionic forms of Nafion 117 membrane. Analysis of the spin–lattice and spin–spin relaxation times temperature dependences allowed us to estimate the correlation times of local water molecules in Li^+, Na^+ and Cs^+ ionic forms of membrane. Diffusion coefficients calculated by Einstein relation were compared with the macroscopic diffusion coefficients measured by PFG NMR. Therefore, macroscopic mass transfer is due to the local jumps of water molecule and movable cations between the charging groups. Jumping frequency is governed by the ion hydration and channel nanostructure (mainly, the distance between sulfonate groups).

NMR measurements have been performed using the equipment of the Multi-User Analytical Center of Problems of Chemical Physics RAS and Science Center RAS in

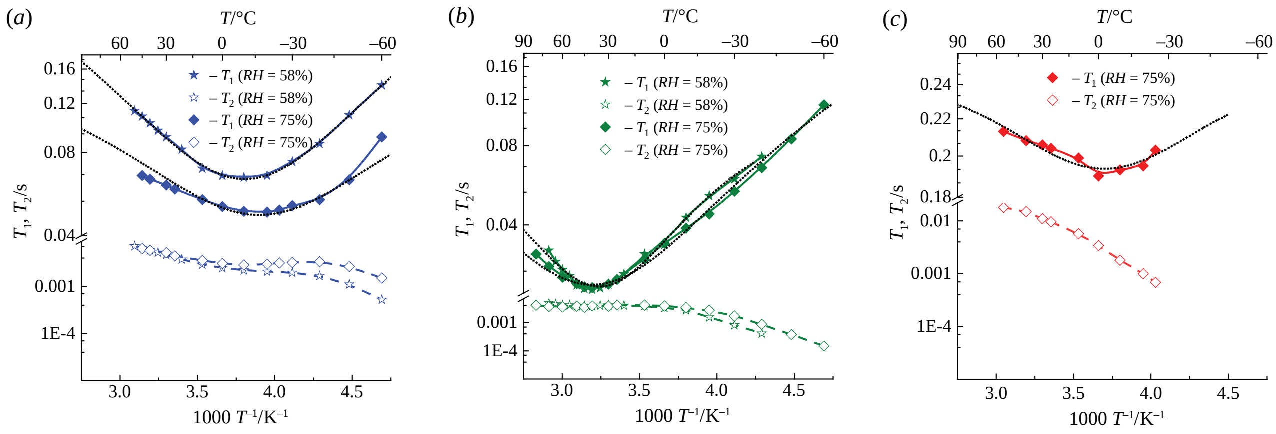

Figure 2 Temperature dependences of water molecules ^{1}H spin–lattice (T_1) and spin–spin (T_2) relaxation times in (*a*) Li^+, (*b*) Na^+ and (*c*) Cs^+ Nafion 117 membrane ionic forms at *RH* = 58% and *RH* = 75%. Dotted curves represent Gaussian functions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.033.

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