Hydration, self-diffusion and ionic conductivity of Li$^+$, Na$^+$ and Cs$^+$ cations in Nafion membrane studied by NMR

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ABSTRACT

Hydration of Nafion 117 perfluorinated sulfonic cation-exchange membrane in alkaline ion forms was investigated by high resolution ^{1}H NMR. Hydration numbers of Li$^+$, Na$^+$ and Cs$^+$ cations were 5 ± 1, 6 ± 1 and 1 ± 0.2, correspondingly for membrane equilibrated with water vapor at 98% RH. As opposed to Li$^+$ and Na$^+$, which form separate ion pair, Cs$^+$ cation directly contacts with membrane sulfonate group. Cation self-diffusion coefficients were measured by pulsed field gradient NMR technique on ^{7}Li, ^{23}Na and ^{133}Cs nuclei for the first time. Self-diffusion coefficients are changed in the next rows Li$^+ \leq$ Na$^+ >$ Cs$^+$. Self-diffusion activation energies of Li$^+$ and Na$^+$ cations are about 20 kJ/mol which is close to water self-diffusion activation energy in these membranes, but Cs$^+$ self-diffusion activation energy is distinctly more (25 kJ/mol). Ionic conductivities calculated on the basis of Nernst–Einstein equation from cation self-diffusion coefficients $1.6 \cdot 10^{-2}$, $2 \cdot 10^{-2}$, $6 \cdot 10^{-3}$ S/cm for Li$^+$, Na$^+$, Cs$^+$ cations, correspondingly, are closely approximating to conductivities measured by impedance spectroscopy: $1.3 \cdot 10^{-2}$, $1.1 \cdot 10^{-2}$, $2.3 \cdot 10^{-3}$ S/cm for Li$^+$, Na$^+$, Cs$^+$ cations, correspondingly, but calculated values are appreciably more compared with experimental meanings.

1. Introduction

Ionic transport in sulfonic cation (−exchange) perfluorinated membrane is controlled by the particularities of the cation hydration. It is especially important at low water content, at the condition when the amount of water molecules per sulfonate group λ is comparable with the counter ion hydration number h ($\lambda \leq h$).

NMR became the method of choice for investigation of ion exchanger's hydration. First results of cation hydration in sulfonic cation resins and in aqueous acid and salt solutions as model systems have been published in the beginning of 1970s, soon after the appearance of commercial NMR spectrometers (1–9). The dependences of the ^{1}H chemical shift of water (and H$^+$ counter ion for acidic ionic form) on humidity and temperature were analyzed. It was shown that water molecules in the first metallic cation hydration sphere are polarized which results to destruction of hydrogen bond network and shift of the averaged water ^{1}H NMR line to higher magnetic field. In the case of acid ionic form the H$^+$ cation forms additional hydrogen bonds which causes shift the resonance signal of protons to lower field. Main attention was

paid to H$^+$ ionic form of cation exchangers. Perfluorinated sulfonic cation Nafion (10–18) and MF-4SC membranes (19–21) attract a special interest. It was suggested that at low water content in sulfonic cation resins (7), Nafion (17) and MF-4SC (19–21) membranes H$^+$ cation tightly binds with two water molecules and forms hydroxonium ion H$_5$O$_2^+$. This hydrated H$^+$ cation is very stable; therefore two hydrated water molecules are retained during sample drying at high temperature (100 °C - 120 °C) to constant weight. The amount of residual water, expressed as a number of water molecules per ionic site λ_0, was measured directly by NMR and was equal to 1.5 ± 0.5 in Nafion (11,17), this result is agreed with the formation of H$_5$O$_2^+$ particle. Some authors have proposed H$_3$O$^+$ ion formation in Nafion membrane at low humidity (10,15).

The hydration numbers in sulfonic cation exchangers were less in comparison with water solutions (6).

NMR relaxation was used to estimate a local water and ionic mobility (17,18,22–24). Translation motion correlation times of water molecules and Li$^+$ cations in MF-4SC membrane were calculated. The comparison of self-diffusion coefficients calculated from correlation times on the

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basis of Einstein equation with experimental self-diffusion coefficients measured by pulsed field gradient NMR has revealed that macroscopic water and cation transfer is controlled by particle jumping between neighboring sulfonate groups in membrane ionic channels (21,22). This jumping frequency is driven by the hydrated ion structure, which by turn strongly depends on the cation nature and membrane humidity.

Water and ionic self-diffusion represent the particular interest because self-diffusion processes namely determine ionic conductivity. Water molecule self-diffusion coefficients dependences on water content and temperature in perfluorinated membranes were measured directly by pulsed field gradient NMR (PFG NMR) technique (13,14,17–22,25–29). Self-diffusion coefficient decreases by several orders of magnitudes when water amount per sulfonate group (λ) is less than four (17,18,20–22).

The dependences of the proton conductivity on temperature and humidity change symbatically with the self-diffusion coefficients of water (17,29–32). Temperature dependence of self-diffusion coefficients is approximated by the Arrhenius equation in the regions above and below 0 °C. The activation energies of the high humidity samples are close to the bulk water activation energy in high temperature region and essentially increase in low temperature region. At low water content self-diffusion activation energies are higher as compared to those in bulk water in the whole temperature range (17,18,21).

It is very important to compare ionic self-diffusion and conductivity data. The overwhelming majority of NMR self-diffusion experiments were carried out for acid form of Nafion membrane on ^{1}H nuclei. In this case PFG NMR measures an average self-diffusion coefficient of water and H^{+} counter ion while proton conductivity determines by H^{+} migration in hydrogen bond network (17). Therefore the direct quantitative comparison of diffusion and conductivity results is next to impossible. From this point of view it is very desirable to measure the self-diffusion coefficients of cation only. This experiment may be realized by PFG NMR technique on alkaline metal cation nuclei [7]Li^{+}, [23]Na^{+} and [133]Cs^{+} (33), unfortunately, these measurements are not known for Nafion membrane. The main reasons are the low magnetic moment and short spin-spin relaxation time of [7]Li, [23]Na, [133]Cs nuclei compare with ^{1}H therefore the hetero nuclear experiments are rather time-consuming.

Our very brief review shows that ^{1}H NMR spectroscopy, NMR relaxation and PFG NMR are very informative techniques for the investigation of the hydration and molecular water mobility at different spatial scales (from tenth nm to μm) in perfluorinated sulfocation exchange membranes. The measurements of one charge cation self-diffusion coefficients are especially important for direct quantitative ionic conductivity calculation. These measurements may be realized by PFG NMR for [7]Li^{+}, [23]Na^{+} and [133]Cs^{+}. Namely, this kind of investigations is our objective. Widely used and studied by the different physical techniques (including NMR) Nafion 117 membrane was selected as a model system.

2. Materials and methods

2.1. Materials

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. As-received membranes are pre-cleaned by boiling in 3 wt% oxygen peroxide (H_2O_2) during 1 h to eliminate organic residues and are rinsed with demineralized water. To guarantee a complete acidification and paramagnetic ion impurities extraction the samples are soaked in aqueous 10 M H_2SO_4 at room temperature during 1 h and rinsed with demineralized water. Finally, the membranes are boiled 1 h in aqueous 1 M HCl and then rinsed with demineralized water. Salt membrane ionic forms prepared by repeated equilibration with aqueous lithium, sodium, cesium chloride 1 M solutions and following rinsed by demineralized water (33). For the required humidity achievement Nafion samples were placed in open
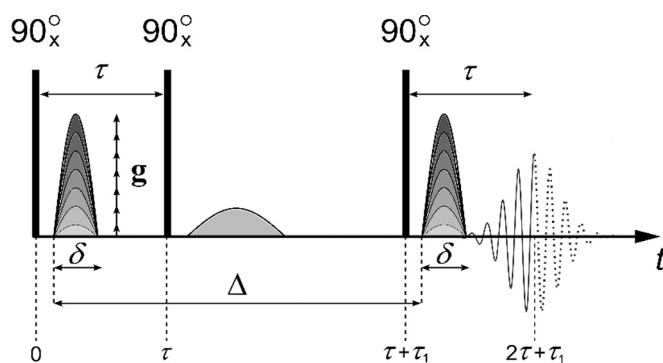

Fig. 1. Stimulated echo pulse sequence with the magnetic field gradient pulses. Here, τ is the time interval between the first and second RF pulses, τ_1 is the time interval between the second and the third ones, Δ is the interval between the gradient pulses, δ is duration of the equivalent rectangular magnetic field gradient pulses, g is the amplitude of the magnetic field gradient pulse (34).

weighing bottle inserted in desiccators in which the relative humidity (*RH*) was determined by the vapor pressure of saturated aqueous $ZnCl_2$ (*RH* is 10%), $MgCl_2$ (*RH* is 33%), NaBr (*RH* is 58%), $NaNO_2$ (*RH* is 64%), NaCl (*RH* is 78%), Na_2CO_3 (*RH* is 95%) salt solutions and water (*RH* is 98%). For NMR measurements the membrane plates with 3 × 40 mm dimension were inserting in hermetic closed NMR sample tubes, which outer diameter was 5 mm. Dry membrane samples were got by drying at 110 °C till the constant weight or equilibration with P_2O_5 at room temperature. Gravimetrical measured water content λ_g is characterized as water molecule amounts per sulfonated group, calculated from Eq. 1 (11,17):

$$\lambda_g = \frac{m_{H_2O} \cdot EW}{m_{dry} \cdot M(H_2O)} \tag{1}$$

where *EW* is the equivalent weight of the membrane considered. In this study we used the value EW = 1100 g/equiv., M (H_2O) = 18 g/mol is the molar mass of water, m_{H2O} is the total mass of water in the membrane and m_{dry} is the mass of the dry membrane.

2.2. Methods

High resolution of Nafion membrane[1]H, [7]Li, [23]Na, [133]Cs spectra were recorded on the AVANCE-III-500 Bruker NMR spectrometer (proton Larmor frequency is 500 MHz) in the temperature region from −60 °C to +25 °C. The ^{1}H chemical shift was calculated relatively bulk water ^{1}H NMR signal at 23 °C (δ_{H2O} = 4.30 ppm relatively TMS), chemical shift measurement error was less than 0.05 ppm.

The self-diffusion coefficients were measured on ^{1}H, [7]Li, [23]Na, [133]Cs nuclei by pulsed field gradient technique at the frequencies 400.22, 155.51, 105.84, 52.48 MHz, respectively. The measurements were carried out on Bruker AVANCE-III-400 NMR spectrometer, equipped with the diff60 gradient unit. The pulsed field gradient stimulated echo sequence shown in Fig. 1 was used. Three 90° pulses produce a stimulated spin-echo at time $2\tau + \tau_1$, where τ is the time interval between the first and second 90° pulses (2.5–3. ms) and τ_1 – interval between the second and the third pulses (6–8 ms). The magnetic field gradient pulses of amplitude g and duration δ (1 ms) were applied after the first and third 90° pulses. The gradient strength g was varied linearly in 32 steps within a range from 0.1 to 27 T/m value. The integrated intensities of spectrum lines were used to obtain the dependence of echo signal attenuation on g^2 (diffusion decay).

For the molecules undergoing unhindered isotropic Brownian motion, the evolution of spin echo signal is described by the following equation.

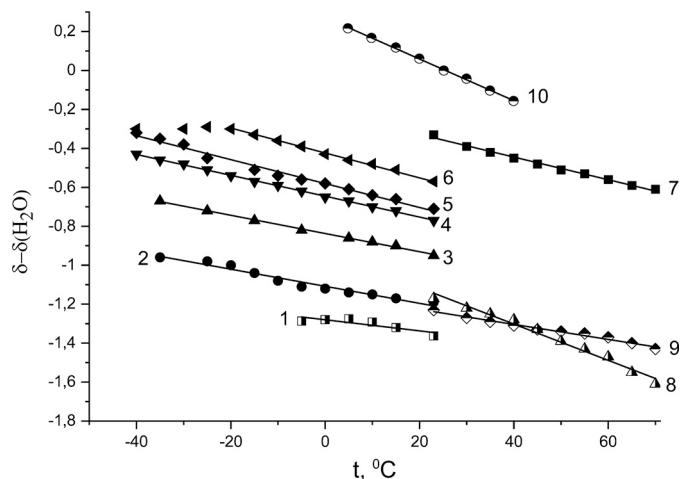$$A(2\tau, \tau_1, g) = A(2\tau, \tau_{1,0}) \cdot exp(-\gamma^2 g^2 \delta^2 t_d D_s) \tag{2}$$

Fig. 2. Temperature dependence of water proton chemical shifts in the Li^+, Na^+ and Cs^+ ionic forms of Nafion membranes at various relative humidity where δ_{H2O} is the bulk water chemical shift $\delta_{H2O} = 4.30$ ppm relatively TMS, at 20 °C: Li^+ ionic form: 1 - $\lambda = 0.9$, 2 - $\lambda = 2.0$, 3 - $\lambda = 4.0$, 4 - $\lambda = 5.7$, 5 - $\lambda = 7.4$, 6 - $\lambda = 10.7$, 7 - $\lambda = 12$; 8 - Na^+ ionic form, $\lambda = 10$; 9 - Cs^+ ionic form, $\lambda = 4$; 10 - bulk water; λ is amount of water molecules per sulfonated group.

where γ is gyromagnetic ratio, $t_d = \Delta - \delta/3$ (10 ms), is the diffusion time, δ is 1 ms, τ is 2 - 3 ms and D_s is the self-diffusion coefficient, τ, τ_1 and g are shown in Fig. 1; $A(2\tau, \tau_1, 0)$ is expressed by the equation.

$$A\left(2\tau, \tau_{1,0}\right) = \frac{A(0)}{2exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right)}$$

where $A(0)$ is the signal intensity after the first radio frequency (RF) pulse (Fig. 1). T_1 and T_2 are the spin-lattice and spin-spin relaxation times, respectively. The T_2 values at 20 °C were about 10, 2 and 4 ms for $^7Li^+$, $^{23}Na^+$ and $^{133}Cs^+$ nuclei, correspondingly. During measurement of echo signal evolution, τ and τ_1 are fixed, and the normalized dependence of A on g A/A_o is analyzed.

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

3. Results and discussion

3.1. High resolution NMR. Hydration

The Li^+, Na^+, Cs^+ ionic form ^1H NMR spectrum is a singlet, which position is shifted to high magnetic field compare with bulk water signal. The NMR line is rather narrow even at low humidity and freezing temperature that indicates on high water mobility, at these conditions. The chemical shift value depends on water content and temperature.

3.1.1. Temperature chemical shift dependence

From ^1H chemical shift temperature dependences hydration numbers of hydrated Li^+, Na^+, Cs^+ ion may be calculated. Relevant techniques were applied to sulfonic cation exchangers (5–9,17–19) and salt aqueous solutions (1–4).

Temperature chemical shift dependences at different water contents are shown in Fig. 2. These dependences are straight lines, which slope increased following by λ increasing; the line slope is highest for bulk water (curve 10 in Fig. 2).

Follow to ^1H NMR temperature investigation of salt aqueous solutions (1–4) and sulfonic cation exchange resins (5,6,9) in salt ionic form the hydration numbers h were calculated from Eq. 3:

Table 1
Hydration numbers h Li^+ cation in lithium form of Nafion membrane at different water contents λ.

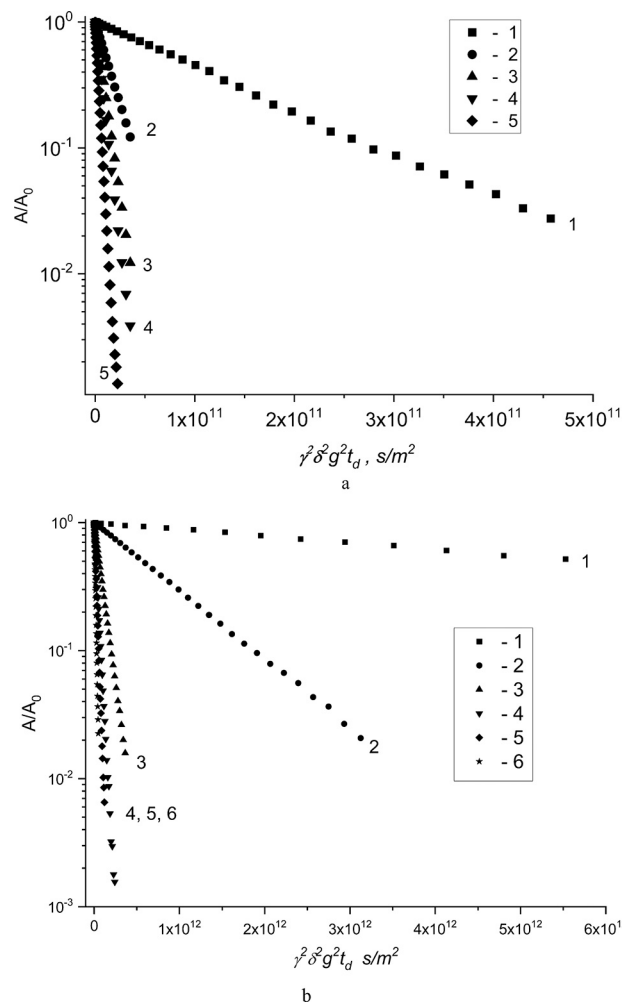| λ, [H_2O/SO_3^-]	0.9	2.0	4.0	5.7	7.4	10.7	12
h	0.6 ± 0.3	1.2 ± 0.5	2.1 ± 0.5	2.6 ± 0.5	2.9 ± 0.5	4.2 ± 1.0	5 ± 1

Fig. 3. a-Spin-echo signal attenuation of water molecule ^1H nuclei dependences on gradient pulsed amplitude $A(g)/A_o$ (diffusion decay) in Li^+ ionic form of Nafion membrane at different water content: 1 - $\lambda = 2.0$, 2 - $\lambda = 4.0$, 3 - $\lambda = 5.7$, 4 - $\lambda = 7.4$, 5 - $\lambda = 10.7$; $\delta = 1$ ms, $\Delta = 10$ ms. b-Spin-echo signal attenuation of ^7Li nuclei dependences on gradient pulsed amplitude $A(g)/A_o$ (diffusion decay) in Li^+ ionic form of Nafion membrane at different water content: 1 - $\lambda = 0.9$, 2 - $\lambda = 2.0$, 3 - $\lambda = 4.0$, 4 - $\lambda = 5.7$, 5 - $\lambda = 7.4$, 6 - $\lambda = 10.7$; $\delta = 1$ ms, $\Delta = 10$ ms.

$$h = \lambda \left[1 - \frac{\frac{d\delta}{dt}}{\frac{d\delta_{H_2O}}{dt}}\right] \tag{3}$$

where λ is the number of water molecules per sulfonate group; δ is the measured ^1H chemical shift; δ_{H_2O} is the bulk water ^1H chemical shift. Hydration numbers h of Li^+ cation in appropriate ionic form of Nafion membranes at different humidity are listed in Table 1.

Hydration numbers are differed with humidity variation. At high water content $\lambda > 10.7$ hydration number h about 4–6, this value is
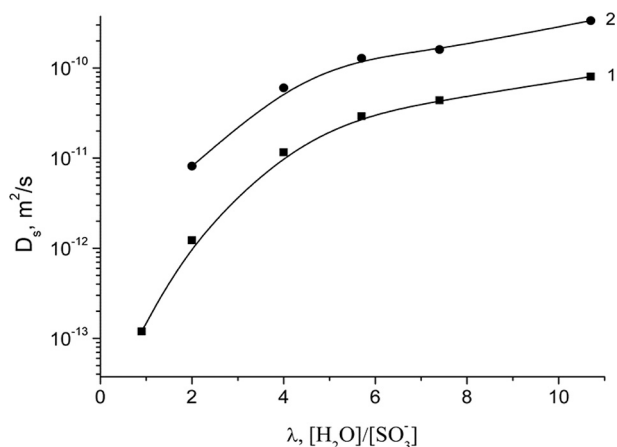
Fig. 4. Self-diffusion coefficients of Li$^+$ ions (curve 1) and water molecules (curve 2) dependences on water content λ in Nafion membrane Li$^+$ ionic form, where λ is water amount per sulfonate group.

closed to lithium cation hydration number in dilute lithium salt aqueous solutions ($h = 5$–6), where Li$^+$ forms a separate ionic pair with anion. With reducing water content Li$^+$ hydration number is decreased and oxygen atom of sulfonate group replace the oxygen of water molecule; thereby a contact ionic pair is created. Sodium cation hydration number h is 6 ± 1 ($\lambda = 10$ at 98% RH) which is the same as h in dilute sodium salt aqueous solutions (3,4,35,36) so the separate ionic pair Na$^+$ − SO$_3^{3-}$ group is formed at these conditions. For Cs$^+$ cation hydration number h is 1 ± 0.2 ($\lambda = 4$ at 98% RH) this value is less compare with h in aqueous solution (3) and in Dowex 50 W (cation resin) (5) ($h = 3$–4). It means that even at maximum water content Cs$^+$ may be interacted with Nafion SO^{3-} group directly and contact ionic pair is forming. This cesium cation hydration particularity is due the fact that compare to lithium and sodium cations Cs$^+$ hydration energy is less than hydration bond energy between water molecules (37).

Hereby in spite of rather crude approaches of proton chemical shift temperature dependences interpretation some important conclusions may be done.

At low water content Li$^+$ and Na$^+$ cations are in direct contact with sulfonate groups while at high water content water molecules are built in between cation and SO^{3-} groups. Cesium cation probably interacts with sulfonate group directly at any water content.

3.2. Pulsed field gradient ^1H ^7Li, ^{23}Na, ^{133}Cs NMR, macroscopic self-diffusion

Self-diffusion of Li$^+$, Na$^+$, Cs$^+$ cations was investigated.

3.2.1. Lithium cations and water molecules self-diffusion

Lithium cations and water molecules self-diffusion in Li$^+$ Nafion ionic form were measured at different water contents. Diffusion decays of ^7Li nuclei of Li$^+$ cation and water molecule ^1H nuclei are shown in Fig. 3.

Spin-echo attenuations were approximated by Eq. 2 in three orders of magnitudes in the whole range of water contents. Self-diffusion coefficients of lithium cation and water molecule dependences on water content λ are given in Fig. 4.

Theses dependences shapes are similar. It may be concluded that translational motions of Li$^+$ cation and hydrated water molecules are correlated as it was indicated in (21). Self-diffusion coefficients both cation and water dramatically decrease since $\lambda < 4$–6, which corresponds to $h = 2$–3. It means that water molecules in the first Li$^+$ hydration sphere may be replaced by sulfonate group oxygen. Therefore Li$^+$ and SO$_3^-$ group forms one-to-one ion pair, which is followed by sharp cation and water mobility drops.
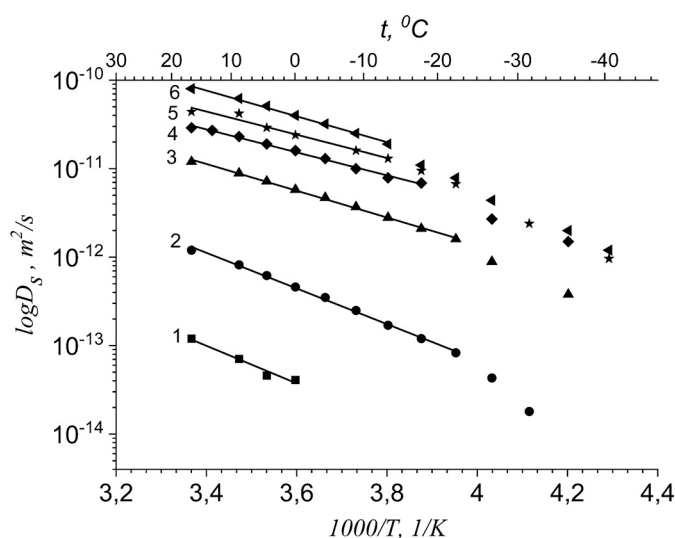

Fig. 5. Li$^+$ cation self-diffusion coefficient temperature dependences for Nafion membrane Li$^+$ ionic form at different water content λ, where λ is water amount per sulfonate group. 1 - $\lambda = 0.9$, 2 - $\lambda = 2.0$, 3 - $\lambda = 4.0$, 4 - $\lambda = 5.7$, 5 - $\lambda = 7.4$, 6 - $\lambda = 10.7$.
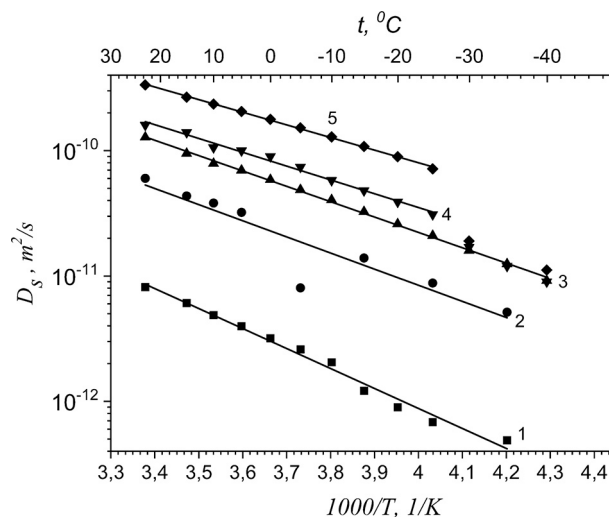

Fig. 6. Water molecule self-diffusion coefficient temperature dependences for Nafion membrane Li$^+$ ionic form at different water content λ, where λ is water amount per sulfonate group. 1 - $\lambda = 2.0$, 2 - $\lambda = 4.0$, 3 - $\lambda = 5.7$, 4 - $\lambda = 7.4$, 5 - $\lambda = 10.7$.

Temperature dependences of Li$^+$ and water molecules at different moisture content are shown in Figs. 5 and 6.

The dependences $D_s(T)$ were approximated by Arrhenius Eq. (4).

$$D_s = D_{s0} \cdot e^{-\frac{E_a}{R \cdot T}} \tag{4}$$

Table 2
Activation energies of Li$^+$ and water molecule self-diffusion in Li$^+$ ionic form of Nafion membrane E_a at different water content λ.

λ, [H$_2$O/SO$_3^-$]	0.9	2.0	4.0	5.7	7.4	10.7
E_a Li$^+$ cations self-diffusion, kJ/mol	40.3 ± 2	38.4 ± 2	28.8 ± 2	25 ± 2	25 ± 2	27.8 ± 2
E_a water molecules self-diffusion, kJ/mol	–	28.8 ± 2	25 ± 2	23 ± 2	21.1 ± 2	19.2 ± 2

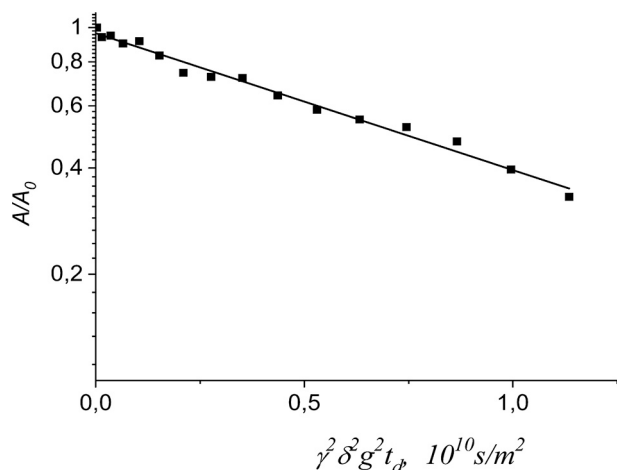**Fig. 7.** Diffusion decay of ^{23}Na nuclei in Nafion membrane Na$^+$ ionic form, *RH* = 98%, t = 20 °C; δ is 1 ms, Δ = 6 ms, τ is 2–3 ms.
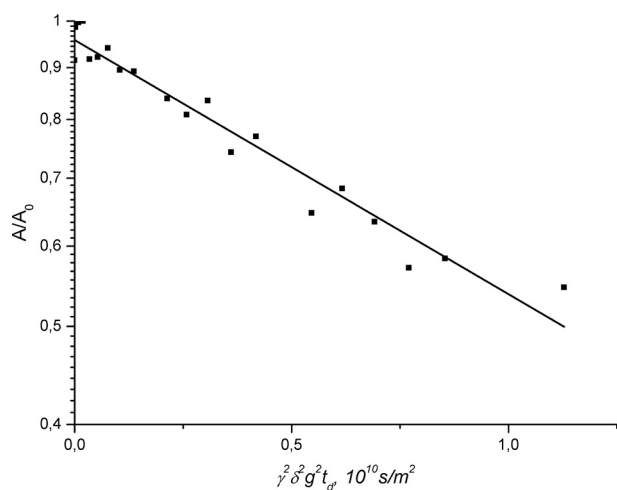

Fig. 8. Diffusion decay of ^{133}Cs nuclei in Nafion membrane Cs$^+$, *RH* = 98%, t = 20 °C; δ is 1 ms, Δ = 10 ms. τ is 2–3 ms.

where D_{s0} is temperature independent, R is gas constant, T is absolute temperature, E_a is self-diffusion activation energy.

Eq. (4) describes well Li$^+$ self-diffusion in temperature region from −10 °C to +30 °C (Fig. 5) and water molecule self-diffusion from −40 °C to +30 °C (Fig. 6). Activation energies at different water content λ summarize in Table 2.

Activation energies E$_a$ increase with hydration degree decreasing. Lithium cation self-diffusion activation energies are essentially more compare to water molecule self-diffusion activation energies.

3.2.2. Sodium and cesium cation self-diffusion

The measurement of Na$^+$ and Cs$^+$ self-diffusion coefficients is more effortful compare to Li$^+$ self-diffusion coefficient. Till now the sodium and cesium self-diffusion data in Nafion membrane are unknown. There are two reasons of these difficulties. First is low magnetic moment of ^{23}Na and ^{133}Cs nuclei. The second is the large quadrupole moment of these nuclei. The main spin relaxation mechanism of ^{23}Na and ^{133}Cs nuclei is quadrupole moment - gradient ligand electric field interaction. We have observed these nuclei diffusion decays in aqueous solution and in sulfocation-exchange membranes (MSC) based on polyethylene sulfonated grafted polystyrene (33), which maximum water content λ is more compare to Nafion membrane. At this condition cation water molecule shell is high symmetric. Therefore electric field gradient is low
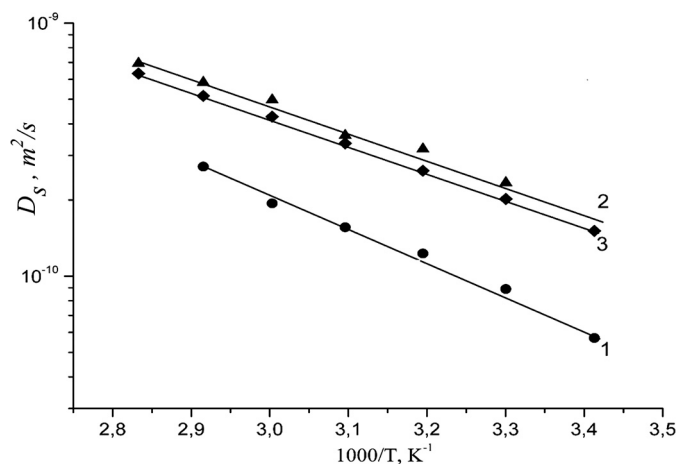

Fig. 9. Temperature dependences of Cs$^+$ (curve 1), Na$^+$ (curve 2), Li$^+$ (curve 3) self-diffusion coefficients in Li$^+$, Na$^+$, Cs$^+$ Nafion membrane ionic forms. *RH* = 98%.

Table 3
Moisture content λ, amount water molecules per cation, self-diffusion coefficients D_s, at 20 °C, self-diffusion activation energies E_a of Li$^+$, Na$^+$ and Cs$^+$ cations in Nafion membrane, MSC membrane at *RH* = 98% and chloride aqueous solutions.

Membrane type	Cation	Moisture content λ, amount water molecules per cation	Cation self-diffusion coefficient at 20 °C D_s, m^2/s	Cation self-diffusion activation energy E_a, kJ/mol
Nafion	Li$^+$	12	$(1.5 \pm 0.1) \cdot 10^{-10}$	20.5 ± 1
	Na$^+$	10	$(2.1 \pm 0.3) \cdot 10^{-10}$	19.3 ± 1.5
	Cs$^+$	4	$(0.6 \pm 0.2) \cdot 10^{-10}$	24.8 ± 1.5
MSC (33,36)	Li$^+$	24	$3.7 \cdot 10^{-10}$	17.6
	Na$^+$	21	$4.4 \cdot 10^{-10}$	18.1
	Cs$^+$	16	$8.3 \cdot 10^{-10}$	16.5
Chloride aqueous solution (36)	Li$^+$	24	$(8.2 \pm 0.3) \cdot 10^{-10}$	17.1 ± 0.5
	Na$^+$	21	$(1.1 \pm 0.2) \cdot 10^{-9}$	18.3 ± 0.6
	Cs$^+$	16	$(1.7 \pm 0.2) \cdot 10^{-9}$	16.8 ± 0.6
bulk water (38)	–	–	$2.02 \cdot 10^{-9}$ m^{2}s^{-1}	

and nuclear spin-spin relaxation time is long enough to observe spin-echo signal. We also succeeded to get spin echo attenuation in Nafion membrane at *RH* = 98%. The examples of ^{23}Na and ^{133}Cs decays of Na$^+$ and Cs$^+$ cations are given in Figs. 7 and 8.

Lithium, sodium and cesium cation self-diffusion coefficient temperature dependences in Nafion membrane at maximum humidity (*RH* = 98%) in the temperature range from 20 to 80 °C are shown in Fig. 9.

These dependences $D_s(T)$ were approximated by Arrhenius Eq. (4). Self-diffusion coefficients at 20 °C, self-diffusion activation energies of Li$^+$, Na$^+$ and Cs$^+$ cations in Nafion membrane are indicated in Table 3. The values of Li$^+$, Na$^+$, Cs$^+$ self-diffusion coefficients and activation energies in MSC sulfonic cation-exchange membrane and dilute chloride aqueous solution are also given for comparison.

Self-diffusion activation energies of Li$^+$ and Na$^+$ cations are about 20 kJ/mol which is close to water self-diffusion activation energy in these membranes (21,39), but for Cs$^+$ activation energy is distinctly more compare with Li$^+$ and Na$^+$ cations. It should be mentioned that in MSC membrane cation self-diffusion activation energies are little less and Cs$^+$ activation energy even smaller than Li$^+$ and Na$^+$ compare with Nafion membrane. Cation self-diffusion coefficients are changed in the next rows Li$^+ \leq$ Na$^+ >$ Cs$^+$ in Nafion; Li$^+ <$ Na$^+ <$ Cs$^+$ in MSC (33,36) and chloride aqueous solutions. Higher Cs$^+$ activation energy and lower self-diffusion coefficient in Nafion compare to aqueous solution and

Table 4

Water content λ, hydration number h, self-diffusion coefficients D_s, calculated conductivity σ_c, measured conductivity σ_e of Li^+, Na^+, Cs^+ cations in Li^+, Na^+, Cs^+ Nafion membrane ionic forms, $t = 20\ °C$.

Ionic form	Water amount per sulfonated group λ	Hydration number h	Cation self-diffusion coefficient D_s, m^2/s	Calculated ionic conductivity, σ_c S/m	Measured ionic conductivity, σ_e S/m
Li^+	12	5 ± 1	$(1.5 \pm 0.1) \cdot 10^{-10}$	1.6 ± 0.1	1.3 ± 0.1
Na^+	10	6 ± 1	$(2 \pm 0.3) \cdot 10^{-10}$	2 ± 0.3	1.1 ± 0.1
Cs^+	4	1 ± 0.2	$(0.6 \pm 0.2) \cdot 10^{-10}$	$(6 \pm 0.2) \cdot 10^{-1}$	$(2.3 \pm 0.3) \cdot 10^{-1}$

MSC membrane may be explained in the following way. As it was mentioned above as opposed to Li^+ and Na^+ Cs^+ cation interact with Nafion SO^{3-} group directly and contact ionic pair is forming. This is the reason of low mobility and high self-diffusion activation energy of cesium cation in Nafion.

3.2.3. Lithium, sodium, cesium cation self-diffusion and ionic conductivity

Ionic conductivities σ_c of Li^+, Na^+ and Cs^+ on the basis of Nernst-Einstein Eq. (5) was calculated in Nafion membranes.

$$\sigma = \frac{N \cdot D \cdot e^2}{k \cdot T} \tag{5}$$

y4where N is the number of charge carriers in m^3; D is the self-diffusion coefficient, m^2/s; e is the electron charge, $1.9 \times 10{-}19 C$; k is the Boltzmann constant, $1.38 \times 10{-}23\ J/K$; and T is the temperature.

Calculated conductivities σ_c was compared with experimental values σ_e measured by impedance spectroscopy. The data are listed in Table 4.

Ionic conductivities calculated from cation self-diffusion coefficients are closely approximating to conductivities measured by impedance spectroscopy, but calculated values are appreciably more compared with experimental meanings. This discrepancy reason may be the next: ionic conductivity is controlled only by cation transfer along applied electric field, but PFG NMR fixes all translational jumping of cation, for instance, cation coming and leaving of sulfonate group.

4. Conclusions

Hydration of alkaline metal cations, water and ionic self-diffusion in Nafion 117 membrane were studied by ^1H NMR spectroscopy and pulsed field gradient NMR on ^7Li, ^{23}Na and ^{133}Cs nuclei. Hydration numbers h of Li^+ and Na^+ counter ions are 5 ± 1 and 6 ± 1, correspondingly at maximum moisture content, which is equal to these cation hydration numbers in dilute salt aqueous solutions, where Li^+ and Na^+ forms a separate ionic pairs with anions. Hydration number of Cs^+ ion is 1 ± 0.2, thereby cesium cation and membrane SO^{3-} groups interact directly, forming contact ionic pair. For this reason Cs^+ translational mobility is essentially low compare with Li^+ and Na^+ translational mobilities, cation self-diffusion coefficients are the next row $Li^+ \leq Na^+ > Cs^+$. Self-diffusion activation energy of cesium ion is more than activation energies of lithium and sodium ions, which is closed to bulk water self-diffusion activation energy. These cation self-diffusion activation energies in MSC membrane (with humidity much more Nafion humidity) and chloride aqueous solutions are independent on cation type and equal to bulk water self-diffusion activation energy. In this case lithium, sodium and cesium cations and anions form separate ion pairs. Cation self-diffusion coefficients are changed in the next row $Li^+ < Na^+ < Cs^+$. Thus there is an opportunity to control ionic mobility by membrane humidity variation, which gives possibility of selective ionic separation. Ionic conductivities calculated from cation self-diffusion coefficients are closely approximating to conductivities measured by impedance spectroscopy, but calculated values are appreciably more compared with experimental meanings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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