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Ab initio study of cationic polymeric membranes in water and methanol

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Abstract The work is devoted to a computational study of three types of cationic polymeric membranes in Li^+-ionic form, in water and methanol environments, at various solvation levels. The studied membranes Nafion, IonClad, and M3 possess the perfluorinated backbone; however, various side chains were terminated with the functional groups of distinctly different ionic strength. The paper discusses the structural features of the membrane-solvent clusters as well as an influence of the side chain nature on the dissociation of the functional groups and the binding energy of the solvent molecules. Additionally, the paper compares the obtained results for Li^+-Nafion membrane in water with the results published earlier for H^+ and Na^+ forms.

Introduction

Ion-exchange membranes are widely used in fuel cell technology, electrodialysis, medical devices, and other various membrane separation processes [1–4]. Numerous papers presented also experimental investigations of ion-exchange membranes applied in the separation of liquid mixtures by pervaporation [5–9]. Cabasso et al. [5, 6] and Godino et al. [7] showed that separation of alcohol/water mixtures using Nafion membrane depends on the type of the counter-ions. The experiments indicated that water is preferentially transported across the Nafion membrane than alcohol. The water flux decreases in the following sequence: $H^+ > Li^+ > Na^+ > K^+ > Cs^+$. Zhao et al. [8] studied an influence of water, methanol, and ethanol on the sorption and transport properties of Nafion membrane in different ionic forms. It was pointed out that the counter-ions affect the amount of the solvents absorbed by the membrane.

Kujawski et al. [9, 10] investigated the influence of the character of the sulfonic group and size of the counter-ion on aliphatic alcohols transport across the membranes Nafion, IonClad, and PESS (based on polyethylene/poly(styrene-co-divinylbenzene)). Both, the stronger acidic character of the sulfonic group and the smaller radius of the counter-ion, provide an easier dissociation of the ion-pairs and enhance the alcohol transport. The dissociation of the ion-pair is easier in the perfluorinated membrane Nafion than in aromatic membranes IonClad and PESS. Also, the diffusion coefficients of aliphatic alcohol are higher in perfluorinated membranes than in aromatic ones [9, 10].

Hamann et al. [11], Koter [12], and Villaluenga et al. [13] investigated experimentally water and methanol uptake by sulfonated cation-exchange membranes. It was reported that Nafion 117 membrane in sodium form can uptake up to 15 water and 21 methanol molecules per sulfonic group. Nandan et al. [14] indicated that Nafion shows unusually large sorption of methanol for the membrane in H^+, Li^+, and Na^+ ionic forms. The solvent uptake decreases with increasing size of the counter-ion. Moreover, studies carried out in 50:50 mol%

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methanol-water mixture confirmed the selective enrichment of water in the membrane phase. Struis et al. [15] found out that permselectivities for methanol and water depend on the counter-ion in the polymer. It was shown that lithium is the best suited as a counter-ion with respect to long-term stability and membrane performance.

Numerous theoretical investigations of perfluorinated sulfonic cationic membranes in the water environment have been performed using quantum chemical and molecular dynamics (MD) methods [16–27].

The aggregation of the sulfonic acid groups of Nafion membrane at different hydration levels was studied by other authors using computer simulations [16–21]. Elliott et al. [16] and Khalatur [17] performed the NVT molecular dynamics simulations and the semi-empirical molecular orbital SCF calculations, respectively. Yamamoto et al. [18] used dissipative particle dynamics (DPD) simulations, whereas Urata et al. [19] and Devanahan et al. [20, 21] carried out the investigation of the hydrated Nafion membrane model using the molecular dynamic (MD) simulations. The hydrophilic sulfonic domains of the membrane bind the water, thus increasing aggregation size, whereas the hydrophobic pendant side chain does not bind the water even at the high hydration level. It was established that the diffusion coefficient of water and counter-ions increases with growing hydration level. These results are found in a good agreement with experiments [19–24]. Khalatur et al. [17] showed that polar sulfonic acid ($-SO_3H$) groups and water molecules build three-layer structure aggregates. The aggregates stability rises with increased hydration. The results of the spectroscopic studies and time-correlated single-photon counting experiments of Moilanen et al. [22], as well as the dissipative particle dynamics (DPD) simulations of Wu et al. [23] and Dorenbos et al. [24], indicate that hydrophilic domains of Nafion membrane grow and the dispersion of water regions around sulfonic acid groups increase with increased hydration level.

Nechaeva et al. [25] performed a computational study based on molecular dynamics (MD) simulations with IR spectral analysis of the dissociation and vibrational frequencies of carboxyl and sulfonic acid groups in the aromatic membranes. The analysis of the obtained results demonstrated that ion transport takes place by breaking the bonds between the acid group and the counter-ion.

The papers [28–33] presented the computational studies using the molecular dynamics simulations (MD) of an interaction of methanol and water with perfluorosulfonated membranes. Vishnyakov et al. [28] and Abroshan et al. [29] demonstrated that both water and methanol formed stable hydrogen bonds with the oxygen atoms of the hydrophilic sulfonic group ($-SO_3^-$). It was noticed that solvent molecules bonded to the sulfonic group form the first solvation shell. The other part of the side chain, including ester oxygen atoms, has hydrophobic character. Urata el al. [30, 31] and Abroshan et al.

[29] pointed out, despite the fact that both water and methanol molecules have the similar attractive energy to the sulfonic groups, that more methanol molecules are located in the vicinity of the hydrophobic polymer matrix than water molecules. Water molecules are preferentially situated closer to the sulfonic group. The papers [32, 33] presented experimental study on the transport properties of hydrocarboned CM2 membrane and perfluorinated sulfonic Nafion membrane in water-methanol mixtures. It was shown that, at methanol mass fraction 30–40 % in the external solution, the water content in perfluorinated membrane Nafion 117 increases. The authors assumed that it happens due to methanol presence, which in opposite to water can interact with the hydrophobic parts of side chains thus expanding the space between them. It leads to an increase in membrane volume and in this way promotes water absorption.

The simulations presented in [34–36] were focused on solvation of the poly(ether ether ketone) (SPEEK) membranes. The simulations indicated that water and methanol clusters can be formed with increasing solvation level. However, in the SPEEK membrane, the solvent clusters are smaller and more isolated than in the perfluorinated the Nafion membrane [35]. In a proton ionic form of the SPEEK membrane, the hydrogen ion is located pronouncedly closer to the sulfonic group than in the Nafion one, what suggests weaker acidic character of sulfonic group in the SPEEK membrane.

In our previous work [26], quantum-mechanical calculations were carried out with the analysis of conductivity for the hydrated membranes: aromatic MK-40 and perfluorinated MF-4SK (analogue of Nafion). The transport properties of the membranes were investigated for Na^+ and H^+ ionic forms. It was found that the dissociation of the ion-pairs and strong water network around the functional group occur in MF-4SK membrane. This finding is consistent with high diffusion coefficient and molar conductivity of counter-ions in MF-4SK membrane compared to the MK-40 aromatic membrane.

The focus of the present paper is to discuss the differences between the interactions of water and methanol molecules with the ion-exchange membranes by quantum chemical calculations. Moreover, taking into account the influence of the nature of the functional groups and the polymeric matrix, we focused on understanding the solvation and dissociation phenomena of the ion-pairs in the equilibrium clusters of ion-exchange membrane models.

The numerical calculations were carried out as a function of the number of solvent (water or methanol) molecules (X, with $X = 0–10$), allowing to get information regarding (i) structural properties of the Nafion, IonClad, and M3 ion-exchange membranes and (ii) binding energy of the solvent molecules (water or methanol) to the functional groups in the investigated ion-exchange membranes. The calculations were performed for the lithium ionic form of the membranes. Moreover, in order to investigate the counter-ion effect, the

simulation results obtained for the Nafion-Li$^+$ membrane in water environment are compared with the earlier reported results for H$^+$ and Na$^+$ ionic forms at various hydration level [26].

Membranes studied

In the study, three cation-exchange membranes were investigated: Nafion, IonClad, and M3. The chemical structures of the membranes are shown in Fig. 1. These membranes possess identical perfluorinated backbone but different side chains and the functional groups with varying ionic strength [9, 10]. Nafion membrane contains ether-linked side chains terminated with sulfonic groups. The backbone chains of IonClad membrane is grafted with poly(styrene sulfonic acid) side chains also terminated with sulfonic group [37]. Membrane M3 is a virtual ionomer, modeled with the same polymer matrix as IonClad, but possessing the carboxyl functional groups. The lithium ionic form of all these membranes was chosen for investigations.

Methods

The theoretical investigation of the membranes was carried out on the reduced models including the lithium counter-ion. For the Nafion membrane, a structural model consists of the reduced backbone and the side chain [(CF$_3$)$_2$–CF–OF$_2$–CF–(CF$_3$)–O–CF$_2$–CF$_2$–SO$_3$–Li$^+$]. The model of IonClad membrane is represented by the reduced backbone and another reduced side chain [(CF$_3$)$_2$–CF–CH(CH$_3$)–C$_6$H$_5$–SO$_3$–Li$^+$]. The M3 membrane is represented by the following model [(CF$_3$)$_2$–CF–CH(CH$_3$)–C$_6$H$_5$–COO–Li$^+$]. The membrane models used for the numerical calculations are indicated by the rectangular boxes in Fig. 1.

The theoretical simulations were performed for the membrane models with lithium counter-ion in the dry state and at various solvation levels with the solvents water or methanol. The number of solvent molecules (water or methanol) per

sulfonic group has been varied from 1 to 10 for all membranes.

The geometries were optimized using the Restricted Hartree Fock (RHF) method with the 6–31++G(d,p) basis set [38]. The calculations of the binding energy of the membrane-solvent complexes were carried out using the local pair natural orbital—coupled-electron pair approximation (LPNO-CEPA/1) with the def2-TZVP basis set [39]. The LPNO-CEPA/1 method was referenced in order to accurately describe weak interactions [40]. The computational study was carried out using the program ORCA [41].

The binding energy E_b was computed from the electronic energy values (E) of the dry and solvated membranes by the following expression:

$$E_b = E_{cluster} - E_{dry} - X \cdot E_{solvent} \quad (1)$$

where X is the number of water molecules in the solvated membrane; $E_{cluster}$, E_{dry}, $E_{solvent}$ are the electronic energies of the solvated membrane with X solvent molecules, of the dry membrane and of one solvent molecule, respectively. In order to compare the different clusters, the binding energy per solvent molecule E_b/X will be also discussed.

Results and discussion

Nafion, IonClad, and M3 membranes in Li$^+$ form in water and methanol

Using the quantum chemical calculations, the following data were analyzed in detail: the geometries of the membrane models and the binding energy of the solvent per solvent molecule as a function of the solvation level (water/or methanol). The distinct attention was focused on the state of the functional groups (also called ion-pairs) consisting of the fixed groups and counter-ions and the water molecules interactions with the functional groups.

Figure 2 displays the optimized model structures of investigated membranes in the dry state, with three water
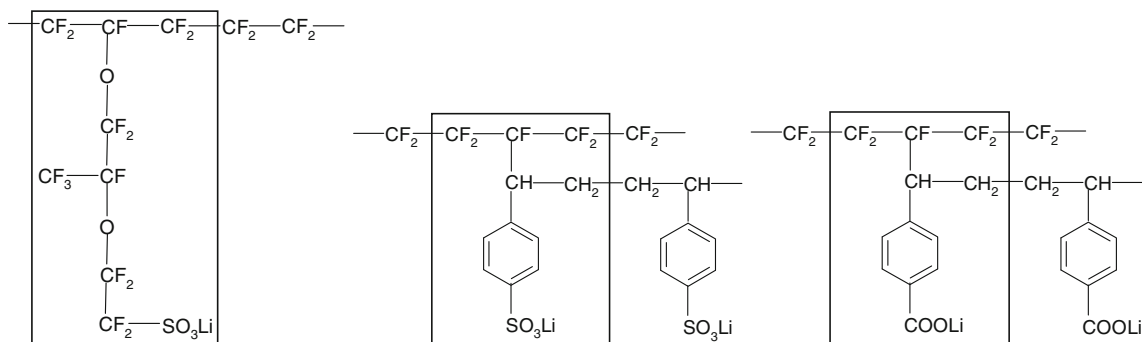

Fig. 1 Chemical structure of the membranes: **a** Nafion, **b** IonClad, **c** M3. The membrane models used in the quantum calculations are marked by the squares
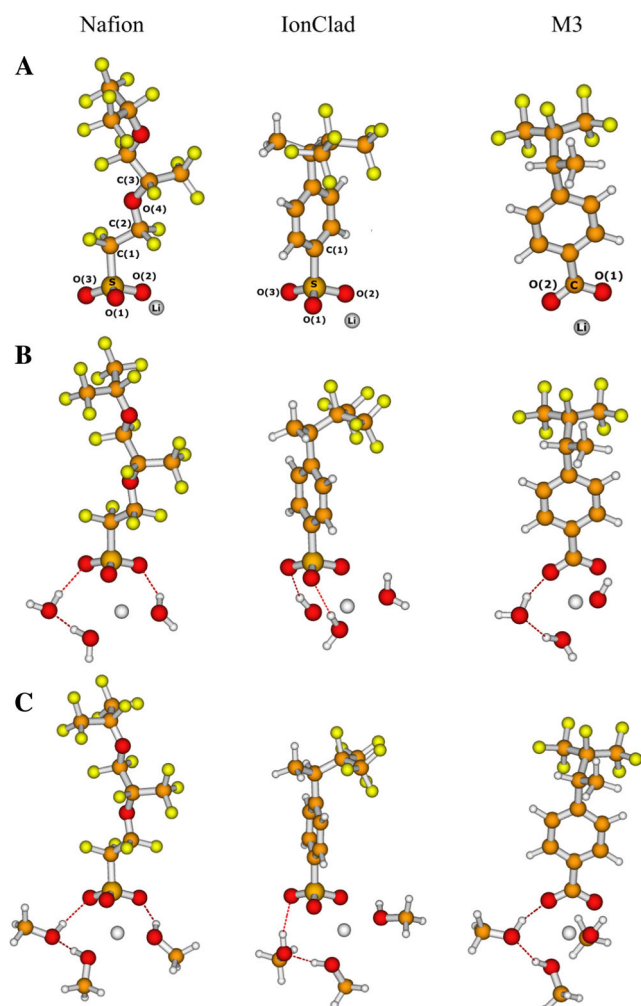
Fig. 2 Calculated geometries of Li$^+$ form membranes: **a** dry state, **b** with three water molecules, **c** and three methanol molecules. Nafion—on the *left*, IonClad—in the *middle*, M3 —on the *right*

Table 1 Geometry parameters of functional groups of calculated membrane models in Li$^+$ form in the dry state and with three solvent molecules

Parameter	Atom/group	Dry membrane		
		Nafion-Li$^+$	IonClad-Li$^+$	M3-Li$^+$
Bond	O(1)-Li$^+$	1.895	1.870	1.846
length (Å)	O(2)-Li$^+$	1.905	1.871	1.846
	S (or C)-O(1)	1.468	1.482	1.252
	S (or C)-O(2)	1.469	1.482	1.252
	S-O(3)	1.416	1.428	
Angle	S (or C)-O(1)…Li$^+$	89.6	89.1	83.5
(deg)	S (or C)-O(2)…Li$^+$	89.1	89.0	83.5
	C-S (or C)-O(1)…Li$^+$	−108.5	−114.4	179.6
	C-S (or C)-O(2)…Li$^+$	108.1	114.4	−179.6
Parameter	Atom/group	3 water molecules		
		Nafion-Li$^+$	IonClad-Li$^+$	M3-Li$^+$
Bond	O(1)-Li$^+$	1.857	3.231	2.011
length (Å)	O(2)-Li$^+$	3.248	1.936	1.981
	S (or C)-O(1)	1.463	1.453	1.242
	S (or C)-O(2)	1.442	1.475	1.253
	S-O(3)	1.437	1.454	–
	H2O(1)…Li$^+$	1.922	1.974	1.984
	H2O(2)…Li$^+$	1.897	1.981	1.940
	H2O(3)…Li$^+$	3.724	1.986	3.458
Angle	S (or C)-O(1)…Li$^+$	125.3	60.3	85.5
(deg)	S (or C)-O(2)…Li$^+$	65.4	115.2	86.5
	C-S (or C)-O(1)…Li$^+$	−155.2	−149.8	179.8
	C-S (or C)-O(2)…Li$^+$	132.5	−176.4	−179.8
Parameter	Atom/group	3 methanol molecules		
		Nafion-Li$^+$	IonClad-Li$^+$	M3-Li$^+$
Bond	O(1)-Li$^+$	1.861	1.951	2.011
length (Å)	O(2)-Li$^+$	3.246	2.230	1.986
	S (or C)-O(1)	1.462	1.468	1.241
	S (or C)-O(2)	1.442	1.466	1.252
	S-O(3)	1.437	1.446	–
	CH3-O(1)H…Li$^+$	1.915	1.942	1.969
	CH3-O(2)H…Li$^+$	1.887	1.918	1.930
	CH3-O(3)H…Li$^+$	3.705	3.750	3.451
Angle	S (or C)-O(1)…Li$^+$	125.0	96.4	85.5
(deg)	S (or C)-O(2)…Li$^+$	65.4	85.4	86.4
	C-S (or C)-O(1)…Li$^+$	−155.3	−129.0	−178.0
	C-S (or C)-O(2)…Li$^+$	132.5	126.8	180.0

molecules, and with three methanol molecules. The geometry parameters of these membrane systems are gathered in Table 1. The comparison of the geometries of the dry sulfonic cationic membranes shows that, on the average, distances S… O in the –SO$_3^-$ groups are slightly larger in the aromatic membrane IonClad (1.46 Å) than in the perfluorinated Nafion membrane (1.45 Å). In the membrane M3, the average value of the bonds C…O in the carboxyl group was equal to 1.25 Å.

Figure 3 presents the distances between the nearest oxygen atom of the functional group and Li$^+$ ion as a function of the number of the absorbed water molecules (on the left) and methanol molecules (on the right). During advancing solvation by water, it was found that uniquely in the perfluorinated Nafion membrane, the lithium ion shifts away from the sulfonic group. The distance –SO$_3^-$…Li$^+$ dramatically increases from 1.90 to 3.70 Å after the membrane absorbed seventh water molecule (Fig. 3). This observed movement of the lithium ion from the sulfonic group in the hydrated Nafion

membrane proves the dissociation of the functional group [9]. Further buildup of the water molecules in the Nafion membrane leads to additional slight increase of the–SO$_3^-$… Li$^+$ distance. In aromatic membranes IonClad and M3, the shortest distances between the lithium and the fixed groups practically do not change (1.85–2.06 Å) over the whole investigated range of the hydration level (Fig. 3). It was also found
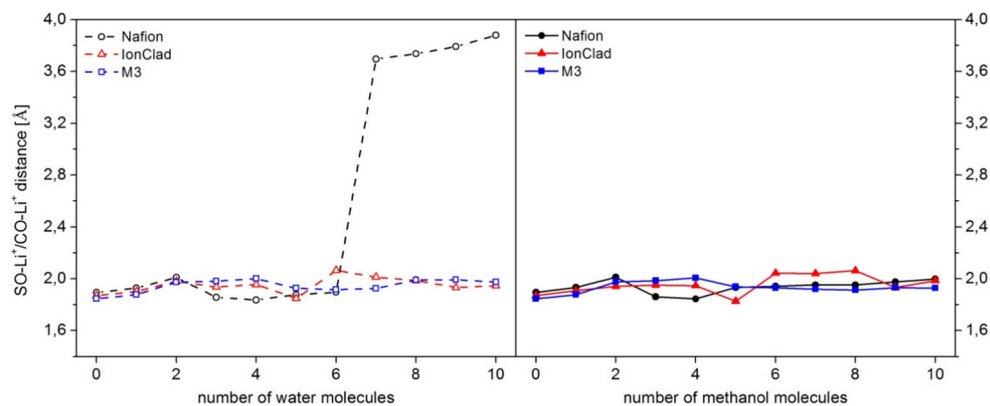
that in course of solvation by methanol, for all three membranes, the distance between the lithium ion and fixed groups was practically invariant over the whole investigated range of the solvation level.

Figure 4 illustrates the calculated geometries of all the three membranes solvated by 10 molecules of water (Fig. 4a) or methanol (Fig. 4b). In the hydrated Nafion membrane, the ion-pair rests in the dissociated state, and some water molecules separate the sulfonic group and lithium counter-ion. In the hydrated aromatic membranes IonClad and M3, the lithium ion remains close to the fixed group in the whole

investigated range of the solvation level. The same situation is observed in the case of all three membranes solvated by methanol: the ion-pairs do not dissociate over the whole studied solvation range.

Figure 5 schematically displays a difference in the formation of the solvation shells around the dissociated and non-dissociated ion-pairs [42]. When the ion-pair dissociates, the solvent molecules are located between the fixed group and the counter-ion separating them. When the ion-pair is non-dissociated, the solvent molecules surround the non-separated ion-pair forming the outer solvation shell [9, 42]. From the

Fig. 4 Calculated geometries of solvated membranes in Li$^+$ form: **a** with ten water molecules, **b** with ten methanol molecules. Nafion—on the *left*, IonClad—in the *middle*, M3—on the *right*

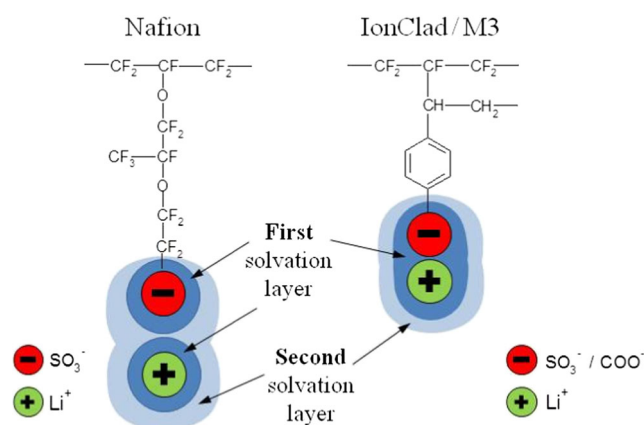Nafion   IonClad   M3
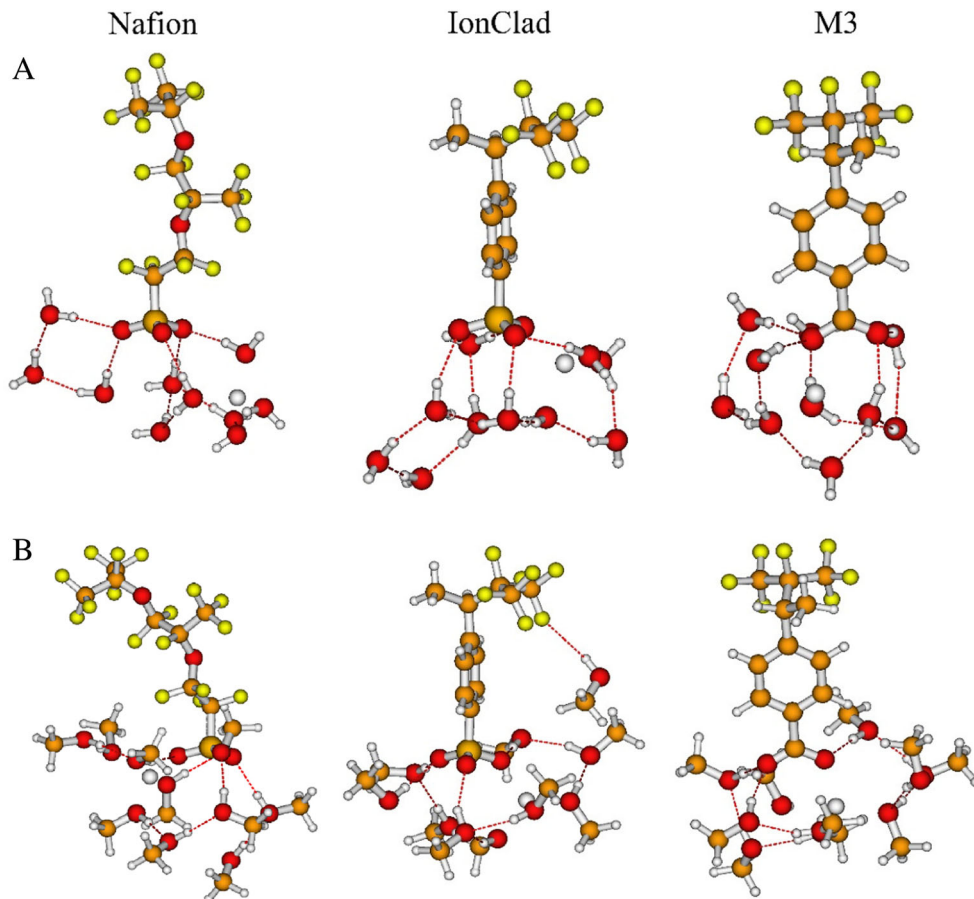
Fig. 5 Scheme of the solvation for dissociated (*left*) and non-dissociated (*right*) ion-pairs in the ion-exchange membranes

calculated geometries of the membranes with ten solvent molecules presented in Fig. 4, the distances between the ion-pairs and the solvent molecules of the first solvation shells were measured. The obtained values are gathered in Table 2.

The average distances between the ion-pairs and water molecules in the hydrated membranes increase in the following order Nafion < M3 < IonClad, while at the solvation by methanol molecules, these distances follow the sequence Nafion < IonClad < M3. It should be mentioned that in the case of the hydrated Nafion membrane, the first hydration shell of the sulfonic group consists of five water molecules, while the first hydration shell of the counter-ion Li^+ is built by four molecules, revealing a tetrahedral coordination. A similar observation is reported in the papers [43, 44] devoted to the computational study of Li^+ in aqueous solution, as well as in a study [45] which investigated the water sorption in Nafion.

The occurrence of the ion-pair dissociation in the hydrated Nafion membrane in comparison with aromatic membranes has already been discussed in earlier works [9, 35]. The sulfonic groups in Nafion membrane are bound to the fluorocarbon vinyl ether side chains. The presence of electron-withdrawing $–CF_2-$ groups in the side chains of Nafion membrane generates stronger acidic and polarizable character of the functional group facilitating its dissociation. Mahajan et al. [35] indicated that polymer matrix in SPEEK and

Nafion membranes has some influence on the separation of the functional groups from another one. It was shown that the separation between the sulfonic groups in aromatic membrane induced by its solvation was hindered by low hydrophobicity of aromatic backbones and low hydrophilic character of the sulfonic groups in SPEEK. Using DFT methods, Sakai et al. [46] and Doan et al. [47] studied the protonated and deprotonated forms of perfluorosulfonic molecules modeling Nafion membrane. It was demonstrated that the deprotonated sulfonic group is more stable than the protonated state by 3.72 kcal/mol (16 kJ/mol). Using LPNO-CEPA/1 method, we found a similar value of 4.17 kcal/mol (17.44 kJ/mol) for Nafion with three water molecules. Sakai et al. [48] analyzed the energetic stability of membrane models of Nafion and SPEEK at low hydration levels (1–3 molecules of water) in terms of the activation energy (ΔE_a) and the enthalpy difference (ΔH) before and after deprotonation of the sulfonic group. It was pointed out that the activation energy of sulfonic groups in the perfluorosulfonic membrane is very low, while ΔE_a and ΔH for the aromatic SPEEK membrane are higher than for the perfluorinated Nafion one. Therefore, the deprotonation step was indicated as a non-favorable in the case of SPEEK. Consequently, it can be calculated that the presence of the benzene ring in the side chains of the aromatic membranes decreases the acidity of their functional groups [9]. However, the dissociation of the functional group does not depend solely on the side chain structure but also on the polarity of the absorbed solvent. This fact results from the observation that the ion-pair of Nafion membrane dissociates, when the membrane is solvated in water, while it does not dissociate in methanol.

Figure 6 depicts the binding energy per one solvent molecule of water and methanol as a function of the solvation level. In Nafion, the binding energy of both water and methanol is slightly higher than for the aromatic membranes IonClad and M3. These computations help also to explain the experimental results, indicating that the Nafion membrane absorbs more methanol and water than the aromatic membrane IonClad. As it can be seen in Fig. 6, for the Nafion and IonClad membranes, the binding energy of water (E_b/X) decreases with increasing hydration level. In the case of membrane M3, where the side chains are terminated with the carboxyl groups, E_b/X rises at low hydration level $X = 1–3$, but the further increase of the hydration ($X = 4–10$) leads to a decrease in the interactions of water with the carboxyl groups. For all three studied membranes, the binding energy of methanol continuously goes down with increasing solvation.

A comparison of the interaction energy of water and methanol with the investigated membranes shows that at solvation level $X = 1–8$, in the perfluorinated membrane Nafion, water molecules are more weakly bound to the functional groups than methanol molecules (Fig. 6). At higher solvation $X = 9–10$, the binding energies of water and methanol are

Table 2 Distances between the counter ions (Li^+), the fixed charge ($–SO_3^-$, $–COO^-$), and closest solvent molecules (water and methanol) in Nafion, IonClad, and M3 membranes at solvation level $X = 10$

Distance between ion-pairs and 10 solvent molecules (Å) in membranes			
10 water molecules	Nafion-Li	IonClad-Li	M3-Li
	$–SO_3-$ Li	$–SO_3$-Li^+	$–COO^-Li^+$
	2.00 1.96	2.66	2.31
10 methanol molecules	Nafion-Li+	IonClad-Li	M3-Li
	$–SO_3$ Li	$–SO_3$-Li^+	$–COO^-Li^+$
	2.49	2.57	2.61

Fig. 6 Binding energy per solvent molecule vs. number of absorbed solvent molecules in Nafion, IonClad, and M3 membranes in Li^+ form
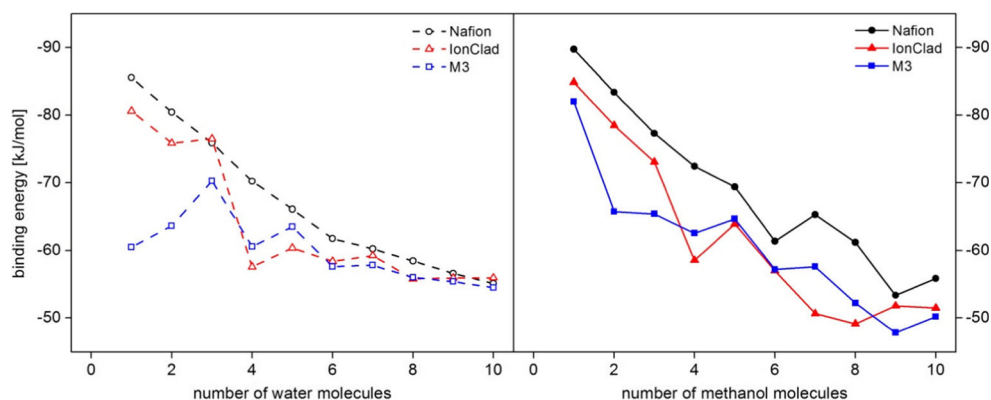
practically the same. In the aromatic membrane IonClad, the first methanol molecule is more strongly bound to the functional group than the first water molecule. Subsequently, at $X = 2$–6, the binding energies of water and methanol have very similar values, whereas, at higher solvation level $X = 7$–10, water is more tightly linked to IonClad than methanol. Very interesting results are observed for the virtual membrane M3. In this case, the carboxyl group interacts significantly more strongly with the first absorbed methanol molecule than with the first water molecule (Fig. 6). At $X = 2$–7, the binding energies of methanol and water possess very comparable values; however at higher solvation level $X = 8$–10, water is more strongly tied to the membrane than methanol.

The experimental results reported by Chaabane et al. [32, 33] showed that membrane CM2, having hydrocarbon side chains, contains less water molecules per sulfonic group ($X = 6.03$ mol H_2O/mol SO_3^-) than membrane Nafion 117 ($X = 8.80$ mol H_2O/mol SO_3^-) with the perfluorinated side chains. Furthermore, Nafion membrane absorbs much more methanol than CM2 membrane. These results correlate well with the binding energies calculated within this work: water and methanol interactions with the hydrocarbon side chain of the IonClad membrane are weaker than with perfluorinated side chain of the Nafion membrane.

Nafion in Li^+, H^+, and Na^+ forms in water

This part of the paper presents a comparison of the structural features of the Nafion membrane in three ionic forms H^+ [26], Na^+ [26], and Li^+ investigated at various hydration level ($X = 0$–10).

Table 3 presents the atom and ionic radii of H/H_3O^+, Li/Li^+, and Na/Na^+ as well as their hydration numbers in aqueous solutions [49–57] and in Nafion membrane determined in the present study. The computed geometries of the membranes hydrated with ten water molecules are demonstrated in Fig. 7. The functional groups in all investigated ionic forms are found in the dissociated state, but the spatial arrangement of the water molecules in the membrane significantly differs and depends on the counter-ion nature (Fig. 7). We found that amount of the water molecules in the first hydration shell of the counter-ions increases with rising atomic radius of the counter-ion in accordance with the sequence $H^+ < Li^+ < Na^+$ (Table 3). The hydration numbers of the counter-ions obtained in the simulation for Nafion membranes are consistent with the values measured for the ions in aqueous solutions. Table 4 demonstrates the distances to the closest water molecules from the counter-ions and the sulfonic groups in Nafion membrane hydrated by ten water molecules. The water molecules are located significantly nearer to the proton than to the alkali ions. But in proton form of Nafion, the distance between sulfonic group and the water molecules is slightly higher than in Li^+ and Na^+ forms. As seen from the Table 4, in all studied ionic forms of the Nafion membrane, the distances between the water molecules and the counter-ions are shorter than the distances determined for the counter-ions in aqueous solutions. In H^+ form of Nafion, the water molecules are located around 1.57 Å from the proton, while in the $H^+(H_2O)_9$ cluster the distance is 2.54 Å, as computed by Bankura et al. [52].

Figure 8 depicts the closest distances between the fixed group and counter-ions ($-SO_3^-…Cat^+$) as a function of the hydration level. In the dry Nafion, the distance $-SO_3^-…Cat^+$

Table 3 Atomic and ionic radii of H, Li, and Na, their hydration number in aqueous solutions [49–57, this study], and Nafion hydrated with ten water molecules

Atom/ion	Atom/ionic radii, [Å]	Hydration number	
		In aqueous solution	In Nafion membrane
H/H_3O^+	0.32/1.54 [49–51]	3.0 [52]	3 [this study]
Li/Li^+	1.52/0.68 [49, 57]	3.3–4.4 [56, 57]	4 [this study]
Na/Na^+	1.86/0.97 [49, 57]	4.5–6.5 [53–55, 57]	5 [this study]

Fig. 7 The geometry of different ionic forms of membrane Nafion-H, Nafion-Li, and Nafion-Na hydrated with ten water molecules. In Nafion-H, the proton is marked by the dashed circle
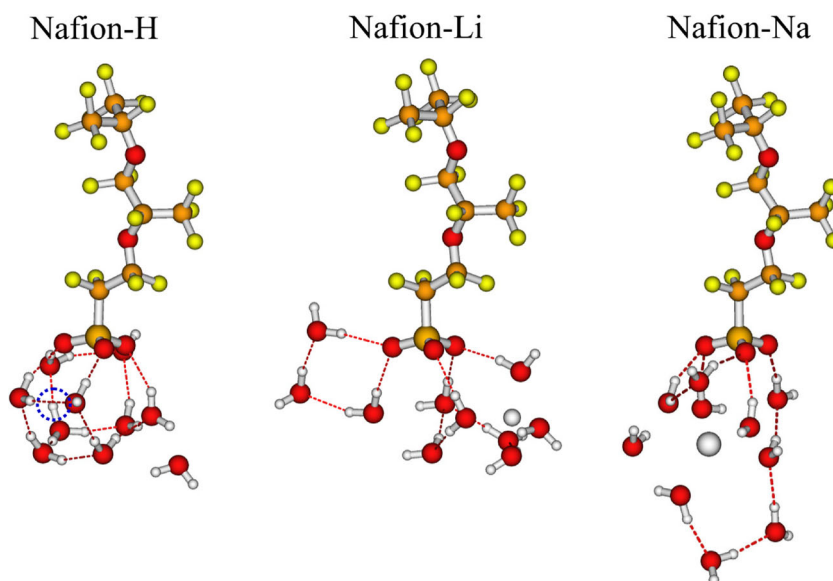
increases with the atomic radius of the counter-ion in the following sequence $H^+ < Li^+ < Na^+$. In the proton form, the distance $-SO_3^-\ldots H^+$ extremely increases, when the membrane absorbs three and five water molecules. At $X = 3$, the proton form of the functional group dissociates. At $X = 5$, the proton jumps to the second layer of the water molecule surrounding the sulfonic group. At hydration level $X > 5$, the proton marginally continues to move away from the sulfonic group with increasing hydration level. In Li^+ and Na^+ forms of the Nafion membrane, the distances $-SO_3^-\ldots Cat^+$ practically do not change at $0 \le X \le 6$. In these ionic forms, the dissociation of the functional groups occurs, when the functional group is surrounded by seven water molecules. The distances $-SO_3^-\ldots Li^+$ and $-SO_3^-\ldots Na^+$ reach comparable values, 3.70 and 3.77 Å, respectively. At higher hydration level $X > 7$, Li^+ and Na^+ ions are located further away from the sulfonic groups than the protons are. The mean distance $-SO_3^-\ldots H^+$ equals 3.46 Å at this hydration range ($X > 7$). It should be mentioned that prior to the dissociation, the hydrogen is connected to the sulfonic group by a covalent bond, while the alkali metal ions Li^+ and Na^+ create ionic bonds. After the dissociation, the proton builds the hydronium ion, which has a significantly larger radius than the proton and also than the

lithium and sodium cations (Table 3). Since the hydronium ion has larger size and lower surface charge density than the studied alkali cations, the hydronium ion is less distanced from the sulfonic group at the higher hydration level ($X \ge 7$).

The water binding energy in Nafion membrane is presented in Fig. 9. The diagram demonstrates the water binding energy per water molecule in Nafion membrane of the three ionic forms investigated, as a function of the hydration level. In general, the binding energy continuously decreases with increasing hydration level (Fig. 9). A pronounced difference in the binding energy is observed at low hydration level $1 \le X \le 4$. At this region of hydration, the water interactions with the membrane are the strongest for the Li^+ form and the weakest for the H^+ form of the membrane. In the whole investigated range of the hydration level ($0 \le X \le 10$), the binding energy per water molecules is stronger for Nafion containing the alkali ions as the counter-ions, because the alkali ions possess quite large surface charge density, which strengthens the electrostatic attraction of the water molecules. The static ab initio calculations are consistent with experimental observations demonstrating that the water diffusion coefficient is higher in H^+ form Nafion than in Na^+ or Li^+ forms [58–60].

Table 4 Minimum distances between the counter-ions (H^+, Li^+, and Na^+), the fixed charge ($-SO_3^-$), and the closest water molecules in Nafion hydrated with ten water molecules [52, 57, this study]

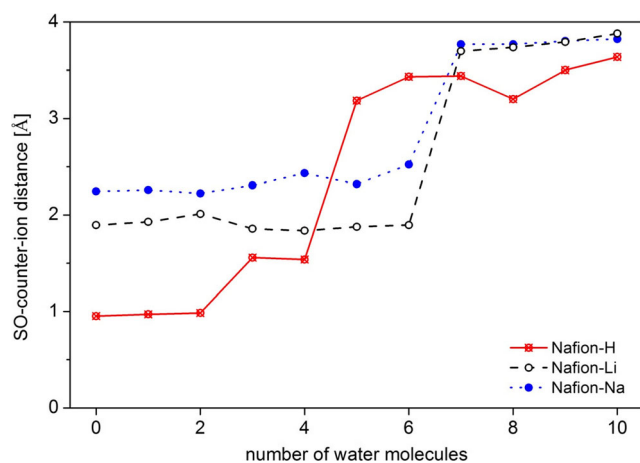| Cation	Distances between cation and water [Å]		Distances between $-SO_3^-$ and water in Nafion membrane [Å]
	In Nafion	In aqueous solution	
H^+	1.53–1.62 [this study]	2.54 [52]	1.92–2.10 [this study]
Li^+	1.94–1.99 [this study]	1.95–2.03 [57]	1.90–2.07 [this study]
Na^+	2.27–2.49 [this study]	2.34–2.50 [57]	1.90–2.03 [this study]

Fig. 8 Minimal distance between sulfonic group and counter-ions in Nafion membrane of different ionic forms: H⁺, Li⁺, and Na⁺ vs. number of absorbed water molecules

Conclusions

The work discusses the interactions of water and methanol molecules with different cationic polymeric membranes as well as the role of the nature of the functional groups and membrane polymeric matrices on these interactions. Using ab initio methods, three cation-exchange membrane models of Nafion, IonClad, and M3 were investigated in Li^+ ionic form, in contact with water and methanol molecules, at various solvation level ($X = 0–10$). The studied membranes possess the perfluorinated backbone, but different side chains terminated with the various functional groups of distinct ionic strength. The simulation of the membranes with lithium as counter-ion showed that in the Nafion membrane, the dissociation of the ion-pairs occurs at the hydration level of seven water molecules. In the aromatic membranes IonClad and M3, no dissociation of the functional groups is observed for the whole investigated range of the hydration level. The presence of the benzene ring in the side chains of the aromatic membranes decreases the acidity of their functional groups. The
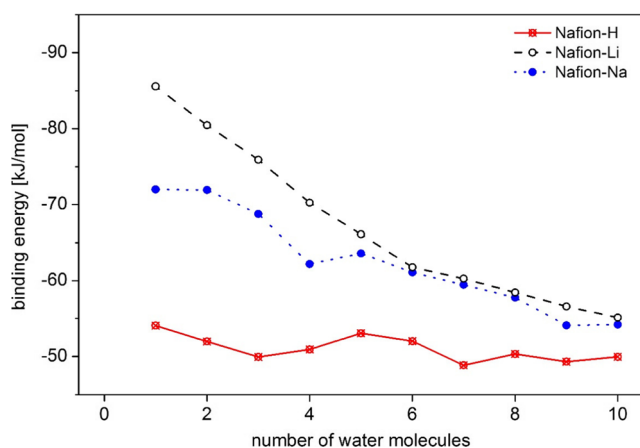
solvation of all three membranes by methanol does not lead to any dissociation of the functional groups. It indicates the strong role of the polarity of the absorbed solvent on the dissociation phenomenon.

It can be assumed that the ability of the functional group to dissociate becomes more pronounced with the following:

1) growing electron density of the polymer side chains, especially when the electronegative group is directly connected to the functional group
2) increasing polarity of the absorbed solvent
3) increasing acidity of the fixed group

The binding energy of the solvent molecules with the membrane generally decreases with increasing solvation level. In the Nafion membrane, the binding energy of water and methanol is slightly higher than in the aromatic membranes IonClad and M3.

The obtained results for Li^+-Nafion in water are compared with earlier published simulation for H^+ and Na^+ forms. In the dry state of Nafion, the distance between the counter-ion and fixed group increases with growing atom radius of the counter-ion as $H^+ < Li^+ < Na^+$ and then increases with rising hydration level. For high hydration levels $X \geq 7$, this distance practically does not depend on the counter-ion nature and is equal to around 3.67 Å. In the Nafion-H^+ membrane, the functional groups dissociate at hydration level of $X = 3$, while in the Na^+ and Li^+ forms, the dissociation proceeds at $X = 7$. In the perfluorinated sulfonate membrane, the binding energy per water molecule increases with rising surface charge density of the counter-ion. Moreover, the water molecules are located closer to the counter-ions in the Nafion membrane than in aqueous solutions.

Fig. 9 Binding energy per water molecule in Nafion membrane in H⁺, Li⁺, and Na⁺ form as a function of the hydration level

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