Effect of the polar–nonpolar liquid mixtures on pervaporative behavior of perfluorinated sulfonic membranes in lithium form

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Edyta Rynkowska [a,b], Joanna Kujawa [a], Corinne Chappey [b], Kateryna Fatyeyeva [b], Larisa Karpenko-Jereb [c], Anne-Marie Kelterer [c], Stéphane Marais [b], Wojciech Kujawski [a,*]

[a] Nicolaus Copernicus University in Toruń, Faculty of Chemistry, 7, Gagarina Street, 87-100 Toruń, Poland
[b] Normandie Univ, UNIROUEN, INSA Rouen, CNRS, PBS, 76000 Rouen, France
[c] Institute of Physical and Theoretical Chemistry, Graz University of Technology, NAWI Graz, Stremayrgasse 9, 8010 Graz, Austria

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ABSTRACT

Two ion-exchange membranes possessing perfluorinated backbone and sulfonic groups (i.e. Nafion® 120 and IonClad™ R4010) with lithium(I) counter-ions were investigated. The interactions between solvents of different polarity and the ion-exchange membranes with various morphologies were taken into account in order to better understand solvation and dissociation phenomena of the ion-pairs.

Pervaporation of polar (i.e. water, methanol)–nonpolar (i.e. methyl acetate, dimethyl carbonate) liquid mixtures was carried out. It was revealed that the increase of the polar component concentration above 2 wt% in the feed mixture leads to dissociation of ion-pairs in Nafion membrane, which is reflected by the rapid increase of the polar component partial flux. In the case of IonClad membrane the dissociation of the ion-pairs during pervaporation was observed only when water was a polar feed component.

The dissociation of ion-pairs was also evidenced in infrared study by observing the shift of symmetric stretching vibrations (ν_s) bands of sulfonic groups to the lower wavenumbers, compared to the membrane in the dry state. The symmetric stretching vibrations (ν_s) bands of the dry Nafion membrane and membrane solvated with water and methanol were equal to 1071 cm^{-1}, 1058 cm^{-1}, and 1054 cm^{-1}, respectively. In the case of IonClad membrane the symmetric stretching vibration (ν_s) bands changed in contact with water from 1047 cm^{-1} (dry membrane) to 1037 cm^{-1}. The dissociation of the ion-pairs did not occur in IonClad membrane equilibrated with methanol, which is also consistent with the result obtained during pervaporation.

1. Introduction

The Nafion membrane is the most frequently used ion-exchange membrane thanks to its excellent chemical stability as well as high proton conductivity [1–4]. Nafion is widely utilized in different processes and devices such as: fuel cells [5,6], electrodialysis [7], electrochemical synthesis [8], sensors [9], electrokinetic energy conversion [10,11], and pervaporation (PV) [12,13]. The studies of the water and aliphatic alcohols uptake and their transport through Nafion and other sulfonated ion-exchange membranes (e.g. IonClad, PESS) indicated that the behavior of molecules transported through the ion-exchange membrane is strongly affected by the nature of counter-ion [14–17] and ion-exchange group [14,18–23]. Numerous studies of ion-exchange membranes were also devoted to investigate sorption and permeation properties in contact with water, alcohols, and with aqueous–organic or organic–organic mixtures [3,15,18,24–26]. Moreover, the permeability of water and methanol [27] and diffusion ability of alcohols [14,16,28] were investigated in order to evaluate the performance of Nafion in pervaporation measurements.

Ion-exchange membranes are applied in pervaporation thanks to their efficiency and their properties which can be tailored, depending on the nature of the counter-ion. Pervaporation enables to

Table 1
The potential applications of pervaporation [35–44].

Type of pervaporation	Possible applications	References
Hydrophilic (separation of water from aqueous–organic mixtures)	Separation water–organic azeotrope mixtures (e.g. water–ethanol, water-2-propanol); dehydration of organic solvents; controlling the equilibrium of the reaction (e.g. esterification)	[39,40,44]
Organic–organic (separation of organic–organic mixtures)	Separation of azeotropic mixtures (e.g. methanol–DMC, ethanol–cyclohexane, ethanol–ETBE, methanol–MTBE); separation of isomers (e.g. xylenes)	[35,38,43]
Hydrophobic (removal of volatile organic compounds (VOCs) from aqueous streams)	Recovery of organic compound from fermentation broth; dealcoholization of beer and wine; removal of VOCs from water	[36,37,41,42]

separate binary or multicomponent liquid mixtures including azeotropic and close-boiling systems (Table 1). PV involves liquid to vapor phase change, therefore that technique is unique among membrane separation processes [29]. During PV permeants are transported from the feed to the permeate side of the non-porous dense polymeric membrane. The difference in chemical potentials of components between two sides of the membrane is a driving force of the mass transfer of permeants. The driving force can be created either by vacuum (vacuum pervaporation, VPV), temperature difference (thermopervaporation, TPV) or using sweep gas (sweeping gas pervaporation, SGPV) [30,31]. In general, the separation by a non-porous membrane is based on the differences in the solubility and the diffusivity of the feed components in the membrane [14,18,19,32–34].

Pervaporation (PV) is an important membrane separation process characterized by a low energy consumption and high selectivity of membranes, which are important advantages over the conventional separation processes like distillation or extraction [44,45]. This technique allows to separate close boiling solvents, azeotrope mixtures, and isomers (Table 1). The exploitation of perfluorinated ion-exchange membranes in organic–organic pervaporation can be an interesting alternative in solving the separation limitations in chemical and petrochemical industry dominated by distillation, adsorption, and absorption [33,45–49]. It is related to the fact that separation by distillation employs selective evaporation and condensation of separated components [50] in contrast to solution-diffusion mechanism in pervaporation. According to the solution-diffusion model, the transport of the components through the membrane consists of liquid sorption into the membrane on the feed side, vapors diffusion through the membrane, and desorption at the permeate side [51]. The comprehensive characterization of ion-exchange membranes is the crucial approach and can lead to broaden the knowledge about the affinity between the ion-exchange membrane structure and its equilibrium, transport, and separation properties.

The ion-exchange membranes were extensively studied in pervaporative separation in order to correlate their morphology and transport efficiency [33,50,52–56]. Lue et al. [50] investigated transport properties of Neosepta®-CMX cation-exchange membrane containing copper ions Cu(II) or sodium ions Na(I) as counter-ions in pervaporation of benzene–cyclohexane liquid mixture. It was shown, that benzene is preferentially transported through the Neosepta in the both sodium and copper-forms. The change of Na(I) into Cu(II) ions resulted in the higher flux of benzene and higher efficiency of separation. It is related to the fact that both sorption and diffusion coefficient of benzene was higher in the case of membrane in Cu(II) form. Kao et al. [33] and Koval et al. [52] performed the studies on transport properties of Nafion in contact with benzene/cyclohexane [33] and styrene/ethylbenzene mixtures [52], respectively. Authors indicated that replacement of sodium counter-ion with silver one in Nafion membrane increases Nafion selectivity and permeability to benzene and styrene, respectively. Zhou et al. [53] carried out the pervaporative separation of ethanol–cyclohexane using the polypyrrole membranes. Two kinds of polypyrrole membranes were tested, i.e.

membrane with the neutral and oxidized cationic state containing hexafluorophosphate as the counter-ion [53]. It was proved that studied membranes are selective toward ethanol within the whole investigated concentration range. Moreover, the oxidized form of membrane possesses higher selectivity than the reduced one, at ethanol feed concentration below 20 wt% [53]. However, both membranes show similar selectivity at higher concentration level of ethanol in the feed. Jiang et al. [54] and Chen et al. [55] carried out the research on pervaporative separation of methanol from triglyme (triethylene glycol dimethyl ether) [54] and methyl t-butyl ether solution [55], respectively, utilizing two different ion-exchange membranes. Jiang et al. [54] pointed out that Nafion membrane was highly permeable and selective for methanol, which is associated with transport of molecules through the cluster-network of Nafion. Since methanol molecules are smaller and more polar than triglyme ones, the facilitated transport of methanol through Nafion ionic channels is observed. Chen et al. [55] applied PSS-Me/Al$_2$O$_3$ composite membrane with sodium (I) and magnesium(II) as counter-ions. The investigated membranes transported methanol selectively from methanol–methyl t-butyl ether feed mixture, whereas the membrane possessing Mg (II) counter-ions revealed higher separation properties than the membrane with Na(I) counter-ion.

Zhou et al. [56] used polypyrrole based membranes doped with hexafluorophosphate (PPy-PF) and p-toluenesulfonate (PPy-PTS), in pervaporative removal of methanol from toluene. The efficiency of the PPy-PF and PPy-PTS membranes in separation of methanol/toluene mixture was compared to the results obtained for these membranes in pervaporative separation of methanol/2-propanol and methanol/MTBE mixtures.

Nafion and IonClad membranes possess similar polymeric backbone made of polytetrafluoroethylene. However, despite that fact Nafion and IonClad membranes reveal significant differences in the transport abilities in contact with aqueous–organic solvent mixtures. Kujawski et al. performed the differential permeation measurement for Nafion® 120 and 117, IonClad™ R4010 and PESS membranes in contact with various aliphatic alcohols [14]. It was stated that although ion-exchange capacity (IEC) of Nafion membrane is lower than that of IonClad, diffusion coefficients of aliphatic alcohols vapors are much greater in contact with Nafion membrane. Tricoli et al. [19] investigated the methanol permeability and proton conductivity of IonClad™ R4010 and IonClad™ R1010. Obtained results were subsequently compared with results for Nafion® 117. It was found that methanol permeability for Ion-Clad membranes is four times smaller than that for Nafion one [19]. It is supposed that this difference between investigated membranes is strongly associated with the ionic strength of sulfonic groups and its polarizability. Sulfonic groups in IonClad membranes are attached to the benzene ring, whereas in Nafion membrane the sulfonic groups are bound to the fluorocarbon vinyl ether side chains resulting in the stronger acidic character of such sulfonic group. Therefore the sulfonic groups in Nafion membrane demonstrate better dissociation ability, resulting at higher permeability of alcohols. The influence of the different ionic strength of functional groups in ion-exchange membranes on the

permeability of water and alcohol were also presented in other studies on sulfonated poly(arylene ether sulfone) (PAES) membrane [21], sulfonated poly(phenylene ether ether sulfone) (SPEES) membrane [20], sulfonated polyetheretherketone (SPEEK) membrane [57], and MK-40 possessing sulfonic groups attached to polystyrene/divinylbenzene copolymer chains [18]. Godino et al. [17] and Cabasso et al. [58] presented that the type of counter-ion in Nafion membrane affects water and alcohol transport through the membrane. It was shown that Nafion membrane is selective towards water, whereas the water flux increased with decreasing atomic number and radius of chosen alkali cations in the following sequence: $Cs^+ < K^+ < Na^+ < Li^+ < H^+$, which is in accordance with results of other authors [15,22,26]. The increasing size of counter-ion causes also a decrease of the solvent uptake [22]. Moreover, Struis at al. [59] revealed that the counter-ion type in the ion-exchange membrane influence the methanol and water permselectivity. The best effectiveness and the stability of the Nafion membrane was found for lithium as a counter-ion [59]. Haldrup et al. [10] and Kilsgaard et al. [11] investigated Nafion and nitrocellulose and sulfonated polystyrene based membranes, respectively, in lithium(I) form in terms of the electrokinetic conversion efficiency. It was shown that thanks to polar electrostatic interactions between lithium ion and water molecules the membranes possessed high permselectivity and high efficiency of electrokinetic energy conversion.

According to our hypothesis, the ion-pairs dissociation phenomenon in the ion-exchange membranes is one of the key factors allowing broad understanding of transport properties during membrane separation processes. In our previous work [60] the Nafion, IonClad, and M3 membranes were investigated using quantum chemistry approach in terms of the ion-pairs dissociation phenomena, taking into account both the structural properties of the ion-exchange membrane (the nature of the functional groups and the polymeric matrix as well as the type of counter-ion) and the different polar character of the solvents (water and methanol). It was found that the dissociation of ion-pairs occurred at the hydration level X=7 for Nafion-Li$^+$ and Nafion-Na$^+$ membrane models [60,61] and at X=3 for Nafion-H$^+$ one [60,61]. On the other hand, in the case of IonClad membrane, the calculations suggested that the solvation with water or methanol did not cause the separation of ion-pairs [60].

The aim of this work was to investigate the influence of structural properties of two ion-exchange membranes possessing the perfluorinated backbone and sulfonic groups (i.e. Nafion-Li$^+$ and IonClad-Li$^+$) on the solvation and separation of ion-pairs in contact with solvents of different polarity during pervaporation. In order to study the dissociation phenomena of the investigated ion-exchange membranes the effect of the feed polar components on the separation effectiveness in the pervaporation of polar (i.e. water, methanol)–nonpolar (i.e. methyl acetate, dimethyl carbonate) liquid mixtures was taken into consideration. The effect of the solvation by solvents of different polarity on the state of ion-pairs was investigated using infrared analysis for the membranes in dry state, in contact with pure water and pure methanol, as well as with water vapors at different relative humidity. The obtained experimental results were compared with the theoretical calculations for Nafion and IonClad membrane models at different solvation levels [60].

2. Materials and methodology

2.1. Membranes

The following two various ion-exchange membranes were used (Table 2): Nafion purchased from du Pont de Nemours and Co.

(USA) and IonClad kindly provided by Pall Corporation (USA). Both membranes possess the perfluorinated backbone (polytetrafluoroethylene – Nafion and poly(tetrafluoro-co-perfluoropropylene) - IonClad) and sulfonic groups as ion-exchange sites. Nafion membrane possesses sulfonic groups attached to the perfluorinated ether-linked side chains, whereas the sulfonic groups in the IonClad membrane are bound to the poly(styrene sulfonic acid) side chains.

Prior to use, the pristine samples of the Nafion membrane were rinsed with deionized water and then were annealed in hot distilled water (80 °C) during 1 h [14]. The annealed Nafion and the pristine IonClad membrane samples were converted into lithium form. Membrane samples were immersed in 4 M HCl solution for 24 h, to exchange all counter-ions into hydrogen ones. Furthermore, membranes were washed with deionized water and immersed in 1 M LiOH solution for 24 h. Before using membranes in pervaporation experiments, samples were rinsed in deionized water to remove the excess of LiOH and dried at the ambient temperature.

2.2. Solvents

Methanol, methyl acetate and dimethyl carbonate were delivered by Avantor Performance Materials Poland S.A. (Gliwice, Poland). Absolute methanol, methyl acetate and dimethyl carbonate of analytical grade as well as RO deionized water were used to prepare following binary solvent mixtures: water–methyl acetate (H$_2$O–MeAc), methanol–methyl acetate (MeOH–MeAc), water–dimethyl carbonate (H$_2$O–DMC), and methanol–dimethyl carbonate (MeOH–DMC). The amount of water in pure absolute methanol is less than 0.01 wt%. The composition of permeates determined by using gas chromatography with thermal conductivity detector indicated water content in MeOH–DMC and MeOH–MeAc mixtures below 0.1 wt% H$_2$O. These negligible amounts of water found in feed and permeate mixtures (MeOH–MeAc and MeOH–DMC) did not distort the obtained results [66]. All solvents were used as received. The differences of physicochemical properties of tested solvents are presented in Table 3. The saturated vapor pressure at 25 °C of water, methanol, and methyl acetate was calculated according to Antoine's equation (Eq. (1)) and in the case dimethyl carbonate according to the Eq. (2) [67].

$$\log P = A - \frac{B}{T + C - 273.15} \tag{1}$$

$$\ln P = \ln P_c + \left(\frac{T_c}{T}\right) + \left(a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5\right) \tag{2}$$

where: A, B, C and a, b, c, d – Antoine's equation constants, T – temperature [K], T_c – vapor/liquid critical temperature [K], P_c – vapor/liquid critical pressure [bar], $\tau = 1 - \frac{T}{T_c}$.

2.3. Pervaporation experiments

The vacuum pervaporation experiments were performed at 35 °C using the standard experimental rig presented schematically in Fig. 1 and described in the detail elsewhere [37,51]. Nafion and IonClad membranes were utilized in pervaporation experiments in lithium form. The binary solvent mixtures, i.e. water–methyl acetate (H$_2$O–MeAc), methanol–methyl acetate (MeOH–MeAc), water–dimethyl carbonate (H$_2$O–DMC), and methanol–dimethyl carbonate (MeOH–DMC) were used as feed mixtures. The content of more polar component in the feed mixture varied within the concentration range 0–10 wt% of MeOH for MeOH–MeAc and MeOH–DMC mixtures. In the case of H$_2$O–MeAc feed mixture,
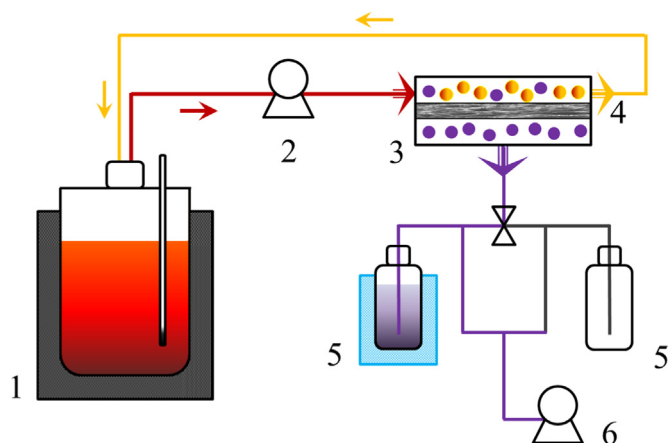
Fig. 1. The scheme of the pervaporation setup: (1) thermostated feed tank, (2) feed pump, (3) membrane module, (4) membrane, (5) permeate traps cooled with liquid nitrogen, (6) vacuum pump [37,51].

water was added up to the concentration equal to around 8 wt% H_2O [73], whereas H_2O–DMC mixture was tested up to 3 wt% of water, as DMC and water form two phase system (miscibility gap) in the concentration range between 3 and 85 wt% of H_2O in the binary H_2O–DMC mixture [74].

Effectiveness of pervaporation process was described using the parameters presented by Eqs. (3)–(7) [37,51,75]:

The total permeate flux (J_t):

$$J_t = \frac{\Delta m_t}{A \Delta t} [\text{g m}^{-2} \text{ h}^{-1}] \tag{3}$$

where: Δm_t – permeate mass [g] collected over Δt period [h], and A – membrane area [m²].

The partial flux of component i (J_i) was calculated using the following formula:

$$J_i = J_t \cdot y_i \tag{4}$$

where: y_i is the weight fraction of i in the permeate.

The separation effectiveness of the membrane in the pervaporative separation of organic–organic and organic–aqueous liquid mixtures was assessed using the separation factor β (Eq. (5)) and enrichment factor EF (Eq. (6)), as suggested recently by Baker et al. [75]:

$$\beta = \frac{y_i/(1-y_i)}{x_i/(1-x_i)} \tag{5}$$

$$EF = \frac{y_i}{x_i} \tag{6}$$

where: x_i – the weight fraction of i in the feed, y_i – the weight fraction of i in the permeate.

Taking into account that membranes possess different thicknesses the thickness-normalized fluxes were calculated:

$$J_{N,i} = J_i \cdot d_i \tag{7}$$

where: d_i is the thickness of the membrane [μm].

2.4. Gas chromatography

The feed and permeate mixtures composition were analyzed using Varian 3300 gas chromatograph with thermal conductivity detector (TCD). Porapak Q packed column was used for analysis. Data were acquired and processed using BORWIN software (JMBS, France).

In order to homogenize two phases H_2O–MeAc and H_2O–DMC samples, dry propan-1-ol or dry acetone of analytical grade were utilized, respectively.

The accuracy of the feed and permeate components analysis by the gas chromatography was evaluated in terms of the sensitivity and the quantitative parameters. The limit of detection (LOD) is defined as the minimum concentration of water and methanol solvent and referred to the signal-to-noise (S/N) ratio equal to 3. The limit of quantification (LOQ) is calculated as a S/N ratio equal to 10 [76]. LODs and LOQs of water and methanol were as follows:

Water: LOD=0.03 wt%, LOQ=0.11 wt%
Methanol: LOD=0.04 wt%, LOQ=0.13 wt%

Relative standard deviations for the repeatability (RSD_r for $n=5$) and the reproducibility (RSD_R $n=9$, 3 operators) in the investigated range of polar component concentrations were following [77]:

Water: $RSD_r < 1.3\%$, $RSD_R < 3.1\%$
Methanol: $RSD_r < 0.8\%$, $RSD_R < 3.0\%$

2.5. Swelling

The swelling of the Nafion and IonClad membranes was investigated in contact with pure water, methanol, methyl acetate, and dimethyl carbonate solvents. Dry membrane samples were immersed into the solvents. After a given period of time membranes were taken out from the solvents, the excess solvent was wiped with paper, and membranes were immediately weighed. The mass swelling degree (SD_W), molar swelling degree (SD_M), and SD_{IEC} – i.e. molar swelling degree relatively to the ion-exchange capacity were calculated according to the Eqs. (8)–(10):

$$SD_W = \frac{W_{wet} - W_{dry}}{W_{dry}} (\text{g solvent/g dry membrane}) \tag{8}$$

$$SD_M = \frac{SD_W}{M_{sol}} (\text{mol solvent/g dry membrane}) \tag{9}$$

Table 2
The main characteristics of investigated membranes [14,15,60,62–65].

Membrane	Chemical backbone	Thickness [μm]	Ion-exchange capacity (IEC)[a] [mmol/g]	K_{dis}
Nafion® 120 (Nafion)	Polytetrafluoroethylene with pendant ether-linked side chains terminated with sulfonated groups	254	0.83	10^3–10^6 [65]
IonClad™ R4010 (IonClad)	Irradiation grafted sulfonated styrene monomers onto poly(tetrafluoroethylene-co-perfluoropropylene) film	67	1.50	3.3 [64]

[a] Data provided by the membrane producer.

Table 3
Physicochemical properties of the solvents used in pervaporation experiments [46,68,69].

Solvent	Boiling temperature	Vapor pressure at 35 °C	Water solubility in the solvent	Relative permittivity at 298 K
	T [°C]	p [bar]	S_w [%w/w]	ε [dimensionless]
H_2O	100 [70]	0.06[a]	–	78.5 [71]
MeOH	64 [72]	0.28[a]	∞	33.1 [68]
MeAc	57 [73]	0.44[a]	8 [73]	6.7 [68]
DMC	90 [69]	0.12[b]	3 [74]	3.1 [69]

[a] Calculated according to the Eq. (1).
[b] Calculated according to the Eq. (2).

Table 4
Values of SD_{IEC} for Nafion and IonClad membranes in contact with pure water, methanol, methyl acetate, and dimethyl carbonate solvents.

Membrane	SD_{IEC}			
	[mol solvent/mol sulfonic group]			
	H_2O	MeOH	MeAc	DMC
Nafion	13.6	27.0	3.4	2.3
IonClad	6.7	5.1	0.2	0.2

$$SD_{IEC} = \frac{SD_M}{IEC}(\text{mol solvent/mol sulfonic group}) \qquad (10)$$

where: W_{wet} and W_{dry} are the weight of the dry and solvent-equilibrated Nafion and IonClad membranes, respectively; M_{sol} is the molecular mass of the solvent; IEC is the ion-exchange capacity of the membrane (Table 2).

2.6. FTIR analysis

FTIR analysis were performed in ATR mode (Ge crystal) using the Nicolet FT-IR apparatus (Thermo Fischer, Avatar 360 Omnic Sampler) in the range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. The IR spectra were recorded for the dry membranes, the membranes equilibrated with water and methanol as well as for the membranes equilibrated with the water vapor from 0 (the dry membrane) to 95% RH.

The position of the symmetric stretching vibration band (ν_s) of the sulfonic group in Nafion and IonClad membranes was determined using Omnic® software (version 5.5) and interpreted according to the literature data [15,78,79].

Table 5
Hansen solubility parameters of Nafion [84] and solvents [32,83] used in pervaporation experiments and calculated values of distance parameter $\Delta_{i,j}$.

Solvent	Hansen Solubility Parameters			Distance parameter			
	δ_d [MPa$^{1/2}$]	δ_p	δ_h	$\Delta_{i,H2O}$ [MPa$^{1/2}$]	$\Delta_{i,MeOH}$ [MPa$^{1/2}$]	$\Delta_{i,MeAc}$ [MPa$^{1/2}$]	$\Delta_{i,DMC}$ [MPa$^{1/2}$]
Nafion	17.4	12.5	9.6	32.9	12.9	6.0	8.8
Water	15.5	16.0	42.3	–	20.3	35.8	34.8
MeOH	15.1	12.3	22.3	20.3	–	15.6	15.1
MeAc	15.5	7.2	7.6	35.8	15.6	–	–
DMC	15.5	3.9	9.7	34.8	15.1	–	–

3. Results and discussion

3.1. Equilibrium and transport properties of membranes in contact with single solvent

The influence of the Nafion and IonClad membranes morphology and the differences in the polarity of solvents was taken into account in order to better understand the state of the ion-pairs of sulfonic groups and lithium counter-ion. In order to indicate an impact of the differences in the investigated membranes structure on the membrane ion-pairs behavior, the sorption measurements of Nafion and IonClad membranes equilibrated with the given pure solvents were performed. Table 4 presents the values of molar swelling degree of Nafion and IonClad membranes in contact with water, methanol, methyl acetate, and dimethyl carbonate.

In general, the degree of swelling is correlated with the solvation of functional groups and it depends on the membrane morphology. The swelling of the Nafion membrane is higher than of IonClad despite the lower ion-exchange capacity of the former one (Table 2). The hydrophobic side chains in the IonClad membrane are shorter than those in Nafion membrane. The short side chains cause the decrease of the free volume of the polymer. Moreover, the sulfonic groups in IonClad are less accessible to the solvent, despite the higher ion-exchange capacity, because they are closely located to the hydrophobic backbone structure (Table 2). This explains, that swelling degree of the IonClad membrane equilibrated with solvents of lower polarity is smaller than that for Nafion one. Taking into consideration Nafion membrane equilibrated with solvents of different polarity, it can be seen that the Nafion swelling is the highest in contact with methanol, despite the fact that methanol is less polar than water (Table 5). The long hydrophobic side chains in Nafion can be partially solvated by the methanol molecules which enhances the swelling abilities of the Nafion membrane. The swelling of sulfonated cation-exchange membranes in contact with water and methanol was investigated by Koter [80] and Hamann et al. [81]. It was shown that SD_{IEC} degree of Nafion 117 in sodium(I) form was equal to 15.4 water and 20.9 methanol molecules per sulfonic group, which is consistent with our findings (Table 4) [80,81]. Moreover, Nandan et al. [22] revealed that the Nafion is characterized by the large methanol uptake in hydrogen(I), lithium(I), and sodium(I) forms, whereas the solvent uptake increased with decreasing radius of the counter-ion.

The behavior of Nafion and IonClad membranes in the dry state and in the contact with water and methanol was also investigated by the infrared analysis. The spectra obtained for the studied membranes confirmed the differences in the strength of sulfonic ion-exchange groups in Nafion and IonClad. The frequency of the symmetric stretching vibration (ν_s) band of the sulfonic groups in Nafion is significantly higher (1071 cm^{-1}) than that of IonClad (1047 cm^{-1}) (Fig. 2) [15].

This difference results from much stronger acidic character of sulfonic groups in Nafion membrane comparing to the IonClad – Fig. 2 – structure B [15]. It is related to the fact that fluorine atoms in the Nafion perfluorinated ether side chains cause the strong electro-attractive effect on the sulfonic anions attached to the side chains, just enhancing the polarization of the sulfonic groups. The equilibrium solvation of the Nafion and IonClad membrane with water shifts the position of the symmetric vibration bands to the lower frequency compared to the dry membrane (Fig. 2 – structure A). This confirms that ion-pairs in Nafion and IonClad dissociate in contact with water (Fig. 2 – structure B). The position of ν_s band of Nafion and IonClad equilibrated with water are equal to 1058 cm^{-1} and 1037 cm^{-1}, respectively. It can be observed the position of the symmetric stretching vibration bands of the
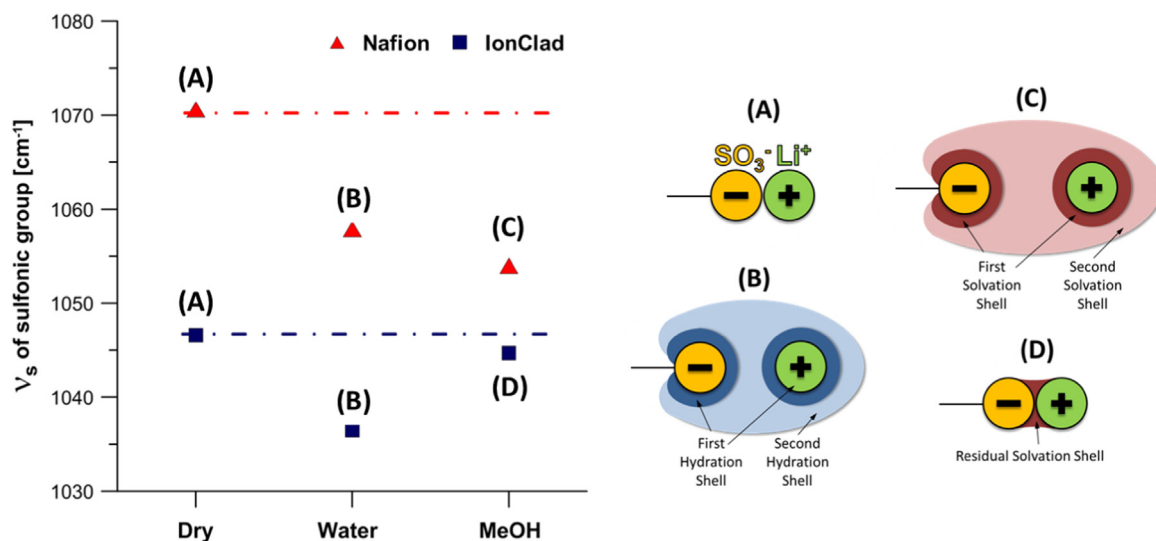
Fig. 2. The influence of water and methanol polarity on symmetric stretching vibration bands (ν_s) in Nafion and IonClad membranes: (A) non-dissociated ion-pair in dry membrane, (B) dissociated ion-pair surrounded by hydration shells, (C) dissociated ion-pair surrounded by methanol solvation shells, (D) non-dissociated ion-pair with residual methanol solvation shell.
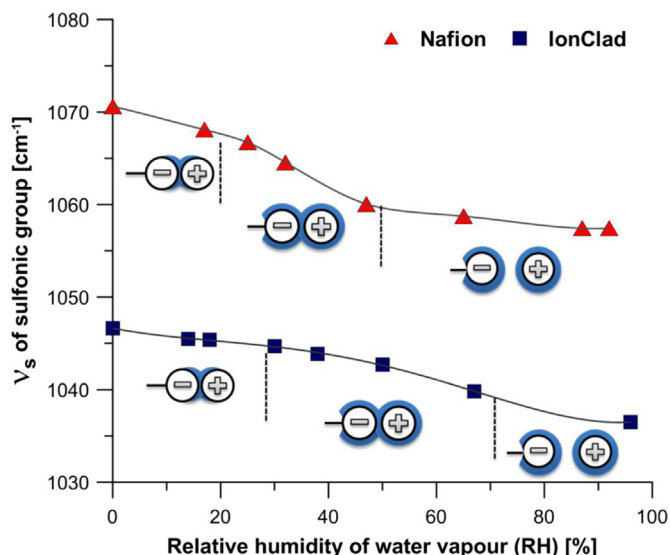

Fig. 3. Influence of water relative humidity (RH) on symmetric stretching vibration bands (ν_s) in Nafion and IonClad membranes.

membranes solvated with methanol shifts only for the Nafion membrane (Fig. 2 – structure C), due to the dissociation of the ion-pairs, and it is equal to 1054 cm^{-1}. In the case of the IonClad membrane, the ion-pairs remains non-dissociated with the residual solvation shell (Fig. 2 – structure D). The infrared analysis revealed the significant differences of the investigated ion-exchange membranes in contact with solvents of different polarity.

In order to investigate in detail the dissociation ability of the hydrated sulfonic ion-exchange groups in the Nafion and IonClad membranes, the infrared analysis of the membranes equilibrated with the water vapors at the various relative humidity was performed. In the case of Nafion membrane an increase of the water vapor RH causes the shift of the ν_s band towards lower wavenumbers, and the solvation shell is formed around the ion-pairs (Fig. 3, Fig. 2 – structure B). When the RH exceeds 50% the complete dissociation of ion-pair occurs (Fig. 3) which is reflected by the significant shift of the ν_s bands towards lower wavenumber by more than 10 cm^{-1}, compared to the Nafion membrane in the dry state. The infrared analysis of IonClad membrane at different RH

revealed that position of the ν_s bands does not change up to 40% RH of water vapors what means that ion-pairs are surrounded by the residual hydration shell. Further increase of the water vapor RH causes the formation of the solvation layer around the sulfonic group and lithium ion, and the ν_s bands shifts slightly. A greater change of the sulfonic ν_s bands compared with the dry IonClad membrane is observed for RH higher than 80%, indicating the total separation of the lithium ion and the sulfonic anion group (Fig. 3, Fig. 2 – structure B). Moreover, the obtained infrared results are consistent with the theoretical computations and indicate the presence of the dissociation of the ion-pairs: lithium cation–sulfonic anion group [60].

The various character of sulfonic group, and thus the different performance and the effectiveness of ion-exchange membranes, can be explained by the different states of ion-pairs, i.e. pair of ion-exchange group and counter-ion, in contact with solvent of different polarity described in detail elsewhere [15,23,26]. The model of the ion-pairs dissociation was proposed by Eignen et al. [23], and subsequently used by Boakye et al. [71], Lowry et al. [26], and Kujawski et al. [14] as well as it is applied within this work, in order to qualitatively describe the behavior of ion-pairs in the investigated membranes during the infrared analysis. The model of ion-pair dissociation illustrates how the dissociation of ion-pairs takes place in membranes with aromatic side chains equilibrated by pure water, while in the case of Nafion membrane it occurs in contact with pure water as well as with pure polar organic solvents (eg. methanol) [14,15,82]. In general, when the ion-exchange membrane possessing aromatic side chain (IonClad or PESS membrane) is in the dry state or is exposed to solvents of very low polarity, the counter-ion is in a direct contact with the ion-exchange group, eventually surrounded by the residual solvation shell. Solvation of the membrane by a polar solvent causes the formation of inner-solvation layer around the counter-ion and sulfonic group pair. The dissociation of ion-pair and presence of solvation layers around separated ions is observed in the membrane equilibrated with the pure solvent of a high polarity or a binary mixture with a relatively high content of polar component [14].

The interactions between membrane material and the solvent can be also discussed based on the Hansen's Solubility Parameters (δ). The solubility parameter describes a cohesive energy which is characterized by δ_h – hydrogen bonding, δ_p – polar, and δ_d –

dispersion interactions (Table 3) [83]. Based on the partial solubility parameters δ_i the distance parameter was calculated (Eq. (11)) which provides the information about the affinity between two components [51,83]. The low value of the distance parameter (Δ) indicates the higher affinity [51,83].

$$\Delta = \left[\left(\delta_{d,i} - \delta_{d,j} \right)^2 + \left(\delta_{p,i} - \delta_{p,j} \right)^2 + \left(\delta_{h,i} - \delta_{h,j} \right)^2 \right]^{0.5} \quad (11)$$

It can be noticed in the Table 5 that all tested solvents are characterized by the similar dispersion cohesion parameter (δ_d), which means that the δ_d does not influence the interactions between solvent and the polymer. The affinity between the investigated substances depends only on the polar (δ_p) and hydrogen bonding (δ_h) parameters.

The pervaporation experiment for Nafion and IonClad membranes in contact with pure methyl acetate and dimethyl carbonate was performed in order to investigate the influence of the non-polar feed component on the transport properties of the studied membranes (Fig. 4). The results obtained during pervaporation showed that thickness-normalized permeate flux of MeAc is significantly higher than that of DMC for Nafion membrane. This can be related with the lower value of distance parameter between Nafion and MeAc than Nafion and DMC (Table 5). Moreover, the polar character of MeAc is higher than that of DMC, which explains the better affinity between Nafion and MeAc. It should be also noted that ion-exchange groups in Nafion are characterized by the high polarizable properties (Table 2) and thus the transport through the membrane is enhanced in contact with MeAc, in contrast to Nafion membrane equilibrated with DMC. Moreover, taking into account so called "apparent" pervaporation properties, the vapor pressure of the permeants is also considered [51]. Thus, the vapor pressure of a given solvent can be the next factor explaining the higher flux of pure MeAc compared to DMC for Nafion membrane (Table 3). In the case of IonClad membrane, the higher thickness-normalized permeate flux is observed for the DMC which is related to the fact that the membrane with lower polarizable character has the higher affinity with solvent of lower polarity.

3.2. Properties of Nafion and IonClad membranes in contact with water–methyl acetate and methanol–methyl acetate mixtures

The separation efficiency of investigated Nafion and IonClad membranes in lithium form during pervaporation of water–methyl acetate mixture is presented in Fig. 5. It can be observed that water is selectively transported through Nafion and IonClad membranes from water–methyl acetate feed solution. The increase of the water content in the feed mixture causes the increase of the water content in permeate for both membranes (Fig. 5), and results in the characteristic sigmoidal shape of the experimental curve. It should be noted that the sigmoidal shape is typical only for ion-exchange membranes reflecting the dissociation of the ion-pairs according to the model proposed by Eignen et al. [23]. The water content in permeate does not change remarkably at the low water concentration in the feed mixture (Fig. 5), while the ion-pairs remain in the direct contact. Further increase of the water content results in the rapid rise of the water content in permeate. This is related to the fact that hydration shells are formed around sulfonic group and lithium(I) ion causing the ion-pair separation and transport pathways formation, facilitating the water transport through the membrane. As it can be seen in Fig. 7A the increase of water content in the feed mixture enhance the methyl acetate transport through the Nafion membrane. Hence, IonClad membrane is more selective than Nafion one in the contact with aqueous–organic feed mixture (Fig. 5, Table 6). This is associated with the fact that addition of water leads to the solvation of the ion-pairs and formation of clusters around sulfonic groups and lithium (I) ion in Nafion membrane. As a consequence of the simultaneous high transport of water and methyl acetate the drop of the Nafion selectivity is observed.

Separation properties of Nafion and IonClad membranes in contact with methanol–methyl acetate mixture are presented in Fig. 6. It can be pointed out that for both investigated membranes methanol is transported preferentially, although values of separation factor β are much lower (Table 7) comparing to the selectivity of both membranes in contact with water–methyl acetate feed mixture (Table 6). However, it can be seen that Nafion in
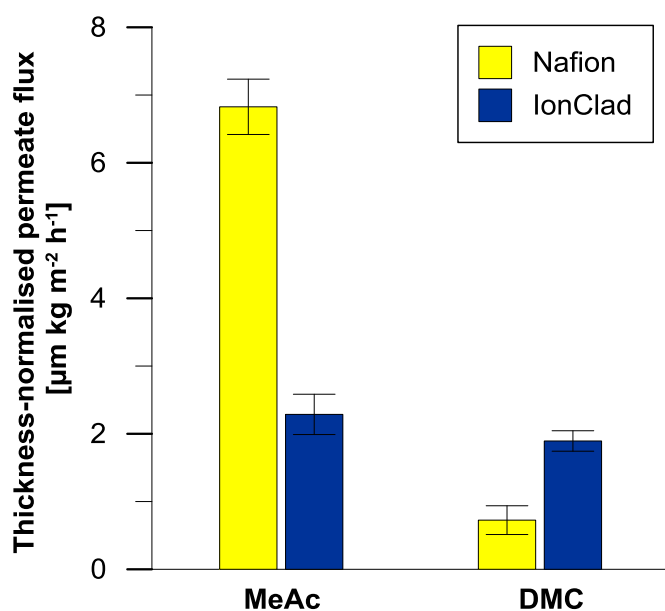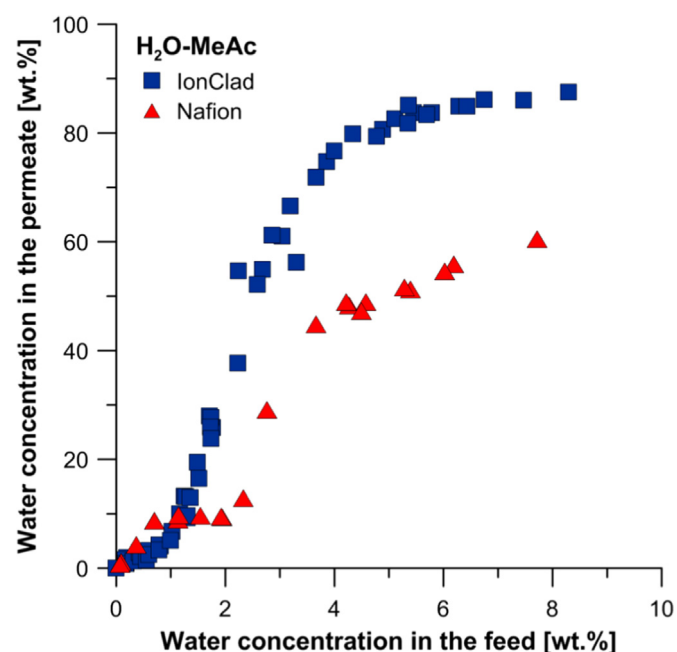

Fig. 4. Comparison of thickness-normalized permeate flux of methyl acetate and dimethyl carbonate for Nafion and IonClad membranes during pervaporation of pure solvents.

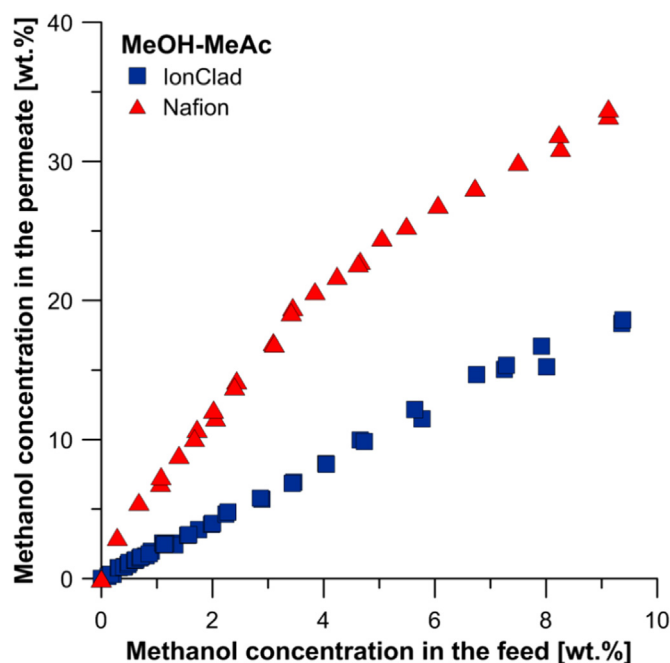Fig. 5. McCabe-Thiele separation diagram for Nafion and IonClad membrane in contact with water–methyl acetate mixture, T=35 °C.

Fig. 6. McCabe-Thiele separation diagram for Nafion and IonClad membrane in contact with methanol–methyl acetate mixture, T=35 °C.

Table 6
Comparison of water content in permeate and water separation factor for Nafion and IonClad membranes in contact with water–methyl acetate feed mixture.

Water concentration in H_2O–MeAc feed mixture [wt%]	Water content in permeate [wt%]		β	
	Nafion	IonClad	Nafion	IonClad
1.0	9.4	6.5	10.2	6.9
2.0	9.4	33.6	5.1	24.8
3.0	34.2	61.1	16.8	50.8
4.0	47.3	76.2	21.5	77.0
5.0	49.9	82.7	18.9	90.9

Table 7
Comparison of methanol content in the permeate and methanol separation factor for Nafion and IonClad membranes in contact with methanol–methyl acetate feed mixture.

Methanol concentration in MeOH–MeAc feed mixture [wt%]	Methanol content in permeate [wt%]		β	
	Nafion	IonClad	Nafion	IonClad
1.0	6.7	2.1	7.0	2.1
2.0	11.9	4.2	6.6	2.1
3.0	16.6	6.3	6.4	2.2
4.0	20.7	8.3	6.3	2.2
5.0	24.2	10.3	6.1	2.2

contrast to IonClad membrane is more selective in contact with feed mixture containing methanol.

The differences in the morphological properties between Nafion and IonClad membranes revealed also the significant differences in the transport of the molecules through the membranes in contact with aqueous–methyl acetate mixture (Fig. 7).

The initial increase of water concentration up to 2 wt% results in the increase of the water in permeate (Fig. 7). Although, it does not cause the significant changes of the water partial fluxes for both membranes (Fig. 7). Further addition of water to the feed

mixture causes the rapid increase of water partial fluxes. Moreover, it can be seen that in the case on IonClad membrane methyl acetate partial flux does not change significantly in the whole investigated range and maintain at around 40 g h^{-1} m^{-2}, whereas in the case of Nafion membrane the increase of water content in the permeate leads to the enhanced transport of the methyl acetate through the membrane reflected by the gradual increase of the partial flux up to 360 g h^{-1} m^{-2} (Fig. 7A).

Taking into consideration the ion-pair dissociation model it can be explained that the lithium(I) ion remains in contact with sulfonic group when the investigated membranes are solvated with the pure methyl acetate (Fig. 7, Fig. 8). Water molecules appearing in the vicinity of ion-pairs at increasing water content in the feed mixture up to 2 wt% cause the formation of the inner solvation layer around the SO_3^- and Li^+ pair. The further increase of water
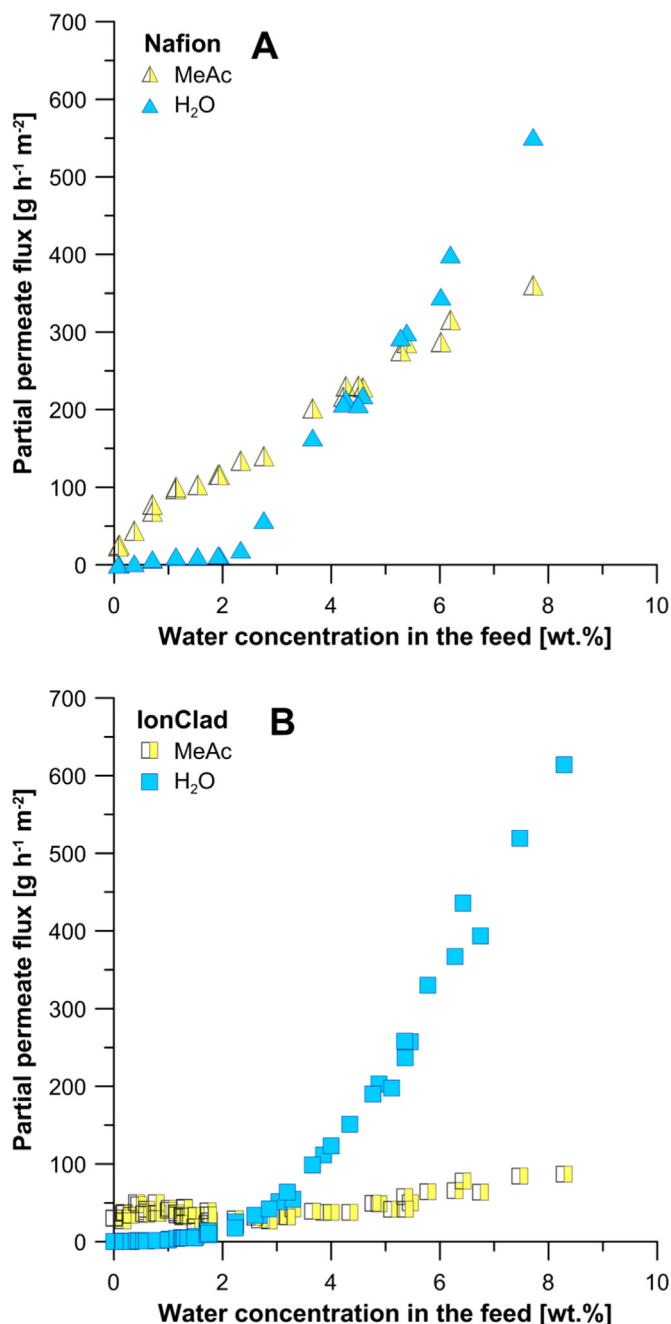

Fig. 7. Partial permeate fluxes of components in contact with Nafion (A) and Ion-Clad (B) membrane vs. water feed concentration.
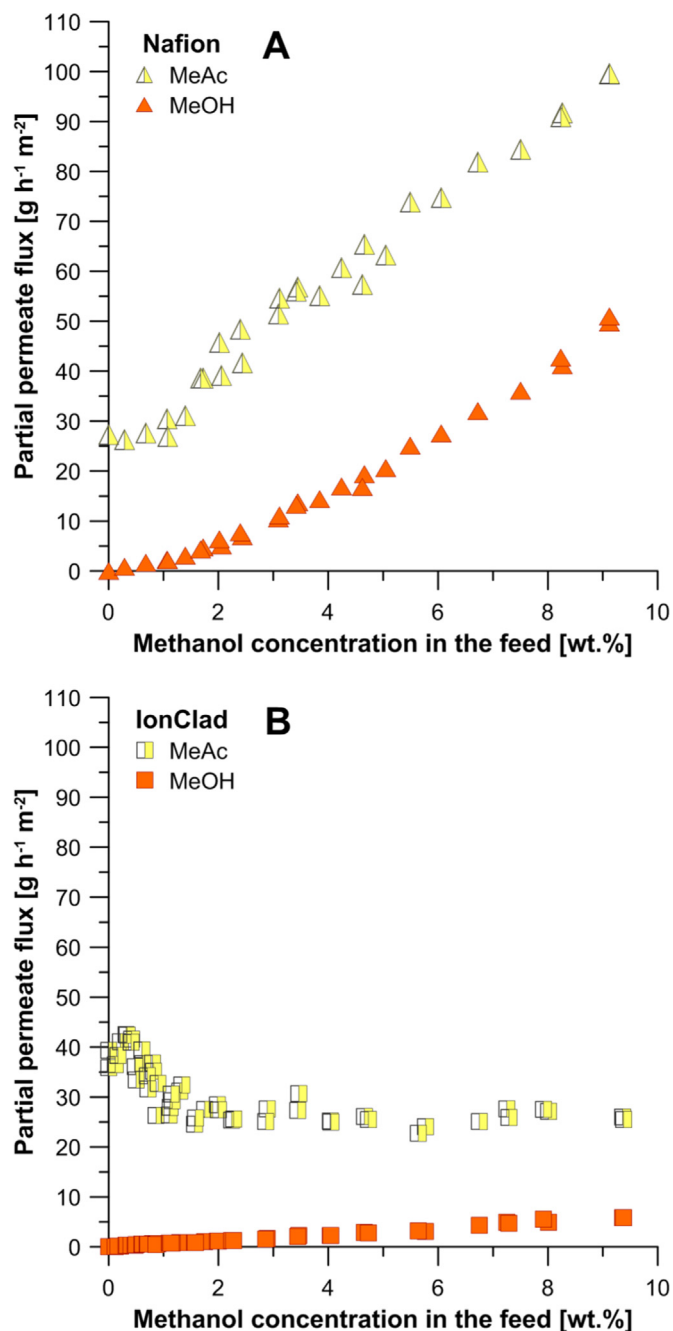
Fig. 8. Partial permeate fluxes of components in contact with Nafion (A) and Ion-Clad (B) membrane vs. methanol feed concentration.

content in the feed mixture induce the separation of SO_3^- and Li^+ by the formation of solvation layers around separated ions (Fig. 2 – structure C). The separation of sulfonic group and lithium(I) ion starts at lower water concentration in the feed mixture in the case of the Nafion membrane in comparison to the IonClad one. The stronger acidic character of sulfonic groups in Nafion membrane, due to the fluorinated side chains connected with functional groups, enhance the dissociation of ion-pairs in the presence of polar solvent [60]. The dissociation constant of the sulfonic acid groups in Nafion ($K_{dis}=10^3$–10^6) [65] is several orders of magnitude higher than that for IonClad ($K_{dis}=3.3$) [64] – Table 2.

Karpenko-Jereb et al. [60] applying the theoretical model found that the dissociation of ion-pairs occurs only for the Nafion membrane, regardless the investigated counter-ion, i.e. hydrogen (I), lithium(I), and sodium(I). The dissociation occurred if the

Nafion was solvated with at least 7 water molecules. The dissociation phenomenon was reflected by the sharp increase of $-SO_3^-$…Li^+ distance from 1.90 to 3.70 Å. It was also shown that $-SO_3^-$…Na^+ system reached comparable value of 3.77 Å for the Nafion membrane solvated with 7 water molecules. The ion-pairs in Nafion membrane in the proton form start to dissociate while Nafion was hydrated with 3 water molecules only. Simultaneously, the first solvation layer around separating ions is formed [60]. When ion-pair of Nafion-H membrane was hydrated with 5 water molecules, proton jumps to the second solvation layer surrounding sulfonic group and hydronium ion [60]. It must be remembered, however, that in the practice Nafion and IonClad membrane sulfonic groups form numerous clusters with solvent molecules [4,85], whereas in the case of the quantum chemistry approach, the isolated single sulfonic groups solvated with 1–10 water and methanol molecules are considered. According to the Mauritz et al. the cluster in Nafion membrane consists of 10 sulfonic acid groups [4]. Therefore, the dissociation of ion-pairs is facilitated and occurs also for the IonClad membrane, what is evidenced by the sharp increase of water flux noticed for water content in the feed mixture higher than 2 wt%.

Inspecting Fig. 8, it can be seen that the flux of the methyl acetate is higher than that for dimethyl carbonate which is related to the greater affinity between pure methyl acetate and Nafion membrane than between dimethyl carbonate and that membrane. This is reflected also by the distance parameters equal to 6 and 8.8 $MPa^{1/2}$ for MeAc and DMC, respectively (Table 5). Moreover, high affinity between Nafion and methyl acetate molecules located at the side chains leads to their facilitated transport through the membrane along the clusters of sulfonic groups and water in contact with water–methyl acetate feed mixture. For the water concentration exceeding 5 wt% water flux is higher than methyl acetate one which also indicates that ion-pairs in Nafion membrane are dissociated. Thus, the transport pathways across the membrane increase and water transport is enhanced [14].

The presence of methanol molecules instead of water ones in the vicinity of sulfonic groups also cause at least partial solvation of ion pairs. However, the transport of methanol molecules through the Nafion and IonClad membranes is significantly lower and hence the decrease of partial fluxes of feed components compared to the results of the membranes in contact with water–methyl acetate was observed (Fig. 8).

The methyl acetate partial fluxes for Nafion membrane equilibrated with MeOH–MeAc and H_2O–MeAc mixture containing around 8 wt% of polar component were equal to 91.7 and 360.6 g h^{-1} m^{-2}, respectively. In the case of IonClad membrane the partial fluxes of MeAc were equal 27.0 and 87.2 g h^{-1} m^{-2} for membrane in contact with MeOH–MeAc and H_2O–MeAc mixture, respectively. This behavior is related to lower polar nature of methanol in comparison with water resulting from the smaller value of the relative permittivity of methanol than water (33.1 and 78.5, respectively) – Table 3 [15]. Moreover, it can be seen that the nature of the sulfonic group of the investigated membranes has the significant influence on the partial fluxes of MeAc, which is reflected by the lower MeAc flux for IonClad membrane than for Nafion one. The dissociation of ion-pairs in the IonClad membrane is hindered in contrast to the Nafion one due to lower acidic polarizable character of sulfonic groups in the IonClad membrane [14,64,65]. An addition of methanol molecules to the feed mixture above 1.5 wt% causes the solvation of the sulfonic groups and lithium ions resulting in their separation which facilitates further the transport of MeAc through Nafion membrane. It is also reflected by the significant increase of the MeAc partial flux (Fig. 8A). The fact that methanol molecules affect the dissociation of ion-pairs in Nafion membrane is explained by the higher polarizable character of its sulfonic groups and stronger tendency to dissociate

even in the presence of pure aliphatic alcohols possessing lower polarity than water [14,15]. The infrared analysis revealed also the dissociation of the ion-pairs in Nafion membrane equilibrated by the pure methanol (Fig. 3). Kujawski et al. observed the dissociation of counter-ion and sulfonic groups pairs also in Nafion-Li$^+$ membrane equilibrated in pure 2-propanol [15].

The pervaporation study revealed that in the case of IonClad an increasing concentration of MeOH in MeOH–MeAc feed mixture decreases the MeAc flux up to MeOH content equal to around 2 wt% (Fig. 8B). The presence of methanol molecules in IonClad membrane cause the replacement of methyl acetate molecules by methanol ones in the solvation shells as evidenced by continuous decrease of methyl acetate partial flux.

Gorri et al. [86] presented the transport properties of the Pervap 2255-30 membrane in the pervaporation of methanol–methyl acetate feed mixture under various methanol content in the feed (2–34 wt%) and temperature (40–60 °C) operating conditions. Authors depicted that in the pervaporative separation of methanol–methyl acetate feed mixture at 60 °C Pervap 2255-30 membrane is methanol selective in the whole investigated concentration range. Moreover, it was pointed out that methanol causes swelling of the investigated membrane significantly, increasing the total flux, and decreasing the separation factor. The separation factor decreases since the swollen membrane allows the simultaneous transport of the methyl acetate and methanol through the membrane [87,88]. In pervaporation of methanol–methyl acetate mixture through Pervap 2255-30 membrane at 40 °C the methanol flux was around 0.6–0.7 kg m^{-2} h^{-1} and the separation factor β was equal to 10. Genduso et al. [89] conducted the studies of methanol–methyl acetate pervaporative separation using polyvinylidene fluoride (PVDF) membrane in contact with methyl acetate feed mixture in the concentration range 11–78 wt% MeOH in the range temperature 30–44 °C. It was indicated that PVDF membrane is selective towards methanol for the methanol content in the feed concentration above 60 wt%, while it was selective towards methyl acetate for higher concentrations of methyl acetate [89]. Avagimova et al. [90] carried out the pervaporative separation of methanol–methyl acetate mixture using the poly(phenylene isophthalamide) (PA) pristine membrane and PA membranes modified with particles of nanodiamond. For all investigated membranes higher methanol concentration in the feed mixture resulted in the increase of the total flux, wherein the separation factor decreased. It is related to the fact that increasing amount of methanol in the feed mixture affects swelling of the membrane, thereby increasing the diffusion of methanol and methyl acetate through the membrane.

3.3. Properties of Nafion and IonClad membranes in contact with water–dimethyl carbonate and methanol–dimethyl carbonate mixture

Results depicted in the Figs. 9–12 confirm that the difference in the polarity of DMC and MeOH or water as well as the nature of sulfonic groups in Nafion and IonClad membrane influence their selective and transport properties. As it was observed for the pervaporation of H$_2$O–MeAc (Fig. 4) the Nafion membrane is more selective than IonClad one in the presence of methanol in the feed mixture. On the other hand, the IonClad membrane possess higher selectivity in the transport of water in comparison to Nafion one.

It can be seen in Fig. 9 that in the case of water–dimethyl carbonate feed mixture water is transported selectively through the both IonClad and Nafion membranes. The water concentration in the permeate increases rapidly while increasing the water content in the feed mixture starting from 1.2 wt% for IonClad (Fig. 11). Moreover, the sigmoidal shape of the curve in the McCabe-Thiele diagram for the IonClad can be also noticed. This is related to the
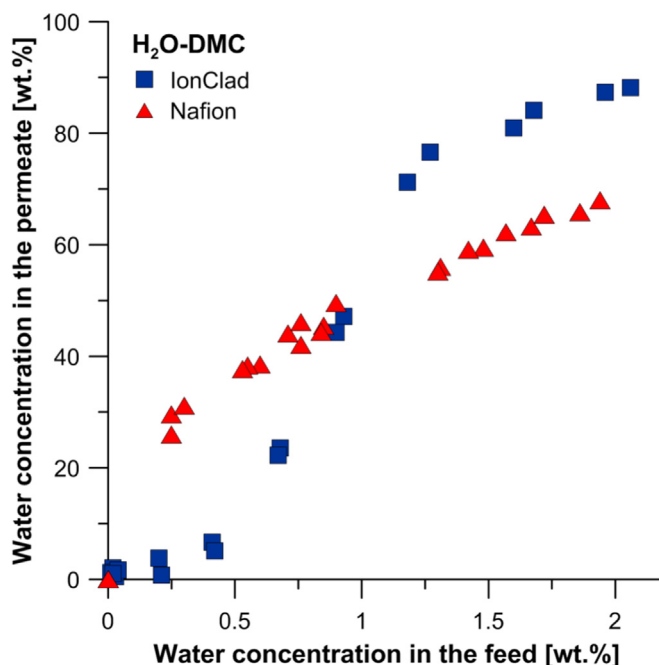

Fig. 9. McCabe-Thiele separation diagram for Nafion and IonClad membrane in contact with water–dimethyl carbonate mixture, T=35 °C.
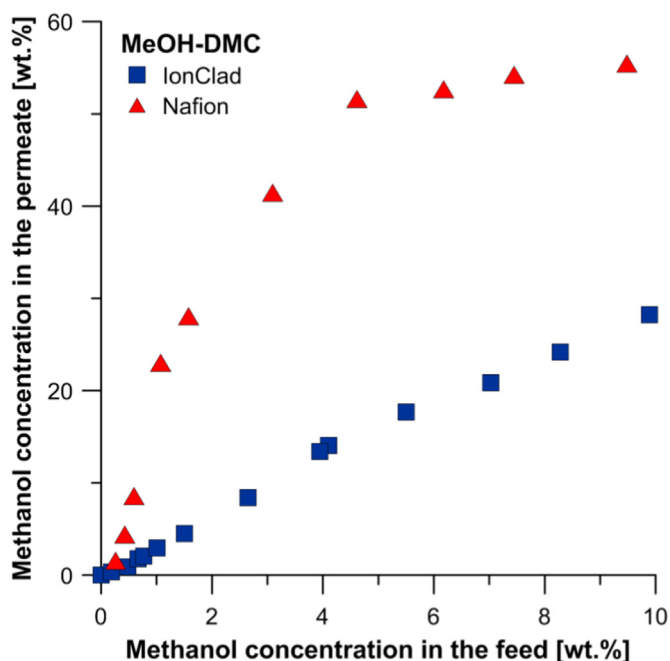

Fig. 10. McCabe-Thiele separation diagram for Nafion and IonClad membrane in contact with methanol–dimethyl carbonate mixture, T=35 °C.

gradual solvation of the ion-pairs in IonClad membrane. In the case of the Nafion membrane the water content in the permeate raises, starting from the low concentration of water in the feed mixture. The higher polarizable character of the sulfonic groups in the Nafion membrane enables the facilitated separation of ion-pairs in the presence of water in the water–dimethyl carbonate feed mixture.

Inspecting the McCabe-Thiele diagram (Fig. 10) it can be seen that methanol is selectively transported by both investigated membranes during pervaporation of methanol–dimethyl carbonate mixture. Moreover, the values of separation factor are equal
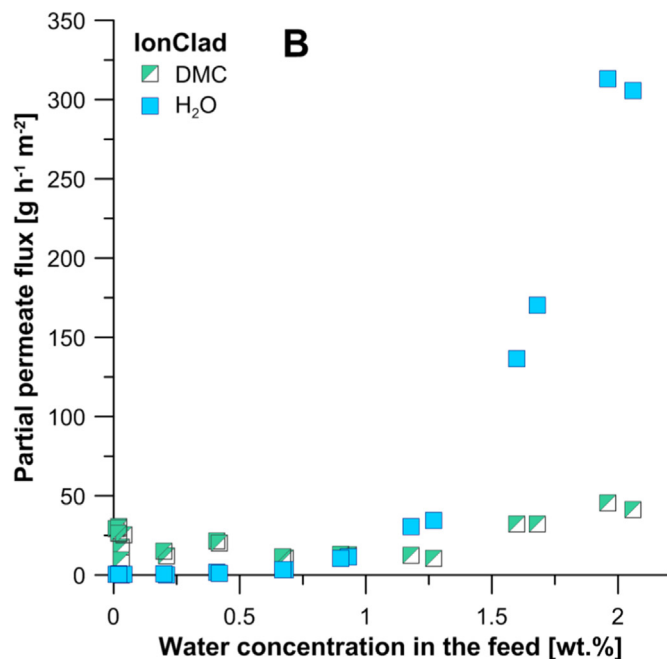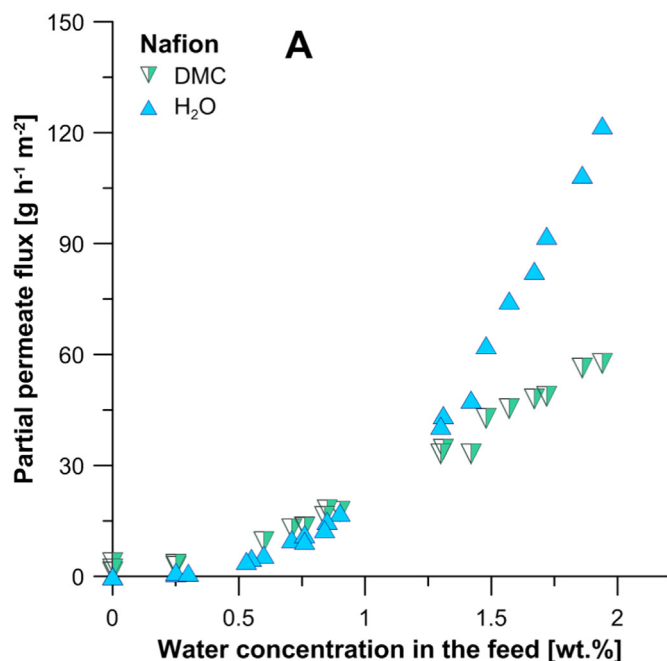
Fig. 11. Partial permeate fluxes of components in contact with Nafion (A) and IonClad (B) membrane vs. water feed concentration.
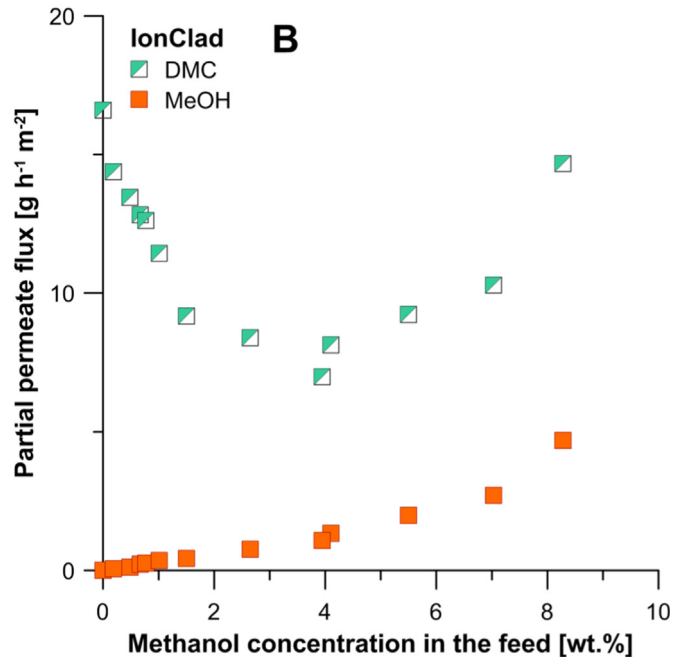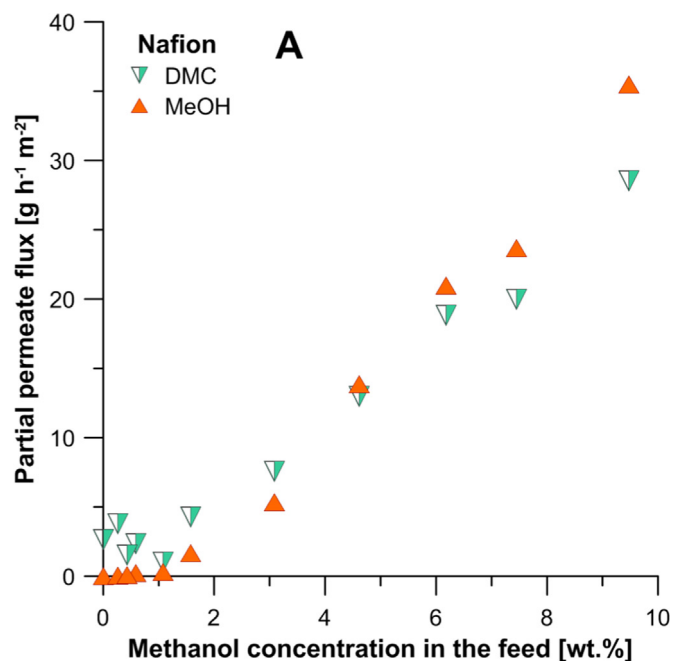

Fig. 12. Partial permeate fluxes of components in contact with Nafion (A) and IonClad (B) membrane vs. methanol feed concentration.

$\beta = 12$ and $\beta = 4$ for Nafion and IonClad membrane, respectively. In the case of Nafion membrane the increase of methanol concentration in the methanol–dimethyl carbonate feed mixture results in the simultaneous increase of methanol and dimethyl carbonate concentration in the permeate for the methanol concentration higher than 1 wt% (Fig. 12). Nafion membrane is in the contact with solvents of low polarity, however the presence of the sulfonic groups with high polarizable ability enable ion-pairs in Nafion membrane to dissociate. Nevertheless, transport of methanol molecules through the Nafion membrane is much lower in comparison to the results of pervaporative separation of methyl acetate-methanol feed mixture in contact with Nafion membrane in the presence of DMC molecules (Fig. 7A, Fig. 8A). Due to lower

polarity of DMC and higher distance parameter $\Delta_{i,j}$ between DMC and Nafion comparing to MeAc (Table 4), the transport properties of Nafion membrane during pervaporation of MeOH–MeAc and MeOH–DMC are different.

The pervaporation of water–dimethyl carbonate was performed up to 2 wt% of water concentration in the feed mixture due to the miscibility gap at the higher water content in dimethyl carbonate (Table 3). The obtained results for Nafion membrane in contact with water–dimethyl carbonate feed mixture showed that the increase of the water content in the feed mixture leads to the concurrent increase of both water and the dimethyl carbonate partial fluxes (Fig. 11A). This can indicate the strong coupling effect between fluxes [91]. The similar behavior of the Nafion membrane

was observed in contact with the water–methyl acetate feed mixture (Fig. 7A). The high affinity of water molecules with sulfonic groups in the Nafion membrane characterized by strong polarizable properties, result in the facile separation of ion-pairs. Transport pathways in the Nafion membrane are enlarged and the molecules of water and methyl acetate can be easily carried across the membrane.

It can be seen that the initial increase of water content up to 1.3 wt% does not change significantly the water partial flux (Fig. 11B) in the case of IonClad membrane. The following addition of water to the feed mixture resulted in the sharp increase of the water partial flux up to $313 \, \mathrm{g \, h^{-1} \, m^{-2}}$, whereas the dimethyl carbonate partial flux remains at the same level. The low partial flux of dimethyl carbonate explains the higher selectivity of the IonClad towards water compared to the Nafion one. Moreover, it can be seen that the raise of the water partial flux occurs at lower water content compared to the pervaporative separation of water–methyl acetate feed mixture.

The slight increase of partial flux of methanol for IonClad membrane can be observed for the methanol concentration in the feed mixture higher than 6 wt% (Fig. 12B). It is in agreement with the fact that IonClad membrane possesses less polarizable sulfonic groups than Nafion one, whereby the dissociation of ion-pairs in the presence of non-polar dimethyl carbonate solvent in the feed mixture instead of methyl acetate is much more hindered. Therefore the much higher amount of polar methanol solvent is required to form solvation shells in IonClad membrane. On the other hand, the flux of dimethyl carbonate decreases initially, then rises for the concentration of methanol higher than 5 wt%. It can be explained by the fact that increasing amount of methanol molecules in the vicinity of sulfonic groups allows the replacement with dimethyl carbonate molecules. Further addition of methanol leads to the formation of the solvation shells around the ion pairs which facilitates the transport of the dimethyl carbonate molecules, and thus the increase of the partial flux of dimethyl carbonate through the IonClad membrane is observed.

Pervaporation of methanol–dimethyl carbonate was investigated also by other authors [92,93]. Wang et al. [92] studied the transport of methanol through the poly(acrylic acid)/poly(vinyl alcohol) (PAA/PVA) blend membranes in the pervaporative separation of methanol/dimethyl carbonate mixture. Authors pointed out that PAA/PVA blend membranes transport methanol preferentially. It was indicated that increase of methanol concentration from 10 to 90 wt% resulted in the increase of methanol flux and the parallel decrease of dimethyl carbonate flux during pervaporation at 60 °C, wherein the separation factor β was increasing reaching the maximum at 60 wt% of methanol. According to the researchers the changes of methanol and dimethyl carbonate fluxes are in a good agreement with the fact that driving force of methanol and dimethyl carbonate increases and decreases, respectively. Increasing methanol concentration in feed cause an increase of swelling degree of the PAA/PVA blend membranes, which also influence pervaporation performance. It was observed, that in the case of the blended membranes at 60 °C for the methanol concentration in the feed mixture equal to 10 wt% methanol, the flux was equal to $580 \, \mathrm{g \, m^{-2} \, h^{-1}}$ with the separation factor β=0.9 (i.e. membrane became DMC selective). Wang et al. [93] investigated the membranes based on poly(vinyl alcohol) crosslinked with glutaraldehyde in terms of their separation properties in pervaporation of feed dimethyl carbonate/methanol mixture for 40–70 wt% of methanol. It was shown that increase of the methanol concentration in the feed influences the increase of methanol flux and decrease of the separation factor for the whole investigated temperature range from 50 to 70 °C. Since the crosslinked membrane possesses the high affinity to methanol, the swollen degree of the membrane increases when the methanol

concentration increase, and thus methanol flux increases. The variation of separation factor with increasing methanol content in the feed is explained in terms of an increase of the free volume in the membrane, which facilitates the transport of dimethyl carbonate through the membrane.

Won et al. [74] investigated also the pervaporative separation of dimethyl carbonate-methanol using the chitosan membranes at the operating temperature 25–55 °C. Methanol concentration in the feed membrane varied in the range 6–70 wt%. It was indicated that methanol is transported selectively through the tested membranes breaking the DMC/MeOH azeotrope (70/30 wt% MeOH/DMC). The selectivity of the chitosan membranes was improved with the crosslinking of the membranes. Moreover, an increase of methanol content in feed mixture results in the increase of the total flux, wherein the separation factor decreases.

Won et al. [74] studied also crosslinked chitosan membranes in the removal of water from dimethyl carbonate at the 1.0–2.6 wt% concentration of water in the feed mixture in the temperature range of 25–65 °C. It was shown that the dehydration of DMC using pervaporation is an effective method, since the water content in the permeation stream was in the range 85–94 wt%. For both studied binary MeOH–DMC and water–DMC mixtures the researchers indicated the significance of the membrane swelling during the pervaporative measurements [74]. In the case of water–DMC mixture, an increase of the operating temperature leads to decrease of the solubility of water in the chitosan membranes. Therefore, the diffusion of components is hindered, and the permeation flux decreases with increasing temperature. The opposite behavior is observed for the chitosan membranes in contact with methanol/DMC mixture. The increase of the temperature of the pervaporation resulted in the increase of the solubility of methanol in the investigated chitosan membranes which was reflected by the increase of the permeation flux [74].

4. Conclusions

This work was devoted to the investigation of the ion-pairs dissociation phenomena in Nafion and IonClad membranes containing lithium(I) as the counter-ions. The dissociation of ion-pairs was described taking into account their behavior during swelling and pervaporative separation of the binary polar-nonpolar solvent mixtures. Two main factors affecting the performance of the membranes in the pervaporation process were revealed:

- the nature of the sulfonic ion-exchange groups,
- the polarity of the solvents.

The easier ion-pairs dissociation and the higher permeability of solvents through the membrane were observed for the Nafion membrane in comparison with IonClad due to the more polarizable character of Nafion. The dissociation of ion-pairs was observed for the Nafion membrane in contact with water-nonpolar and methanol-nonpolar binary mixtures, which was reflected by the rapid increase of the partial flux of water component. In the case of IonClad membrane, the dissociation of ion-pair occurred only in the presence of water as a polar feed component.

It should be noted that results obtained during pervaporation of water–dimethyl carbonate, methanol–dimethyl carbonate as well as water–methyl acetate and methanol–methyl acetate mixtures indicate the characteristic sigmoidal shape of the flux-feed composition curves, namely the rapid increase of components fluxes in the increasing content of polar component. The unique behavior occurs with ion-exchange membranes during dissociation of ion-pairs. The transport of the molecules in ion-exchange membranes is related to the ion-pairs dissociation ability of the

membrane. In the case of other membranes swelling of the membrane plays the crucial role in the transport of the molecules during pervaporation.

The infrared analysis confirmed that the strength of the sulfonic groups in Nafion and IonClad membranes has influenced the localization of the symmetric stretching vibrations while equilibrium in pure solvents in liquid and vapor state. It was revealed that the ion-pair in both membranes were dissociated in contact with pure water. Though, the ion-pairs in the IonClad membrane equilibrated with pure methanol remained non-dissociated in contrast to the Nafion one.

Acknowledgments

Nomenclature

Symbols

A	membrane area [m^2]
a, b, c, d	Antoine's equation constants
A, B, C	Antoine's equation constants
d_i	thickness of the membrane [μm]
EF	enrichment factor
J_i	partial flux of component [kg m^{-2} h^{-1}]
$J_{N,i}$	thickness-normalized partial permeate flux [μm kg m^{-2} h^{-1}]
J_t	total permeate flux [g m^{-2} h^{-1}]
K_{dis}	dissociation constant
M_{sol}	molecular mass of the solvent [g mol^{-1}]
P	vapor pressure at 25 °C [bar]
P_c	vapor/liquid critical pressure [bar]
SD_{IEC}	molar swelling degree relatively to the ion-exchange capacity [mol solvent/mol sulfonic group]
SD_M	molar swelling degree [mol solvent/g dry membrane]
SD_W	mass swelling degree [g solvent/g dry membrane]
S/N	signal-to-noise ratio
S_w	water solubility in the solvent [%w/w]
T	temperature [K]
T_c	vapor/liquid critical temperature [K]
W_{dry}	weight of the dry membrane [g]
W_{wet}	weight of the solvent-equilibrated membrane [g]
x_i	weight fraction of i in the feed
y_i	weight fraction of i in the permeate

Greek letters

β	separation factor
δ	Hansen's Solubility Parameters [MPa$^{0.5}$]
δ_d	dispersion interactions [MPa$^{0.5}$]
δ_h	hydrogen bonding interactions [MPa$^{0.5}$]
δ_p	polar interactions [MPa$^{0.5}$]
$\Delta_{i,j}$	distance parameter [MPa$^{0.5}$]
Δm_t	permeate mass [g]
ε	relative permittivity at 298 K [dimensionless]
ν_s	symmetric stretching vibration [cm^{-1}]
τ	parameter used in the Eq. (2)., $\tau = 1 - \frac{T}{T_c}$

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