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

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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

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Abbreviations: FTIR-ATR, Attenuated Total Reflection with Fourier Transform Infrared (FTIR-ATR) Spectroscopy; IEC, ion-exchange capacity [mmol/g]; LOD, limit of detection; LOQ, limit of quantification; PA, poly(phenylene isophthalamide); PAA, poly(acrylic acid); PAES, poly(arylene ether sulfone); PF, hexafluorophosphate; PPy, polypyrrole; PTS, p-toluenesulfonate; PV, pervaporation; PVA, poly(vinyl alcohol); PVDF, polyvinylidene fluoride; RH, relative humidity; RSD_r, relative standard deviations for the repeatability; RSD_R, relative standard deviations for the reproducibility; SGPV, sweeping gas pervaporation; SPEEK, sulfonated polyetheretherketone; SPEES, sulfonated poly(phenylene ether ether sulfone); TDC, thermal conductivity detector; TPV, thermopervaporation; VOCs, volatile organic compounds; VPV, vacuum pervaporation

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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_2O_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 IonClad 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