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Influence of hydrophobization conditions and ceramic membranes pore size on their properties in vacuum membrane distillation of water–organic solvent mixtures

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ABSTRACT

The initially hydrophilic micro- and macroporous ceramic membranes were successfully hydrophobized by grafting with fluoroalkylsilane (FAS) molecules. The influence of diverse parameters (e.g. type of molecule, duration of grafting, concentration of FAS solution, type of solvent) on the resulting hydrophobic surface was investigated. The liquid entry pressure of water (LEPw) was used as a measure of the hydrophobization efficiency. The prepared membranes were subsequently investigated in vacuum membrane distillation (VMD) process using pure water and water–organic solvent solutions as feed mixtures. It was found that permeate flux of pure water is strictly correlated with LEPw value. The selectivity of membranes in contact with water–organic mixtures depends strongly on the pore size of the hydrophobized membrane. Microporous membrane are much less efficient in the separation of organics from water (separation factor of ethyl acetate – EtAc in the range 1.3–30) comparing with macroporous ones (separation factor of EtAc in the range 32–60). The results were also discussed assuming the various mechanism of transports through porous ceramic membranes. These latter results were additionally compared with the results obtained for hydrophobic polymeric membranes (separation factor of EtAc in the range 25–450).

1. Introduction

Polymeric membranes found numerous practical applications – from a simple dead-end microfiltration through reverse osmosis and pervaporation to hemodialysis or the sophisticated enzymatic membrane bioreactors [1–5]. However, polymeric membranes cannot be utilized at elevated temperatures or drastic chemical conditions, because of the limited thermal stability and chemical resistance [1–3]. Ceramic membranes offer several advantages over polymeric ones, such as mechanical resistance, chemical inertness, non-swelling behavior, thermal stability and the possibility of the uncomplicated cleaning [6–12]. An inorganic membrane can be described as an asymmetric porous multilayer material formed by a macroporous support, that provides the mechanical resistance, and successive thin layers deposited on it. These membranes, different in pore diameter, are applied in microfiltration [13–15], ultrafiltration [16–18], nanofiltration [19,20], gas separation [21–23] or even in hydrophilic pervaporation [4]. Inorganic membranes are prepared from various materials such as ceramics, zeolites, carbons, glasses and metals [24–26].

Nowadays, both dense polymeric and porous ceramic membranes are used in the separation of mixtures of liquid mixtures [26–29]. In the case of dense polymeric membranes the technique is called vacuum pervaporation [26,27,30,31]. However, in the case

Abbreviations: A, membrane area [m^2]; AAA, alkoxyalkylsilanes; AKD, aklylketene dimer; β, separation factor; BuOH, butanol; EtAc, ethyl acetate; EtOH, ethanol; FAS, fluoroalkylsilanes; J_t, total permeate flux; LEP, liquid entry pressure; m_t, total weight of the compound in the permeate [kg]; MTBE, methyl-tert buthyl ether; MWCO, molecular weight cut-off; MWPE-CVD, microwave plasma-enhanced chemical vapor deposition; Δp, vapor partial pressures of transported components [kPa]; p_i^f, partial pressure of component i in feed [kPa]; p_i^p, partial pressure of component i in permeate [kPa]; PSI, process separation index; t, permeation time [h]; T_f, feed temperature [°C]; VMD, vacuum membrane distillation; VPV, vacuum pervaporation; x_i, mass fractions of the compound i in the feed; y_i, mass fractions of the compound i in the permeate

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of micro, meso and macro porous hydrophobic ceramics, the term of vacuum membrane distillation seems to be more appropriate [32–36].

Vacuum pervaporation is recognized as a separation process in which a binary or multicomponent liquid mixture is separated by a partial vaporization through a dense polymeric membrane [37,38]. The selectivity of the process results from the selective sorption and selective diffusion of one on the feed components (according to the solution–diffusion model) [39–41]. The driving force for the mass transfer of permeants from the feed side to the permeate side of the membrane is a difference in chemical potentials of components, created by applying a vacuum on the permeate side of the membrane. There are three main areas of the potential applications of vacuum pervaporation:

- hydrophilic pervaporation – utilized for the removal of water from binary or multicomponent mixtures, particularly those forming water–organic azeotropes (e.g. water–ethanol, water–isopropanol or water–pyridine) [42–45]. Hydrophilic pervaporation reached an industrial level, especially for ethanol and isopropanol dehydration [46,47].
- hydrophobic pervaporation - applied mainly for the removal of volatile organic compounds from water [38,48–50]. This type of pervaporation can be also used in the analytical and diagnostic applications [51–53].
- organic–organic pervaporation - utilized to the separation of binary or multicomponent mixtures of organic solvents [54–57]. The organic–organic pervaporation was successfully applied at the industrial scale for the separation of methanol-methyl t-butyl ether [58–61]. The prospective large-scale applications of the organic–organic pervaporation is related with the petrochemical industry, especially in the area of the separation of aromatic and aliphatic hydrocarbons [62–64].

The vacuum membrane distillation (VMD) process is in the principle very similar to hydrophobic vacuum pervaporation (Fig. 1). The main difference results from the type of the membrane used and the mechanism of the separation. In VMD process the lyophobic porous membranes are used and the separation is govern by the liquid–vapor equilibrium. VMD process is mainly used for the desalination, the concentration of solutions and the removal of organics from water [65–73].

Ceramic membranes are usually prepared using metal oxides like alumina, titania or zirconia [8,25,42,49,74–76]. Such materials exhibit however a hydrophilic character resulting from the presence of the hydroxide groups on the membrane surface [24,25,77]. These hydrophilic groups can be utilized in the reaction leading to the conversion of the membrane character from the hydrophilic into hydrophobic one.

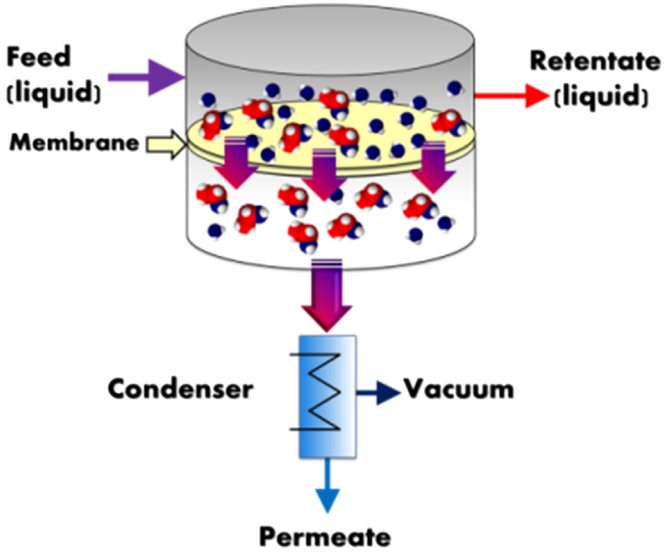

Fig. 1. The principle of the separation in hydrophobic vacuum pervaporation (VPV) and vacuum membrane distillation (VMD).

The change of hydrophilic character into the hydrophobic one is nowadays of a particular interest. A number of methods have been developed to create hydrophobic surfaces, like solidification of melted aklylketene dimer (AKD) [78], plasma modification, microwave plasma-enhanced chemical vapor deposition (MWPE-CVD), anodic oxidization of aluminum [79–83]. However, in the case of porous ceramic materials, the modification using low-surface-energy materials is the most often utilized method [6,7,16,35,43,55,81].

Fluoroalkylsilanes (FAS) are the group of compounds, which can be efficiently used in the enchancing of the hydrophobic character of different surfaces [42,67,84–86]. Moreover, the investigation of the orientation and self-assembly of different FAS was presented in scientific literature [87]. The researchers [88] performed studies on intrusion and extrusion of water in porous silica modified with FAS. Picard et al. [25,42,76,89] reported the grafting process of FAS on the surface of alumina, titania, zirconia and silica membranes.

Usually, the condensation reaction is performed using a hydrophobic compounds such as perfluoroalkylsilanes (FAS) or alkoxyalkylsilanes (AAS) [25,42,50,65,76,89]. The both FAS and AAS possess an appropriate reactive group, like methoxy group (–OCH_3), ethoxy group (–OC_2H_5) or chlorine atom. As a result of the reaction, a nanolayer of hydrophobic brush is obtained [25,49,50,67,76,86,89]. The extent of resulting hydrophobicity depends of the type of the grafting molecules, type of the metal oxide as well as on the grafting conditions (concentration of grafting solution, time of grafting, temperature) [24,25,76,77,81,85,86,89].

The aim of this work was to investigate the influence of the porosity of ceramic membrane (with MWCO of 5 kD and 300 kD), type of the grafting molecule and the grafting conditions on the resulting transport and selective properties of FAS modified membranes in the removal of volatile organics from water. In this research two various FAS molecules were used: $C_6F_{13}C_2H_4Si(OC_2H_5)_3$ and $C_{12}F_{25}C_2H_4Si(OC_2H_5)_3$ – denoted hereafter as C6 and C12, respectively. Grafting was performed by a condensation reaction using FAS solutions in ethanol or chloroform at room temperature. The resulted hydrophobic membranes were subsequently utilized in vacuum membrane distillation of water and water–organic solutions.

2. Experimental

2.1. Materials and methods

The commercial tubular titania, alumina and zirconia submeso- and macroporous membranes with MWCO of 5 kD and 300 kD were purchased from Pall Exekia (France). 150 mm long samples of tubular membranes with external/internal diameter of 10/7 mm were used in the research. For membrane characterization, planar ceramic titania 5 kD and 300 kD membranes provided by the same company were used.

The following two kinds of FAS compounds were delivered by Apollo Scientific (UK):

- 1H,1H,2H,2H-perfluorooctyltriethoxysilane – $C_6F_{13}C_2H_4Si(OC_2H_5)_3$ – denoted as C6;
- 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane – $C_{12}F_{25}C_2H_4Si(OC_2H_5)_3$ – denoted as C12.

C6 and C12 and their solutions were kept under an inert

atmosphere of argon to prevent self-condensation of FAS molecules. Chloroform (stabilized by 1% ethanol), ethanol and acetone were purchased from Riedel-de-Haën (France). Butanol and ethyl acetate were supplied from Avantor Performance Materials Poland S.A. (Poland). All compounds and chemicals were applied as received.

2.2. Grafting procedure

Grafting of membranes was conducted according to the following procedure. Prior to the main grafting process, the samples of TiO_2 membranes were first rinsed with water, ethanol and acetone successively for 5 min. and subsequently dried in an oven at 100 °C. The clean and dry samples of membranes were immersed in C6 or C12 solutions of given concentration for various periods of time at room temperature. Once the grafting was completed, samples were taken out from the solution, rinsed again in water, acetone and ethanol, dried at 100 °C and stored in the air. After each grafting or regrafting step, the value of liquid entry pressure of water (LEPw) was determined. Finally, the grafted membranes were utilized in the vacuum pervaporation or vacuum membrane distillation processes.

2.3. LEP measurements

The efficiency of grafting was initially assessed by liquid entry pressure of water (LEPw) measurements [66,90], using a laboratory setup presented in Fig. 2. The modified dried membrane sample was placed in the module (6) and water from the tank (3) was circulating through the lumen side of the membrane, applying a circulating pump (4). The pressure in the system was continuously increased by using the pressurized nitrogen (1). The experiment was run until first drops of water were observed on the shell side of the membrane. The pressure at which water starts to be transported through the membrane is referred as liquid entry pressure of water (LEPw) for a given membrane sample. Values of LEPw were determined for each membrane, after each single stage of grafting. According to Eq. (1) the LEPw depends on the pore size of the membrane, surface tension of penetrating liquid and contact angle. In the case of hydrophobic membranes, LEPw is directly related to the hydrophobicity level of modified membranes.

$$\mathrm{LEP}_w = \frac{2\gamma_L}{r_{max}} \cos\theta_{ef} \tag{1}$$

where: LEP_w is the pressure difference at the liquid–gas interface, γ_L is the surface tension of liquid, r_{max} is the maximal radius of the membrane pores, and θ_{ef} is an effective contact angle.

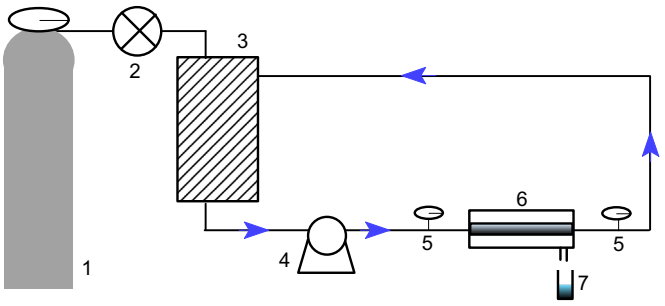

Fig. 2. LEP_w experimental rig. 1 – compressed nitrogen, 2 – valve, 3 – thermostated feed tank, 4 – circulating pump, 5 – manometer, 6 – membrane module, 7 – glass cylinder.

2.4. Membrane characterization

Pristine and grafted planar ceramic membranes were characterized by measurements of apparent contact angle (CA) applying a sessile drop method (5 μl drop of pure liquid) described in detail elsewhere [77,85]. All experiments were done at room temperature using goniometer PG-X (FibroSystem AB). The apparent contact angle values were established by Image J software (Image J, NIH – freeware version), with an accuracy of $\pm 2°$. The results presented are the averages from 20–30 measurements. Using the contact angle values for water and glycerol, surface free energy values were calculated as described elsewhere [77,85].

An atomic force microscope (AFM) equipment was used to surface analysis of planar membranes (NanoScope MultiMode SPM System and NanoScope IIIa i Quadrex controller – Veeco, Digital Instrument, UK). Tip scanning mode was used for the surface roughness determination of samples. The root mean squared (RMS) roughness was used as a parameter describing heterogeneity of the samples. In this study, scan size areas were equal to 5 μm × 5 μm.

In order to determine a membrane pore size a nitrogen adsorption/desorption analysis (ASAP 20120) using BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) models were utilized [24,77]. Samples were characterized before and after hydrophobization process. Before the sorption tests, samples of membranes were degassed at 90 °C for 2 h. The experimental protocol of this analysis was presented in our previous work [24].

2.5. Vacuum pervaporation/vacuum membrane distillation experiments

Prior to vacuum pervaporation and vacuum membrane distillation experiments the modified membranes underwent conditioning procedure by performing experiments with pure water, until the constant flux was observed. Usually 5–7 hours of the process was needed to rich the constant permeate flux of water [91]. This procedure was utilized to wash out all the FAS molecules which did not react with the ceramic surface and were only adsorbed on the membrane surface and in the membrane pores. The details of the procedure are described elsewhere [50,91].

The conditioned hydrophobized ceramic membranes were subsequently applied in VPV and VMD processes. VPV and VMD experiments were performed using the same laboratory rig, described in the detail elsewhere [50,91]. The tubular membrane was mounted in the stainless steel module. The thermostated feed was circulating between the feed tank and the module at the constant flow rate. Feed contacted the tubular membrane from the lumen side. Permeate was collected in the two parallel cold fingers cooled by liquid nitrogen, what enabled the continuous operation of the setup. The vacuum was created by a vacuum pump, ensuring that pressure on the permeate side was below 4 mbar.

Initially, the value of pure water flux was determined for each modified and conditioned hydrophobized membrane sample. Subsequently, VPV/VMD experiments were realized using aqueous solution of ethanol (EtOH), ethyl acetate (EtAc) and butanol (BuOH). Experiments were conducted for water–EtOH mixtures in the concentration range 0–20 wt% EtOH and in the concentration range 0–4 wt% organics in the case of other solvents. The composition of feed and permeate solution was determined by applying the gas chromatography [31,49]. The permeate fluxes of water were determined gravimetrically [31,49] – Eq. (2).

The effectiveness of separation process was determined by using the following parameters:

total (J_t) permeate flux as defined by Eq. (2) [37]

$$J_t = \frac{\Delta m_t}{A \cdot \Delta t} \quad (2)$$

where: m_t is total weight of the compound in the permeate [kg], A is the membrane area [m^2], t is the permeation time [h].

separation factor β defined by Eq. (3) [41]

$$\beta = \frac{y_i/(1-y_i)}{x_i/(1-x_i)} \quad (3)$$

where: y_i and x_i are mass fractions of the compound i in the permeate and feed.

The driving force in VPV and in VMD depends on the values of vapor partial pressures of transported components (Eq. (4)) [37]

$$\Delta p_i = p_i^f - p_i^p \quad (4)$$

where: p_i^f is partial pressure of component i in feed (f) [kPa], p_i^p is partial pressure of component i in permeate (p) [kPa].

Total flux (J_t) and separation factor (β) can be combined into the so called Process Separation Index (PSI), according to Eq. (5):

$$PSI = J_t(\beta - 1) \quad (5)$$

The transport through the membrane and the selectivity of separation process is also dependent on a number of physico-chemical parameters of solvents, like molar volume, saturation pressure, solubility parameter or dielectric constant. Table 1 collates the chosen physico-chemical data of the solvents used in this research.

3. Results and discussion

3.1. Characterization of pristine and modified TiO_2 5 kD and 300 kD membranes

Table 2 presents the values of LEPw measured for 5 kD and 300 kD membranes modified in various conditions. It is evident that the concentration of grafting solution is the most important factor influencing LEP_w. Membranes grafted from diluted solutions show relatively low values of LEP_w. Time of grafting is also an important factor affecting the resulting LEP_w value. As it can be seen from Fig. 3, with increasing grafting duration, the value of LEP_w increased reaching eventually a constant value after ca. 4000–5000 min of modification. This phenomenon is related to the fact that there is a limited number of active hydroxyl groups available on the surface of ceramics [77]. In order to assess the impact of grafting process on the membrane morphology, pore size diameter were determined for pristine and chosen hydrophobized tubular membranes (Table 3). According to the achieved data, it can be concluded that after grafting process the pore size of the ceramic membranes decreased. This observation is related to the attachment of the fluoroalkylsilanes molecules on the membrane surface and inside the membrane pores. As a consequence of this modification, the membrane tortuosity increased what corresponds to an increase of the LEP_w value of grafted membranes (Table 2).

Table 1
The values of the physico-chemical properties of the used solvents.

Solvent	M [g mol^{-1}]	V_M [cm^3 mol^{-1}]	p° at 25 °C [hPa]	δ [MPa]$^{0.5}$	ε
Water (H_2O)	18.01	18.1	23.39	47.8	80.1
Ethanol (EtOH)	46.07	58.4	78.89	26.5	24.3
Butanol (BuOH)	74.12	91.5	9.33	23.1	17.8
Ethyl acetate (EtAc)	88.11	97.7	126.12	18.2	6.02

Table 2
Grafting conditions of 5 kD and 300 kD titania, zirconia and alumina ceramic membranes and the resulting LEPw values.

Membrane	Grafting conditions				Relative LEP [bar]
	Grafting molecules	Grafting time [h]	Concentration of grafting agent[M]	Solvent	
Ti-5 kD	C6	5	0.05	CH_3Cl	1
		15	0.05		2
		35	0.05		4
Ti-5 kD	C6	72	0.01	EtOH	2
		96	0.1		14
Ti-5 kD	C6	72	0.01	CH_3Cl	1
		72	0.1		11
Ti-5 kD	C12	5	0.05	CH_3Cl	3
		15	0.05		4
		35	0.05		4
Ti-300 kD	C6	5	0.05	CH_3Cl	1
		15	0.05		2
		35	0.05		3
Ti-5 kD	C12	72	0.01	CH_3Cl	2
		72	0.5		16
Ti-300 kD	C12	5	0.05	CH_3Cl	2
		15	0.05		3
		35	0.05		4
Al-5 kD[49]	C6	5	0.05	CH_3Cl	1
		10	0.05		2
		15	0.05		3
Al-5 kD[49]	C12	5	0.05	CH_3Cl	3
		10	0.05		4
		15	0.05		4
Zr-5 kD[49]	C6	5	0.05	CH_3Cl	3
		10	0.05		4
		15	0.05		5
Zr-5 kD[49]	C12	5	0.05	CH_3Cl	4
		10	0.05		7
		15	0.05		10
Zr-300 kD[49]	C6	5	0.05	CH_3Cl	2
		10	0.05		3
		15	0.05		5
Zr-300 kD[49]	C12	5	0.05	CH_3Cl	2
		10	0.05		4
		15	0.05		6

Membranes which were subsequently utilized in VMD were also characterized more in detail. Planar ceramic membranes were used in order to determine contact angle (CA), surface free energy (SFE) and roughness (RMS). The obtained data were gathered in Table 3. Based on these results (Table 3) it can be concluded that modification process (time and type of grafting agent) have an important impact on the resulting membrane properties (CA, SFE and RMS). Increasing grafting time contributed to an increased value of contact angles and the diminution of surface free energy

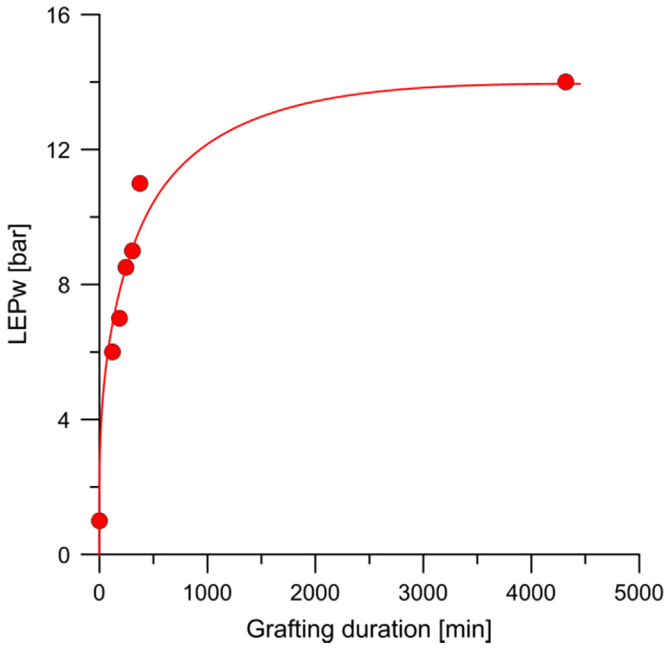

Fig. 3. Correlation between duration of grafting and LEPw. TiO_2-5 kD membrane. Grafting conditions: PFAS-C6, concentration: 0.1 M.

Table 3
Physicochemical properties of grafted ceramic membranes.

Membrane	Grafting time [h]	Pore size [nm]	CA [deg]	SFE [mN m $^{-1}$]	RMS [nm]
Ti-5 kD pristine	**0**	**4.8**	**~40**	**186**	**42**
Ti-5 kD-C6	5	–	110	58.0	25
	10	–	116	45.1	20
	15	3.0	130	30.9	16
Ti-5 kD-C12	5	–	115	50.8	19
	10	–	120	40.9	15
	15	1.6	134	25.1	7
Ti-300 kD pristine	**0**	**187.0**	**~40**	**186**	**62**
Ti-300 kD-C6	5	–	116	47.0	38
	10	–	140	18.8	22
	15	185.0	145	14.4	17
Ti-300 kD-C12	5	–	122	38.2	26
	10	–	146	14.4	16
	15	183.6	148	12.6	10

of the membranes. Moreover, as a result of hydrophobization process by fluoroalkylsilanes, the reduction of surface roughness is observed (Table 3). It must be remembered that a membrane morphology plays an important role and influences the membrane properties. Membranes possessing bigger pores (300 kD) were characterized by slightly higher contact angle values and higher roughness. On the Ti-300 kD membranes modified by C6 and C12 for the duration >15 h, highly hydrophobic surfaces were produced. These surfaces were characterized by contact angle higher than 145° and quite low roughness in the range of 10–22 nm.

Furthermore, a closer inspection of Eq. (1) leads to the conclusion that LEPw should increase with a diminution of pore diameter and with an augmentation of the contact angle value. According to our results published elsewhere [65], the pore diameter of grafted membranes is indeed lower than that in the pristine material. It was also found that the contact angle for water increases with duration of grafting [6,85]. Comparing the data presented in Table 2, as well as those available in the literature, it can

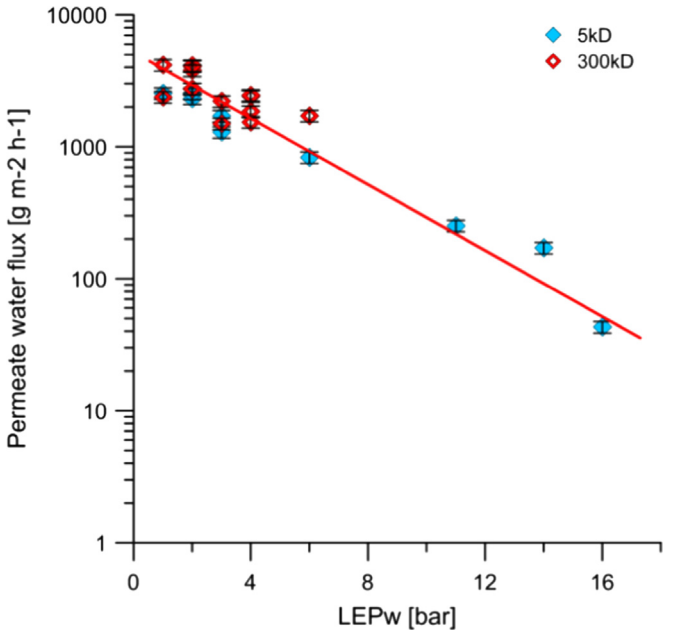

Fig. 4. Permeate flux vs LEP_w for 5 kD and 300 kD membranes grafted with C6 and C12 molecules.

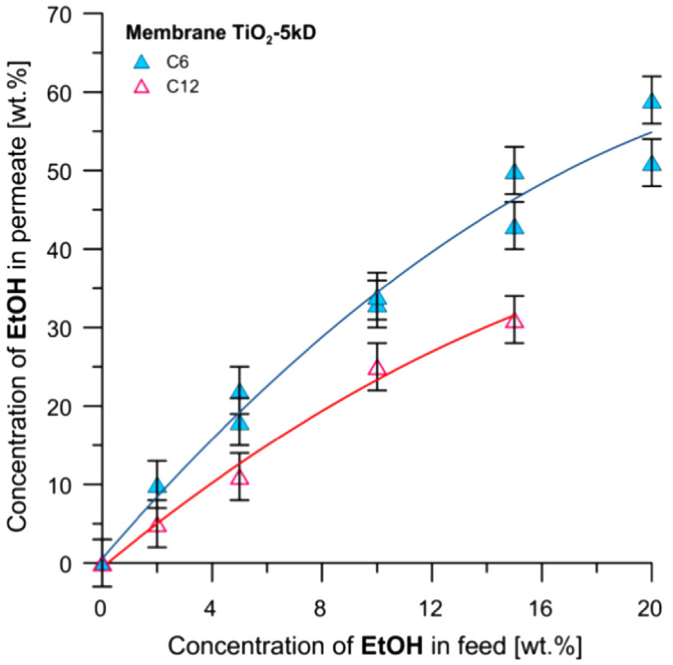

Fig. 5. Composition of feed and permeate in EtOH–water systems.

be additionally stated that in case of membranes with higher pore size (300 kD) the resulting values of LEPw are lower [65].

3.2. Transport properties of hydrophobized membranes in contact with pure water

The conditioned modified membranes were initially tested in contact with pure water, performing the vacuum membrane distillation experiments. During these experiments, the flux of pure water was determined and correlated with LEP_w values. The results obtained for all modified membranes (5 kD as well as 300 kD) are shown in Fig. 4. It can be noticed that the water permeate flux decreased exponentially with increasing LEP_w value, independently on the grafting conditions, type of PFAS molecules

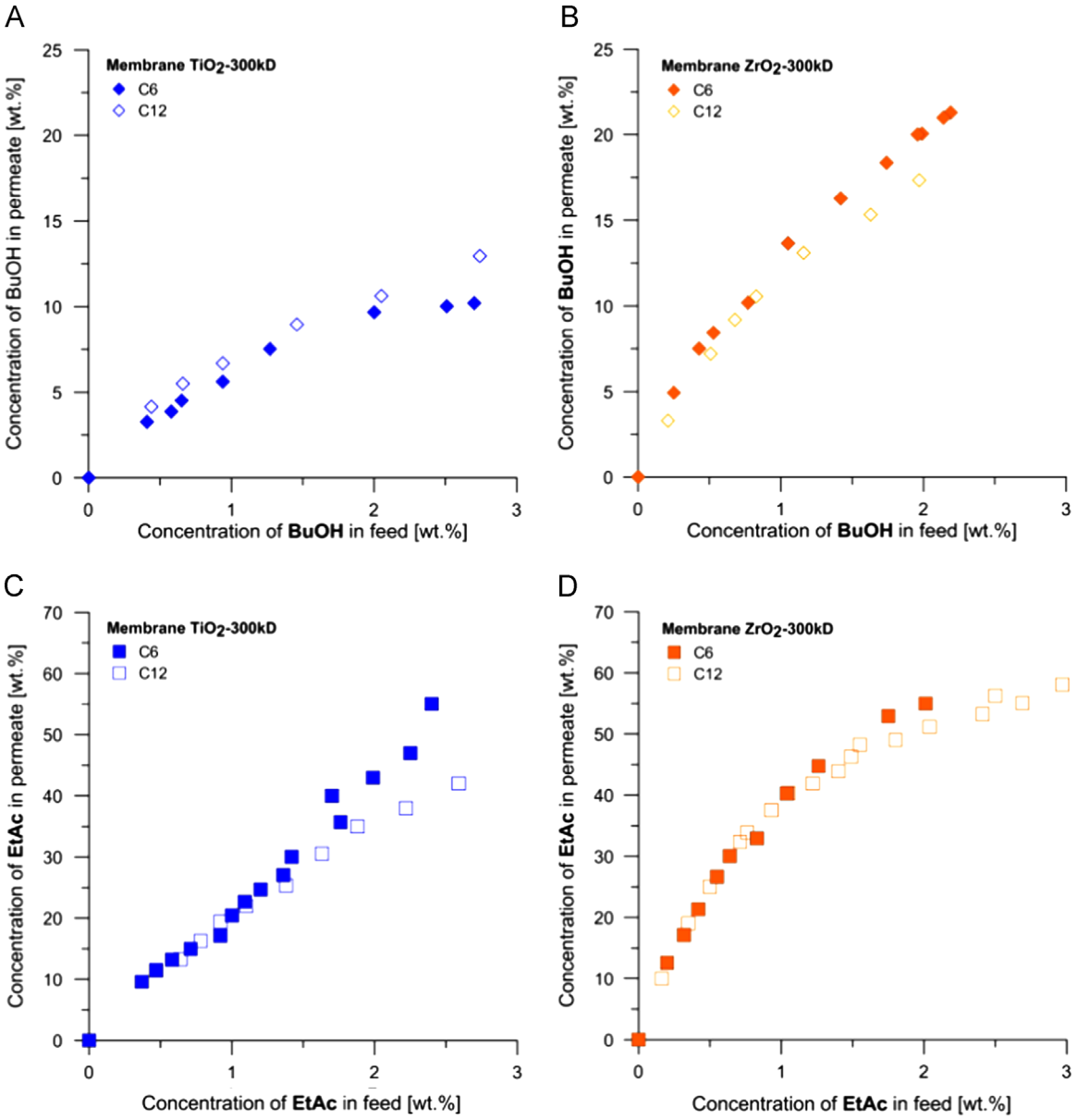

Fig. 6. Composition of feed and permeate in organic–water systems.

and the type of the membrane. This fact is very important concerning the potential practical applications of modified membranes. Membranes with higher fluxes are usually more effective in the separation of liquid mixtures.

3.3. Separation and transport of aqueous organic mixtures in contact with 5 kD and 300 kD membranes modified by C6 and C12 molecules

Fig. 5 presents the separation diagram of TiO_2-5 kD ceramic membrane modified with C6 and C12 molecules, in contact with water–ethanol mixture. As it can be seen permeate is enriched in ethanol for the both investigated membranes. However, the concentration of ethanol in permeate is higher in the case of membranes grafted by C6 molecules.

The different observations are made in the case of VMD experiments with more porous membranes (300 kD ≈ 200 nm) – Fig. 6. In that case, the selectivity of membranes is practically independent on the type of grafting molecules (Fig. 6), however it depends to some extent on the type of ceramics (ZrO_2 or TiO_2). The difference between membranes results from the different amount of hydroxyl groups available on the membrane surface and the structure of pores [85]. Furthermore, comparing the results for water–butanol and water–ethyl acetate mixtures it can be seen that the selectivity is higher in the case of organic solvent possessing higher vapor pressure (Table 1).

To discuss more in detail the differences in the selectivity between micro- and macroporous hydrophobic membranes, the values of separation coefficient determined for various hydrophobized ceramic and polymeric hydrophobic membranes in contact with 2 wt% EtAc in water are gathered in Table 4. Additionally, the values of process separation index (PSI), calculated according to Eq. (5) are also reported. PSI allows to compare the efficiency of various membranes applied in a given separation process [92]. Furthermore, separation coefficient (β=330) resulting from vapor–liquid equilibrium was added for a comparison [93]. Presented data highlights the differences between various types of membranes and allowed to speculate on the presumed mechanism of separation.

The resulting selectivity of a macroporous membrane (300 kD ≈ 200 nm) is a superposition of selectivity related first of all to the vapor–liquid equilibrium (at the pore entrance) and selectivity

Table 4
Comparison of the effectiveness of hydrophobic polymeric and hydrophobized ceramic membranes with liquid–vapor equilibrium in the separation of water–EtAc mixture.

	EtAc conc.[wt%]	T_f [°C]	β_{EtAc}	PSI [kg m^{-2} h^{-1}]	Ref.
Vapor liquid equlibrium	2	30	330	N/A	[96]
Ceramic membranes					
Ti-300 kD-C6	2.0	35	40	546	This work
Ti-300 kD-C12	2.0	35	32	344	This work
Zr-300 kD-C6	2.0	35	60	637	This work
Zr-300 kD-C12	2.0	35	50	241	This work
Ti-5 kD-C6	2.0	35	30	190	[50]
Ti-5 kD-C12	2.0	35	1.7	0.8	[50]
Zr-5 kD-C6	2.0	35	26	27	[49]
Zr-5 kD-C12	2.0	35	1.5	0.04	[49]
Al-5 nm-C6	2.0	35	8	18	[49]
Al-5 nm-C12	2.0	35	1.3	0.4	[49]
Polymeric dense membranes					
PDMS (Pervap 1060)	2.0	53	300	294	[38]
Zeolite filled PDMS (Pervap 1070)	0.5	53	450	150	[38]
Pebax-4033	0.5	53	25	2.4	[38]
Ethylene-vinyl acetate copolymer	2.5	30	118	130.9	[93]
P(VDF-HFP)/PP(Acetone)	4.0	30	180	295	[94]
P(VDF-HFP) (DMAc)	3.0	30	80	32	[95]
PDMS-PMHS/alumina	5.0	40	140	73	[96]
P(VDF-HFP)/ [bmim]BF4(5 wt%)	5.0	65	121	563.3	[97]
P(VDF-HFP)/ [bmim]BF4(1 wt%)	5.0	65	99	375.1	[97]

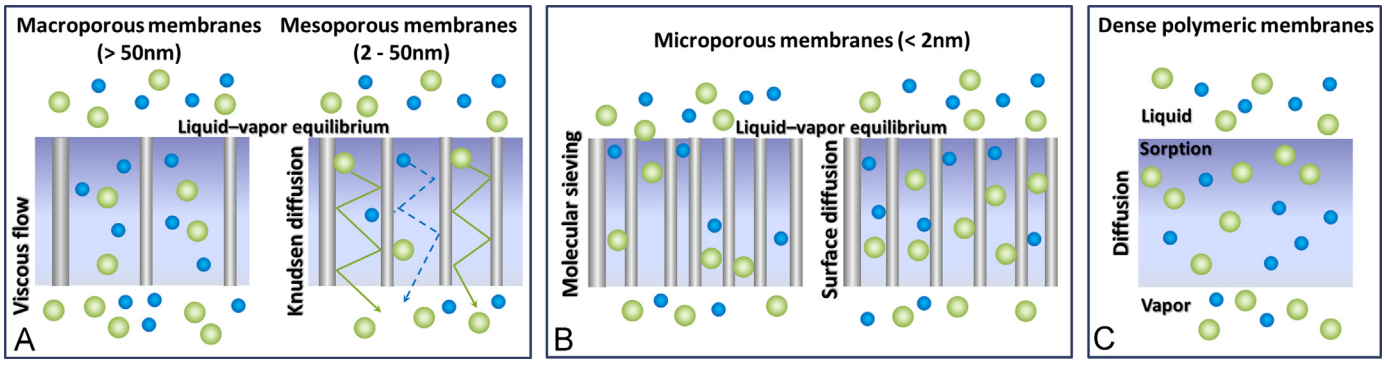

Fig. 7. Comparison of separation mechanisms in VMD and VPV. A – VMD with hydrophobic macroporous ceramic membranes; B – VMD with hydrophobic microporous ceramic membranes; C – VPV with dense hydrophobic polymeric membranes. L–V – liquid–vapor equilibrium.

associated with the Knudsen diffusion and/or the viscous flow (Fig. 7A) [34,98–100]. The separation factor for water–EtAc mixture is in the range of 30–60 and this value reflects the strong influence of Knudsen diffusion and/or viscous flow on the resulting separation, because transport through the hydrophobic macroporous membranes favors smaller molecules (i.e. water). If the pore size of ceramic membranes is decreased to the microporous range (5 kD ≈ 2–4 nm) the selectivity of membrane is drastically reduced. The separation factor of membranes grafted with C12 molecules is lower than 2. The separation factor for membranes grafted with C6 molecules is also inferior ($\beta \approx 8$–30) than that for macroporous hydrophobic membranes. It can be stated that in the case of vacuum membrane distillation with 5 kD membranes, the selectivity of membranes grafted by C6 is higher than that grafted by C12 molecules. The lower selectivity of membranes grafted by C12 results from the fact that C12 brush is denser and transport of organic molecules is limited to much higher extent than in the case of membranes modified by C6 molecules (Fig. 7B). Moreover, for microporous ceramic membranes (2–4 nm) hydrophobized by FAS molecules, the mechanism of separation is a combination of LV equilibrium (at the pore entrance) followed by a surface diffusion or molecular sieving – Fig. 7B [30,41,98].

It is also interesting, that the best separation results were obtained for dense polymeric membranes during hydrophobic pervaporation process – Table 4, Fig. 7C [38,101]. The separation in the dense membranes is described by a solution–diffusion mechanism [30,41,102]. The solution–diffusion mechanism assumes the selective sorption of components into the membrane at feed side, followed by the selective diffusion of sorbed components through the membranes (Fig. 7C). In the case of hydrophobic pervaporation, sorption favors more hydrophobic molecules (ethyl acetate), however diffusion always facilitates smaller molecules [48,50].

Khayet and Matsuura compared vacuum pervaporation and vacuum membrane distillation using PVDF dense and porous membranes [98]. Authors prepared porous membranes of various pore sizes in the meso- to macroporous range (10–220 nm). It was stated, that in VMD process the transport occurs both in pores and through the dense part of polymers. Authors correlated the transport and selectivity of the process with the pore size of the membranes, and similarly indicated that with decreasing pore size the selectivity and fluxes were decreasing [98].

4. Conclusions

Hydrophobization of the ceramic membranes with various porosity was successfully performed using perfluorosilanes with different length of fluorocarbon chain. Effectiveness of grafting was expressed by determining LEPw. It was stated that LEPw is

dependent on several parameters like time of grafting, concentration of grafting solution, type of solvent used, and the length of PFAS molecule. The membranes were subsequently used in the vacuum membrane distillation process of pure water and water–ethyl acetate mixture. The strong correlation between measured liquid entry pressure of water and water flux indicates that transport properties of hydrophobized membranes would depend mainly on LEPw. The selectivity of membranes in the separation of water–organic mixture depends strongly on the pore size of the hydrophobized membrane. Microporous membrane are much less efficient in the separation of organics from water (separation factor of ethyl acetate – EtAc in the range 1.3–30) comparing with macroporous ones (separation factor of EtAc in the range 32–60). The results were also discussed assuming the various mechanism of transports through porous ceramic membranes. Results were additionally compared with the results obtained for hydrophobic polymeric membranes (separation factor of EtAc in the range 25–450). PSI indices obtained for macroporous ceramic membranes were in the same range as these calculated for dense polymeric membranes, regardless the different separation mechanism. Results indicate that in the practical applications vacuum membrane distillation with macroporous membranes would be as effective as pervaporation with hydrophobic polymeric membrane. It should be however remembered that during membrane distillation process the wetting of the pores is one of the limitations of the wider used of this membrane process.

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