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WETTING OF SUPPORTS BY IONIC LIQUIDS USED IN GAS SEPARATION PROCESSES

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Abstract. Ionic liquids were found to be selective solvents for separation of gases. They are widely used in supported ionic liquid membranes (SILMs) technology, especially in gas separation and purification processes. This work has characterized commercially available porous membranes employed in such purposes. Characterization of supports and membrane phases was carried out in order to determine factors influencing membrane stability. Scanning electron microscopy (SEM) was used to determine morphology of membrane surface. In this work wetting of the polymeric support with [Emim][TfO], [Emim][Tf₂N], [Bmim][TfO] and [Bmim][Tf₂N] and swelling of the membrane impregnated with ionic liquids have been investigated.

keywords: imidazolium ionic liquids, liquid membrane, wettability

1. Introduction

Supported liquid membranes (SLMs) have been an object of growing interest in recent years. They present several advantages in separation processes, such as requirement of very small quantities applications. The reason of this state is mainly low stability (Kemperman et al., 1996). Mechanisms of instability are reported in the literature (Kocherginsky et al., 2007). Stability is mostly affected by loss of liquid membrane phase from the support (Naplenbroek et al., 1992). Due to the fact that membrane phase is kept in the membrane pores by capillary forces, it is obvious that this process can be either evaporation, dissolution in surrounding phases or high pressure difference. These effects have influence on flux and selectivity of the system (Takeuchet et al., 1987; Zha et al., 1995). Stability of SLMs depends on the properties of polymeric or ceramic support, membrane phase, possible carriers and operating conditions. Physicochemical properties of membrane phase play important role in membrane stability. Proper choice of these materials can improve significantly system lifetime. Problems mentioned above can be avoided by using ionic liquids as a membrane phase filling pores of the support. Some researchers report that water

concentration in organic phase is also important in SLMs stability, whereas when it is less than 15 g/l it shows proper stability (Zha et al., 1995).

In recent years ionic liquids have been widely used as an alternative to traditional organic solvents in catalysis, as a reaction media and in separation and purification processes. Ionic liquids have many unique properties, for example, they have non-measurable vapor pressure, they are non-flammable and liquid in a wide range of temperatures, they solvate wide range of organic and inorganic species (Earle et al., 2000; Marsh et al. 2004; Pernak, 2000). Ionic liquids give a possibility of adjusting their physicochemical properties by choosing proper ions. Proper choice of organic phase allows to avoid the problem of solvating IL in receiving phase and only the excess amount of ILs from the membrane surface is removed (De Los Rios, 2007; 2009). These properties give SILMs advantage over traditional SLMs (Fortunato et al. 2004; Gan et al, 2006; Hernandez-Fernandez et al., 2009). Non-measurable vapor pressure allows to overcome the problem with loss of membrane phase by evaporation. Since ILs consist of large asymmetric organic cation and small anion and this structure prevents crystallization, they are liquid in a wide range of temperatures. As mentioned above, stability depends on capillary forces that is why size and morphology of membrane pores affect the stability (Kemperman et al., 1996). Minimum transmembrane pressure required to push out the impregnating phase from membrane pores is given by the Young–Laplace equation:

$$P = \frac{2 \cdot \gamma \cdot \cos \theta}{r}, \quad (1)$$

where: γ is the interfacial tension, θ is the contact angle, r is the pore radius.

This equation is true for cylindrical pores. Commercially available membranes have highly irregular pores geometry. Calculated pressure is then higher than real critical level. It can be concluded that generally membranes with smaller pore size are more stable than those with bigger pores.

This work focused on the use of polymeric porous membranes which can be applied as support for liquid membranes. Experimental procedures based on capillary rise method are widely used for porous media characterization (i.e. pore radius, contact angle). Measurements of penetration distance and liquid mass increase are two main experimental methods, in which Washburn equation is a basic instrument to analyze the obtained results (Trong et al., 2005; 2006). Capillary rise method was used for contact angle determination for polymeric material wetted by ionic liquids. Influence of imidazolium-based ionic liquids composition on wettability of porous supports was investigated. The family of 1-alkyl-3-methylimidazolium compounds ($C_n\text{mim}$) with variable alkyl chain lengths in cation and changeable anions were taken into account.

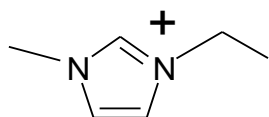
2. Experimental

2.1. Material, experimental apparatus and method

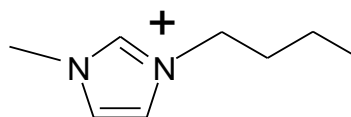
Seven ionic liquids were used in this study: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][Tf₂N], 1-ethyl-3-methylimidazolium trifluoromethanesulfone [EMIM][TfO], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf₂N], 1-butyl-3-methylimidazolium trifluoromethanesulfone [BMIM][TfO]. All chemicals were supplied by Merck Chemicals Company, Darmstadt, Germany with purity higher than 99%. The molecular structures of ILs cations and anions used in this study are shown in Fig.1 and Fig.2.

In order to determine the effect of chemical structure of the ionic liquids on wetting, different alkyl chain lengths of the cations and different anions were selected.

Polymeric supports: the four hydrophilic membranes were used: GH Polypro (polypropylene) - PP, FP VericelTM (polyvinylidene fluoride) - PVDF, NylafloTM (polyamide) - Nylon, Supor[®] (polyethersulfone) - PES, (Pall, Gelman Laboratory, USA). Table 1 shows the physicochemical properties of polymeric supports used in the experiments declared by Pall, Gelman Laboratory.

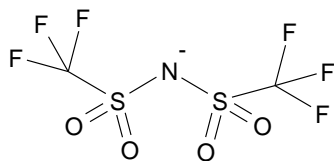


1-ethyl-3-methylimidazolium [Emim]

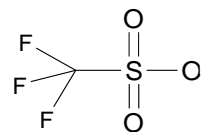


1-butyl-3-methylimidazolium [Bmim]

Fig. 1. Structure of ionic liquids cations used in the experiments



bis(trifluoromethylsulfonyl)imide [Tf₂N]



trifluoromethanesulfone [TfO]

Fig. 2. Structure of ionic liquids anions used in the experiments

Table 1. Physicochemical parameters of polymeric supports reported by producer

Support	Density [kg/m ³]	Pore size [μm]	Porosity [%]	Thickness [μm]
PP	900	0.2	80	92
PVDF	1790	0.2	80	123
Nylon	1130	0.2	80	110
PES	1370-1510	0.2	80	148



SEM characterization

The scanning electron microscope (SEM) Philips-FEI XL 30 ESEM (Environmental Scanning Electron Microscope) was used to determine the morphological properties and the pore size distribution. Before the SEM observation, the samples of supports were dusted with ultrathin layer of gold which significantly improved the quality of obtained images. Fig.4 (a), (b), (c) and (d) are SEM micrographs of the supports – polypropylene PP, polyvinylidene fluoride PVDF, polyamide Nylon, polyethersulfone PES (5000x) (scale bar = 5µm).

IR spectra of PP membrane

PP support has a hydrophilic, modified surface. The manufacturer (Pall) does not provide information about the type of modification. Membrane surface modification was calculated by ATR (Attenuated Total Reflection) technique on camera - FT-IR Spectrometer Tensor using zinc selenide optics and diamond crystal (Golden Gate's snap Specac). Analyses were performed using the following parameters: the spectral range 4000 - 600 cm⁻¹, resolution 2 cm⁻¹, the number of scans: 64. Figure 5 shows the IR spectra.

Thickness of the membrane and swelling in ionic liquids

Thickness of the membrane after immobilization step was determined by optical method using Epi-fluorescent Microscope L3001 with a compatible digital camera, Power Shot A650 IS. This method allows to measure the change of the thickness of the polymer after immersing it in ionic liquid for 24h. Glass holder was used to place the membrane in z direction to measure thickness.

Wetting of the membrane

The capillary rise method is based on the Washburn approach that has been derived from the Poiseuille equation:

$$dV = \frac{r^4 \cdot \Delta P \cdot \pi}{8\eta \cdot h} dt \quad , \quad (2)$$

and the Washburn equation:

$$h^2 = \frac{r \cdot \gamma \cdot \cos \theta}{2\eta} t \quad . \quad (3)$$

Additionally, the following simplifications are employed in the capillary rise method:

- a) the flow is laminar and stationary,
- b) there is no slip, i.e. no flow on the solid body - liquid interface,
- c) no internal pressure.



One way of determining contact angle value is an investigation of two liquids – reference and examined (Studebaker, 1955). For reference liquid:

$$h^2 = \frac{r\gamma_0}{2\eta_0} t_0. \quad (4)$$

When two beds are identical, r is constant, and for another liquid we have:

$$h^2 = \frac{r\gamma_1 \cos \theta}{2\eta_1} t_1. \quad (5)$$

Dividing equation (4) by (5) we obtain:

$$\cos \theta = K \frac{t_0}{t_1}, \quad (6)$$

where

$$K = \frac{\gamma_0 \cdot \eta_1}{\gamma_1 \cdot \eta_0}, \quad (7)$$

where

t_0 , γ_0 , η_0 are time of penetration, surface tension and viscosity of reference liquid, and t_1 , γ_1 , η_1 are time of penetration, surface tension and viscosity of liquid investigated, respectively.

The apparatus for the capillary rise experiments is shown in Fig. 3.

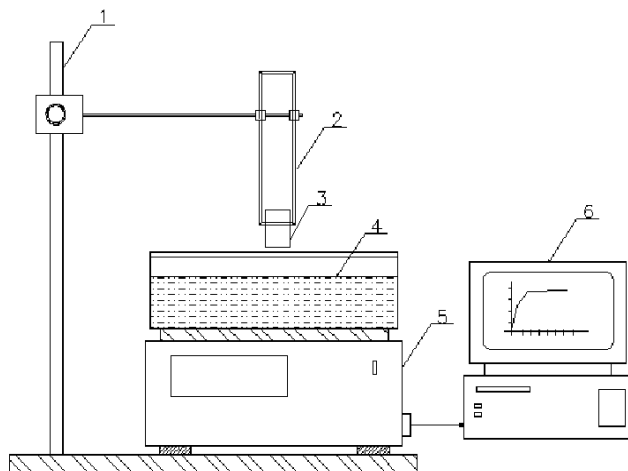


Fig. 3. Capillary rise measuring apparatus: 1 - support, 2 – glass matrix holder, 3 – polymeric membrane, 4 – vessel with ionic liquid, 5 - balance, 6 -computer



In the experiment, polymeric membrane samples sized 10x10 mm were cut out. The line at 5 mm height was made. The sample was placed in a glass holder. The increase in height of liquid penetrating into polymeric membrane and decrease in mass of the liquid in a container was recorded every second using timer and electronic balance, attached to a computer. The time $t = 0$ approximately corresponded to the moment of membrane submersion in the wetting liquid. The time of penetration up to 5 mm of membrane was measured. The experiments were repeated eight times (two times for each side) and the mean value was calculated. Based on measurement of ionic liquid penetration time in polymeric support, angle values were calculated using Equations 5 and 6. The results are shown in Table 2.

The second method for contact angle determination was the dynamic sessile drop method. The surface tensions of the ionic liquids were determined by the pendant drop method using Tensiometer Kruss DSA 10. Dynamic sessile drop study determines the largest contact angle possible without increasing solid/liquid interfacial area by adding volume of liquid dynamically. This maximum angle is the advancing angle θ_a . Volume is removed to produce the smallest possible angle, the receding angle θ_r . The difference between the advancing and receding angle $\theta_a - \theta_r$ is the contact angle hysteresis. The results are shown in Table 3.

3. Results and discussion

In the experiments imidazolium ionic liquids with different anions and cations were applied. Selected ionic liquids are widely used in gas separation technology. Imidazolium salts containing alkyl fluoride anions: bis(trifluoromethanesulfonyl) amide ([Tf₂N]) and trifluoromethanesulfonate ([TfO]) selectively separate carbon (IV) oxide from other gases, for example methane (Anderson et al., 2007; Anthony et al., 2005; Baltus et al., 2004; Bara et al., 2009; Bates et al., 2002; Chin et al., 2006; Joskowska et al., 2010; Joskowska et al. 2011).

The morphology of commercial membranes was studied by SEM. SEM (Fig.4) micrographs present highly porous material. The pores are heterogenic and not cylindrical.

Figure 4 indicates, that the 0.2 μm pore size declared by the manufacturer is not the size of the smallest pores, but the average size of all the pores in the membranes.

IR spectra illustrate intense stretching vibrations of C-H bond - methyl group at 2951 cm^{-1} (asymmetric) and 2868 cm^{-1} (symmetric) and methylene group at 2919 cm^{-1} (asymmetric) and 2839 cm^{-1} (symmetric) are visible in the IR spectra of PP membrane (Fig. 5). Stretching vibrations of the double bond occurred at 1728 cm^{-1} . IR spectra shows also intense bending vibrations of symmetric methylene group at 1453 cm^{-1} and bending vibrations of asymmetric methyl groups at 1376 and 1358 cm^{-1} .

Therefore, it can be concluded that the surface of PP membrane is modified with compounds containing C-O-C bonds, as evidenced by the emergence of asymmetric stretching vibration of C-O-C bond at 1256 cm^{-1} and asymmetric at 1105 cm^{-1} band



swing vibration of methyl groups below 1000 cm^{-1} . IR spectra of PVDF, PES and Nylon membranes perfectly fit to the IR spectra of model sample.

Contact angle θ is a quantitative way of showing wettability of solid with liquid. It is geometrically defined as an angle formed at tri-phase border liquids – gas – solid. The low value of contact angle indicates spreading of liquid on a surface – good wettability; high value indicates weak wettability. If the contact angle is below 90° it can be concluded, that liquid wets solid. If the angle is over 90° , liquids does not wet solid.

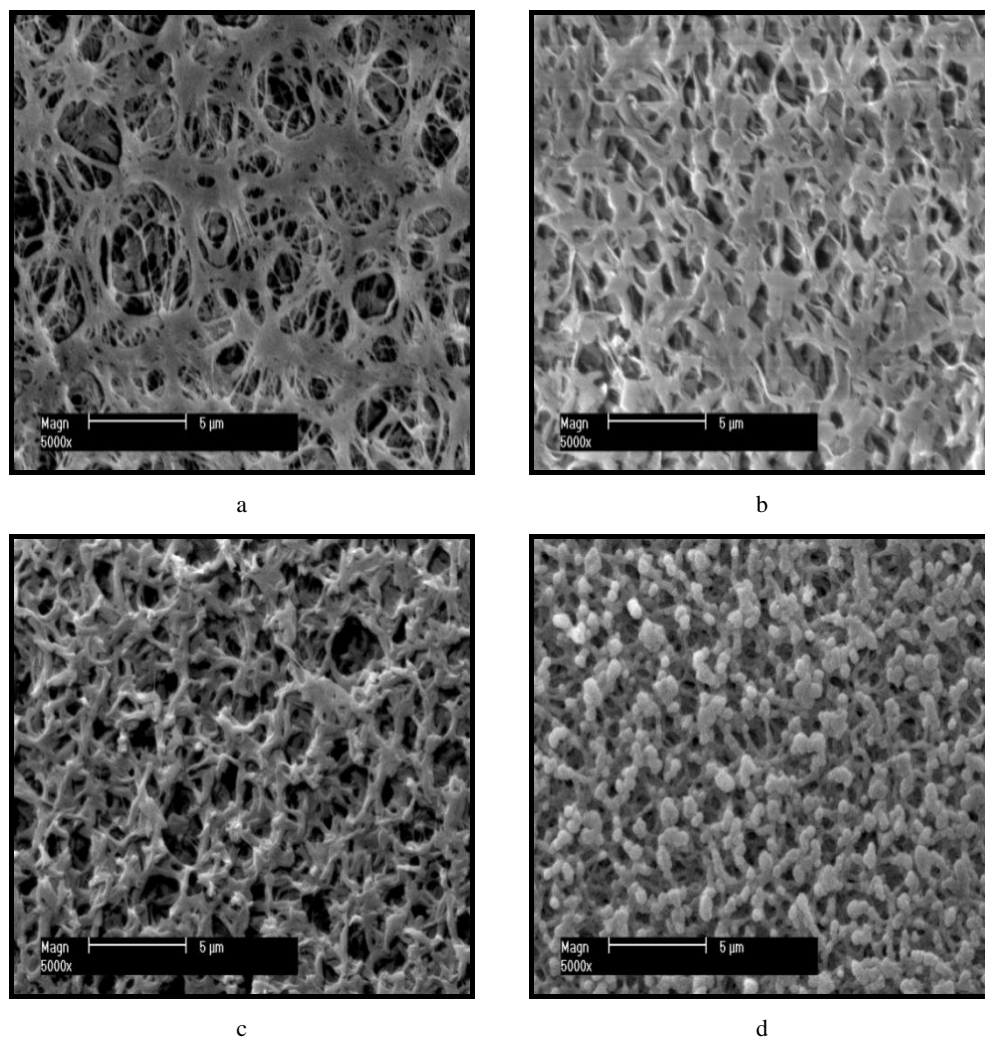


Fig. 4. Scanning electron micrographs of (a) PP, (b) PVDF, (c) Nylon, (d) PES (500x) (scale bar = $5\ \mu\text{m}$)

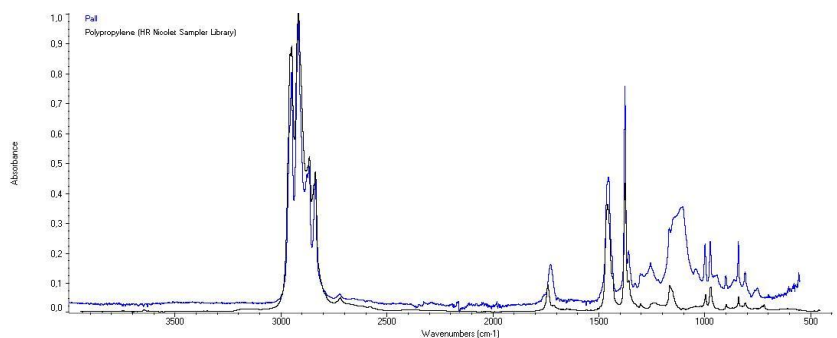


Fig. 5. IR spectra of PP membrane

Table 2. The physicochemical properties and time of penetration of reference liquids

Support	Reference liquid	Surface tension, N/m	Viscosity, Pa·s	Time of penetration, s
PES	Hexane	0.0179	0.00029	2
PVDF	Hexane	0.0179	0.00029	5
Nylon	Toluene	0.0278	0.00055	4
PP	Methanol	0.0221	0.00054	4

Table 3. The physicochemical properties of ionic liquids and contact angle determination by Washburn equation

Ionic Liquid	Surface tension [N/m]	Viscosity [Pa·s]	Support	Time of penetration t_1 [s]	k	$\cos\theta$	θ [deg]
[EMIM][Tf ₂ N]	0.041	0.026	PES	367	38.2	0.208	78
			PVDF	471	38.2	0.406	66
			Nylon	209	31.5	0.602	53
			PP	212	25.3	0.478	61
[EMIM][TfO]	0.044	0.040	PES	297	55.7	0.239	66
			PVDF	707	55.7	0.332	67
			Nylon	247	45.8	0.492	42
			PP	213	36.9	0.374	46
[BMIM][Tf ₂ N]	0.037	0.032	PES	444	53.0	0.489	76
			PVDF	799	53.0	0.802	71
			Nylon	354	43.6	0.977	60
			PP	376	35.1	0.681	68
[BMIM][TfO]	0.034	0.070	PES	530	129.7	0.489	61
			PVDF	809	129.7	0.802	37
			Nylon	437	106.7	0.977	12
			PP	505	86.0	0.681	47



Capillary rise experiments were carried out in order to investigate wettability of the polymeric support by selected ionic liquids. The first experiment including water, toluene, ethanol, methanol, isopropanol, acetone, hexane and cyclohexane was done in order to determine a reference wetting liquid for each support. Methanol was the best penetrating liquid for PP, hexane for PES and PVDF. For Nylon membrane toluene (see table 2) occurred to be the best. Based on the time of penetration in polymeric matrix measurements of reference liquids and examined ionic liquids, contact angles values were calculated (see table 3). For all the examined ionic liquids wettability decreases in following order Nylon > PP (except for BMIM TfO) > PVDF > PES. The lowest value of contact angles for all supports has been determined for BMIM TfO. Contact angle, θ , increases as the surface tension of the ionic liquid, γ increases. Similar findings have been reported earlier by Sedev (2011).

The Washburn equation presents linear dependence of squared height of liquid penetration in capillary and time of the experiment. However, in the case of porous system, Washburn established the model of system as a bunch of cylindrical capillaries. Capillary radius r is then the average or effective pores radius. Another simplification in Washburn method is connected with flow which should be laminar and stationary and without flow in the phase boarder.

Examined polymer supports do not meet Washburn assumptions. Therefore, sessile drop method was used.

Values of contact angles calculated from sessile drop contact angle measurements are below 20° , therefore all the ionic liquids examined are suitable for perfect wetting of supports (table 4). The best wettability was observed for Nylon membrane, successively for PP, PVDF and PES.

Assumption of best wetting for liquids with the lowest surface tension was confirmed ([Bmim][TfO]). Increase in ionic liquid hydrocarbon chain in cation structure does not affect wettability.

Taking into account values of contact angles (table 4) it can be concluded that each of chosen supports is perfectly wetted by ionic liquids.

Izak et al. (2007) observed that degree of swelling of the membrane can be related with the water activity of the ionic liquid. The measured water content of ionic liquids used was [Emim][TfO] – 1.370%, [Bmim][TfO] – 0.134%, [Emim][Tf₂N] – 0.001%, [Bmim][Tf₂N] – 0.109%. However, ionic liquids are highly hygroscopic and we have to keep in mind that water content can change during the experiment (Izak et al., 2007).

All the investigated supports show higher thickness after immobilization with ionic liquid. According to presented data it can be concluded that the longer is hydrocarbon chain in the cation structure, the higher swelling effect is observed. However, Nylon membrane shows similar thickness for all ionic liquids used in this study. Thickness of PVDF membrane was difficult to measure due to transparency of the membrane when immobilized with ionic liquid as indicated by standard deviations values. Such



behavior of polymeric membranes can affect mechanical stability of the membranes and affects value of maximum possible gas pressure without breaking of support.

Table 4. Contact angle determination by sessile drop method

Ionic Liquid	Support	Advancing angle θ_a [deg]	Receding angle θ_r [deg]	Hysteresis $\theta_a - \theta_r$ [deg]
[EMIM][Tf ₂ N]	PES	16.6±0.2	9.6±0.2	7.0
	PVDF	12.5±0.7	7.4±0.1	5.1
	Nylon	10.3±0.5	6.8±0.6	3.5
	PP	12.3±0.5	7.8±0.6	4.5
[EMIM][TfO]	PES	14.5±0.6	8.3±0.2	6.2
	PVDF	15.5±0.6	8.4±0.19	7.1
	Nylon	14.2±0.3	8.1±0.2	6.1
	PP	11.8±0.9	5.6±0.7	6.2
[BMIM][Tf ₂ N]	PES	16.9±0.2	8.2±0.2	8.7
	PVDF	19.2±0.5	10.9±0.5	8.3
	Nylon	10.7±0.4	8.4±0.3	2.3
	PP	13.9±0.4	8.0±0.3	5.9
[BMIM][TfO]	PES	15.5±0.2	8.1±0.2	7.4
	PVDF	18.3±0.6	10.4±0.7	7.9
	Nylon	8.1±0.3	6.6±0.1	1.5
	PP	10.5±0.3	8.8±0.5	1.7

Table 5. Thickness of pure and immobilized with ionic liquid membranes

Support	Ionic Liquid	Thickness [μm]
PES	none	117.73 ± 2.52
	[EMIM][Tf ₂ N]	133.52 ± 8.56
	[EMIM][TfO]	138.40 ± 2.07
	[BMIM][Tf ₂ N]	148.85 ± 4.50
	[BMIM][TfO]	144.17 ± 1.93
PVDF	none	159.92 ± 1.83
	[EMIM][Tf ₂ N]	179.95 ± 5.34
	[EMIM][TfO]	170.01 ± 2.80
	[BMIM][Tf ₂ N]	186.78 ± 3.89
	[BMIM][TfO]	204.57 ± 7.37
Nylon	none	114.51 ± 3.24
	[EMIM][Tf ₂ N]	121.10 ± 3.62
	[EMIM][TfO]	122.61 ± 3.27
	[BMIM][Tf ₂ N]	117.15 ± 2.34
	[BMIM][TfO]	119.15 ± 3.29
PP	none	74.57 ± 2.29
	[EMIM][Tf ₂ N]	86.93 ± 2.31
	[EMIM][TfO]	82.39 ± 2.63
	[BMIM][Tf ₂ N]	105.80 ± 6.44
	[BMIM][TfO]	104.80 ± 5.63



4. Summary

Properties of commercial membranes characterized in this study affect the effectiveness of gas separation processes based on supported ionic liquid membranes. One of the major factors affecting such processes is membrane stability. Stability of systems is then characterized for example by pressure resistance, wettability and swelling of the support. Wettability of polymeric support with ionic liquids was examined. The results show that it is possible to use ionic liquids as the membrane phase in the supported ionic liquid membranes and to apply such systems for selective separation of carbon dioxide from other gases (Joskowska et al., 2010).

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