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WETTING PROCESSES IN SUPPORTED IONIC LIQUID MEMBRANES TECHNOLOGY

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Abstract: Ionic liquids are widely used in supported ionic liquid membranes technology, especially in gas separation and purification processes. This work characterizes the ability of ionic liquids to wet commercially available porous supports used for such purposes. Characterization of supports and membrane phases was carried out in order to determine factors influencing wetting process. Experimental method based on capillary rise is widely used for porous media characterization (i.e. pore radius, contact angle). Measurements of penetration distance or liquid mass are two main experimental methods, in which the Washburn equation is a basic instrument to analyze the obtained results. However, polymeric porous supports do not meet Washburn assumptions and the method is loaded with human errors, so the sessile drop method was used. The rate of wetting influences swelling effects and therefore changes in permeation path during gas separation processes are observed. Influence of ionic liquids structure on wetting and swelling of porous supports was investigated. The families of 1-alkyl-3-methylimidazolium ($C_n\text{mim}$), ammonium (N_{nmn}), 1-alkyl-1-methylpyrrolidinium ($C_n\text{Pyr}$) and 1-alkylpyridinium ($C_n\text{Py}$) compounds with variable alkyl chain lengths in cation structures and changeable anions were taken into account in wetting and swelling experiments.

Keywords: ionic liquid, supported ionic liquid membrane, contact angle, wettability, swelling

Introduction

Supported liquid membrane (SLM) is a two phase system of porous support and liquid phase held in the membrane pores by capillary forces (Walczyk, 2006). Industrial application of liquid membrane systems usually covers usage of ethanolamine (MEA), diethanolamine (DEA), chloroform, dichloromethane, tetrachloromethane, chlorobenzene and toluene. These traditional solvents present high absorption capacity of CO_2 at low temperature and under pressure (Schaffer et al., 2011). However, they also present high heat absorption, corrosiveness (Kittel et al., 2009), high vapor pressure, lack of possibility of recovery and high toxicity. Pure MEA vapor pressure is

about 64 Pa. However, while using water solutions, vapor pressure is much higher. DEA acute toxicity in the form of LD₅₀ is from 1.41 g/kg to 2.83 g/kg (Expert Panel of the Cosmetic Ingredient, 1983), DEA is irritant to skin, eyes and cause systemic toxicity mainly in liver, kidney, red blood cells and the nervous system following oral and/or dermal exposure of laboratory animals (Gamer et al., 2008). Therefore, while using these traditional organic solvents several disadvantages can be observed such as secondary stream pollution or loss of membrane phase caused by vaporization or displacement of liquid from the pores under transmembrane pressure (Teramoto, 2000). Many efforts have been made to improve the lifetime of SLMs. Gelation, applying top layers or replacing traditional solvent to ionic liquid (IL) were employed to prevent instability mechanisms (Danesi et al., 1987; Naplenbroek et al., 1992). Great issue is noticed in using ionic liquids as a replacement for toxic, flammable and volatile organic solvents. Calculated vapor pressure for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in 298K is $12 \cdot 10^{-6}$ Pa (Berthod et al., 2008). Ionic liquids are class of solvents that are composed of large asymmetric organic cation and smaller organic or inorganic anion. Ionic liquids present many unique properties, they have negligible vapor pressure, they are non-flammable and stay liquid in a wide range of temperatures, moreover ILs solvate many of organic and inorganic species (Cadena et al., 2004). These properties make them very attractive in many industrial applications. However, complete design of industrial processes using ILs can be performed only having knowledge on their physicochemical properties such as viscosity, density or surface tension.

Ionic liquids present surface tensions lower than those observed for traditional solvents as water, however these values are still much higher than observed for organic solvents (Sohn et al., 2000). Freie et al. (2007) presented the dependence of surface tension on the strength of interactions between cation, anion and hydrogen bonds.

Ionic liquids also have higher viscosity than other typical solvents used in separation processes. Dynamic viscosity of ILs in room temperature is situated in a range from about 10 mPa·s to 500 mPa·s. In comparison, viscosity of chloroform, tetrachlorocarbon and ethanolamine in 293K is 0.89; 16.1; and 20 mPa·s respectively (Wasserscheid and Keim, 2000; Chiappe and Pieraccin, 2005).

Properties of ionic liquids mentioned above give supported ionic liquid membranes (SILMs) predominance over traditional SLMs (Gamer et al., 2008; Letcher, 2007; Hernandez-Fernandez et al., 2009). SILMs present several advantages, such as requirement of very small quantities of solvent and high selectivity. Key aspect in obtaining satisfying effectiveness and long membrane lifetime is the proper choice of ionic liquid and polymeric or ceramic support. Properties of both affect the processes of obtaining useful supported ionic liquid membrane. Perfect wetting of supports with ionic liquids is required for complete pores saturation and applying high operating pressures without pushing the liquid out of the pores. Contact angles of some ionic



liquids are described in the literature, for example on Si wafers (Tadkaew et al., 2011), PTFE and glass (Nguyen et al., 2012; Cichowska-Kopczynska et al., 2013).

This work characterizes the ability of ionic liquids to wet polymeric porous supports and the rate of swelling of these supports that are used in SILMs technology. Wetting of supports affects membrane stability, whereas swelling effect causes fluctuations in gas diffusion path. Experimental method based on capillary rise is widely used for porous media characterization (i.e. pore radius, contact angle). Measurements of penetration distance and liquid mass are two main experimental methods, in which Washburn equation is a basic instrument to analyze the obtained results (Dang-Vu and Hupka, 2005; Ferraris et al., 2001). However, this method is loaded with human errors, so the sessile drop method was used for measurements. The families of 1-alkyl-3-methylimidazolium ($C_n\text{mim}$), ammonium ($N\text{nnnn}$), 1-alkyl-1-methylpyrrolidinium ($C_n\text{Pyr}$) and 1-alkylpyridinium ($C_n\text{Py}$) compounds with variable alkyl chain lengths in cation structures and changeable anions were taken into account in order to discuss the influence of ionic liquids structure on wetting and swelling of porous supports.

Materials

Several imidazolium, ammonium, pyridinium and pyrrolidinium ionic liquids were used in this study:

- 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Emim][Tf₂N],
- 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [Emim][TfO],
- 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf₂N],
- 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][TfO],
- 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Hmim][Tf₂N],
- trimethylbutylammonium bis(trifluoromethylsulfonyl)imide [N1114][Tf₂N],
- triethylbutylammonium bis(trifluoromethylsulfonyl)imide [N2224][Tf₂N],
- triethylhexylammonium bis(trifluoromethylsulfonyl)imide [N2226][Tf₂N],
- triethyloktylammonium bis(trifluoromethylsulfonyl)imide [N2228][Tf₂N],
- 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BPyr][Tf₂N],
- 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [HPyr][Tf₂N],
- 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BPyr][TfO]
- 1-butylpyridinium bis(trifluoromethylsulfonyl)imide [BPy][Tf₂N],
- 1-hexylpyridinium bis(trifluoromethylsulfonyl)imide [HPy][Tf₂N].

All chemicals were supplied by IOLITEC, Heilbronn, Germany with purity about 99%. The molecular structures of ILs cations and anions used in this study are shown in Figs. 1–2.

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.



The four hydrophilic membranes were applied: GH Polypro (polypropylene) – PP, FP VericeITM (polyvinylidene fluoride) – PVDF, NylafloTM (polyamide) – PA, Supor® (polyethersulfone) - PES, (Pall, Gelman Laboratory, USA). The surface of PP membrane occurred modified with compounds containing C-O-C bonds, so the surface of PP membrane is also hydrophilic. This was evidenced by IR spectra previously (Joskowska et al., 2012).

Table 1 presents the physicochemical properties of polymeric supports declared by Pall, Gelman Laboratory.

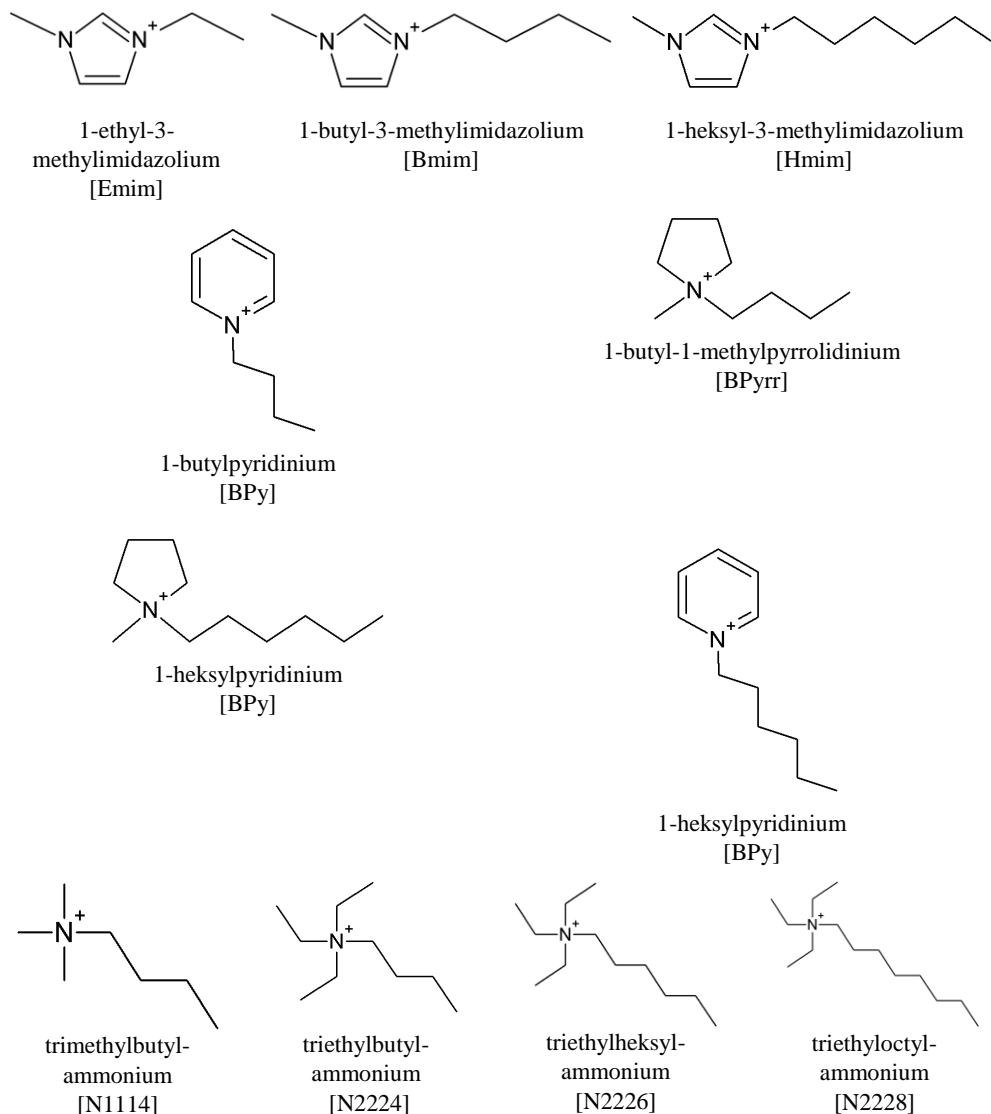


Fig. 1. The structure of ionic liquids cations used in the experiments



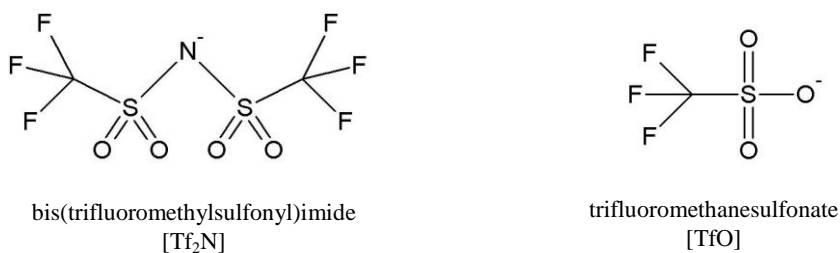


Fig. 2. The structure of ionic liquids anions used in the experiments

Table 1. Physicochemical parameters of polymeric supports*

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

* data provided by producer

Experimental

Wetting experiments

Contact angles of porous and powdered materials are usually measured using capillary rise method. However, as we have indicated in the previous paper, examined support do not meet assumptions of Washburn equation (Joskowska et al., 2012). In this paper contact angle determination was carried out using the dynamic sessile drop method. The size of membranes pores is much smaller than the drop size, therefore the method could be applied. Dynamic sessile drop study determines the largest contact angle possible without increasing solid/liquid interfacial area by dynamically adding volume of liquid. This maximum angle is the advancing angle θ_a , whereas 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 shape of air/liquid interface of a drop is detected using digital system and matched to a numeric model (Sohn et al., 2000). The results are shown in Fig. 9.

The surface tensions of the ionic liquids were determined by the pendant drop method using Tensiometer Krüss DSA 10. The uncertainty of the surface tension measurements was ± 0.2 mN/m.

Traces of water and volatile contaminants were removed from ionic liquids in a vacuum dryer in 353 K for 24 h. The measurements were carried out in 298 K and the relative humidity of the air was 60-70%. The humidity of the air can affect the values of measured surface tension due to hygroscopicity of ILs, therefore the time of

stabilization was not longer than 5 min to minimize the effect. Still, measured values can be loaded with error following the water content fluctuations. The changes in water content after the experiment were not recorded.

Swelling rate experiments

Swelling rate of polymeric supports was determined on the basis of thickness of supports saturated with ionic liquids. Polymer supports and ionic liquids were kept in vacuum dryer VacuCell 55, according to procedure described in literature (Hernandez-Fernandez et al., 2009; Fortunato et al., 2004; 2005). Degassed polymeric supports were saturated with 0.1 cm^3 of ionic liquids per 1.0 cm^2 of support surface. The excess of ionic liquid was removed from membrane surface using blotting paper until the mass of immobilized membrane was stable. Thickness was determined by optical method. The accuracy of this method is better than gravimetric due to difficulties in removing excess ionic liquid from the surface. Measurements were conducted using epi-fluorescent microscope L3001 equipped with digital camera with high resolution. Membrane was placed in glass holder in Z direction according to the procedure described in literature (Izak et al., 2007). Swelling rate was determined using optical method by measuring thickness of the membrane after 2, 24, 72 and 120 hours from the immobilization procedure. In the time intervals between each measurement membranes were kept in a dessicator containing self-indicating silica gel. The humidity of air in the dessicator was 19%.

Results

Wetting experiments

Values of ionic liquids surface tension are located between values for alkanes and for water. There is a large number of publications dealing with surface tension of ionic liquids. Vakili-Nezhaad et al. performed experiments of effect of temperature on the surface tension, density and viscosity of 1-butyl-3-methylimidazolium combined with thiocyanate and tetrafluoroborate anions and 1-hexyl-3-methylimidazolium with tetrafluoroborate and hexafluorophosphate anions and they reported a decrease of physicochemical parameters as the temperature increased (Lee and Prausnitz, 2010). Sanchez et al. provided data on the temperature effect on physicochemical properties of imidazolium, pyridinium and pyrrolidinium ionic liquids, and observed the same trends (Khupse and Kumar, 2010). Similar conclusions were published by Klomfar et al. on the behavior of 1-alkylimidazolium based ionic liquids with hexafluorophosphate anion (Klomfar et al., 2009). The values reported in the literature for the same ionic liquids can differ significantly. The reason is water content in the ionic liquid. Moreover no direct relation between surface tension and alkyl chain length is observed. Sedev performed the attempt to provide an empirical description of the dependence of surface tension and molecular volume. The data set was approximated



with the equation $\gamma = a + bV_M^{-4}$ (Sedev, 2011), where γ is the surface tension and V_M is the molecular volume that was derived from molecular weight (M) and density (ρ) on the basis of the following equation: $V_M = M/(\rho \cdot N_A)$. This approximation is only a guide for the eye. Though, molecular volume is affected by the length of the alkyl chain, other factors should be taken into account when describing the correlation of surface tension and IL structure, like the distribution of intermolecular attractive forces. Moreover, it was reported that ammonium and phosphonium ionic liquids present no correlation between surface tension and molecular volume. It is confirmed by this research (Fig. 3).

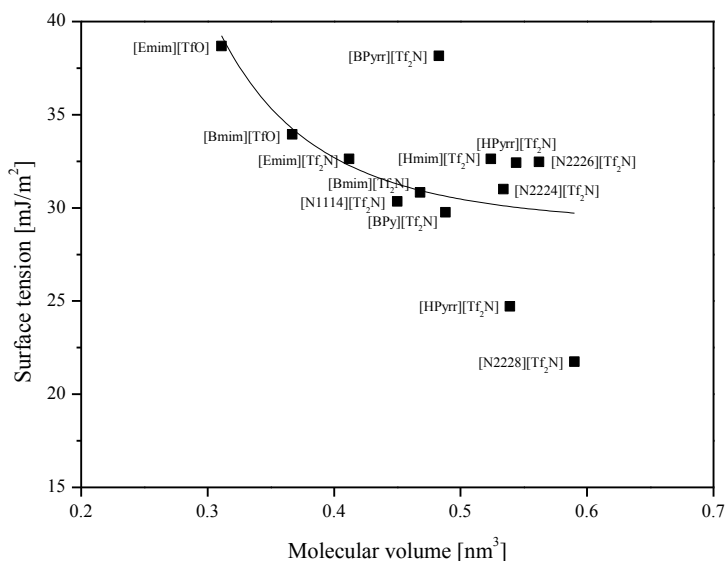


Fig. 3. Surface tension of selected ionic liquids at 298 K

The sessile drop method showed that advancing contact angles of all examined membranes in most cases are below 20 deg. These values demonstrate very good wettability of supports with ionic liquids used in the experiments. Contact angles for imidazolium and pyrrolidinium increase with the alkyl chain length in the ionic liquid cation structure (Figs 4–5). The opposite situation was recorded for ammonium and pyridinium ionic liquids (Figs 6–7).

The parameter deciding on this behaviour is ionic liquid polarity. The polarity of ILs is very sensitive to temperature changes (Lee and Prausnitz, 2010). It has been noticed that the polarity of pyridinium and pyrrolidinium ionic liquid decreases with temperature and this situation is in contrast to that observed for phosphonium ILs (Khupse and Kumar, 2010).



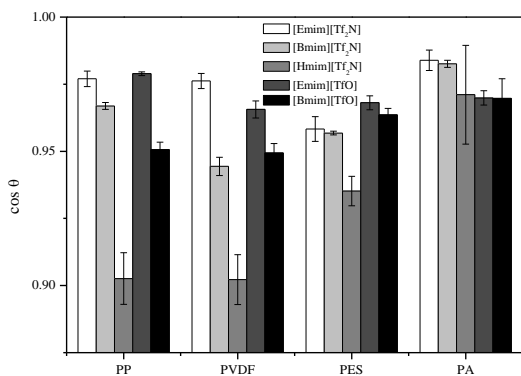


Fig. 4. The relation of carbon atoms number of $[C_n \text{mim}][\text{Tf}_2\text{N}]$ based ionic liquids and $\cos \theta$

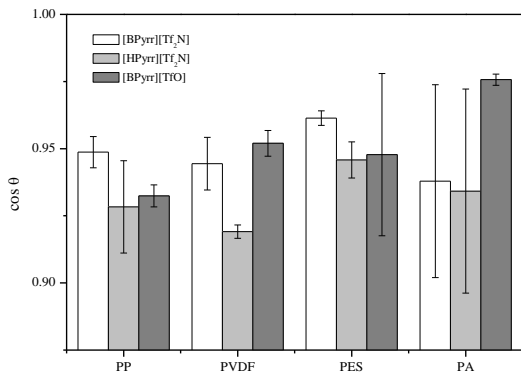


Fig. 5. The relation of carbon atoms number of $[C_n \text{Pyr}][\text{Tf}_2\text{N}]$ ionic liquids and $\cos \theta$

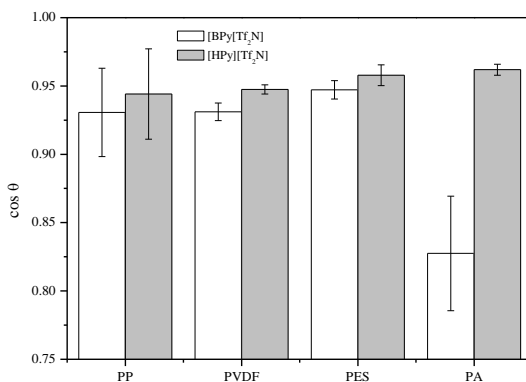


Fig. 6. The relation of carbon atoms number of $[C_n \text{Py}][\text{Tf}_2\text{N}]$ ionic liquids and $\cos \theta$



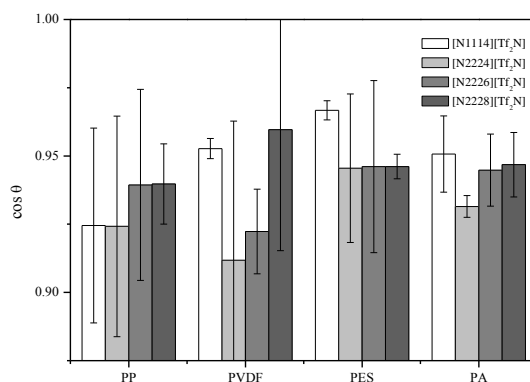


Fig. 7. The relation between carbon atoms number of [Nnnnn][Tf₂N] ionic liquids and $\cos \theta$

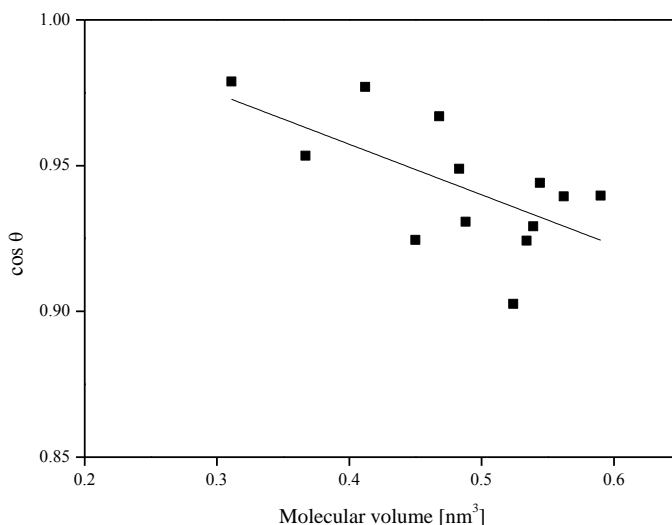


Fig. 8. The dependence of advancing contact angle on polypropylene support on molecular volume of the liquid

Figure 8 presents the overall trend of increasing contact angle value with the increase of molecular volume of ionic liquid and this behavior is preserved for all of examined supports. In most cases the best wettability was obtained for PA support and successively for PP, PES and PVDF.

Supports examined in this study do not meet Young equation foundations, the drop remains in the metastable state and therefore the hysteresis is observed. The hysteresis value is a result of the thermodynamic hysteresis that is dependent on the surface roughness and heterogeneity, and the second one that is the dynamic hysteresis connected to chemical interactions of liquid and solid, penetration of liquid into

polymer pores and the ability of atoms or functional groups to change its positions. The first component is not affected by the time of liquid drop – solid contact, whereas dynamic hysteresis is, and moreover is dependent on the properties of polymer and ionic liquid. The hysteresis of contact angle measured on the PA support was the lowest (Fig. 9), therefore it can be concluded that the heterogeneity and porosity of the PA support surface is the lowest of all examined supports, whereas the highest is observed for PVDF.

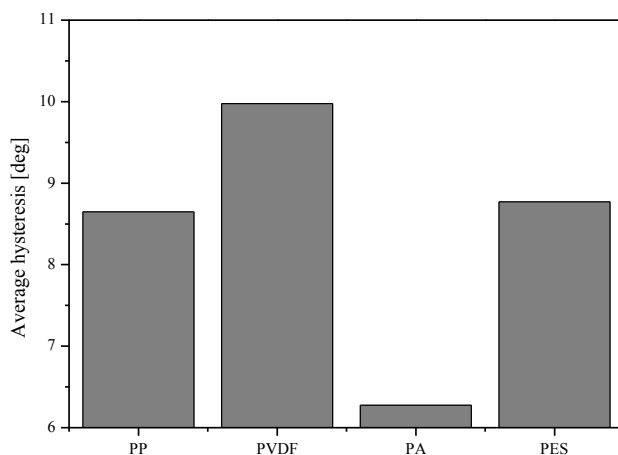


Fig. 9. The average hysteresis of contact angles for examined supports

Swelling rate experiments

Izak et al. (2007) stated, that rate of support swelling depends on the water content in ionic liquid. Therefore, before each experiment, ionic liquids were remained in the vacuum dryer in 343 K for 12 hours. However, swelling effect was observed even if extremely dried ionic liquids were used. Still, the water content could change during the experiments due to water vapor absorption from the atmosphere (Poleski et al., 2013). All the investigated supports showed higher thickness after saturation with ionic liquid. Swelling behavior of polymeric membranes can affect mechanical stability of the membranes and affects value of maximum possible gas pressure without support breakage (Cichowska-Kopczynska et al., 2013).

The obtained results suggest that the longer hydrocarbon chain in the cation structure is, the higher swelling effect is observed. Ionic liquid penetrates into the support pores between polymer particles and fibers and reorientates functional groups, so the particles in the ionic liquid-polymer interface reach the minimum of free interface energy. The longer alkyl chain length the greater space is occupied with the ionic liquid and the greater polymer expansion is observed. Taking into account swelling of the supports, it is observed that the polypropylene support gains similar



thickness immediately after impregnation for all ionic liquids used in the study and it can be assumed that the hysteresis is dependent only on the roughness and heterogeneity of support surface. Further changes in thickness of the supports are

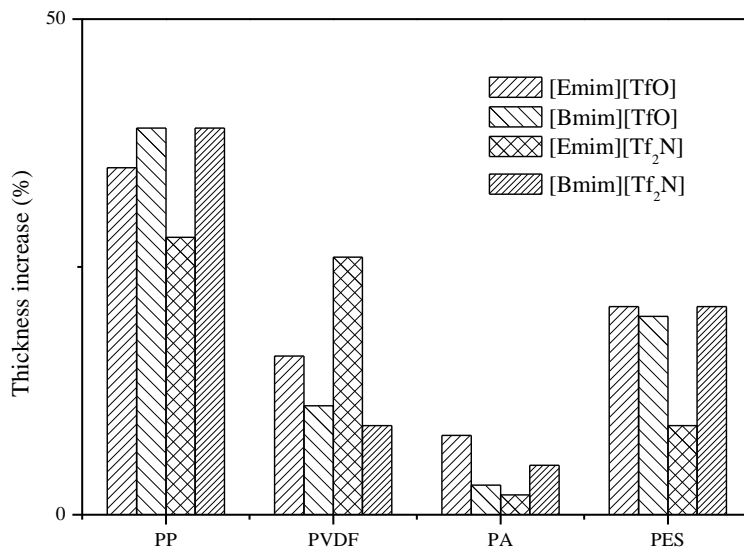


Fig. 10. Thickness increase of supports saturated with imidazolium ionic liquids

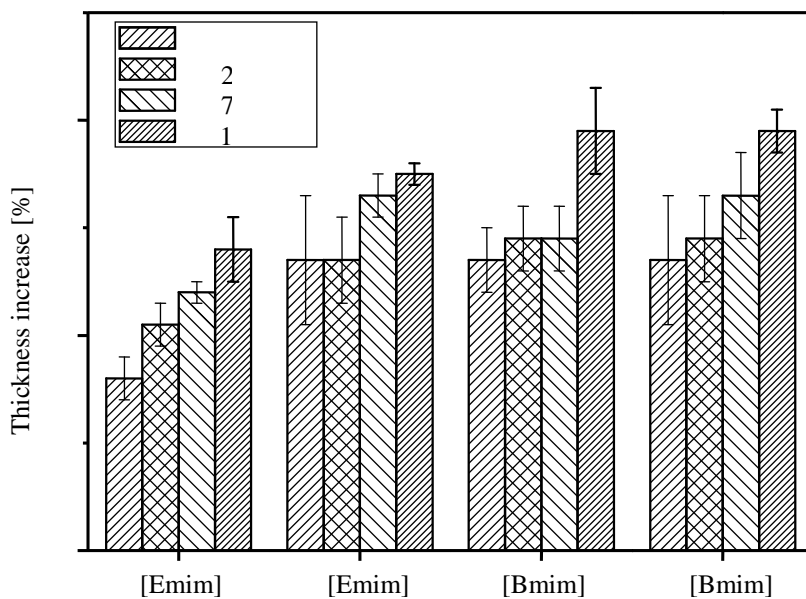


Fig. 11. Thickness increase of polypropylene support saturated with imidazolium ionic liquids



connected to the liquid penetration into the free space between polymer molecules and reorientation ionic liquid structure to the position that is energetically favorable. Polypropylene supports gain about 30–40% of thickness and yet PA ones gain only about 4%, nevertheless wetting of PA occurred to be the best.

The highest thickness increase was observed during two hours since the saturation with ionic liquid was performed. Again, the slight correlation with alkyl chain length and the type of anion is visible for imidazolium ionic liquids in contrast to ammonium, pyridinium and pyrrolidinium. Presumably, this is the consequence of heterogeneity of supports, differences in the structure of each support used in the experiments and possible water gaining from air in the dessicator between measurements. After 120 h since the saturation of supports with ionic liquids, supports gain their terminal thickness. There is no further thickness increase observed.

Conclusions

As indicated by this research, obtaining good effectiveness of the separation process requires proper support and membrane phase, forming stable supported ionic liquid membrane. One of the issues that have to be taken into consideration when choosing proper system should be wettability of the polymeric or ceramic supports in order to ensure that the liquid is not pushed out of the support pores in high pressures. It has been revealed that porous polymer supports are perfectly wetted with ionic liquids, however degradation of polymers is observed in a form of swelling. The surface tension, viscosity, density and contact angles can be tuned by selection of proper combination of cation and anion. Our results confirmed the results of Sedev (2011), hinting that the surface tension of ionic liquids is not directly affected by the alkyl chain length and other factors should be taken into account when describing the correlation of surface tension and IL structure, like the distribution of intermolecular attractive forces. Polymeric supports used in this study occurred to be suitable in order to low values of contact angles. However, due to the high rate of swelling that occurs, mechanical stability should be taken into account. The selection of suitable support is crucial in the development and obtaining highly stable supported ionic liquid membranes.

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