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# Separation of Fluids by Nonporous Membranes

název disertace

Komise pro obhajoby doktorských disertací v oboru chemické inženýrství

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## Abstract

This DSc thesis summarizes results and also the potential of separation of fluids through nonporous membranes. Two membrane separation techniques are involved, namely the pervaporation and the gas or vapor separation. Special attention is focused on ionic liquids, which have a growing potential in both previously mentioned fields. The ionic liquids can act as a separation medium in the form of supported ionic liquid membranes or selective components of a mixed membrane matrix. When using such kind of membrane for separation of the aqueous liquid solutions, it is necessary to cover these membranes with a hydrophobic thin layer of polymer and form the so-called “multiphase membrane”. This kind of membrane can enhance production of organic substances from fermentation if pervaporation is on-line connected to the process. The positive influence of the ionic liquid content on the permeation flux and diffusion coefficients of permeants through the supported ionic liquid membranes by pervaporation has already been proven. Moreover, the ionic liquid can successfully be used as a new class of solvent for chemical reactions. Their main advantage in downstream separation processes is negligible vapor pressure at normal conditions and temperature stability, which is the reason why they are often called the green solvents. During the integrated esterification reaction in the ionic liquid coupled with the pervaporation process water can be selectively removed using a hydrophilic membrane and yield of the esterification can be significantly increased.

Nowadays separations of various gaseous and organic vapors from air have been within the gradually growing interest of many companies and research teams. Furthermore, the ionic liquid membranes supported here help improve separation and permeation properties and in certain cases ($CO_2/H_2$; $CO_2/CH_4$) overcome the upper bound limit in Robeson plot. The mixed matrix membrane where carbon nanotubes or carbon fibers were incorporated also improved their mainly mechanical properties.

However, ionic liquids are still much more expensive than classical solvents, which hindered their practical application in full-scale processes. Therefore, the end of this DSc thesis focuses on water as a separation medium in the commercially available hydrophilic reverse osmosis membrane. During the author`s research, great effort was invested to the practical application of separation of fluids by pervaporation and the gas or vapor permeation. Although the selectivity of the “water-swollen membrane” is lower than in the case of supported ionic liquid membranes, separation is cheaper. It is a great advantage of water condensing and water-swollen membranes since the real full scale-application is mainly a matter of economy. The new technology must be cheaper than the previous one. The way of

the water-swollen membrane technology from the laboratory scale through the pilot plant to the small-industrial scale is described at the end of this thesis.

## Content

# 1. Introduction

Nowadays membrane separation processes represent a relatively new type of unit operation for selective separation of fluids. The membrane usually acts as a semi-permeable barrier and the separation is based on different physical-chemical properties. Membrane separation processes have already been used widely in chemical industry worldwide. Companies involved in membrane processes earn billions US$ every year and this market has continuously been growing. Membrane separation methods show a good potential for separation of fluids because they are typically energy favorable. Furthermore, properties of membranes can be adjusted by incorporation of additives to prepare material with optimal properties for the particular separation. This DSc thesis is focused on the separation of fluids by pervaporation and the gas or vapor permeation through nonporous membranes.

Pervaporation is one of the most commonly used membrane separation techniques for separation of liquids [1,2]. This technique is limited to relatively volatile compounds and can be used successfully in the case of natural substances, e.g. for separation/recovering of natural aroma from apple juice [3,4] or dehydration of organic solvents [5].

Gas and vapor separation processes offer a number of benefits over other gas separation technologies [6]. A membrane is a selective semipermeable barrier that allows different gases, vapors or liquids to move through it at different rates. It usually consists of a thin polymeric film. The present DSc thesis introduces two innovative approaches to enhance the membrane performance beyond the current state of art. The basic principle of the membrane is to selectively restrict the motion of molecules passing through it so that some molecules move more slowly than others, or are excluded. A wide range of mechanisms is available for this restriction; for example, size variability of molecules, affinity for the membrane material, and permeation driving forces – typically concentration or a pressure difference [6]. Each component of a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material [7]. If the selective barrier is a liquid, it is called a liquid membrane. The innovative aspect of this work focuses on the intermediate between the solid and the liquid phase, either by strong swelling of the polymer phase with liquid water or by stabilizing the liquid phase of the ionic liquids by a gel-forming polymer.

The aim of this DSc thesis is to summarize new perspectives of incorporation of ionic liquids into the polymer porous/nonporous support to enhance their separation properties of fluid mixtures and also to introduce a cheaper alternative - “water condensing membrane” or “water-swollen membrane” - developed in our laboratory. Chemical engineering aspects are emphasized during the description of permeates transport through the nonporous membranes. The thesis is based on 23 original papers and 3 patents, indicated as O or P (own + number). The research summarized in this thesis was supported by ten projects in which I participated as the principal investigator from various grant agencies (EU, GA ČR, MPO, MŠMT).

## 2. Theory of permeates transport through nonporous membranes

Thomas Graham studied gas permeation through polymers in 1829 already and in 1866 he formulated the “Solution diffusion process” [1]. This process involves three successive steps:

1. Upstream partitioning of the feed components between the liquid mixture and the swollen upstream layer of the membrane, i.e. **selective sorption.**
2. **Selective diffusion** of the penetrants through the unevenly-swollen permselective membrane.
3. Permeate **desorption**, which takes place on the downstream surface of the membrane.

In 1855 Adolf Fick formulated the law of mass diffusion by the analogy to Fourier’s law of heat conduction:

$$J = -D\frac{\partial c}{\partial z} \qquad (2.1)$$

$J$ represents penetrant flux, for one dimensional diffusion; $D$ – gas diffusion coefficient; $\delta c/\delta z$ – concentration gradient applied across the membrane.

Von Wroblewski based on Stefan and Exner gas permeation theory presented a quantitative solution to the Graham’s solution-diffusion model [8]. The dissolution of gas was based on Henry’s law of solubility, where the concentration of gas in the membrane was directly proportional to the applied gas pressure:

$$C = S\,p \qquad (2.2)$$

Under steady state conditions, and assuming diffusion and solubility coefficients to be independent of concentration, gas permeation flux can be expressed as:

$$J = -DS(\frac{\Delta p}{\mathrm{z}}) = -P(\frac{\Delta p}{\mathrm{z}}) \qquad (2.3)$$

($\Delta p/z$) represents applied pressure gradient across membrane thickness ($z$); $P$ – defined as gas permeability of the membrane. The conventional unit for expressing $P$ is Barrer, where 1 Barrer = $10^{-10}$(cm$^3$(STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$).

The knowledge of permeability of polymer materials plays an important role for their utilization in industry. The possibility to estimate the permeability coefficients of not only gases but also organic vapors from sorption data without the need to perform permeation experiments was proven [O1].

By the end of the twentieth century, a great attention was paid to the field of diffusion, sorption and permeation through polymer membranes due to the fact that these basic phenomena play a very important role in designing of chemical engineering processes in membrane separation. Therefore, it is necessary to understand and precisely describe the mixing of polymer and liquid molecules.

Several models as Flory–Rehner equation, UNIFAP model, and modified Maxwell–Stefan equations [9]) were compared and it is possible to conclude that all used models were able to semi-quantitatively describe pervaporation fluxes and separation ability, as was preliminary discussed in detail in my Ph.D. thesis.

On the basis of the results [O2] and experience with a very precise description of pervaporation processes, during which coupled diffusion may occur (usually one component permeating much faster than the other ones), the use of modified Maxwell–Stefan equations is recommended. The advantage of this approach is also in the use of only one adjustable parameter (coupled diffusion coefficient $D_{ij}$). However, from the technological point of view, Flory–Rehner equation and UNIFAP model should be sufficient in such situations when it is necessary to know dominant pervaporation flux and when the pervaporation data are unknown [O2].

# 3. Ionic liquids in pervaporation processes

## 3.1. Influence of ionic liquid content on separation properties

Room temperature ionic liquids (RTILs) have been recognized as a possible environment-friendly alternative to classical organic solvents, mainly due to their non-measurable vapor pressure, good thermal stability and ability to solubilize a large range of organic molecules and transition metal complexes [10].

Downstream processing still continues to be one of the major challenges not only in chemical and biotechnological production processes but also in wastewater treatment [10]. The aim of our work is to combine the recent development in the field of membrane technology, e. g. nanofiltration [11], liquid membranes [12] or pervaporation [O3-O6], with the use of RTILs for providing novel solutions in downstream processing or process intensification. RTILs have currently been explored as a new reaction media for chemical synthesis or electrochemical applications. RTILs seem to have a large potential in downstream processing, especially when applied in a form that requires only a small amount of them, e.g. in supported liquid membranes [13]. The special property of RTILs that makes their application in liquid membranes attractive for pervaporation is their negligible vapor pressure at room temperature [14]. Pervaporation is considered a perspective and a modern membrane process for separation of various liquids or vapor mixtures.

Supported ionic liquid membranes (SILMs) offer a range of possible advantages:

1. Molecular diffusion is higher in ionic liquids than in polymers due to the presence of charged ions, which are responsible for more selective and often faster transport of especially polar permeates through the semi-permeable membrane;
2. the selectivity of the separation can be influenced by variation of the liquid - especially tunable ILs offer the advantage of a wide variety of properties [15];
3. owing to their special mixing behavior, ILs as liquid membranes easily allow three-phase systems; contrary to the extraction, only a small amount of liquid is necessary to form the liquid membrane, thus allowing even the use of more expensive materials;
4. owing to the usage of the ceramic nanofiltration (NF) module, concentration polarization [14] can be diminished by a rough liquid membrane surface.

The novel hydrophobic ionic liquid tetrapropylammonium tetracyano-borate $[(C_3H_7)_4N]$ $[B(CN)_4]$, which has a quite large cation and a relatively small, but very stable anion, with the melting point about 60°C was prepared [16,17].

Firstly, the transport of the solute (1,3-propanediol) from aqueous mixture through an empty ceramic NF module under low pressure at room temperature (22°C) was evaluated. The module with pore size 0.9 nm was then impregnated by $[(C_3H_7)_4N][B(CN)_4]$ at 70 °C inside the burette. Pervaporation experiments with an impregnated module were then performed under the same conditions. The whole separation process was monitored by gas chromatography in the classical pervaporation arrangement [O3].

The ceramic NF module with $[(C_3H_7)_4N][B(CN)_4]$ was stable under low pressure (20 Pa) in aqueous solution for 92 hours. The IL was then flushed out from the pores by water. To improve the stability and also the selectivity, the NF module with IL was immersed for 1 hour in dimethylpolysiloxane, viscosity of 350 cSt (at 25°C). Both sides of the module made of $TiO_2$ got coated and the hydrophobicity and also selectivity of this set-up increased dramatically [P1], as can be seen in Fig. 1.

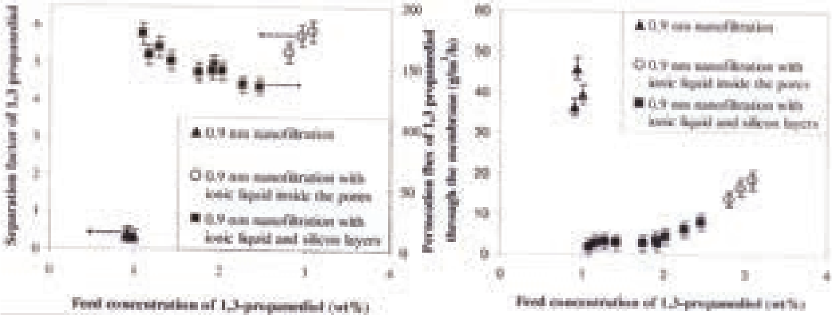

**Fig. 1:** Comparison of 1,3-propanediol separation factor (left) and permeation flux (right) with its feed concentration during NF; using the NF ceramic module with the 0.9 nm pores filled with IL; using the NF ceramic module with the 0.9 nm pores filled with IL and both sides coated with silicon [O3].

The instability of SILMs in contact with aqueous solutions, which has limited their commercial application so far, has been solved by dimethylpolysiloxane coating [P1]. By using the "***multiphase membrane***" in NF ceramic module, the separation factor of the solute increased from 0.4 up to 177. On the contrary, the average permeating flux of the solute decreased from 34.3 g $m^{-2}$ $h^{-1}$ to 3.86 g $m^{-2}$ $h^{-1}$, which follows a typical trade off. Although the separation process with the multiphase membrane was one order of magnitude slower, its selectivity increased by more than two orders of magnitude, which shows a great potential for improving downstream separation processes. The pervaporation of the system was checked after nine months and no changes in transport properties were observed, which indicates a very high stability of the multiphase membrane [O3]. The binary system used as a case study (removal of 1,3-propanediol from aqueous solution) has a practical application in biotransformation processes, where the fermentation broth from *K. pneumoniae* is normally used [O4].

Another product of biotransformation and fermentation processes can be possibly used as biofuel in the practical industrial application. Namely ***biobutanol*** (similar heat enthalpy as gasoline), the main product of acetone, butan-1-ol, ethanol (ABE) fermentation, and it is also the primary inhibitory product affecting the bioconversion. The selectivity of the biobutanol separation in liquid membranes is not based on the solid support of a given membrane but on the properties of the liquid [18]. *Clostridium acetobutylicum*, a Gram-positive bacteria, is well known for its ability to produce solvents such are acetone, butan-1-ol and a very small amount of ethanol. The ABE fermentation had been used in the industrial scale until the middle of the last century [19]. However, high substrate costs and inconvenient product recovery rates caused a termination of the commercial fermentation.

Therefore, focused on the most effective downstream separation process for ABE fermentation e.g. the pervaporation was chosen. To achieve even more efficient ABE removal by pervaporation, the ionic liquid–polydimethylsiloxane (IL–PDMS) membrane, which has better separation properties than classical polymer membrane, was prepared [O4].

The task was to test different supported ionic liquid–PDMS membranes with liquid mixtures from which organic compounds were removed by vacuum pervaporation. As can be seen in our publication [O5], using polydimethylsiloxane–1-ethenyl-3-ethyl-imidazolium hexafluorophosphate (PDMS–IL1) and polydimethylsiloxane–tetrapropyl-ammonium tetracyano-borate (PDMS–IL2) as the supported ionic liquid membranes in an ultrafiltration ceramic module, in comparison with a polydimethylsiloxane membrane, the enrichment factor of butan-1-ol increased from 2.2 (PDMS) to 5.3 (PDMS–IL1) and to 10.9 (PDMS–IL2) at 0.4 %w/w botan-1-ol concentration in feed mixture.

The enrichment factor is defined as: $\beta_i = w_i^P/w_i^F$ (3.1)

$w_i^F$ representing weight fraction of the component $i$ in the feed and $w_i^P$ representing weight fraction of the component $i$ in the permeate.

Moreover, the separation process with IL–PDMS membranes was faster than that of PDMS neat membrane. Therefore, higher selectivity and permeability showed a good potential for the improvement of downstream separation processes. The pervaporation of the system was checked after five months and no changes in transport properties or stability of the SILM were observed. The composition of the ternary system that was used as a case study (the removal of acetone and butan-1-ol from aqueous solution) has a practical application in biotransformation processes where the fermentation broth from *C. acetobutylicum* is normally used [20-23].

The sorption experiments at a wide interval of relative vapor pressures $(p_{rel}=p/p^0)$ were performed gravimetrically by two sorption apparatuses equipped with the calibrated quartz so-called McBain's spiral balances for two ionic liquids at the Institute of Chemical Technology in Prague. Namely the integral diffusion coefficients $D$ were obtained by fitting of experimental data by Eq. (3.2), which was derived by solving the second Fick law under appropriate initial and boundary conditions [24,25]:

$$\frac{Q_\tau}{Q_\infty} = 1 - \frac{8}{\pi^2} \times \sum_{i=0}^{\infty} \frac{1}{(2i+1)} \exp\left[ -\frac{(2i+1)^2 \pi^2 D \tau}{L^2} \right] \tag{3.2}$$

$Q_\tau$ representing mass uptake at time $\tau$; $Q_\infty$ the mass uptake at time of reaching the sorption equilibrium; $L$ the membrane thickness; $\tau$ - time of sorption

The diffusion coefficients of butan-1-ol in IL-PDMS are displayed in Fig. 2 (left). It is obvious that the diffusion coefficient is much higher (one order of magnitude) in IL-PDMS than in the PDMS membrane. However, this difference decreased at higher relative pressure of butan-1-ol. On the contrary, the sorption isotherms are identical for IL-PDMS and PDMS membranes (Fig. 2, right side). Therefore, it can be stated that the higher permeation flux (Fig. 3, left side) is probably caused by a higher diffusion coefficient of butan-1-ol in IL-PDMS membranes.

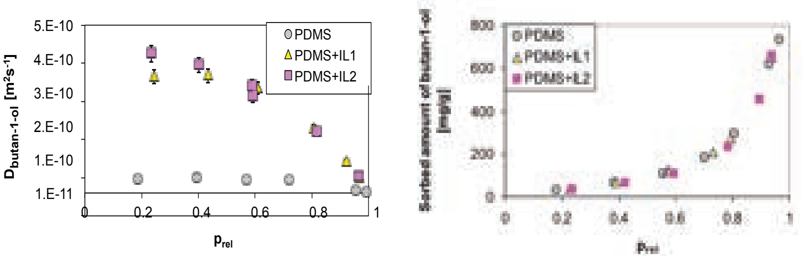

**Fig. 2.** Dependence of butan-1-ol diffusion coefficient (left) and sorption isotherm (right) on relative pressure. o PDMS; Δ PDMS+1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; □ PDMS + tetrapropylammonium tetracyano-borate ionic liquid [O5].

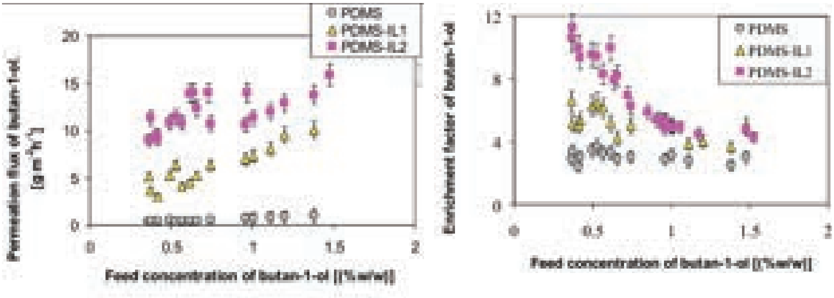

**Fig. 3**. Dependence of butan-1-ol permeation flux (left) and enrichment factor (right) on feed concentration. o PDMS; Δ PDMS+1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; PDMS + tetrapropylammonium tetracyano-borate ionic liquid [O5].

Permeation flux is defined as $J_i = J\,w_i^P$, where $J$ represents total permeation flux through the supported ionic liquid membrane and $w_i^P$ the weight fraction of the component $i$ in the permeate. Permeation flux of butan-1-ol increased with the increase of butan-1-ol concentration in the feed for all measured membranes. In downstream processes, lower selectivity is usually obtained for higher flux. However, this was not observed in the case when IL-PDMS and PDMS were compared only. The concentration of feed and permeate was measured every 24 h of the continuous experiment whereas higher concentration of butan-1-ol in the permeate was obtained always when IL was inside the polymer membrane (Fig. 3, right side). Again, this was probably caused by higher diffusion of butan-1-ol, which was transported in IL-PDMS faster than in virgin PDMS. Enrichment factor of butan-1-ol for IL-PDMS membranes increased with the decrease of butan-1-ol concentration in the feed. For the PDMS membrane, the enrichment factor was constant within the measured range of butan-1-ol concentration [O5].

What is highly remarkable is the fact that IL–PDMS membrane has significantly better separation properties than PDMS membrane itself. Particularly the tetrapropylammonium tetracyano-borate IL has much better separation properties and permeation flux than 1-ethenyl-3-ethyl-imidazolium hexafluoro-phosphate IL, although a much lower amount of IL could be immobilized inside PDMS polymer due to the IL immiscibility limitation with PDMS. The free radical polymerization reactions conducted in ionic liquid are faster than in classical molecular solvents and they tend to yield polymers with higher weight [O5].

The influence of the ionic liquid content on separation properties of pervaporation membranes was studied in details [O6]. The polydimethylsiloxane membranes containing 0, 10, 20 or 30 wt.% of ionic liquid benzyl-3-butylimidazolium tetrafluoroborate (abbreviated [BBIM][$BF_4$]) were used for the separation of butan-1-ol from water. Compatibility and homogeneity of ionic liquid in polymer membrane was studied by Differential Scanning Calorimetry (DSC) at the Institute of Macromolecular Chemistry, Czech Academy of Science. DSC measurements showed that PDMS and [BBIM][$BF_4$] are not compatible; therefore, PDMS-[BBIM][$BF_4$] membranes (though optically homogeneous) contain amorphous and crystalline phases of PDMS and also a dispersed phase of [BBIM][$BF_4$].

Pervaporation selectivity increased and the butan-1-ol flux through the membrane raised with the increased content of [BBIM][$BF_4$] in the PDMS-[BBIM][$BF_4$] membranes (see Fig. 4).

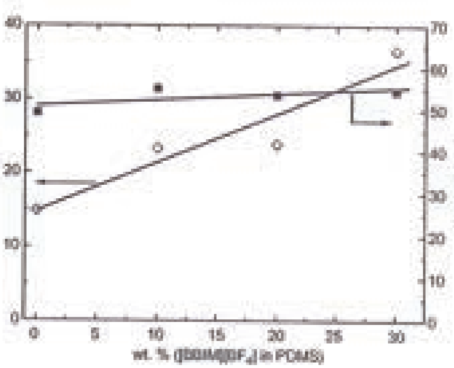

**Fig. 4.** Dependence of separation factor $\alpha_{bw}$ and total permeation flux *J* on [BBIM][BF$_4$] content in PDMS membrane (pervaporation experiment) [O6].

Since the equilibrium separation factor in liquid was nearly independent of the ionic liquid amount in PDMS, diffusion was the major factor contributing to pervaporation selectivity from butan-1-ol + water mixture. The PDMS-[BBIM][BF$_4$] membrane showed high stability as well as selectivity (the separation factor raised up to 37, if 30 wt.% of ionic liquid was accommodated in PDMS) during all experiments.

In another study [O7], the effect of ionic liquid benzyl-3-butylimidazolium tetrafluoroborate to the equilibrium of butan-1-ol vapor sorption in PDMS and the effect of the ionic liquid content on sorption and desorption kinetics of butan-1-ol at 37°C was evaluated. The model was based on the generalized Fick's second law [26,27] solved at time dependent boundary conditions occurring in the apparatus (Eq. 3.3).

$$\frac{\partial \phi_i}{\partial \tau} = \frac{\partial}{\partial x}\left( D\phi_i \frac{\partial \ln(a_i)}{\partial \phi_i} . \frac{\partial \phi_i}{\partial x} \right) \tag{3.3}$$

Where $\phi_i$ and $D$ is the volume fraction and diffusion coefficient of a sorbate ($i$) in a polymer, respectively and $a_i$ means the activity - defined as the ratio of the equilibrium pressure to the saturated vapor pressure at the same temperature. Based on the equilibrium relation between the sorbate activity and its volume fraction in the polymer, the term $\phi_i \partial \ln(a_\mathrm{i})/\partial \phi_i$ imposes the concentration dependence on the overall diffusion coefficient. Hence, the choice of the equilibrium sorption model determines the concrete form of Eq. (3.3).

This approach provided a satisfactory approximation of the data on sorption and desorption kinetics of butan-1-ol vapor in PDMS and in the PDMS–ionic liquid blends; the resulting values of diffusion coefficient depended on the choice of the equilibrium vapor sorption model. The significant decrease of butan-1-ol diffusion coefficients at equilibrium activities above approx. 0.6 indicated anomalous sorption and desorption of butan-1-ol at higher concentrations in the membranes investigated. The increased content of the benzyl-3-butylimidazolium tetrafluoroborate ionic liquid in the PDMS based membranes positively influenced the equilibrium concentration of butan-1-ol in such membranes over the whole butan-1-ol vapor activity interval and, at the same time, reduced the butan-1-ol diffusion coefficients.

### 3.2. Swelling of ionic liquid polymer blend membranes

Swelling is the process of dissolution of a polymer in a defined solvent [O8]. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces are high, due to crosslinking, crystallinity or strong hydrogen bonding, this is all what happens. However, if these forces are overcome by the introduction of strong polymer–solvent interactions, a second stage, the dissolution of the polymer, can take place [28]. The process of swelling results actually from the balance between repulsive and attractive phenomena. These phenomena may include: the thermodynamic mixing between the neat polymer and the solvent; the interaction between fixed charged groups and free ions, as happens in proton-exchange membranes (as Nafion® membrane, which was our case study); the elastic force of the polymer and also inter-chain attractive forces.

The expansion of the polymer takes place due to the entropic diffusion of its constituent chains and their counter-ions [29]. On the other hand, swelling is countered by elastic forces within the polymer chain and inter-chain attractive forces. Overall, polymer–solvent systems tend to reach the minimum of the Gibbs energy of mixing, $G_{mix}$, which is the driving force of the process.

The unique equipment designed for direct measurement of membrane swelling was constructed at the Institute of Chemical Technology Prague [O8]. This equipment is a reliable and powerful tool to follow the kinetics and equilibrium of solute/solvent uptake by flat membranes. This technique reveals to be particularly adequate for studying situations where anisotropic swelling occurs (see Fig. 5); other techniques based on the overall volume or mass change are not able to account for this effect and to quantify it. In Fig. 5, a very interesting observation is displayed: the Nafion membrane is exposed to distilled water, which exhibits a clear anisotropic swelling, i.e. it swells much more in the transverse direction ($x$) than in the casting direction (*y*). Interestingly, when being exposed to "pure" ionic liquid the membrane swells isotropically (see Fig. 5).

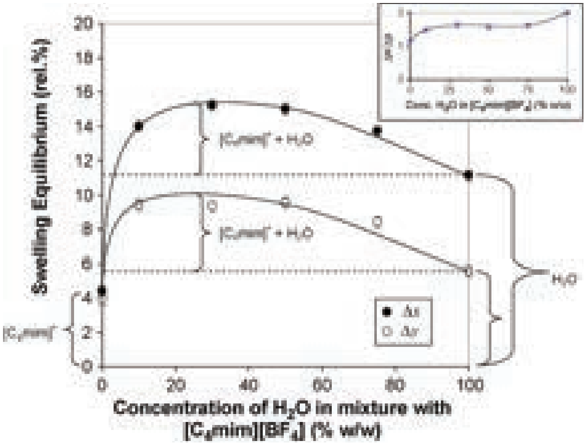

**Fig. 5.** Swelling equilibrium data of a Nafion membrane exposed to binary mixtures of $H_2O$ and $[C_4mim]$ $[BF_4]$ at 25°C. "*y*" corresponds to the membrane casting direction [O8].

A fully reversible process is supposed to occur inside the Nafion membrane during dehydration, which was experimentally confirmed. From Fig. 6, it may be concluded that the swelling process is fully reversible when the membrane is exposed to "deswelling" conditions; as it can be observed, after "deswelling" the ***Δ**x* and ***Δ**y* values came to zero.

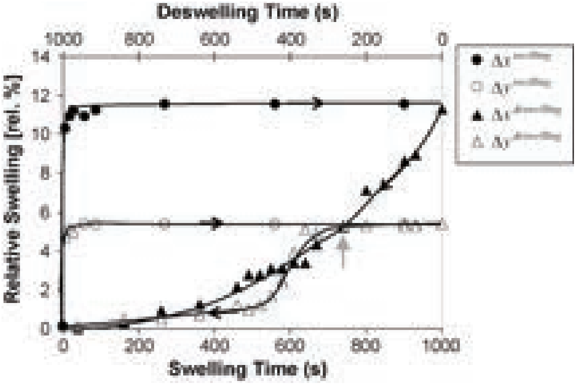

**Fig. 6.** Anisotropic swelling and "deswelling" kinetics of a Nafion membrane in $H_2O$ at 25°C. "*y*" corresponds to the membrane casting direction [O8].

Furthermore, the kinetics of "deswelling" observed is extremely interesting: first, it is worth noticing that the "deswelling" process is much slower than swelling, which can be explained by the fact that the water inside the Nafion membrane is partially involved in solvation processes inside ionic clusters making their molecules more bounded and structured; second, it seems clear that "deswelling" in the *x* direction starts immediately whereas "deswelling" in the *y* direction starts only when $\Delta x \approx \Delta y$ (see grey arrow in Fig. 6). Actually, this behavior suggests that contraction of Nafion in the casting (*y*) direction is only possible when the initial membrane spatial coherence is reacquired. Due to the elastic forces present in the Nafion network, contraction in the *x* direction proceeds when it starts in the *y* direction. On the contrary, "deswelling" of the Nafion membrane exposed to a binary mixture of water and [C$_4$mim] [BF$_4$] is not reversible at all (Fig. 7).

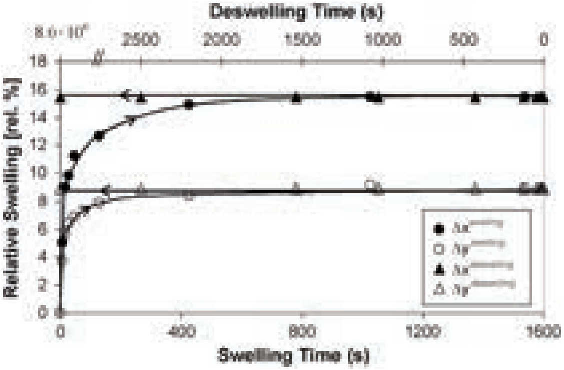

**Fig. 7.** Anisotropic swelling and "deswelling" kinetics of a Nafion membrane in a binary mixture of [C$_4$ mim] [BF$_4$ ] and $H_2O$ (50%/50% (w/w)) at 25°C [O8].

In this case the term "swelling" must be used with caution because, in fact, a ion-exchange process is taking place when Nafion uptakes the ionic liquid cation. Even after the period of 100 days under "deswelling" conditions, swelling of the Nafion membrane was not reversed [O8]. Taking into consideration the knowledge gathered in this work, this result can be interpreted as a consequence of the highly bounded water inside the membrane matrix. As it is known, RTILs exhibit extremely low vapor pressure, which explains why swelling due to RTIL solubilisation inside the membrane is not reversible.

Additionally, it seems that all water uptaken during the swelling process is most likely strongly solvating the cation from the RTIL inside the Nafion structure. The established interactions are sufficiently strong and stable to impede water to leave the Nafion membrane. The results obtained, when studying swelling of Nafion membranes, also show how the process of molecular solubilisation and swelling can be influenced by the fabrication conditions used during the manufacturing process. This aspect is particularly important regarding the fact that the swelling process itself may also reflect on the transport properties of the polymer. Considering the Nafion membranes, transport properties are obviously of high importance and may determine the performance concerning applications in low resistance devices such as fuel cells and transducers.

Understanding the swelling behavior of thin films is therefore essential for the comprehensive design of membrane processes, from a better control of the nanoscale properties of materials towards membrane macroscale applications [O8].

In another study with the same optical equipment, it was demonstrated that even a very small amount of inorganic salt present in methanol–water mixture is sufficient to cause a restriction of Nafion swelling [O9]; in several cases it may even stop the swelling process completely.

Room temperature ionic liquids (RTILs) have currently been studied as relatively new alternative reaction media for chemical synthesis and electrochemical applications [O10]. Owing to their extremely low vapor pressure, high ionic conductivity and thermal stability, large electrochemical window and ability to solubilize a large range of organic molecules and transition metal complexes [27], RTILs are regarded as the new media able to replace some traditional solvents. Their extremely low vapor pressure is regarded as a precious advantage over conventional solvents because the contamination of the atmosphere can be avoided.

In another work, simple ***group contribution method*** allowing the prediction of dimensional changes of Nafion membrane upon its immersion into liquid medium had been developed [O11]. The contributions of the structural units were determined by minimization functions $S_A$ and/or $S_B$:

$$S_X = \sum_{i=1}^{m}\left(X_{\exp,i} - X_{calc,i}\right)^2 \text{ and } S_Y = \sum_{i=1}^{m}\left(Y_{\exp,i} - Y_{calc,i}\right)^2 \tag{3.4}$$

where $i$ represents the sequence number of the compound from the evaluation set; $X_{exp,i}$ - experimental value of the relative expansion in the transverse casting direction; $Y_{exp,i}$ - experimental value of the relative expansion in the casting direction; $X_{calc,i}$ - calculated value of the relative expansion in the transverse casting direction; $Y_{calc,i}$ - calculated value of the relative expansion in the casting direction; $m$ - number of compounds. The Microsoft EXCEL

Solver was used for the parameters determination.

The values of 13 contributions for individual membrane relative expansions were determined on the basis of experimental data on relative expansion of Nafion membrane in 26 organic liquids (evaluation set). The predictive ability of the proposed contribution method was tested by comparing the calculated values of relative expansion for 12 independent compounds (testing set) with the experimental ones. The obtained results are in a good agreement with experimental data. Maximum differences between experimental and calculated values are almost the same, only twice greater than the experimental error [O11]. Another interesting aspect, which can be deduced from our swelling experiments, is that the assumption of ideal sorption behavior cannot be used. The change in the membrane volume caused by a contact with a liquid medium calculated under the assumption of ideal mixing of polymer with binary liquid mixture is not the same as that obtained from the dimensional changes of the membrane on swelling. The difference, attributed to the polymer–liquid medium interactions, is expressed as the percentage of the additively calculated volume in the dependence on the bulk solution composition [O11].

### 3.3. Surface modified ionic liquid polymer blend membranes

The main drawback of using ionic liquids results from their usually high viscosity, which limits momentum and mass transport significantly and has negative impacts on reaction kinetics and separation rates. This problem is also important when processing RTILs by membrane processes, namely by pervaporation, where significant solute ***polarization*** of concentration occurs near the membrane surface. To overcome this problem, it is necessary to improve external mass transfer conditions in the reaction/feed media, which is usually achieved by employing energy-intensive approaches that may involve the use of high feed flow rates (pumping energy) and/or spacers and (macroscopic) static mixing promoters.

Therefore, the ***3D topography of membranes*** was under the study at the New University of Lisbon [O12] since they can offer a unique opportunity to introduce a microscopic static mixing effect, which can promote micro-turbulence at the membrane surface and diminish concentration polarization via that.

It is also important to stress that solute recovery from ionic liquids by pervaporation is a particularly interesting process because only the solutes permeate the membrane and are recovered in the permeate, while the solvent (the RTIL) does not permeate due to its extremely low vapor pressure [30,31]. For this reason, a solvent-free separation process is achieved, while different solutes present in the feed may be recovered differently in the permeate due to their specific affinity to the membrane.

Fluid flows over selective dense membranes develop, at the microscale, three-dimensional interfaces, which are the subject to three-dimensional forces. Therefore, the ability to create microstructures with modulated 3D topography may significantly improve the control over momentum and mass transport phenomena taking place at the membrane's interface. The development of selective dense membranes of urethane–urea elastomers with three-dimensional relief microstructures, based on the emergence of smooth features when the polymer is exposed to UV light and defined extensional stress conditions, was discussed. The technique developed allows for fabrication of microstructures over large areas, with topographic modulation of features with characteristic dimensions (see Fig. 8).

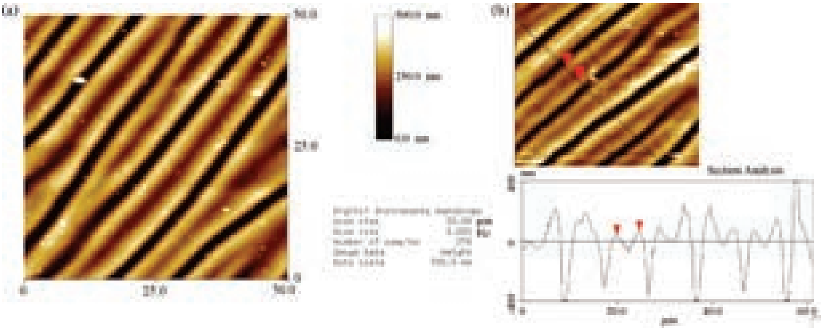

**Fig. 8.** Characterization of a modified PU/PBDO-UV membrane by atomic force microscopy (AFM) before (a) and after (b) a pervaporation experiment [O12].

During the immersion studies it was also necessary to study the swelling behavior of the membranes under the different conditions applied and to compare their behavior with an unmodified flat membrane. The swelling studies were performed by using an optical method developed at the Department of Physical Chemistry of the Institute of Chemical Technology in Prague [O8]. It may be concluded that swelling of both unmodified membranes (PU/PBDO) and surface-modified membranes (PU/PBDO-UV) when immersed into pure hexyl acetate is minimal (see Fig. 9). The swelling of all membranes was found to be isotropic in all measured mixtures. From Fig. 9 it can be seen that the kinetics of swelling is faster in the modified PU/PBDO-UV membrane, although swelling equilibrium data seem very similar. The results observed suggest that the increase of the top surface area (this increase was calculated to be of around 4%, see Fig. 10) is not the only significant feature involved in enhancing swelling kinetics. Possibly, microphase segregation, characteristic of elastomer materials, may play a significant role as well. The surface modification procedure seems to induce the formation of different micro-segregation domains with soft (hydrophobic) and hard (hydrophilic) polymeric components of the elastomer material [O12].

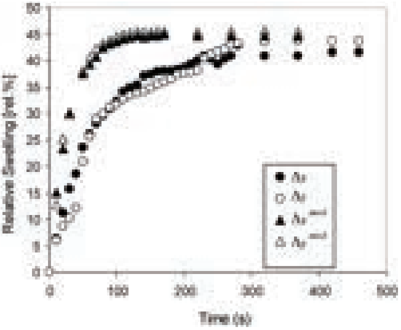

**Fig. 9.** Swelling kinetics of PU/PBDO membranes and surface-modified PU/PBDOUV membranes in hexyl acetate at $T = 25^{\circ}$C (swelling in the transverse casting direction ($\Delta x$) and in the casting direction ($\Delta y$) [O12].

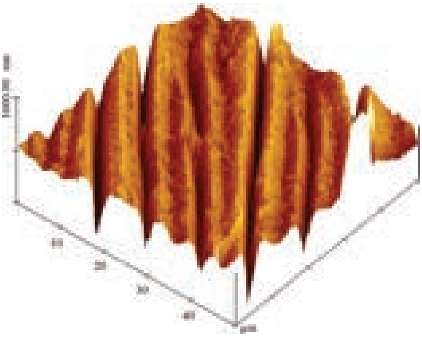

**Fig. 10.** AFM topography image (50µm×50µm scan with an image surface area of 2598 µm$^2$) of a modified PU/PBDO-UV membrane after a pervaporation experiment. [O12].

One possible explanation for the differences observed is that the UV irradiation induces soft/hard segregation, with hydrophilic components at the surface valleys and hydrophobic components at the surface peaks, whereas mechanical stretching cycles induce the opposite segregation [32].

The effect of surface modification and feed flow rate on the flux of hexyl acetate versus the weight fraction of hexyl acetate in the feed. A quantitative analyses of the results obtained allow to conclude that the solute flux increase of 15% was obtained by operating with a higher feed flow rate e.g. Reynolds number. Additionally, the use of the surface modified membrane led to the increase in the solute flux by 14%, which is well above the value of 4% that may be attributed to an augment of the membrane surface area due to membrane roughness. This increase in the solute flux has to be granted to improve fluid dynamic conditions due to micro-turbulence at the membrane surface; still, we should not exclude a possible effect related with the micro-segregation of urethane/urea domains in the membrane polymer, which may also affect the overall solute affinity towards the membrane [O12].

These nano-structured surfaces are particularly interesting for the use in nanobioapplications such as tissue culture and biosensors, where orientation of a molecular/nano-dimension becomes relevant. Applications for improved external mass transfer, as discussed in this work, are also extremely interesting both at a nano- and at a micrometer scale, making it possible to minimize concentration polarization effects – either associated with solute depletion or with solute concentration increase at the membrane interface – leading to better fluxes and improved selectivity [O12].

## 4. Pervaporation in hybrid processes

In recent years, pervaporation has established itself as one of the most promising membrane technologies. Pervaporation offers potential solutions in a wide range of applications from the well-established dehydration of organic compounds to the recovery of organic compounds from water and the separation of organic mixtures [30].

Classical solvents used in esterification reactions (such as toluene and dichloromethane) evaporate into the atmosphere with detrimental impacts on the environment and the human health. They are also flammable and their low boiling points hinder their utilization. Therefore, the use of these solvents is restricted to a low temperature range leading to lower reaction kinetics.

### 4.1. Chemical engineering application – Enhanced esterification conversion

The goal of this work is to evaluate the potential for conversion enhancement of esterification reaction by selective recovery of a reaction product from an ionic liquid reaction medium by means of pervaporation [O13]. The integrated process modeling is also discussed. It enables prediction of the influence of process variables on the esterification reaction. An interesting preliminary work dealing with the enzymatic esterification reaction has already been published [33,34]. The case study selected in this work involves the esterification of (−)-borneol with acetic acid in order to produce (−)-bornyl acetate. This compound is a valuable chemical for industries using fragrances for soaps, bath products and air fresheners; above all (−)-bornyl acetate is used as the intermediate for the production of Camphor.

***The integrated esterification-pervaporation process*** was carried out. Only trace amounts of acetic acid and (−)-bornyl acetate were detected in the permeate. The amount of (−)-borneol permeating through the PVA membrane was about 1.5% w/w of the total water content in the permeate. To close the material balance and mathematically simulate the esterification reaction coupled with pervaporation, it is necessary to know all molar fluxes through the membrane (e.g. the flux of water and (−)-borneol). The flux of water through the

PVA membrane was obtained by performing independent experiments where the RTIL [$C_4$mim][$BF_4$] was dried by pervaporation under the same experimental condition as the other experiments and monitored by Karl–Fisher titration.

The consumption of reactants, namely (−)-borneol and acetic acid, was faster during the integrated process than during esterification without pervaporation [O13]. The influence of the process variable $R = S_M / V$ ($S_M$ – membrane area, $V$ – volume of the reactor) on the conversion of acetic acid to (−)-bornyl acetate is displayed in Fig. 11.

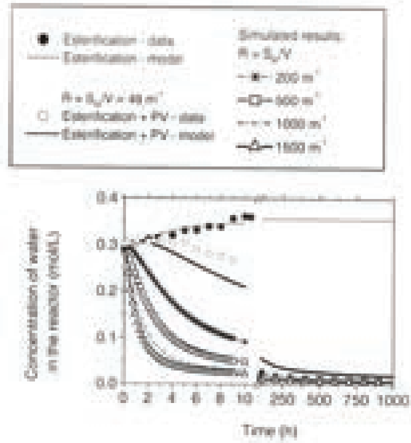

**Figure 11.** Effect of the $S_M/V$ ratio on the conversion to (−)-bornyl acetate [O13].

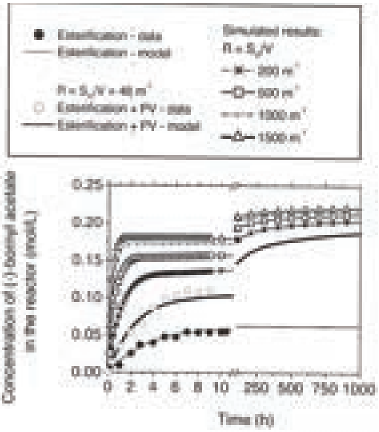

**Figure 12.** Effect of the $S_M/V$ ratio on the water concentration of the reaction medium [O13].

From the model simulation (curves), it can be seen that the $S_M/V$ ratio has a significant impact on the kinetics of the reaction. It can also be observed (Fig. 11) that the numerical simulation of the model is able to predict the integrated esterification process adequately and the effect of the variable $S_M/V$ as well. From the observing these Figs. 11 and 12, it may be concluded that due to the removal of water by continuous pervaporation, it was possible to increase the reaction conversion from 22 to 44% [O13] (increase by a factor of 100%).

### 4.2. Increased productivity of fermentation by pervaporation

Pervaporation can be another ***successful hybrid process***. It has already proved to be one of the best methods to remove a small amount of organic solute out of a water solvent directly connected with fermentation. To get even more effective aceton-butanol-ethanol

(ABE) removal from *Clostridium acetobutylicum* fermentation culture, the IL-PDMS nonporous membrane was prepared [O4]. This membrane showed high stability as well as selectivity during all experiments with real fermentation broth. Using this membrane, it was possible to remove butan-1-ol and acetone from the culture supernatant more effectively, as described by others [35,36]. It was possible to remove more butan-1-ol and acetone than the *C. acetobutylicum* was able to produce. As it can be seen from Fig. 13, butan-1-ol concentration in the permeate increased more than five times in comparison with the concentration in the culture vessel.

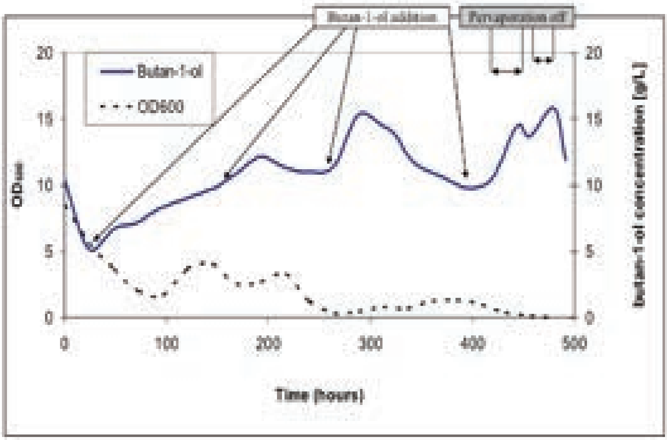

**Figure 13.** Dependence of optical density and butan-1-ol concentration in the feed on time of fermentation [O14].

When butan-1-ol concentration started to be lethal for the cells (about 18 g/l of butan-1-ol in feed), the continuous ABE removal was started (pervaporation was switched on). Nevertheless, when pervaporation was switched off the butan-1-ol amount in the culture vessel increased, and the optical density dramatically decreased (see Fig. 13). In addition, the other products of ABE fermentation (ethanol, acetone) were enriched several times in the permeate as well. Distillation is a traditional technology for separating alcohols from dilute biomass fermentation broths. However, pervaporation is an alternative, which may have energy and capital cost advantages relative to distillation, especially for smaller scale systems or at lower concentrations of the feed. Liu et al. [37] reported that from an application point of view, the PEBA membrane can be used to extract butanol and to a lesser extent ethanol and acetone from the ABE fermentation broth by pervaporation.

Overall solvent productivity of fermentation connected with continuous product removal by pervaporation was 2.34 g $l^{-1}$ $h^{-1}$. To prove the effectiveness of our setup, the fermentation reaction on the limiting values of butan-1-ol concentration (15.82 g $l^{-1}$) to see if the bacteria could still be alive under these conditions was ran. In our study it was proven experimentally that this concentration was already lethal for the bacteria. Considered together, the *C. acetobutylicum* continuous fermentation setup used together with the indicated pervaporation technique would guarantee an increase in fermentation stability and higher production of biobutanol [O4].

## 5. Gas and vapor permeation

Gas separation is the most frequent process that utilizes ionic liquids and permanent gases ($N_2$, $CH_4$, $CO_2$, $H_2$) are usually separated. These gases are present in natural gas, biogas etc. so their separation is still a highly discussed topic. $CO_2$ is the gas that is most frequently separated by ionic liquid membranes because of its high affinity to ionic liquids. Many articles dealing with solubility, diffusivity and permeability of $CO_2$ in the ionic liquid membranes have already been published, e.g. [O14].

### 5.1. Ionic liquid polymeric gel membranes

Ionic liquid membranes are usually prepared in the form of supported liquid membranes [O3, O4], in which the pores of a porous membrane are saturated with the room temperature ionic liquid (RTIL). In such membranes, the ionic liquid is trapped inside the pores by capillary forces. Although evaporation of IL can be excluded, if such membranes come in contact with a liquid phase, for instance in pervaporation discussed in the previous part, they can lose the ionic liquid from the inside part of the polymer network due to swelling and leaching into the liquid phase. The dissolving of ILs from the membrane has to be considered further when the ionic liquid membrane is in a longer contact with organic vapor at higher concentrations. To avoid this problem polymerized room-temperature ionic liquids membranes [38,39] were prepared. These polymerizable RTILs are more stable but they require particular polymerizable groups and sophisticated membrane preparation techniques [O15]. The fluoroelastomeric polymer p(VDF-HFP) formed stable gels in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][$Tf_2N$]) [O15], enabling the successful preparation of resistant free-standing membranes by solution casting of the polymer/ionic liquid mixture, followed by controlled solvent evaporation. The membranes consist of the thermo-reversible polymeric gel in which crystallization of p(VDF-

HFP) was responsible for the network structure, as supported by DSC and X-ray diffraction analysis. The polymer showed a good compatibility with the IL and may swell up to 30% at room temperature while it becomes soluble at 90ºC or higher depending on the concentration of IL. The presence of IL in the polymer caused a decrease of the elastic modulus of several orders of magnitude and a significant reduction of the break strength over the entire concentration range. However, the maximum deformation initially increased to over 1000% and then decreased to IL content above 40%. It happened due to the compromise between increased elasticity of the gel leading to higher elongations, and the reduced break strength leading to lower mechanical stability. DSC analysis showed a strong decrease in the polymer melting point in the gel as a function of the IL content and a decrease in the overall melting enthalpy. Nevertheless, normalized for the polymer concentration, the melting enthalpy tends to increase at higher IL concentrations, presumably due to more efficient chain folding as a result of the lower viscosity and higher mobility of the polymer chains in the IL solution. The gas permeability strongly rose with the IL concentration (Fig. 14) and the transport of larger and more condensable species was favored over that of smaller molecules. Subsequently, the separation changed from the diffusion-controlled process to the solubility controlled one. For this reason, the $CO_2/H_2$ selectivity is unusually high (Fig. 14), offering perspectives for the application of these membranes in environments where carbon dioxide must be separated from hydrogen while the latter remains at high pressure [O15].

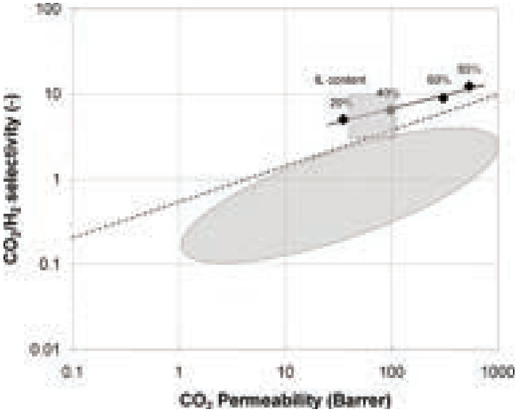

**Figure 14**. Robeson diagram for the gas pair $CO_2/H_2$ indicating the experimental points of the present work (diamonds). The approximate range for common homopolymers (ellipse) and for poly(ethylene glycol) and poly(propylene glycol) derivatives (square) [O15].

Another work evaluated the possibility to tailor gas separation properties of elastomeric block copolyamide membranes by means of RTIL, based on the 1-n-alkyl-3-methylimidazolium cation. Polymeric gel membranes were prepared by adding from 20 to 80 wt.% of 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][$CF_3SO_3$] to Pebax®1657 and Pebax®2533 [O16]. The gas transport through these dense films obeys the solution-diffusion mechanism. The solubility in the polymer matrix depends on the chemical interactions between permeant and polar groups of the copolymer, for which reason rubbers are generally more permeable than glassy polymers. The diffusivity is related to the mobility of the polymer chains and to their packing density or free volume, which allows the passage of the permeant molecules. Both polymers showed relatively high $CO_2$ permeability, which is generally attributed to high solubility of $CO_2$ in the polyether phase [40,41].

The gas transport properties of the less permeable Pebax®1657 were significantly affected by the ***presence of the IL resulting in a strong increase in the permeability of all gases and a slight decrease in the selectivity for most gas pairs***. The plasticization of the polymer by the IL limits the role of less permeable hard blocks of the co-polymer, reducing the weak size-sieving ability of the neat polymer. The highest selectivity is observed for $CO_2/N_2$ separation, for which the selectivity decreases from about 60 to about 40 while $CO_2$ permeability increases fourfold upon addition of the ionic liquid to the system in agreement with the typical Robeson's Upper bound behavior [42]. The absolute values remain slightly below the upper bound for this gas pair (Fig. 15). For Pebax®2533-based membranes, the IL did not influence transport properties of the polymer matrix much [O16].

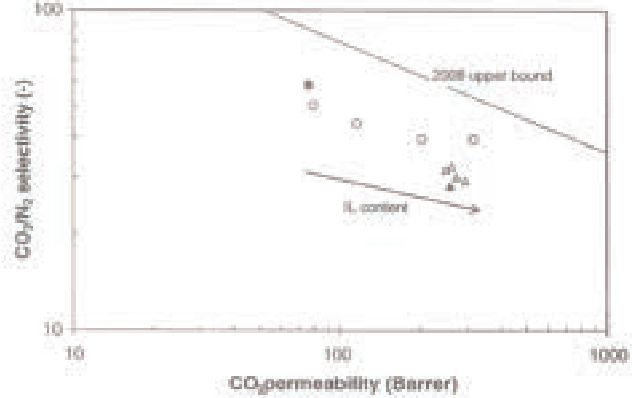

**Figure 15.** Robeson diagram for the $CO_2/N_2$ pair and the IL blend membranes based on Pebax®2533 (Δ), and Pebax®1657 (○). Filled symbols represent the pure polymer.

Ionic liquid membranes usually consist of a porous support saturated with the room temperature ionic liquid. The ionic liquid is typically trapped inside the pores by capillary forces [43]. Such membranes suffer from limited tolerance for pressure difference across the membrane in gas separation processes. Therefore, they might not be suitable for example in $O_2/N_2$ separation typically operated at several tens of atmospheres whereas they might be suitable for low pressure applications like flue gas or biogas treatment, involving $CO_2/N_2$ and $CO_2/CH_4$ separation [44]. Polymerised room-temperature ionic liquids [45,46] or systems in which the IL is dispersed [O4,O5,O6] or absorbed in a dense polymeric membrane [47] can be a valid alternative. The creation of a polymer gel in which the IL is entrapped in the tight spaces between individual polymer chains or clusters thereof can be a successful approach to stabilize the ionic liquid in a polymeric matrix. Several polymers are suitable to form gels in combination with ionic liquids [48] or they spontaneously absorb considerable amounts of ILs [49]. The next work presented a comprehensive discussion on the transport properties of gases and vapors in the ionic liquid gel membranes with the aim to provide a deeper insight into the basic transport parameters and their correlation with membrane structural properties [O18]. A novel data on the solubility and diffusion coefficients, obtained by time lag analysis, as well as the transport properties of a large collection of vapors were presented there. It was proved that the ionic liquid [EMIM][$Tf_2N$] acts as a plasticizer for the p(VDF-HFP) copolymer. In polymer gel membranes of p(VDF-HFP)/[EMIM][$Tf_2N$] blends, the presence of the IL strongly enhances the permeability of permanent gases, mostly because of the drastic increase in the diffusivity. For the first time it was also demonstrated that the correlation of Young's modulus and the permeability or diffusion coefficient can be used as the evidence for a transition in the transport mechanism. This analysis reveals that above approximately 60 wt.% of IL the gas transport mechanism becomes solubility controlled rather than diffusion controlled. In this regime, larger and more condensable species like $CO_2$ permeate preferentially over smaller molecules such as hydrogen. The IL enhances both solubility selectivity and the diffusion selectivity for the $CO_2/H_2$ gas pair. The relatively high $CO_2$ permeability at an IL content of 80 wt.% (4500 Barrer) coupled with an interesting $CO_2/H_2$ selectivity (12.3) makes these membranes the interesting candidates for such applications where $CO_2$ has to be removed from a $H_2$ rich stream and where $H_2$ must remain at high pressure in order to limit the re-compression costs. Vapor permeability has been studied in the membrane containing the highest IL content (80 wt.%). The behavior of the IL rich membrane in terms of vapor transport is between that of glassy membranes, with a diffusion-controlled mechanism, and that of rubbers, with a solubility-controlled mechanism. The solubility controlled mechanism dominates over those species which interact most strongly with the membrane matrix such as alcohols and water vapor. The highest permeability is observed for polar species such as alcohols and water. These properties open perspectives for the use of these membranes in the removal of vapors from gas streams. Application tests with realistic mixtures are needed to confirm the potential of these membranes [O17].

## 5.2. Mixed matrix membranes

Next possibility to modify polymeric membranes is mixing nanoparticles with polymers to obtain nanocomposite membranes or mixed matrix membrane containing a polymeric membrane mixed with RTILs.

These ***mixed matrix membranes containing a polymeric membrane mixed with RTILs*** can be formed by blending for example the fluoroelastomer p(VDF-HFP) with a mixture of the RTIL [EMIM][$Tf_2N$] and the RTIL [HdMIM][$Tf_2N$] ionic liquids [O18]. The impact of the ionic liquids loading and the temperature on pure gas transport properties was then studied. The fluoroelastomeric polymer p(VDF-HFP) formed the most stable gels in the ionic liquid [EMIM][$Tf_2N$], enabling the successful preparation of resistant free standing membranes by solution casting of the polymer/ionic liquid mixture, followed by controlled solvent evaporation. High concentrations of [HdMIM][$Tf_2N$] tend to give fragile porous samples at low temperature. The density and thermal properties of the blend membranes evidence better compatibility of the short alkyl chain IL with the polymer matrix. Gas transport properties showed a discontinuity around the melting point of the [HdMIM][$Tf_2N$] (see Fig. 16).

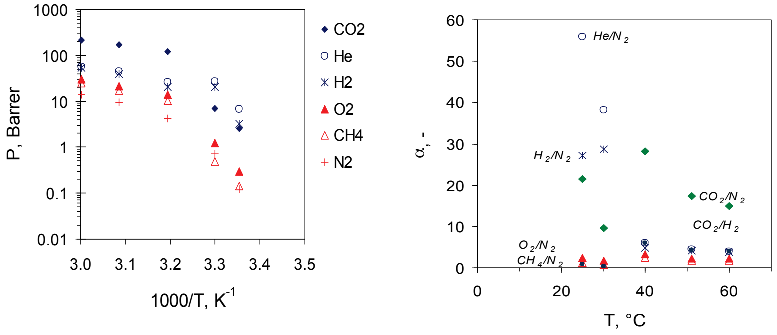

**Figure 16**. Dependence of permeability (left) and the corresponding permselectivity (right) of six permanent gases as a function of the IL mixture content and temperature (40 wt% of the [EMIM][$Tf_2N$]/[HdMIM][$Tf_2N$] mixture) [O18].

Arrhenius behavior was observed above the melting point. At high [HdMIM] content solidification of the IL mixture caused defective and non-selective membranes at low temperature. The contribution to the gas transport of the long chain IL was ‘‘excluded’’ operating at temperatures below its melting point whereas it had a key importance when operating above this temperature. These polymer gel/ILs blends are attractive for continuously varying the transport properties of a polymer, favorably manipulating molecular transport and selectivity. Moreover, ***by changing the temperature, different behaviors can be established for the same membrane.*** These membranes can be used also for pervaporation processes that were discussed in a detail in parts 3 and 4. The ionic liquid [Hdmim] [$Tf_2N$] was more suitable for pervaporation of limonene/carvone mixture in ethanol, where both flux and enrichment factors of essential oils increased with a higher IL content. Traces of water in the feed mixture strongly increased the permeation rate and selectivity of the preferentially permeating components (limonene, carvone) due to a viscosity reduction by strong interaction of water with the ionic groups of the IL [O18].

Another complex study of the operation of ***supported ionic liquid membranes*** from practical point of view was made based on our long term experience [O19]. It was shown that supported ionic liquids used as the case study ([emim][$Tf_2N$] and [emim][dca]) are selective for the binary mixture of $CH_4$/$CO_2$. Unfortunately, the literature provides certain pure ionic liquid data which are mainly focused on $CO_2$ and there is a lack of data for $CH_4$. The main problem seems to be the lack of data concerning diffusion coefficients of gases in supported ionic liquids membranes and, consequently, there are no correlations available between the transport properties and the molecular properties of the gas and of the IL in porous support. The data available in literature are measured and calculated for pure ionic liquids only but there is no reasonable way how to apply them to the supported ionic liquid membranes. All the literature data sets overestimate at least twice the membrane performance in terms of permeability and selectivity. Such a discrepancy brings the supported ionic liquid membranes into an inconvenient position from the point of view of practical application because it is not possible to design a process reliably although the supported ionic liquid membranes are comparable in separation characteristics to the best polymeric membrane (see Robeson plot in Fig. 17). The possible reasons why the theoretical models overstate the real values of permeation fluxes are summarized below:

- The mass transfer resistance of the support is not negligible, as often assumed.
- Some pores of the support are not opened for permeation.
- The structure of the support obstructs the maximal saturation of the liquid with the

gas; in other words, the initial concentration of the gas in the liquid does not reach the expected equilibrium value.

None of these reasons should be totally excluded.

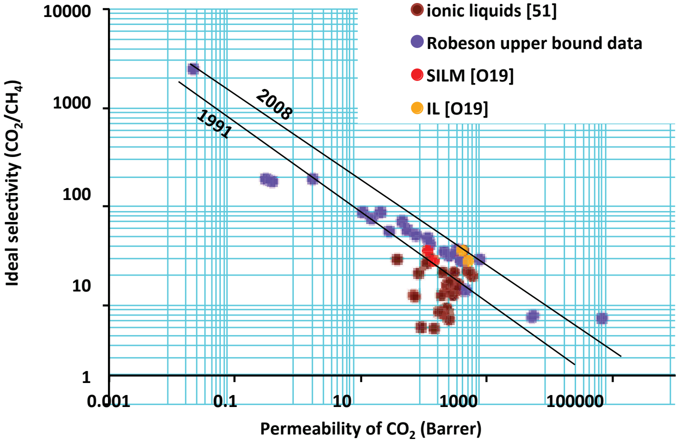

**Figure 17.** Robeson upper bound data and ionic liquid membrane data [O19].

A simple model of transport of gases through the liquid membrane in permeation cell was suggested. It showed that in the used pressure range (150–350 kPa), the mass transfer coefficient may be assumed constant with reasonable accuracy. The model could be applied in the scale-up of the process because it takes into account the decrease in the driving force that occurs along the membrane.

This decrease is not really significant in the lab scale process, where the membrane area is small, but it may be important in larger scale processes, especially when the high enrichment of retentate is required. Generally, it can be concluded that the ionic liquid membranes are convenient for gas separation processes but it is necessary to rely on the data connected to the supported liquid membranes themselves rather than on the data of pure (free) ionic liquids [O19].

In another recent study, gas and vapor transport properties were studied in ***mixed matrix membranes*** containing elastomeric ethylene-octene copolymer (EOC) with three types of carbon fillers: virgin or oxidized multi-walled carbon nanotubes (CNTs) and carbon fibers (CFs) [O20]. Gas and vapor transport measurements in ethylene-octene copolymer membranes show that the EOC is organophilic material that can be potentially used for a membrane vapor separation from air or for some gas separations involving mixtures of highly condensable and lighter species.

The addition of carbon nanotubes and carbon fibers had a relatively little effect on the transport properties of light gases and a modest effect on the transport of vapors. For light gases, the carbon fillers acted as impermeable obstacles and gas permeability slightly decreased in a similar fashion as predicted by the Maxwell model. For vapors, the behavior was opposite and the addition of a small amount of carbon filler caused an increase in permeability. At the same time, the CNTs and especially the CFs enhanced the Young's modulus of the blends more than ten-fold at the highest loading tested (30%) while both the tensile strength and the maximum deformation presented a maximum near the filler content of 10%. Thus, the carbon fillers enhanced the mechanical resistance of the membranes, maintaining or even improving their transport properties. If this behavior is maintained under operating conditions, as may be expected, the presence of carbon fillers will counteract the effect of plasticization of the membranes by vapor sorption, which often compromises the performance of conventional membrane systems. Therefore, the reported membranes are potentially suitable candidates for vapor removal from permanent gas streams [O20].

### 5.3. Water condensing and water-swollen membrane

Many different ionic liquids have been used to separate methane from carbon dioxide, as obvious above or in literature elsewhere [48-51], and their effectiveness has been proved. However, ionic liquids appear to be too expensive for biogas treatment on an industrial scale. We proposed a new method of biogas membrane separation called the "condensing-liquid membrane" (CLM) [P2]. It was proved later that this method is rather universal and can be used for separating polar/nonpolar gases [P3]. This type of membrane has a significant advantage over the usual liquid membrane [O21]. The removal of unwanted and toxic gases from the feed stream is realized continuously and the membrane surface is also continuously refreshed with condensed water to avoid contamination of the perm-selective membrane; furthermore, condensed water passing through the membrane ensures selectivity of the whole separation.

The CLM is in fact a liquid (water in this case) condensing on a porous hydrophilic membrane as a result of the temperature difference of the membrane and water-saturated biogas feed. The main difference between the CLM and an immobilized liquid membrane lies in the fact that the condensing membrane is being regenerated during its continuous operation.

The feed mixture of gases (raw biogas from a sewage plant, see Table I) is saturated by water vapor. The porous membrane (the optimal pore size must be found) has to be cooled enough to make the liquid condensation in its pores.

**Table I.** Composition of raw biogas before and after separation

| Compounds | Units | Feed | Retentate | Permeate |
|---|---|---|---|---|
| Flow rate of streams | (mL/min) | 10.08 | 8.88 | 1.30 |
| Sum of aromatic hydrocarbons | ($mg/m^3$) | 87.1 | 7.92 | 23.8 |
| Sum of chlorinated and aliphatic hydrocarbons | ($mg/m^3$) | 8.26 | 2.00 | 3.80 |
| Hydrogen sulphide | ($mg/m^3$) | 7.95 | <0.91 | <0.61 |
| Sum of siloxane (in water vapor) | ($mg/m^3$) | 130 | 9.10 | 13.0 |
| Hydrogen sulfide | (vol.%) | 0.34 | 0.19 | 1.34 |
| Water | (vol.%) | 3.40 | 2.51 | 16.5 |
| Carbon dioxide | (vol.%) | 27.2 | 21.3 | 67.6 |
| Methane | (vol.%) | 67.6 | 76.0 | 14.5 |

Measured at a feed flow rate of 10 $mLmin^{-1}$ of raw biogas at 27°C with the porous membrane at 14°C. The minor gases are also dissolved in condensing water.

Based on the experiments, it can be stated that with the higher feed flow rate the steady state was achieved more quickly; however, as the residence time of biogas in the permeation cell was shorter, the methane concentration in the retentate was lower. In other words, when the residence time was shorter, a smaller amount of preferentially permeating components (carbon dioxide, hydrogen sulfide) was able to penetrate through the CLM. The driving force of the separation was the difference in chemical potential, which in our case was a function of concentration and pressure. The permeation fluxes of the main biogas components in our laboratory-scale apparatus at a pressure difference of 200 kPa were $J_{CH4} = 1.3\ Lm^{-2}h^{-1}$ and $J_{CO2} = 6.1\ Lm^{-2}h^{-1}$ through a hydrophilic porous Teflon membrane with 65% porosity, pore diameter 0.1 μm, membrane thickness 30 μm, and initial feed flow rate 10 $mLmin^{-1}$. The separation factor was $\alpha = 4.67$, which is higher than the with a polyimide membrane value ($\alpha = 3.95$) published so far [52]. Therefore, the optimal conditions must be further investigated to balance the cost-effectiveness of the industrial process. Because of the demand for the lowest cost of separation a membrane suitable for biogas treatment has to be as cheap as possible. Following the idea of the CLM, water seems to be the ideal liquid from the processing point of view. Its presence in all types of biogas, which is usually seen as a disadvantage, thus changes into an indisputable advantage and necessity. The selectivity of the condensing membrane is given by the different solubilities of methane and carbon dioxide in water. Other minor compounds present in raw biogas (hydrogen sulfide, mercaptanes, and siloxanes) are much more soluble in water than in methane. Porous hydrophilic Teflon is a support on which water is able to condense and is not involved in the separation; however, it is rather expensive. The CLM is able to separate more undesirable components from biogas in one separation step. Water vapor from biogas is used to refresh the membrane because it condenses on the feed side of the membrane and is partially removed from the permeate side of the membrane by sweeping gas (nitrogen). Thus, the CLM is a new and revolutionary change in biogas upgrading. The hydrogen sulfide, mercaptanes and siloxanes are mostly removed from the feed stream by condensing water (see Table I). In case of membrane modules being long enough (larger membrane area) it would be possible to enrich raw biogas up to natural-gas quality (minimum 95% of methane content). The CLM can also be used under unfavorable conditions in which other polymeric membranes could be contaminated or destroyed by aggressive substances [O21].

Based on feasibility study, we can conclude that the above describe method is not cheaper than the classical method for biogas purification for example water or amine scrubbing or PSA adsorption. The main disadvantages are small permeate fluxes of $CO_2$ through CLM membrane and the cost of hydrophilic Teflon® membrane. Therefore, a new thin and cheap membrane is necessary to find. This kind of membrane can be find in Reverse osmosis field because they are produced in huge quantity (several millions of square meters per year) mainly for desalination units in the Middle East. Moreover, these kinds of membranes are not only very cheap but have also a very thin dense selective layer enabling their permeate flux (in our case $CO_2$ and $H_2S$) being much faster.

The condensing water on the swollen thin film hydrophilic composite membrane (TFC) creates, in fact, a separation barrier and separates $CO_2$, $H_2S$ and $CH_4$ from biogas due to their different solubility in water (see Fig. 18) [O22]. In order to achieve spontaneous condensation of water, the temperature of the TFC membrane must be below the dew point of biogas feed. The contact of TFC surface with water causes swelling of the polyamide thin dense film. During the impregnation, the porous support was also saturated with water but this water evaporated during the experiments, so the TFC membrane had to be cooled enough to make the liquid condense on its surface.

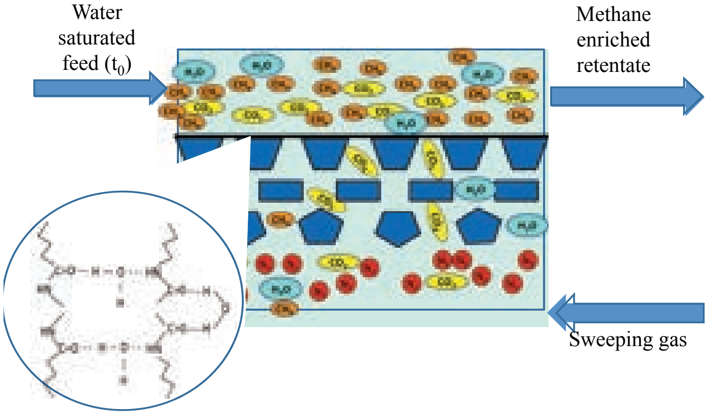

**Figure 18.** Scheme of function of condensing water membrane on thin film composite reverse osmosis membrane [O22].

Dry membranes were found to be impermeable for both gases. For SEM characterization, the little stripes of membrane were dried and then impregnated under vacuum with epoxy resin (see Fig. 19).

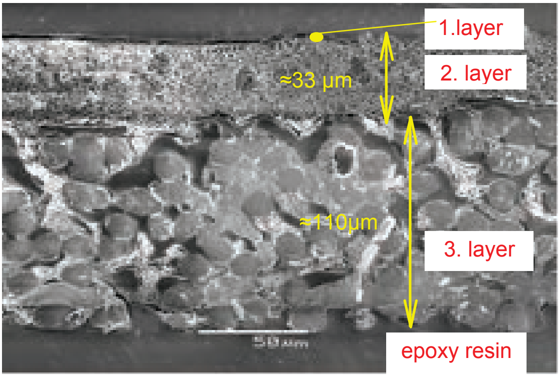

**Figure 19.** SEM image of the TFC membrane: On the top of the first layer is skin polyamide 1µm thin, then polysulfone layer 33µm thick and 110µm polyester layer [O22].

As obvious from Fig. 19, this TFC membrane is much thinner than the hydrophilic Teflon membrane [O22]. The preliminary test of the temperature influence on the permeation flux was carried out by the binary mixture with 67 vol.% of methane and raw biogas. The results show that there is a difference in the membrane performance by using raw biogas and binary mixture. Permeation fluxes of methane and carbon dioxide in raw biogas increase with the increasing temperature. By applying 400 kPa the pressure difference on the reverse osmosis membrane (a swollen skin layer on a dry support) it is possible to obtain even more than 95 vol.% of $CH_4$ in the retentate stream. The significant difference in solubility and permeability of methane and of raw biogas impurities (carbon dioxide, hydrogen sulfide) in and through the water layer causes the effective $CO_2/CH_4$ separation. The presented work represents an innovative approach to the relatively inexpensive production of biomethane from sewage biogas or even agro-biogas.

Unequivocal evaluation of tested supported liquid membranes (ionic liquid and water) may be done by a comparison of the so-called productivity of permeation, which is simply a product of permeance (or permeability) and selectivity. The advantage of this value is that the membrane is characterized by a single number, which compiles both basic characteristics [53]. The comparison of productivity of permeation for $CO_2$ and $CH_4$ calculated for tested membranes is presented in Table II.

**Table II**. Productivity of permeation of tested supported liquid membranes [53]

| | **Productivity of permeation of $CO_2$ (GPU)** | **Productivity of permeation of $CH_4$ (GPU)** |
|---|---|---|
| [emim][$Tf_2$N] in PVDF | 24.75 | 1.98 |
| [emim][dca] in PVDF | 33.12 | 1.61 |
| CWM in Teflon® | 19.69 | 1.87 |
| **Water swollen TFC®** | **223.0** | **10.0** |

A continuous study of this perspective method is in progress. A comparative study of low-pressure and high-pressure reverse osmoses (RO) membranes has been made [O23]. The simultaneous removal of carbon dioxide and hydrogen sulphide from agro-biogas using water–swollen thin hydrophilic film composites from two industrial producers has been studied. The results show that the hydrogen sulphide permeance was higher than that of carbon dioxide, owing to its higher solubility in water. The advantage of this membrane separation is that no pre-treatment of the feed gas is needed to remove the water vapor before the gas separation step, unlike the others, for instance glassy polymer membranes, which often lose performance due to plasticization by water vapor. The TFC membranes show good perm-selectivities when the feed stream contains at least 85% relative humidity, which condenses onto the membrane surface and guarantees that the membrane remains continuously wet during its operation [O23]. In case of low-pressure RO membranes, the permeance of hydrogen sulphide and carbon dioxide significantly increased within the pressure range from 130 to 170 kPa, above which, a plateau was reached for both gases. Since the methane permeance was virtually pressure independent, the corresponding selectivities with respect to methane show the same trend as the permeance. Interestingly, $H_2S$ show a nearly identical trend as $CO_2$ the perm-selectivity of $H_2S$ over $CO_2$ is close to 1 and show a marginal decrease, probably caused by a weak coupling effect. The comparison of both the support porosity and the SEM/EDX membrane analysis with obtained perm-selectivities suggests that a good water–swollen membrane should have the following features [O23]:

- high porosity of the membrane support layer,
- significant decrease in the size and number of the biggest pores caused by water swelling,
- good swelling of the selective skin polyamide layer,
- presence of a sufficient number of amido groups inside the upper layer of the hydrophilic composite.

Based on our studies [O21, O22, P2], a pilot plant operating with high pressure RO membrane was designed at the Prague central sewage plant and sponsored by ČEZ. The goal of this pilot plant was to scale up all the process and use spiral wound modules instead of a flat sheet membrane. After the 18-months-long testing, the concept was successfully proven.

In 2013 the private company Jinpo Plus Inc. constructed, in cooperation with Česká Hlava Ltd., Škoda Energy Inc. and Institute Chemical Process Fundamentals ASCR, v.v.i. a fully automatic unit with the capacity of 3 Nm$^3$/h (see Fig. 20 and their parameters Table III).

Nowadays, long-term stability tests are in a progress in Technological Park in Jihlava. A feasibility study must be done based on full-scale data that will be collected within half a year of continuous tests.

**Table III**. Parameters of unit with capacity 3 Nm$^3$/h of biogas at Technological Park, Jihlava

| **Parameters** | **Production of 1 Nm$^3$ of biomethane** |
|---|---|
| Electricity consumption | 0.531 kWh |
| Membrane area | 2 m$^2$ |
| Water consumption | 0.17 l/m$^3$ |

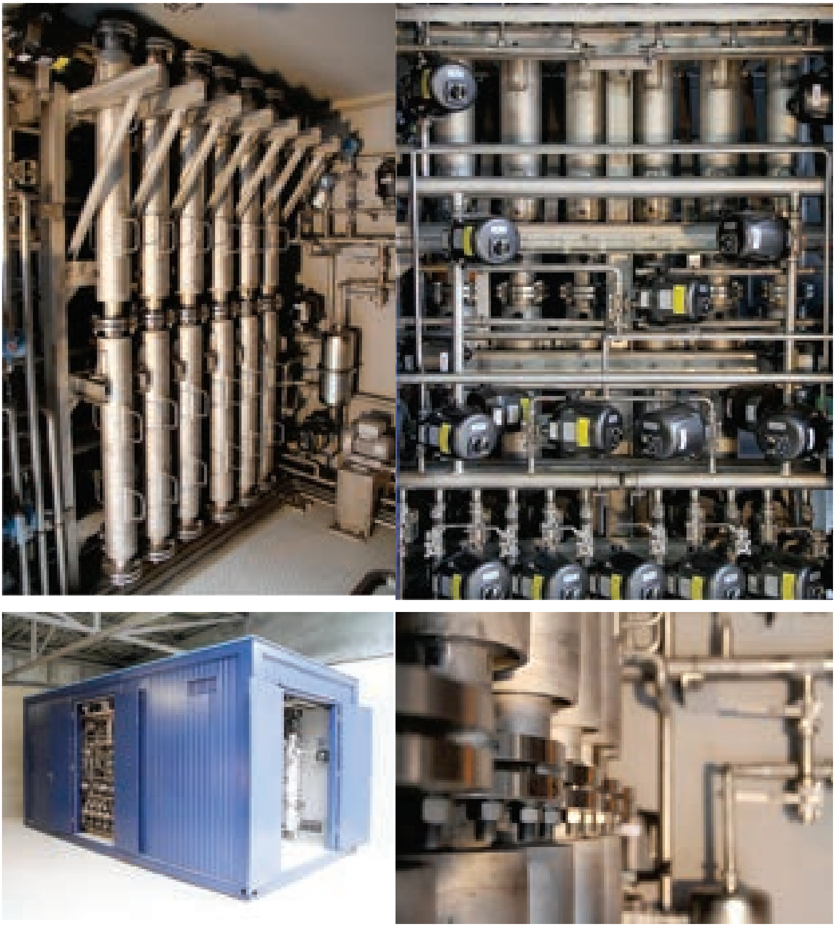

**Fig. 20.** Fully automatic unit with capacity 3 $Nm^3/h$ of biogas at Technological Park, Jihlava

# 6. Patents used in this thesis:

P1. Izák P., Kragl U., Köckerling M.; “Multiphase membrane”; University of Rostock, Germany, 2006. DE 10 2006 024 397 B3.

P2. Izák P., Poloncarzova M., Vejrazka J.; "The method and the apparatus for methane enrichment of biogas from sewage plant and agriculture" PCT-437 2011

P3. Izák P., Poloncarzova M., Vejrazka J.; "The method and apparatus for gas mixture separation" PCT-438 2011

# 7. Original papers used in this thesis

O1. Friess K., Šípek M., Hynek V., Sysel P., Bohatá K., Izák P.: Comparison of Permeability Coefficients of Organic Vapors through Non-Porous Polymer Membranes by Two Different Experimental Techniques. *J. Membr. Sci.* **240(1-2)**, 179-185 (2004).

O2. Izák P., Bartovská L., Friess K., Šípek M., Uchytil P.: Comparison of Various Models for Transport of Binary Mixtures through Dense Polymer Membrane. *J. Polym.* **44(9)**, 2679-2687 (2003).

O3. Izák P., Köckerling M., Kragl U.: Stability and Selectivity of a Multiphase Membrane, Consisting of a Dimethylpolysiloxane on Ionic Liquid, Used in the Separation of Solutes from Aqueous Mixtures by Pervaporation. *Green Chem.* **8(11),** 947-948 (2006).

O4. Izák P., Schwarz K., Ruth W., Bahl H., Kragl U.: Increased Productivity of Clostridium Acetobutylicum Fermentation of Acetone, Butanol, and Ethanol by Pervaporation through Supported Ionic Liquid Membrane. *App. Microbiol. Biotechnol.* **78(4),** 597-602 (2008).

O5. Izák P., Friess K., Hynek V., Ruth W., Fei Z., Dyson J.P., Kragl U.: Separation Properties of Supported Ionic Liquid-Polydimethylsiloxane Membrane in Pervaporation Process. *Desalination* **241(1-3),** 182-187 (2009).

O6. Kohoutová M., Sikora A., Hovorka Š., Randová A., Schauer J., Tišma J., Setničková K., Petričkovič R., Guernik S., Greenspoon N., Izák P.: Influence of Ionic Liquid Content on Properties of Dense Polymer Membranes. *Eur. Polym. J.* **45(3),** 813-819 (2009).

O7. Vopička O., Hynek V., Friess K., Izák P.: Blended Silicone-Ionic Liquid Membranes: Transport Properties of Butan-1-ol Vapor. *Eur. Polym. J.* **46(1),** 123-128 (2010).

O8. Izák P., Hovorka Š., Bartovský T., Bartovská L., Crespo J.G.: Swelling of Polymeric Membranes in Room Temperature Ionic Liquids. *J. Membr. Sci.* **296(1-2),** 131-138 (2007).

O9. Randová A., Hovorka Š., Izák P., Bartovská L.: Swelling of Nafion in Methanol–Water–Inorganic Salt Ternary Mixtures. *J. Electroanal. Chem.* **616(1-2),** 117–121 (2008).

O10. Randová A., Bartovská L., Hovorka Š., Friess K., Izák P.: The Membranes (Nafion and LDPE) in Binary Liquid Mixtures Benzene + Methanol - Sorption and Swelling. *Eur. Polym. J.* **45(10),** 2895-2901 (2009).

O11. Randová A., Bartovská L., Hovorka Š., Poloncarzová M., Kolská Z., Izák P.: Application of the Group Contribution Approach to Nafion Swelling. *J. Appl. Polym. Sci.* **111(4),** 1745-1750 (2009).

O12. Izák P., Godinho M.H., Brogueira P., Figueirinhas J.L., Crespo J.G.: 3D Topography Design of Membranes for Enhanced Mass Transport. *J. Membr. Sci.* **321(2),** 337–343 (2008).
O13. Izák P., Mateus N.M.M., Afonso C.A.M., Crespo J.G.: Enhanced Esterification Conversion in a Room Temperature Ionic Liquid by Integrated Water Removal with Pervaporation. *Sep. Purif. Technol.* **41(2),** 141-145 (2005).
O14. Kárászová M., Kačírková M., Friess K., Izák P.: The new progress in separation of gases and liquids by membranes with ionic liquids: A review. *Sep. Purif. Technol.* **132**, 93-101 (2014).
O15. Jansen J.C., Friess K., Clarizia G., Schauer J., Izák P.: High Ionic Liquid Content Polymeric Gel Membranes: Preparation and Performance. *Macromolecules* **44(1),** 39-45 (2011).
O16. Bernardo P., Jansen J.C., Bazzarelli F., Taselli F., Fuoco A., Friess K., Izák P., Jarmarová V., Kačírková M., Clarizia G.: Gas Transport Properties of PEBAX$^{®}$/Room Temperature Ionic Liquid Gel Membranes. *Sep. Purif. Technol.* **97,** 73-82 (2012).
O17. Friess K., Jansen J.C., Bazzarelli F., Izák P., Jarmarová V., Kačírková M., Schauer J., Clarizia G., Bernardo P.: High Ionic Liquid Content Polymeric Gel Membranes: Correlation of Membrane Structure with Gas and Vapour Transport Properties. J. *Membr. Sci.* **415**, 801-809 (2012).
O18. Jansen J.C., Clarizia G., Bernardo P., Bazzarelli F., Friess K., Randová A., Schauer J., Kubička D., Kačírková M., Izák P.: Gas Transport Properties and Pervaporation Performance of Fluoropolymer Gel Membranes Based on Pure and Mixed Ionic Liquids. *Sep. Purif. Technol.* **109**, 87-97 (2013).
O19. Kárászová M., Šimčík M., Friess K., Randová A., Jansen J.C., Růžička M., Sedláková Z., Izák P.: Comparison of Theoretical and Experimental Mass Transfer Coefficients of Gases in Supported Ionic Liquid Membranes. *Sep. Purif. Technol.* **118,** 255–263 (2013).
O20. Sedláková Z., Clarizia G., Bernardo P., Jansen J.C., Slobodian P., Svoboda P., Kárászová M., Friess K., Izák P.: Carbon Nanotube and Carbon Fiber-Reinforcement of Ethylene-Octene Copolymer Membranes for Gas and Vapor Separation. *Membranes* **4(1)**, 20-39 (2014).
O21. Poloncarzová M., Vejražka J., Veselý V., Izák P.: Effective Purification of Biogas by Condensing-Liquid Membrane. *Angew. Chem.-Int. Edit.* **50(3),** 669-671 (2011).
O22. Kárászová M., Vejražka J., Veselý V., Friess K., Randová A., Hejtmánek V., Brabec L., Izák P.: A Water-Swollen Thin Film Composite Membrane for Effective Upgrading of Raw Biogass by Methane. *Sep. Purif. Technol.* **89,** 212-216 (2012).
O23. Dolejš P., Poštulka V., Sedláková Z., Jandová V., Vejražka J., Esposito E., Jansen JC., Izák P., Simultaneous Hydrogen Sulphide and Carbon Dioxide Removal from Biogas by Water–swollen Reverse Osmosis Membrane, *Sep. Purif. Technol.* **131**, 108-116 (2014).

# 8. References

1. Mulder M.: Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, Boston, London, 1998.
2. Rautenbach R., Albrecht R.: Membrane Processes, John Wiley & Sons Ltd., Chichester, New York, Brisbane, Toronto, Singapore, 1989.
3. Börjesson J., Karlsson H.O.E., Trägårdh G., *J. Membr. Sci.*, (1996) **119**(2): p. 229.
4. Bengtsson E., Tragardh G., Hallstrom B., *Food Science and Technology*-Lebensmittel-Wissenschaft & Technologie (1992) **25**(1): p. 29.

5. Izák P., Kárászová M. Pervaporace. In: Membránové procesy (Zdeněk Palatý, Ed.). Vysoká škola chemicko-technologická v Praze: Praha, 2012. p. 231.
6. Bernardo P., Drioli E., Golemme G., *Ind. Eng. Chem. Res.*(2009) **48** (10): p. 4638.
7. Freemantle M., *Chem.Eng. News*: 2005. **40** (83): p. 49.
8. Stannett V., *J. Membr. Sci.* (1978) **3**: p. 97-101.
9. Izák P., Bartovská L., Friess K., Šípek M., Uchytil P., *J. Polym*. **44(9)** (2003): p. 2679.
10. Crespo J.G., Böddeker K.W., Membrane Processes in Separation and Purification, Kluwer Academic Publisher, Dordrecht (1994): p. 165
11. Kröckel J., Kragl U., *Chem. Eng. Technol.*, (2003) **26**: p. 1166.
12. Branco LC., Crespo JG., Afonso CAM., *J. Chem. Eur.* (2002) **8**: p. 3865.
13. Fortunato R., Afonso CAM., Reis MAM., Crespo JG., *J. Membr. Sci.* (2004) **242**: p. 197.
14. Afonso CAM., Crespo JG., Green Separation Processes, Wiley-VCH, Weinheim, (2005).
15. Heintz A., *J. Chem. Thermodynamics*, (2005) **37**: p. 525.
16. Küppers T., Bernhardt E., Willner H., Rohm H. W., Köckerling M., *Inorg. Chem.*, (2005) **44:** p. 1015.
17. Welz-Biermann U., Ignatzev N., Bernhardt E., Finze M., Willner H., WO 2004/072089 A1, Merck Patent KGaA, Germany, 2004.
18. Huang RYM. (Ed.), Pervaporation Membrane Separation Processes, Elsevier, Amsterdam, 1991: p. 322.
19. Rose A.H., Industrial Microbiology, Butterworths, London, 1961: p. 160.
20. Bahl H., Andersch W., Gottschalk G., *Eur. J. Appl. Microbiol. Biotechnol.* **15** (1982): p. 201.
21. Durre P., *Appl. Microbiol. Biotechnol.* **49** (1998): p. 639.
22. Qureshi N., Maddox I.S., *Food Bioproducts Process*. **83** (2005): p. 43.
23. Bahl H., Andersch W., Gottschalk G., *Eur. J. Appl. Microbiol. Biotechnol.* **17**(73) (1983): p. 201.
24. Crank J., The Mathematic of Diffusion, Clarendon Press, Oxford, 1975.
25. Crank J. and Park GS., Diffusion in Polymers, Academia Press, London, 1968.
26. Zeng Ch., Li J., Li P., Chen T., Lin Y., Wang D., et al. *Chem. Eng. Sci.* (2006) **61**: p. 1892.
27. Neogi P., Kim M., Yang Y. Diffusion in solids under strain, with emphasis on polymer membranes. *AIChE J.* (1986) **32**: p. 1146.
28. Billmeyer Jr. FW., Textbook of Polymer Science, J. Wiley & Sons, New York, 1984.
29. Tanaka T., Fillmore DJ., *J. Chem. Phys.* (1979) **70**: p. 1214.
30. Freemantle M., New Horizons for Ionic Liquids, C&EN, (2001): p. 21.
31. Schafer T., Rodrigues CM., Afonso CAM., Crespo JG., *Chem. Commun.* (2001) **17**: p. 1622.
32. Teixeira P., Trindade AC., Godinho MH., Azeredo J., Oliveira R., Fonseca JG., *Biomater. Sci. Polym. Edn.* (2006) **17**: p. 239.
33. Bélafi-Bakó K., Dormo N., Ulbert O., Gubicza L., *Desalination* (2002) **149**: p. 267.
34. Gubicza L., Nemestóthy N., Fráter T., Bélafi-Bakó K., *Green Chem.* (2003) **5**: p. 236.
35. Qureshi N., Maddox IS., *Food Bioprod Process* (2005) **83**: p. 43**.**
36. Soni BK., Soucaille P., Goma G., *Appl. Microbiol. Biotechnol.* (1987) **25**: p. 317**.**
37. Liu F., Liu L., Feng X., *Sep. .Pur. Tech.* (2005) **42(3)**: p. 273**.**
38. Bara J.E., Lessmann S., Gabriel CJ., Hatakeyama, ES., Noble RD.; Gin DL., *Ind. Eng. Chem. Res.* (2007) **46:** p. 5397.
39. Bara J.E., Hatakeyama SE., Gin DL., Noble RD., *Polym. Adv. Technol.* (2008) **19:** p. 1415.
40. Car A., Stropnik C., Yave W., Peinemann KV., *J. Membr. Sci.* (2008) **307:** p. 88.

41. Lin H., Van Wagner E., Freeman BD., Toy LG., Gupta RP., *Science* (2006) **311(5761):** p. 639.
42. Robeson LM., *J. Membr. Sci.* (2008) **320:** p. 390.
43. Branco LC., Crespo JG., Afonso CAM., *Chem. Eur. J.* (2002) **8:** p. 3865.
44. Scovazzo P., Havard D., McShea M., Mixon S., Morgan D., *J. Membr. Sci.* (2009) **41:** p. 327.
45. Bara JE., Lessmann S., Gabriel CJ., Hatakeyama ES., Noble RD., Gin DL., *Ind. Eng. Chem. Res.,* (2007) **46:** p. 5397.
46. Bara JE., Hatakeyama SE., Gin DL., Noble RD., *Polym. Adv. Technol.,* (2008) **19:** p. 1415.
47. Yoo S., Won J., Kang SW., Kang YS., Nagase S., *J. Membr. Sci.,* (2010) **363:** p. 72.
48. Ueki T., Watanabe M., *Macromolecules* (2008) **41:** p. 3739.
49. Hua X., Jianbin T., Blasig A., Youqing S., Radosz M., *J. Membr. Sci.,* (2006) **281:** p. 130.
50. Bara JE., Gabriel CJ., Hatakeyama ES., Carlisle TK., *J. Membr. Sci.,* (2008) **321:** p. 3.
51. Scovazzo P., Havard D., McShea M., Mixon S., Morgan D., *J. Membr. Sci.,* (2009) **327:** p. 41.
52. Harasimowicz M., Orluk P., Zakrzewska-Trznadel G., Chmielewski AG., *J. Hazard. Mater*., (2007) **144:** p. 698.
53. Kárászová M., *PhD theses*, Institute of Chemical Technology in Prague, (2012) p. 83.