



EUROPEAN COMMISSION
RESEARCH DG

MARIE CURIE MOBILITY ACTIONS
INDIVIDUAL DRIVEN ACTIONS
FINAL SCIENTIFIC/MANAGEMENT REPORT

FINAL SCIENTIFIC REPORT

Type of Marie Curie action:	Marie Curie Intra European Fellowship
Title of the Project:	Liquid Membranes and Ionic Liquids for Selective Downstream Processing
Duration of fellowship/appointment/training period (Start Date – End Date¹):	01/02/2005 – 31/01/2007

OBJECTIVE OF THE RESEARCH

The objective of the project was to investigate the development and application of supported liquid membranes on the base of ionic liquids. The proposed study of the pervaporation process was focused on the possibility to gain experimental data, which will contribute to better understanding and description of transport of a multi-component mixture through a membrane. The aim of the project was the study of transport in membranes during the pervaporation process and finding of an appropriate model for description of the permeate transport through non-porous membranes.

WORK PERFORMED (MENTIONING ALSO UNSUCCESSFUL APPROACHES AND UNFORESEEN DEVELOPMENTS) AND RESULTS

As support for ionic liquid we decided to use the ultra- and nanofiltration ceramic membranes, which are chemically, thermally and mechanically stable. We developed a special procedure to impregnate the pores of chosen membranes. One side of the ceramic membrane is blocked by Teflon stopper and the other side is connected to a vacuum pump. The whole module is placed into the burette and the ionic liquid is poured around. When vacuum is applied into the module, the ionic liquid is pulled into the pores of the ceramic membrane.

The binary system for selective separation that we 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. At the feed side binary mixture (water + 1wt% 1,3-propanediol) is well mixed and low pressure of 20 Pa at the permeate side was applied. The permeate was condensed in the cold trap and pervaporation flux was determined by classical gravimetric method. The concentration of 1,3-propanediol in the feed was monitored by gas chromatography and a FFAP polar capillary column was used. The only problem with the set-up was a long term stability of the liquid in the pores. The following hydrophobic ionic liquids (ILs) have been used:

Ceramic module	<i>Stability of supported ionic liquid (hours)</i>			
	$C_{14}H_{24}N^+BF_4^-$	$C_4mim^+PF_6^-$	$C_8H_{26}N_2^+B(CN)_4^-$	$C_{27}H_{54}F_6N_2O_4S_2$
Pore size (nm)				
200	0.1	-	-	-
60	0.5	-	-	-
5	-	1.3	1.9	-
0,9	1.2	2.4	3.5	0.15

As it can be seen from the table above, the ionic liquids stayed in the pores of ceramic module just for a short time – ranging from a few minutes up to 3.5 hours as a maximum. Water emulsifies the ionic liquid and then the ionic liquid is washed out from the pores.

We have tried two ways to solve this instability of the supported ionic liquid membranes (SILMs): One possibility how to improve hydrophobicity and stability of IL inside the pores of the ceramic module, lies in preparation of a new hydrophobic IL with higher melting point. The novel hydrophobic IL, tetrapropylammonium tetracyanoborate ($[(C_3H_7)_4N][B(CN)_4]$), which has a quite large cation and a relatively small, but stable anion, with the melting point about 60°C was prepared. The potassium tetracyanoborate was heated in water and an equal amount of tetrapropylammonium bromide was added at 50°C. A viscous IL was obtained after extraction with and removal of dichloromethane on a rotary pump. Firstly, we evaluated the transport of the solute (1,3-propanediol) from aqueous mixture through an empty ceramic nanofiltration module under low pressure at room temperature (23°C). The ceramic nanofiltration module with pore size 0.9 nm was then impregnated by $[(C_3H_7)_4N][B(CN)_4]$, at 70°C inside the burette. Then we performed pervaporation experiments under exactly the same conditions with an impregnated module.

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

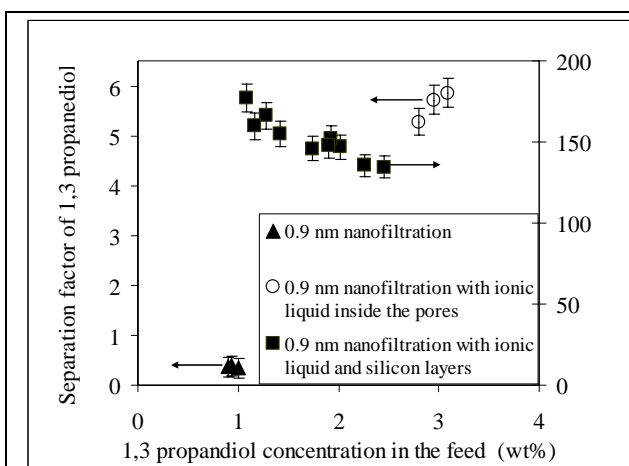


Fig. 1. Comparison of 1,3-propanediol separation factor with its feed concentration, during NF (▲); using the NF ceramic module with the 0.9 nm pores filled with IL (○); using the NF ceramic module with the 0.9 nm pores filled with IL and both sides coated with silicon (■).

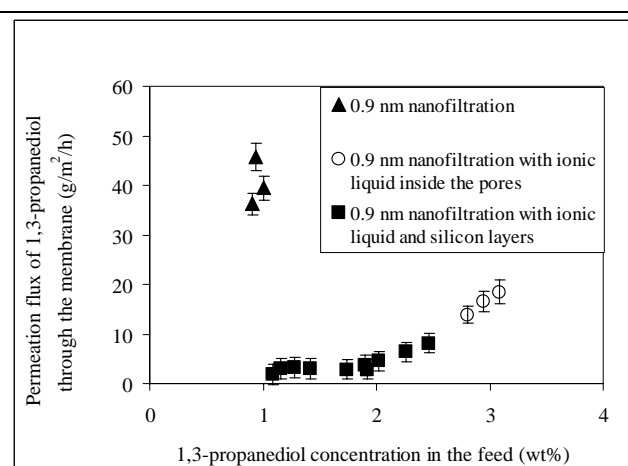


Fig. 2. Comparison of 1,3-propanediol permeation flux with its feed concentration during NF (▲); using the NF ceramic module with the 0.9 nm pores filled with IL (○); using the NF ceramic module with the 0.9 nm pores filled with IL and both sides coated with silicon (■).

As can be seen the separation factor of 1,3-propanediol increased from 0.38 to 5.91, when IL was inside the pores, and up to 177, when the whole ceramic module with IL was coated by dimethylpolysiloxane. The instability of SILMs in contact with aqueous solutions, which has limited their commercial application so far, has been solved by dimethylpolysiloxane coating. On the other hand, the average permeating flux of the solute decreased from 34.3 g/m²/h to 3.86 g/m²/h. Although the separation process with multiphase membrane was in 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 we did not see any changes in transport properties, which indicate a very high stability of the multiphase membrane [1].

Another approach how to stabilize ILs inside the porous membranes is to polymerize ionic liquid inside the pores by adding of certain amount of polymer (polydimethylsiloxane) and a crosslinking agent (dibutyltin dilaurate) to IL. This will change properties and IL is much more stable against water emulsification. The ceramic ultrafiltration module with 1-ethenyl-3-ethylimidazolium hexafluorophosphate ionic liquid and polydimethylsiloxane (PDMS) blend inside the pores was stable under low pressure in aqueous solution of acetone and 1-butanol for more than five months. The pervaporation separation characteristics (Figure 3 and Figure 4) obtained with PDMS - IL blend were compared with another ceramic ultrafiltration module made from TiO₂, which was impregnated with PDMS only. The pervaporation of the ternary system (acetone-1-butanol-water) was carried out at 23°C and a low pressure of 20 Pa.

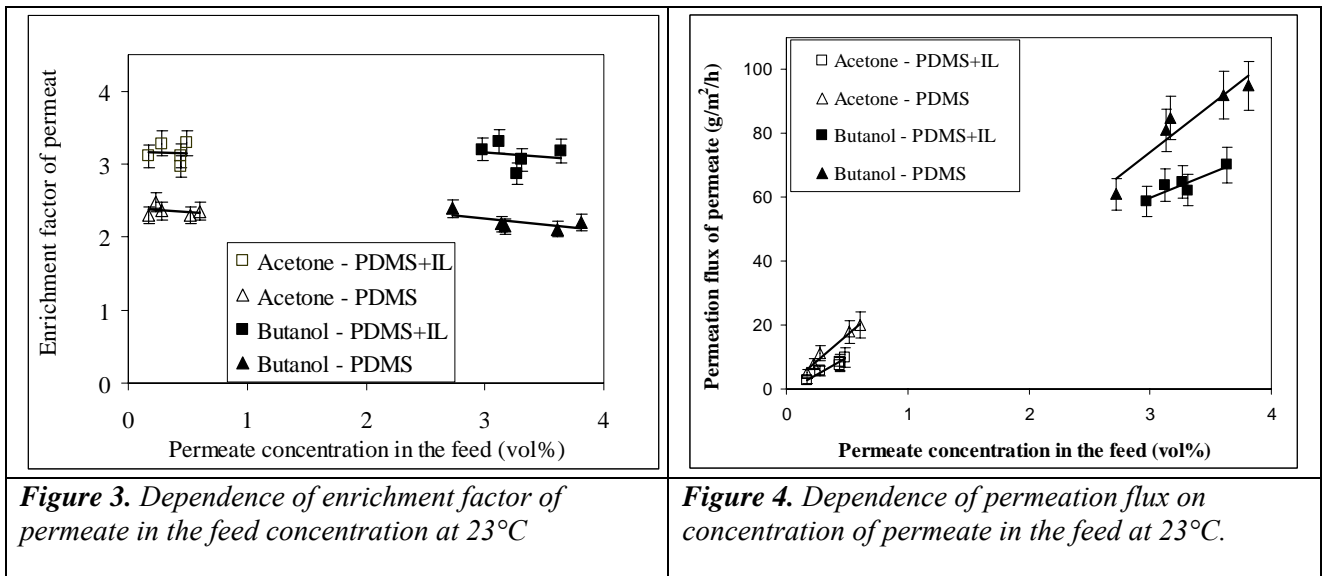


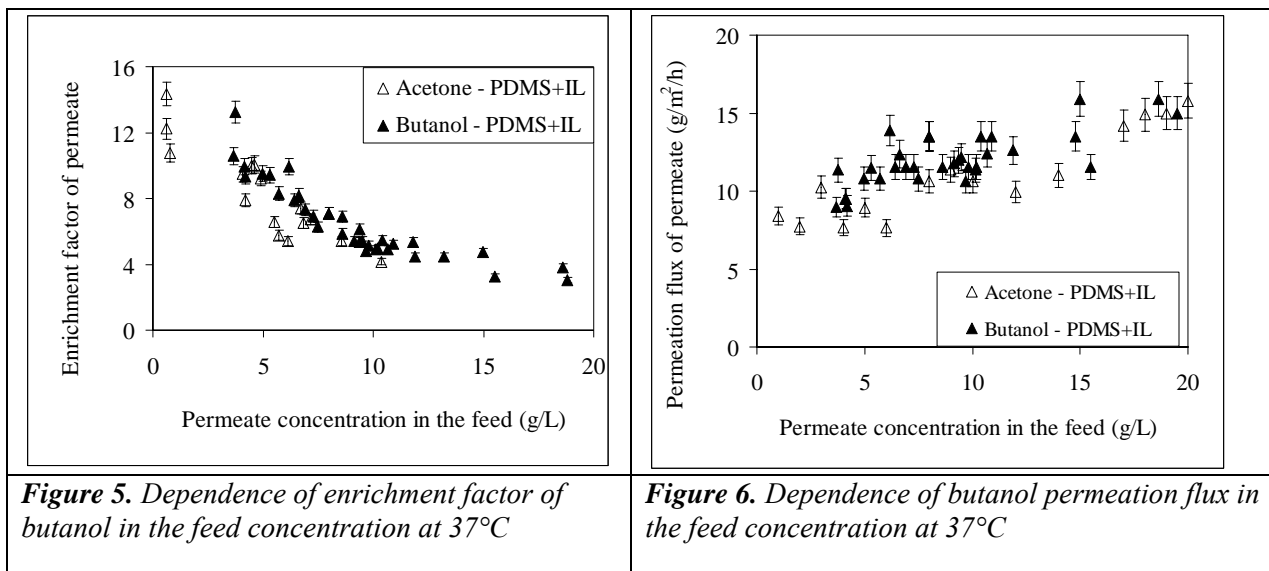
Figure 3. Dependence of enrichment factor of permeate in the feed concentration at 23°C

Figure 4. Dependence of permeation flux on concentration of permeate in the feed at 23°C.

As it can be observed from Figure 3, the enrichment factor of acetone increased from 2.3 to the average value 3.2, when 50 wt% of IL was mixed in PDMS and anchored inside the 30 nm pores of ceramic ultrafiltration module. In case of 1-butanol, the enrichment factor was improved from 2.2 to 3.1 due to the higher selectivity of IL-PDMS blend than the PDMS supported membrane. Figure 4, which represents the speed of the separation, shows that 1-butanol permeates a little bit faster through PDMS than through PDMS-IL blend supported membrane. The same trend can be observed in the case of acetone. The permeation flux of 1-butanol and also acetone increases linearly with the concentration of each permeate in the feed. The slope of the permeating flux for both permeating components is almost the same, indicating similar fluxes of acetone and 1-butanol through supported ionic liquid membranes. During five months of measurements, no decrease in the stability and separation of this set-up was observed. Especially noteworthy is the fact that ionic liquid-PDMS blend has significantly better separation properties than PDMS membrane itself [2]. The free radical polymerization reactions conducted in ionic liquid are faster than in classical

molecular solvents and they tend to yield polymers with higher molecular weight. The exact impact on the mechanism of the polymerization, caused by replacement of traditional solvents with ionic liquids, is not yet fully understood, but includes reduced termination rates (partly due to solvents with higher viscosity), increased propagation constants, and low chain transfer constants. The ionic liquid also introduces to the polymer charged ions, which are responsible for more selective transport of the permeates through the semi-permeable membrane.

The biotransformation processes, where the *Clostridium acetobutylicum* was grown in continuous culture under phosphate limitation (0.74 mM) at a pH of 4.3 (we could not use previous IL because at acidic and aquatic conditions PF_6^- anion would undergo hydrolysis producing HF and PO_4^{3-}), glucose was fermented to butanol as the major products. This fermentation product is main inhibitor for *Clostridium acetobutylicum* growth. Therefore butanol was continuously and “in situ” removed from fermentor by pervaporation separation technique (Figures 5 and 6) and helped to increase the conversion of glucose. Supported ionic liquid–Polydimethylsiloxane blend membrane was used as a selective barrier in pervaporation process at 37°C. The ultrafiltration membrane (pore size 60 μm) was impregnated by 15 wt% of novel ionic liquid ($[(\text{C}_3\text{H}_7)_4\text{N}][\text{B}(\text{CN})_4]$) and 85 wt% of polydimethylsiloxane. The selected supported ionic liquid membrane indicates a very high stability over six months during all measurements. When real fermentation broth with more than 20 different compounds and micro-organisms was used we could not employ multiphase membrane because the permeation flux of butanol was not sufficient enough to avoid deadly butanol concentration inside the fermentor.



Diffusion coefficients and preferential sorption of butanol and acetone were measured for ionic liquid–Polydimethylsiloxane blend membranes. All dependencies were mathematically described and then introduced into Maxwell-Stefan equations. A modified Maxwell-Stefan model, which takes into account the non-ideal multi-component solubility effect, concentration dependent diffusion coefficients of all permeating components and diffusion coupling can describe the pervaporation process very well [3].

This work demonstrates the potential of using pervaporation to enhance biotransformation process. In particular, the use of ionic liquids is rather interesting in combination with pervaporation because, in this case, the separation is more effective and more environmentally friendly.

LITERATURE

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- [2] P. Izák, M. Köckerling, U. Kragl; 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 (2006) 947-948
- [3] P. Izák, K. Schwarz, K. Friess, S. Hovorka, W. Ruth, H. Bahl, U. Kragl; Pervaporation of fermentation broth and modelling based on Maxwell Stephan equations, *publication in preparation*