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Short communication

# Selective removal of acetone and butan-1-ol from water with supported ionic liquid–polydimethylsiloxane membrane by pervaporation

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**Abstract**

The use of ionic liquid–polymer in supported ultrafiltration membrane in vacuum pervaporation has been verified. The ultrafiltration membranes were impregnated by two ionic liquids (1-ethenyl-3-ethyl-imidazolium hexafluorophosphate and tetrapropylammonium tetracyano-borate) and polydimethylsiloxane. These new and very stable supported ionic liquid–polymer membranes were used for separation of ternary mixtures butan-1-ol–acetone–water by vacuum pervaporation. In comparison with polydimethylsiloxane membranes, the average enrichment factor of butan-1-ol increased in both cases. This higher selectivity shows a good potential for improving pervaporation separation process.

*Keywords:* Ionic liquid; Supported polymer membrane; Pervaporation; PDMS membrane

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## 1. Introduction

This communication is focused on the products of biotransformation and fermentation processes, where practical application in industry is possible. The compound of interest is biofuel, namely BIObutanol, 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 separation in liquid membranes is not based on the solid support of a given membrane, but on the properties of the liquid [1]. Supported ionic liquid membranes offer a range of possible advantages: (1) molecular diffusion is higher in ionic liquids than in polymers. (2) The selectivity of the separation can be influenced by variation of the liquids, especially ionic liquids offer the advantage of a wide variety of properties. (3) Ionic liquids as liquid membranes allow three-phase systems easily due to their special mixing behaviour. (4) Contrary to the extraction, only small amounts of liquids are necessary to form the liquid membrane, thus allowing also the use of more expensive materials. (5) Due to their good thermal stability, reactive processes may take place at high temperatures (up to around 250 °C), which leads to faster kinetics in the case of endothermic reactions. (6) The usage of nano-, ultra- and microfiltration ceramic modules could help to diminish concentration polarization due to a rough liquid-membrane surface.

*Clostridium acetobutylicum*, a Gram-positive bacteria, is well known for its ability to produce solvents acetone, butan-1-ol and a very small amount of ethanol. The ABE fermentation had been used in industrial scale until the middle of the last century [2]. However, high substrate costs and inconvenient product recovery rates caused a termination of the commercial fermentation. In the seventies, high oil prices caused a return of interest in the clostridial ABE fermentation. In 1983, Bahl et al. [3] showed that the growth of *C. acetobutylicum* in a chemostat culture with an excess of glucose and a limitation of phosphate led to the highest glucose consumption and product concentration. In spite of this, the product concentration is still limited due to the toxicity of the products of fermentation, especially of butan-1-ol.

A traditional technology for separating alcohols from dilute biomass fermentation broths is distillation. However, down-

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stream processes represent an alternative, which may have energy and capital cost advantages relative to distillation, especially for smaller scale systems or at lower feed concentration. A development of a membrane system with suitable flux and selectivity characteristics plays a critical role in achieving practical utility for pervaporation due to cost considerations [4]. Qureshi and Maddox compared several downstream processes integrated with ABE fermentation for product removal: namely perstraction, liquid–liquid extraction, gas-stripping and also pervaporation [5]. They concluded that pervaporation and gas-stripping appeared to be the most promising product recovery techniques coupled with fermentation.

Therefore we focused on the most effective downstream separation process for ABE fermentation—the pervaporation. To achieve even more efficient ABE removal by pervaporation we prepared the ionic liquid–polydimethylsiloxane (IL–PDMS) membrane, which has better separation properties than classical polymer membrane. To the best of our knowledge, the first application of supported ionic liquid membranes for gas separations was reported by Noble and co-workers [6]. The first report about the molecular interactions between room-temperature ionic liquids (RTILs) and Nafion and PDMS membranes, proving that in contact with these polymers RTILs behaved like electrolytes rather than solvents, was published already in 2005 [7]. Scovazzo et al. concluded that combining the RTILs negligible vapor pressure with the ability to produce application specific RTILs possess the potential for producing highly selective membranes with high permeabilities in comparison to classical polymer membranes [8]. The hydrophobic ionic liquid was introduced as the third phase between the aqueous phase and the plain PDMS membrane for improving mass-transfer of acetic acid from its aqueous matrix to the PDMS membrane by Yu et al. [9]. Their primary results indicated that the ionic liquid as an extractant prior to pervaporation was favorable for improving the permeate selectivity and the permeate flux of acetic acid compared with using only a plain PDMS membrane.

Our task was to test different supported ionic liquid–PDMS membranes with liquid mixtures, from which organic compounds were removed by vacuum pervaporation.

## 2. Experimental

The synthesis of 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate (IL1): 1-ethenyl-3-ethyl-imidazolium bromide [10] (20.3 g, 0.1 mol) and sodium hexafluorophosphate (16.8 g, 0.1 mol) was mixed in water (75 ml), forming a suspension. After vigorously stirring at room temperature for 2 h, the suspension was filtered. The solid was washed with water (3 × 10 ml) and the product was dried under vacuum at 30 °C for 24 h. Yield: 95%, m.p. 76 °C. In situ recrystallization by slow cooling of an over-heated fluid from 80 °C to room temperature over a period of 24 h gave single crystals suitable for X-ray determination.

50 wt% of 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid was mixed with 50 wt% polydimethylsiloxane. The PDMS was prepared by mixing a solution of RTV 615A and RTV 615B (General Electric) in a 10:1 ratio at 60 °C for 0.5 h. The second supported ionic liquid membrane was prepared from a 15 wt% of tetrapropylammonium tetracyano-borate ionic liquid (IL2) [11] and it was mixed with 85 wt% of PDMS (the maximum amount of IL to get a homogeneous polymer). As a support matrix for the polymer–IL membrane the ceramic ultrafiltration module made from $TiO_2$ with pore size 60 nm was used as well. The ceramic asymmetric modules were 500 mm long with external diameter of 10 mm and effective area of 0.011 $m^2$. They were made by Inopor GmbH, Germany. The membrane was then impregnated by this viscous blend of IL and PDMS inside the burette for 0.5 h. The impregnated membrane was then taken out from the burette and cooled down to the room temperature and left to cure for 24 h. 18 ml of IL–PDMS blend (the same amount for both IL tested in this work) was kept in the ceramic module during all the time necessary for the experiments.

The pervaporation experiments were performed with the impregnated module at 23 °C. The concentration of the permeates was first detected by gas chromatographic analyses (GC) and then by high-pressure liquid chromatography (HPLC). Samples for analyses of the content were extracted from the feed and the cold trap (permeate) at regular time intervals—usually every 8 h. Internal standard was used for all samples. The contents of butan-1-ol and acetone were determined by using HPLC-method in ion exclusion mode. The operating parameters used: HPLC-column: Aminex HPX-87H 300 × 7.8 mm (Bio-Rad, USA), mobile phase: sulfuric acid 0.006 M, temperature: 65 °C, detection by refractive index. The measurements were carried out using HPLC-equipment of “Knauer GmbH” (Berlin-Germany). An external standard calibration was used as quantification method.

The ceramic ultrafiltration module with PDMS–IL1 and PDMS–IL2 membrane inside the pores was stable under low-pressure 20 Pa in aqueous solution of acetone and butan-1-ol for more than five months. We did not record any formation of hydrofluoric acid from IL1 and any change in weight of the IL–PDMS inside the module during our experimental condition (pH 7, 23 °C).

## 3. Results and discussion

The pervaporation separation characteristics (Figs. 1 and 2) obtained with PDMS–IL membranes were compared with another ceramic ultrafiltration module made from $TiO_2$, 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. As it can be observed from Fig. 1, the enrichment factor of acetone ($\beta_i = w_{i\mathrm{P}}/w_{i\mathrm{F}}$, where $w_{i\mathrm{P}}$ is the weight fraction of component $i$ in the permeate and $w_{i\mathrm{F}}$ is the weight fraction of component $i$ in the feed) increased from 2.3 to the average value 3.2, when 50 wt% of 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate was mixed in PDMS and anchored inside the 60 nm pores of ceramic ultrafiltration module. In case of butan-1-ol, the enrichment factor was improved from 2.2 to 3.1 because the selectivity of IL1–PDMS membrane is higher than the one of PDMS supported membrane. When 15 wt% of tetrapropylammonium tetracyano-borate ionic liquid was mixed with 85 wt% of PDMS, the enrichment factor of acetone increased from 2.3 up to 7.9 (when 0.4 wt% of ace-

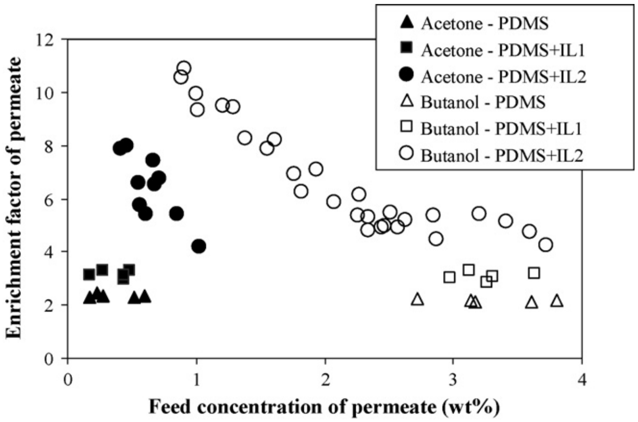

Fig. 1. Dependence of enrichment factor of permeate on feed concentration at 23 °C. (▲) Acetone in PDMS; (■) acetone in PDMS + 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; (●) acetone in PDMS + tetrapropylammonium tetracyano-borate ionic liquid; (△) butan-1-ol in PDMS; (□) butan-1-ol in PDMS + 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; (○) butan-1-ol in PDMS + tetrapropylammonium tetracyano-borate ionic liquid.

tone in the feed) and the enrichment factor of butan-1-ol from 2.2 up to 10.9 (when 0.9 wt% of butan-1-ol in the feed). The enrichment factor increased with decreasing permeate content in the feed. The similar results were obtained by Liu et al. who reached with polyether block amide membrane (PEBA 2533) the selectivity of butan-1-ol even 11.6 at 1.03 wt% of butan-1-ol in the feed at 23 °C [12]. However the permeating flux of butan-1-ol was 6.6 $\mathrm{g\,m^{-2}\,h^{-1}}$ in PEBA 2533, which is much lower then 24 $\mathrm{g\,m^{-2}\,h^{-1}}$ in PDMS–IL2 at 1.03 wt% of butan-1-ol in the feed at 23 °C.

Fig. 2, which represents the speed of the separation, shows that butan-1-ol permeates a little bit faster through PDMS than through PDMS–IL1 and PDMS–IL2 membranes. The same trend can be observed in case of acetone. The permeation flux of butan-1-ol ($J_i = Jw_{i\mathrm{P}}$, where $J$ is total permeation flux through the supported ionic liquid membrane (SILM)) and also acetone increases with the concentration of each permeate in the feed. The slope of the permeation flux for both permeating components is almost the same, indicating similar fluxes of acetone and butan-1-ol through SILMs with their concentration in the feed. During five months of measurements, no decrease (the weight of the module did not change) in the stability and separation of this set-up was observed. Especially noteworthy 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 hexafluorophosphate IL, even when (immiscibility limitation with PDMS) we could immobilize inside of PDMS polymer much lower amount of IL. 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 [13]. 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 [14], and low chain transfer constants [15].

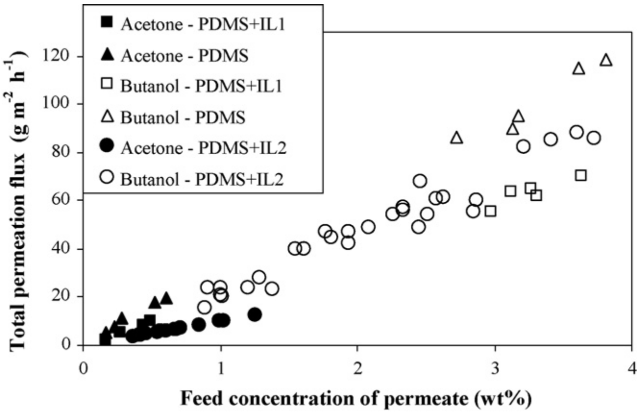

Fig. 2. Dependence of permeate permeation flux on feed concentration at 23 °C. (▲) Acetone in PDMS; (■) acetone in PDMS + 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; (●) acetone in PDMS + tetrapropylammonium tetracyano-borate ionic liquid; (△) butan-1-ol in PDMS; (□) butan-1-ol in PDMS + 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate ionic liquid; (○) butan-1-ol in PDMS + tetrapropylammonium tetracyano-borate ionic liquid.

## 4. Conclusions

In summary, by using polydimethylsiloxane-1-ethenyl-3-ethyl-imidazolium hexafluorophosphate and polydimethylsiloxane–tetrapropylammonium tetracyano-borate 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 3.1 (PDMS–IL1) and to 10.9 (PDMS–IL2). In case of acetone, the enrichment factor increased from 2.3 (PDMS) to 3.2 (PDMS–IL1) and to 7.9 (PDMS–IL2). Although the separation process with IL–PDMS membranes are a little bit slower, its higher selectivity show 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 we 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 [16].

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