REACTIVE & FUNCTIONAL POLYMERS

Vapour sorption and permeation behaviour of supported ionic liquid membranes: Application for organic solvent/water separation

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ABSTRACT

The imidazolium-based ionic liquids (ILs) (1-*n*-alkyl-3-methylimidazolium tetrafluoroborate, where n = 4, 6–8, 12) were synthesized and characterized in terms of their spectral characteristics, thermal stability, and water, ethanol and cyclohexane vapour sorption behaviour. It was found that the highest hydrophilic character had IL with the shortest alkyl chain on the cation. At the same time, the IL thermal stability was decreased with the increase of the cation alkyl chain length. D'Arcy and Watt and NRTL sorption models allowed to well describe the vapour sorption experimental data.

The supported ionic liquid membranes (SILMs) were prepared by impregnation of the porous poly(vinylidene fluoride) (PVDF) membrane with the synthesized ILs. The sorption capacity of PVDF was found to increase after its swelling in IL. An experimental evaluation of the SILMs permeability was carried out for water, ethanol and cyclohexane. The effect of operation parameters such as temperature and concentration of the permeant was studied. It was observed that the presence of the IL strongly influenced the permeability performance of the membrane by reducing the pore sizes and changing the hydrophobic/hydrophilic balance. It is found from the permeation kinetics curves that the SILMs have high potential for separation of organic solvent/water mixtures.

1. Introduction

Membrane technology is one of the most important topic in today's research and practical use. Liquid membrane processes have been suggested as a clean technology due to the following characteristics: high selectivity, high intensity and productivity as well as low emissions and low energy requirements [1]. Besides, higher liquid phase diffusivity allows to improve significantly the permeability compared to most solid state counterparts. Thus, the use of liquid membranes arouses interest for the separation technology [1–5].

The supported liquid membranes (SLMs) may be prepared by porous substrate swelling in the liquid transport media. The transport of components between the two bulk phases separated by the membrane is a continuous process with the stationary membrane phase. Despite the very promising perspectives, the SLMs are used only on a very limited practical scale. This fact originates from the lack of stability of such kind of membranes under long-term application [3,4], caused by removal of the liquid phase filling the membrane pores. The removal is caused by solubility of the liquid phase in the adjacent aqueous solutions and/or by different pressures on the two opposite sides of the membrane. The consequence of this loss is the fact that either the

permeability of the membrane is reduced or the liquid membrane function disappears.

Several methods have been developed to overcome the instability problems of the SLMs, among them the gelation of the liquid membrane phase [6], the application of thin polymer layers on top of porous membranes by means of interfacial polymerization [7], etc.

The ionic liquids (ILs) are a new generation of extractants that are formed by a nanosymmetrical or unsymmetrical organic cation such as imidazolium, *N*-alkylpyridinium, alkylphosphonium, etc. and an inorganic or organic anion such as halides, nitrate, tetrafluoroborate, trifluoromethylsulfonate, etc. The ILs exhibit unique properties compared to other compounds, such as relatively high viscosity, very low vapour pressure under ambient conditions, and high thermal stability (over 300 °C). Depending on the anion and substitute groups of cation, the ILs can solubilize alcohols, alkyl halides, carbonyl compounds and transition metal complexes [8]. So, the ILs are considered as an interesting and clean alternative to volatile organic solvents [5,8].

Taking all foregoing into account, one can conclude that the supported ionic liquid membranes (SILMs) have an advantage over the other SLMs due to the ILs negligible loss through vaporization. The developments in forming SLMs based on ILs seem to be very promising

[9–17]. It has been shown that the SILM based on Nylon® and 1-butyl-3-methylimidazolium tetrafluoroborate is successfully used in the selective separation and demonstrates the excellent stability after a week of operation using *n*-hexane/*n*-hexane and *n*-hexane/*tert*-butyl methyl ether as surrounding phases, feeding and receiving, respectively [11]. However, when *n*-hexane/dimethyl sulfoxide (DMSO) is used as a contacting phase, almost all IL is lost out of the membrane. The decrease of the SILM stability is explained by the increase of the polarity of the solvent used as a receiving phase. Matsumoto et al. used the SILM based on 1-*n*-butyl-3-methylimidazolium hexafluorophosphate for the aromatic hydrocarbon (benzene, toluene, *p*-xylene) separation [17]. They found that the selectivity of aromatic compounds was greatly improved following the order of the increasing hydrophobicity of the ILs. It was assumed that the permeation rate was controlled by the distribution step from the feed to the membrane solution. Izák et al. compared the diffusion coefficient of butan-1-ol in polydimethylsiloxane (PDMS), PDMS/1-ethenyl-3-ethylimidazolium hexafluorophosphate and PDMS/tetrapropyl-ammonium tetracyanoborate membranes [18]. They came to the conclusion that the incorporation of the ILs in PDMS film improved the diffusion coefficient of butan-1-ol in PDMS and that the maximum enrichment factor of butan-1-ol reached 12. The significantly better separation characteristics of PDMS/IL membranes may be explained by the fact that the IL forms the narrow channels inside PDMS and the transport of buthan-1-ol through the membrane is realized through them. The embedding of 1-butyl-3-methylimidazolium tetrafluoroborate in poly(vinylidene fluoride hexafluoropropene) (PVDF-HFP) membrane enhanced the separation performance for ethyl acetate/water mixtures – the increase of the separation factor from 75.8 to 143.9 for the membranes with 0 and 5 wt.% of IL, respectively, was observed [19]. The SILM containing 1-butyl-3-methylimidazolium hexafluorophosphate demonstrated remarkable selectivity for the separation of secondary and tertiary amines [20]. The same membrane showed good long-term stability and selectivity (15–25 depending on the sample feed rate) for the separation of toluene and cyclohexane with a transmembrane pressure of about 1 bar [13]. The SILMs are particularly promising for the separation of carbon dioxide from industrial gas mixtures [4,5,10,14,16,21]. The high solubility of CO_2 in the ILs results from the formation of the weak Lewis acid/base complex with CO_2 acting as an electron-pair acceptor for the cation of the IL and with the anion of the IL as an electron-pair donor [14]. The compatibility within different ILs also affects the solubility of carbon dioxide. The use of the ILs with free amine groups (1-(3-aminopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide or trifluoromethylsulfonate) facilitates the transport of carbon dioxide through the SILMs resulting in selectivity values > 100 for the separation of CO_2 and methane and > 15 – for CO_2 and hydrogen [21,22]. One can say that the results already obtained for the SILMs are quite favourable in terms of selectivity characteristics and membrane stability compared to the traditional SLMs.

The aim of the present work is to assess the efficiency of several SILMs based on PVDF in the organic solvent/water separation. For this purpose, 1-*n*-alkyl-3-methylimidazolium tetrafluoroborate (*n* = 4, 6–8, 12) ILs were synthesized and their spectral properties as well as thermal stability were analyzed. The water vapour sorption measurements of the ILs were performed in order to evaluate their hydrophilic/hydrophobic character. Also, organic (ethanol and cyclohexane) vapour sorption characteristics of the ILs were determined as a function of the IL structure and the vapour sorption behaviour was described from the modelling of the sorption isotherms. The SILMs were prepared by impregnation of the commercial porous PVDF membrane with synthesized imidazolium-based ILs. The vapour permeation flux through the SILM was measured and analyzed in order to evaluate the SILM performance for separating organic solvent/water mixtures.

Table 1
Synthesized 1-*n*-alkyl-3-methylimidazolium tetrafluoroborate ILs.

Name	Abbreviation	Structure	Molecular weight, g/mol
1-butyl-3-methylimidazolium tetrafluoroborate	BMIM-BF₄		226.02
1-hexyl-3-methylimidazolium tetrafluoroborate	HexMIM-BF₄		254.08
1-heptyl-3-methylimidazolium tetrafluoroborate	HepMIM-BF₄		268.10
1-octyl-3-methylimidazolium tetrafluoroborate	OMIM-BF₄		282.13
1-dodecyl-3-methylimidazolium tetrafluoroborate	DMIM-BF₄		338.23

2. Experimental

2.1. Materials

PVDF polymer porous membrane from Millipore™ was used as a support for the SILM. The polymer membrane was 70% porous with the nominal pore size of 0.45 µm and the thickness of 125 µm. 1-methylimidazole (> 99.0%, Fluka), 1-bromobutane (> 99.0%, Sigma-Aldrich), 1-chlorohexane (> 99.5%, Fluka), 1-chloroheptane (> 95%, Fluka), 1-bromooctane (> 99%, Fluka), 1-bromododecane (> 97%, Aldrich), tetrafluoroboric acid (50% in H_2O, Fluka), ethyl acetate (> 98%, Fluka), absolute ethanol (> 99.8%, Sigma-Aldrich), cyclohexane (> 99.0%, Sigma-Aldrich), dichloromethane (> 99.8%, Fluka) and sodium sulfate (anhydrous, > 99.0%, Sigma-Aldrich) were used as received without any additional purification. Ultrapure deionized Milli-Q® water (18.2 MΩ·cm, Millipore®) was used.

2.2. Synthesis of the ILs

The studied ILs (Table 1) have been synthesized according to the procedure described in [23]. The ILs were characterized qualitatively for purity by NMR spectroscopy (see Supporting information).

2.3. Preparation of the SILM

The SILMs were prepared by placing the PVDF membrane into a container with the ionic liquid. The membrane was allowed to swell in the IL for at least 5 h. It has been shown previously that this period of time is sufficient enough to fill the membranes' pores completely. The SILM was then removed from the container and the IL excess was eliminated by blotting.