Journal of Membrane Science 518 (2016) 178–191

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Scalable application of thin film coating techniques for supported liquid membranes for gas separation made from ionic liquids

Judith Grünauer [a], Volkan Filiz [a,*], Sergey Shishatskiy [a], Clarissa Abetz [a], Volker Abetz [a,b]

[a] Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany
[b] University of Hamburg, Institute of Physical Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form
29 June 2016
Accepted 4 July 2016
Available online 5 July 2016

Keywords:
Ionic liquid
Supported liquid membrane
Thin film coating
Landau-Levich equation
CO_2 separation

ABSTRACT

The application of commercial polyacrylonitrile (PAN) membranes as matrix material for ionic liquids (ILs) for gas separation tasks is reported and morphological characteristics for supported liquid membrane stability are discussed. The compatibility of membrane components was investigated and two thin film coating techniques, dip coating and spin coating, were compared. The dip coating technique has proven to fulfill the requirement of membrane stability, as well as pin-hole free coating and thin coating thickness. The thickness of the ionic liquid layer in the membrane could be assessed by means of a modified Landau-Levich approach. Overall liquid membranes supported by PAN with a narrow pore size distribution achieved remarkably good results especially in combination with 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) ionic liquid and are showing the way to commercially scalable supported liquid membrane application.

1. Introduction

The consumption of fossil fuels for energy production is still one of the most significant sources for CO_2 exhaust [1] and contributes decisively to global warming. Therefore research efforts have to provide new perspectives for efficient handling of stationary CO_2 emission. Although the question of CO_2 storage or other methods of utilization is not yet answered conclusively, it is crucial to develop powerful separation processes in order to separate CO_2 from other gases such as nitrogen to facilitate efficient storage efforts [2,3].

One option for the separation is the application of membranes suited for gas separation tasks. Of particular interest are polymeric membranes because they are easy to produce, at low cost [4] and they can be tuned according to the separation process requirements. But there is a limitation for the application of polymeric membranes which is namely the “Robeson upper bound” [5] revealing a tradeoff between permeability and selectivity. Numerous research attempts have been undertaken to overcome this boundary mainly by introduction of solid or liquid filler materials in order to either boost selectivity [6] or permeability [7] beyond the limits of the Robeson upper bound.

A method to maintain high permeabilities for CO_2 and improve the selectivity for CO_2 at the same time is the use of nitrogen atoms containing liquids as filler materials. The filler can be introduced as a blend component or only in case of liquids fillers as a main gas transfer medium in the pore of porous membranes. The resulting membrane then is called supported liquid membrane (SLM).

The lone electron pair of the nitrogen atom of e.g. liquid amines interacts with CO_2 [8] and establishes therefore a specific interaction with the quadrupole of CO_2. This effect leads to high CO_2 solubility as well as good diffusion due to the low viscosity of the liquid. Nevertheless amines have a number of shortcomings including the requirement of high temperature for regeneration, their corrosive nature, a mostly low boiling point that leads to material losses and a limited number of regeneration cycles because of amine degradation in the presence of water and air.

Powerful alternative to amines are ionic liquids (IL). These are organic compounds, which have a salt-like structure, although they are liquid at room temperature [9]. Due to their ionic nature ionic liquids do not evaporate and have found commercial applications as surfactants or lubrication agents, as charge transmitters or as so-called “green” solvents. Often their cation is a quaternary amine, an imidazole or pyridine. Commonly used anions are halogenides, BF_4^-, PF_6^- or NO_3^- but a number of other structures are also known. The optimal choice is mainly influenced by the application since they can be tuned towards the desired functionality [10]. With regard to CO_2/N_2 separation quaternary amines will not serve well due to the absence of the lone electron pair at the nitrogen atom. Therefore mostly imidazole-based ionic liquids are under investigation since their permselectivity can be as high

---

* Corresponding author.
E-mail address: volkan.filiz@hzg.de (V. Filiz).

http://dx.doi.org/10.1016/j.memsci.2016.07.005

as 60 [11].

The application of ionic liquids in membrane technology is mainly limited to the supported SLM concept [12–14] or as blend material dispersed in a polymer matrix [15]. But so far no industrial application for ILs in membranes is reported. This could be ascribed to the still pending stability concerns during operation [16–18] as well as the lack of suitable coating mechanisms, since most conventional SLM preparation processes employ non-continuous methods [19–21].

A number of commercial and non-commercial porous membranes [22] have been tested for their application as SLM matrix. Poly(vinylidene fluoride) and polyethersulfone [23] based ultra- and micro-filtration membranes are among the most common. A material that has not been in the discussion for SLM yet is polyacrylonitrile (PAN) [24]. PAN is known to be chemically stable and ultrafiltration membranes can be obtained via the phase inversion process. [25]. PAN membranes are on many occasions used as microporous support for thin film composite membranes [26,27]. By choice of solvent(s) and process parameters the pore size and pore size distribution as well as the tendency to form “fingerlike” cavities (macrovoids) or a spongy substructure can be tuned [28]. Due to the more polar nature of PAN [29] compared to polypropylene or poly(vinylidene fluoride) it can be assumed that the compatibility with ionic liquids is good and this is an important consideration to achieve distinctive stability characteristics [30].

In a previous work of our group [31] it was shown that the combination of ionic liquids and porous polymeric membranes gives stable SLMs. For the sake of this investigation the matrix material was changed from an isoporous membrane material to a commercially available membrane (PAN) to assure a good scale up potential. Nevertheless the layer thickness of the liquid in the porous support was too high resulting in low membrane permeance not fit for practical application [33] but having selectivities close to the ideal values. Hence the thickness of these SLM comprises the whole porous structure of 30 μm or even more and was not like in integral-asymmetric membranes consisting of only a few hundred nanometers [32]. Therefore the membrane permeance was too low for practical application. The solution to this problem is a significant reduction of the IL layer, in an ideal case close to values characteristic for modern thin film polymeric composite membranes [34]. Nevertheless, it must be emphasized that the charging of the matrix has to be as reproducible as possible to assure uniform performance. In this work ILs with good selectivities and superior gas transport properties were investigated. Important for the selection was also the low viscosity to promote the potential coating success.

In order to identify a robust filling method it is advisable to have a look into frequently used coating technologies for polymer thin film coating. The viscosity of the coating solution is a limiting factor for the choice of deposition. Well qualified for low viscosity thin film coatings are inkjet printing, spin coating, gravure coating and dip coating just to mention the most prominent. [35]. Not all of them have been discussed with regard to ILs and most of the coating techniques have addressed the issue of dense film coating. In beads preparation for CO_2 removal also spray coating of ionic liquids was discussed [36] but it is unclear which degree of homogeneity can be achieved.

Many researchers have reported spin coating for the production of thin films. Mostly it is utilized for membrane production on a laboratory scale [37]. However, the widest spread application of spin coating is the deposition of thin layers in electronic applications [38] such as layer fabrication for organic light emitting diodes on rigid or flexible substrates. Existing research showed the applicability for the deposition of thin IL films onto wafer and was to investigate tribological characteristics [39] or lubrication potential [40] but no membrane application.

Dip coating on the other hand is an equally well-established coating technique for example for sol-gel coating to meliorate glasses. Frequently it is executed on a rigid substrate [41] and it is considered as a non-continuous process [42] but it can be transferred to a role based process [43,44]. Generally, dip coating can be applied in a wide range of viscosities and coating speeds [45]. This process is widely used in production of thin film composite membranes giving the possibility to obtain continuous defect free layers on the surface of porous and non-porous supports with characteristic thickness ranging from several μm down to 50 nm [46]. Several studies have documented that dip coating can be used for the coating of ILs on dense substrates [40,47].

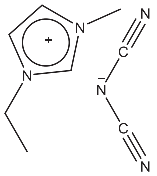
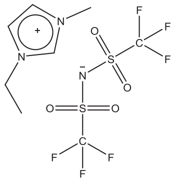
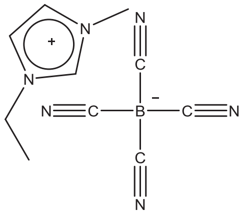
Both coating techniques have not yet been considered for thin film deposition of IL for the fabrication of SLM based on porous polymeric membranes. The aim of this study is to explore the applicability of spin coating and dip coating for the deposition of ILs. This work will provide a coherent procedure for solute-assisted thin film deposition of ionic liquids onto a porous substrate and thereby provide stable gas separation membranes. Aspects regarding the stability as well as membrane morphology will be covered. Furthermore, a theoretical framework to assess the thickness in IL thin film coating on porous substrates will be presented.

2. Materials

Ionic liquids (Tab. 1) 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM Tf2N), solvents and other chemicals were purchased from Sigma-Aldrich Chemie GmbH and used as received, unless otherwise noted. 1-Ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB) was purchased from Merck. No additional drying steps of the ILs were undertaken prior to use. Their purity was given with ∼98%. Characteristic features of the ionic liquids are presented in Table 1.

The polyacrylonitrile (PAN) membranes were produced in house from the same polymer batch (∼300.000 g/mol) [53] with

Table 1
Ionic liquids used in this study and their physical properties.

Abbreviation	Structure	Molecular mass (g/mol)	Viscosity 25 °C (cP)	Density 25 °C (g/ml)
EMIM DCA		177.1	21[48]	1.10[49]
EMIM Tf2N		391.3	37[50]	1.51[49]
EMIM TCB		226.1	15[51]	1.04[52]