Journal of Membrane Science 470 (2014) 494–503

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Investigation of gas permeation properties of film forming polymeric ionic liquids (PILs) based on polybenzimidazoles

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A R T I C L E I N F O

Article history:
Received 11 May 2014
Received in revised form
26 July 2014
Accepted 30 July 2014
Available online 6 August 2014

Keywords:
Polymeric ionic liquid
Polybenzimidazole
Gas permeation
Membranes for CO_2 separation

A B S T R A C T

Polymeric ionic liquids (PILs) are emerging as new generation membrane materials for CO_2 separation. Gas permeation properties of a recently developed PIL family based on three structurally different polybenzimidazoles (PBIs) possessing excellent film forming characteristics are reported. Effects of cationic backbone and anions on gas permeation properties of PILs using pure gases (He, H_2, N_2, CH_4 and CO_2) were examined at 20 atm upstream pressure and correlated with their physical properties. In comparison to the parent PBIs, PILs exhibited generally higher CO_2 permeability, without largely affecting CO_2 based selectivity. Some of these PILs exhibiting high P_{CO_2}/P_{CH_4} selectivity and P_{H_2}/P_{CO_2} approaching ~1 indicated dominance of CO_2 sorption over diffusion. The CO_2 sorption specificity of these PILs was distinctly observed based on their improved S_{CO_2}/S_{N_2}, S_{CO_2}/S_{CH_4} and S_{CO_2}/S_{H_2} selectivity than their parent PBIs. A large variation in permeation properties of PILs based on a common polycation but different anions indicated that anions play a crucial role on governing gas permeation properties of these PILs.

1. Introduction

The global warming due to the increased atmospheric CO_2 concentration resulting from fossil fuel consumption is becoming an important environmental issue today [1]. Carbon capture and storage (CCS) from large point sources such as power plants is one of the options for reducing anthropogenic CO_2 emission; however, currently the capture alone will increase the energy requirements of a plant. [2]. Several techniques such as absorption, adsorption, cryogenic distillation and membrane-based separation have been proposed for the CO_2 capture [3]. Although this has been studied extensively, exploration of more convenient and feasible methods for CO_2 capture remains a challenging pursuit [4]. Traditional CO_2 capture by chemical absorption using aqueous amine solutions is highly energy intensive, owing to the thermodynamic properties and high enthalpy of absorption [5,6]. If conventional aqueous monoethanolamine (MEA) technology is to be applied to postcombustion CCS processes at coal-fired power plants, it is estimated that power output would likely drop by 30% or more, driving down efficiencies while significantly increasing the cost of energy [7]. In this context, development of newer materials for techno-economic CO_2 separation becomes highly important [4,8]. Such new material development would be helpful not only for CO_2 capture from the flue gas, but also in other applications such as natural gas sweetening, enhanced oil recovery, water gas shift reaction, etc. In some of these applications, membrane based separation processes are proved to be advantageous over conventional processes due to their operational simplicity, high reliability, light weight and modular nature leading to easy scale-up, lower capital costs and most importantly, environment friendly nature owing to the physical nature of separation (except for membrane contactors, where physical nature of separation may not be applicable) [3,9–12]. A long term sustainability of the membrane material while maintaining its high CO_2 selectivity under different environmental conditions is a major challenge and needs to be addressed in order to make the membrane based processes techno-economically viable.

CO_2 permeation through polymeric membranes largely relies on its interactions with the membrane material. In the recent literature, ionic liquids (ILs) are shown to possess high CO_2 sorption and are being proposed as the promising CO_2-selective separation media [1,4,8]. Although IL based supported membranes have been demonstrated, they possess serious drawbacks such as poor stability (IL drain) leading to inadequate long-term performance and operations possible only at low pressures [12–15]. In order to overcome these drawbacks, incorporation of IL character in polymer backbone is emerging as a promising option. These new generation materials, viz., ‘polymeric ionic liquids’ (PILs) exhibit good CO_2 sorption, faster adsorption–desorption rates than ionic liquids and appreciable thermal stability [1,4,15–17]. Unfortunately, most of the demonstrated PILs are based on aliphatic

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http://dx.doi.org/10.1016/j.memsci.2014.07.076
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backbone and either are unable to form film due to brittle nature [1,18–20] or obtained membranes could be evaluated only at lower pressures of ~2 atm [14,18,19,21,22]. Efforts are on towards transforming them into a membrane by employing methodologies such as crosslinking or copolymerization for their effective testing into a flat film form [19]. A mechanically stable membrane was obtained by grafting polyethylene glycol (PEG) on to PILs [18]. Casting of the IL monomer on a porous polymer support followed by its UV polymerization is also reported [10,19]. Gas separation performance of the resulting membranes could be measured at only low pressure (~1–2 atm upstream pressure) owing to their fragile nature. Li et al. have prepared composite membrane of PIL and IL by using crosslinking methodology [12]. The attempted approaches towards obtaining film forming PIL led to reduced IL group density per repeat unit of a PIL, low pressure-withstand ability of formed films and generally known lowering of permeability by crosslinking of a polymer. These limitations dictate a need of an alternate approach for synthesizing PILs so that benefits of incorporating IL character into them could be better extracted.

We have recently demonstrated an altogether different methodology of obtaining film forming PILs possessing rigid and fully aromatic backbone [23,24]. The *N*-quaternization of polybenzimidazoles (PBIs) by methyl iodide followed by its metathesis (anion exchange reaction using Ag/Li salt of anions of interest) offered quantitative anion exchange. Obtained PILs possessed excellent film forming ability (except those based on Ac^- and Bz^- as anions) with appreciable mechanical properties, enhanced solvent solubility (than their parent PBI), appreciable thermal stability, highly attractive CO_2 sorption and CO_2 permeability [23,24]. They were amorphous, in spite of possessing distinct ionic character. This is a niche characteristic for evaluating their gas permeation property, as it is well known that crystalline domains present in a polymer are impermeable [25]. The CO_2 solubility coefficients of these PILs were placed distinctly above than those of reported PILs [23]. Obtained results conveyed a need for detailed permeation property analysis of this new family of PILs. Such analysis would involve not only permeation, but also sorption and diffusion characteristics of different gases, which became objective of the present work. PILs based on three structurally different PBIs (viz., PBI-I, PBI-BuI and ABPBI) and different promising anions were evaluated for understanding effects of variations in their cationic backbone and anions on gas sorption and permeation properties.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine (DAB, 99%), 3,4-diaminobenzoic acid (97%), isophthalic acid (IPA, 99%), 5-*tert*-butylisophthalic acid (BuI, 98%), sodium hydride (60 % dispersion in mineral oil), dry dimethyl sulfoxide (DMSO, 0.01% H_2O, 99.9%), silver tetrafluoroborate ($AgBF_4$, 99.99%), lithium bis(trifluoromethane)sulfonimide ($LiTf_2N$, 99.95%), silver acetate (CH_3COOAg, 99%), silver trifluroacetate (CF_3COOAg, 98%), silver heptaflurobutyrate (C_3F_7COOAg, 97%), silver benzoate (C_6H_4COOAg, 99%), silver methanesulfonate (CF_3SO_3Ag, 99%), silver trifluromethanesulfonate (CF_3SO_3Ag, 99.95%), silver *p*-toluenesulfonate ($C_6H_4CH_3SO_3Ag$, 97%) and silver nitrate ($AgNO_3$, 99.99%) were procured from Aldrich Chemicals, Germany. The polyphosphoric acid (PPA, 84% P_2O_5) was procured from Alfa Aesar, USA. The methyl iodide (99%), potassium thiocyanate (KSCN, 98%) and sodium chloride (NaCl, 99%) were procured from S.D. Fine Chemicals, India. Pure gases, viz.; He, H_2 and N_2 (minimum purity of 99.9%) were procured from Vadilal Chemicals Ltd. India, while CH_4 and CO_2 (99.995% purity) were procured from Air Liquide, USA.

2.2. PIL synthesis and membrane preparation

Polybenzimidazoles were synthesized by polycondensation reaction of DAB and isophthalic acid (PBI-I) or 5-*tert*-butylisophthalic acid (PBI-BuI) as reported earlier [26]. A self-condensation of 3,4-diaminobenzoic acid (DABA) offered ABPBI [27]. The detailed procedure for PBI synthesis is given in the Supporting information. The *N*-quaternization of PBI-I, PBI-BuI and ABPBI was performed as reported earlier [24]. Polymeric ionic liquids (PILs) were obtained by metathesis (exchange of iodide anion of a quaternized PBI by another anion of interest, as given in the Supporting information).

The dense membranes of PILs were prepared by solution casting using 3% (w/v) DMAc solution (except for [TMPBI-I][I], in which case, the solvent was DMSO) at 80 °C for 18 h under dry condition on a flat glass surface. After initial evaporation of the solvent, formed membrane was peeled off, dried in a vacuum oven at 100 °C for a week and stored in the desiccator till further use (average thickness: 34–40 μm).

2.3. Gas permeation and sorption

The permeability measurement using pure gases (He, H_2, N_2, CH_4 and CO_2) was carried out by a standard variable volume method at upstream gas pressure of 20 atm and at 35 °C; while maintaining the permeate side at the atmospheric pressure [26]. Membrane samples (5 cm in diameter) after removing from the vacuum oven were immediately mounted in the permeation cell. The gas permeability was calculated using the following equation:

$$P = \frac{Nl}{(p1 - p2)} \tag{1}$$

where '*P*', the permeability coefficient, is expressed in Barrer, '*N*' is the steady-state penetrant flux (cm^3/cm^2 s), 'p_1' and 'p_2' are the feed and permeate side pressures (cm Hg), while '*l*' is the membrane thickness (cm). The permeability measurements were repeated with at least 4 different membrane samples prepared under identical conditions and the data averaged. The variation in permeability from the average was maximum 15%, depending upon the gas analyzed.

The pure gas sorption isotherms using H_2, N_2, CH_4 and CO_2 were obtained at 35 °C using an equipment that consisted of the dual-volume, single-transducer set up based on a pressure decay method [28,29]. The estimated uncertainty of this setup is up to 1.7% [29]. The gas sorption is described by Eq. (2). The dual mode sorption parameters (k_D, b and C'_H) were determined by non-linear regression analysis of the experimentally determined data at varying pressures up to 20 atm [29]

$$S_A = \frac{C}{p} = K_D + \frac{C'_H b}{(1 + bp)} \tag{2}$$

where C is gas concentration in the polymer, p is the applied gas pressure, k_D is Henry's solubility coefficient, C'_H is the Langmuir saturation constant and b is the Langmuir affinity constant. The solubility coefficient (S) and solubility selectivity (S_A/S_B) were determined at 20 atm. The permeability coefficient for a particular gas along with its solubility coefficient at 20 atm was used to estimate the diffusivity coefficient ($D_A = P_A/S_A$).

3. Results and discussion

3.1. Gas permeation properties

All PIL membranes sustained high upstream pressure (20 atm) during their gas permeation analysis. Such high pressure sustainability