Journal of Membrane Science 459 (2014) 264–276

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Mixed gas sorption in glassy polymeric membranes: II. CO_2/CH_4 mixtures in a polymer of intrinsic microporosity (PIM-1)

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ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form
22 January 2014
Accepted 4 February 2014
Available online 11 February 2014

Keywords:
PIM-1
Intrinsic microporosity
Gas transport
Solubility
Mixed gas

ABSTRACT

The individual solubility of CH_4 and CO_2 from binary gas mixtures was measured at 35 °C and up to 35 bar in a polymer of intrinsic microporosity (PIM-1), at different compositions of the gas phase (from 0 to 50 mol% of CO_2). The experiments were conducted on a pressure-decay apparatus equipped with a gas chromatograph, allowing a highly flexible measuring procedure. The gas solubility was plotted versus gas phase composition, total pressure, gas fugacity and second gas concentration. The mixed gas solubility of both species, CH_4 and CO_2, is lower than the pure gas value at the same fugacity, but the reduction of methane solubility due to the presence of CO_2 is generally more significant. Such behavior is due to the fact that CO_2 has normally higher solubility than methane: indeed the depression of the solubility coefficient with respect to the pure gas value is similar for both gases, when reported at the same concentration of the second gas. The real, mixed gas solubility selectivity is in general higher than the ideal value calculated from pure gas behavior. The ratio between real and ideal solubility selectivity increases with CO_2 concentration in the membrane, according to a single mastercurve, reaching a maximum value of 4, and it also increases with the ratio between CO_2 and CH_4 concentration in the membrane. In particular, as in the case of other glassy polymers, the real solubility selectivity of CO_2 over CH_4 is higher than the ideal value if $c(CO_2) > c(CH_4)$, and it is lower than the ideal value if the opposite condition holds true. Such behavior occurs because the competition for sorption is normally less effective on the more abundant penetrant in the polymer. A selectivity–solubility performance plot can be drawn for this system.

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1. Introduction

The separation and removal of carbon dioxide from methane gaseous streams is a process of extreme industrial importance. Such a separation is required in natural gas or biogas treatment in order to increase the heating value and reduce the volume of gas to be transported. In the past two decades, the application of membranes to the removal of CO_2 from methane, e.g., in natural gas and biogas processing, has been under the attention of membrane scientists [1–4]. Membrane technology may be more advantageous than conventional absorption of acid gases in basic solvents, and pressure swing adsorption (PSA), for small-to-medium scale separations and those not requiring stringent product purity. In particular, it is highly desirable to explore membrane materials which can selectively remove CO_2 from gas mixtures, thereby maintaining CH_4 at or near feed pressure to avoid gas recompression [1,2].

The performance of a polymeric membrane for gas separation is expressed by its gas permeability and gas pair selectivity, which must be considered together with other important factors such as chemical and mechanical resistance [5]. The determination of permeability and selectivity of membrane materials in conditions as close as possible to the real operating conditions is essential for the design of membrane separation processes of gaseous mixtures and to identify the most appropriate range of conditions, and also to understand the fundamental mechanisms governing the transport processes. To this aim, it is important to point out that the interactions between gases play an important role in membrane gas separation, especially when swelling and/or polar gases are considered, and the transport parameters measured from pure gas experiments often differ significantly from those measured in the mixed gas state [6]. Therefore, the gas transport parameters required for the design of membrane separation processes must

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http://dx.doi.org/10.1016/j.memsci.2014.02.003
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be measured or estimated in mixed gas conditions. Consequently, several works report permeability of gases from multicomponent gas mixtures, in promising membrane materials [7–12].

Gas permeability in dense membranes is the product of the solubility and diffusivity contributions, as the permeation process requires dissolution of the gas inside the solid phase, together with diffusion through the polymer matrix under a driving force. Selectivity in a binary gas mixture is the product of solubility selectivity, dependent upon the different sorption levels of each gas inside the matrix, and diffusivity selectivity, which is essentially associated with the different sizes of each gas penetrant. These two factors can have different relative importance, depending upon the polymeric membrane material considered. In low-medium free volume glassy polymers, the most relevant contribution is diffusivity selectivity, and correspondingly these polymers are more permeable to the smaller molecules. However, there is an entire class of more novel polymeric materials, characterized by high free volume values, which shows the opposite behavior, with little size sieving character and more predominantly solubility selective. This effect may also result in the so-called reverse selectivity, with the larger molecules having higher permeability than the smaller ones. Of course such effects become important when the CO_2/CH_4 gas pair is considered, as these two gases have similar values of the molecular kinetic diameter and therefore the diffusivity selectivity, based on size, is not far from unity. On the other hand, CO_2 has higher condensability than methane, and the solubility selectivity in polymers is favorable to CO_2: such contribution can even be augmented by incorporating functional groups into the polymeric matrix capable of interacting more specifically with CO_2.

According to the Robeson upper-bound trade-off plot, among the membrane materials having the highest performance for CO_2/CH_4 separations are polyimides, PIM-based polymers and PTMSP [5].

In particular, the latter polymers lie in the region of ultrahigh permeability (around 5000 Barrer for PIM-1 and 10,000 Barrer for PTMSP) and low-medium CO_2/CH_4 selectivity (around 18 for PIM-1 and around 4 for PTMSP). The solubility selectivity values reported range from 3 to 5 [13] for PIM-1, and from 2 to 3 in PTMSP, according to the pure gas solubility measurements [14]. The diffusivity selectivity is estimated to be around 5 for PIM-1 and slightly higher than unity (around 1.5) for PTMSP [15].

It is thus clear that the solubility selectivity and diffusivity selectivity have similar weightings in determining the overall selectivity performance: actually in both PTMSP and PIM-1, the pure gas data seem to indicate that solubility selectivity is equal to or higher than diffusivity selectivity for the CO_2/CH_4 couple. It is thus evident that an accurate estimation of the solubility and of the solubility selectivity in these matrices is fundamental to evaluate and explain mixed gas permeation behavior at different operating conditions.

In this study we focus on the behavior of polymers having intrinsic microporosity (PIMs), which are promising materials, having high permeabilities and moderate selectivities [16,17]. For example, a permselectivity of ca. 12–25 was reported for the equimolar carbon dioxide/methane mixture being separated on a PIM-1 membrane at 25 °C up to the pressure of ca. 33 atm [18]. The permselectivity CO_2/CH_4 of a membrane functionalized with pendant tetrazole groups (TZPIM) decreases with the increasing feed pressure and, at the same time, does not reveal significant difference between the ideal and real permselectivity in those conditions [13].

The aim of the present work is to assess, in a wide range of compositions and pressures, the solubility properties of CO_2/CH_4 mixtures absorbed in films of PIM-1. In particular, we study and determine the effect of mixture composition, pressure, second component fugacity and concentration on the solubility and solubility selectivity values, as well as on the deviation from the corresponding pure gas properties.

In our previous work [19] it was shown that the solubility selectivity for CO_2/CH_4 mixed gases in PTMSP can be significantly higher than that evaluated from pure gas conditions, up to 4–5 times. That behavior is due to significant competition between the two penetrants for polymer sorption, which is in favor of the most abundant penetrant, usually CO_2. In PTMSP, pure gas behavior is approximately similar to that of CH_4 mixtures diluted with low levels of CO_2, which may occur in relatively pure natural gases. For CO_2 molar fractions higher than 5–10%, which are present in many natural gas and biogas feed streams, the solubility of methane is much lower than the corresponding pure gas solubility value and the solubility selectivity based on pure gases can be highly underestimated.

It is well known that the measurement of mixed gas solubility and diffusivity is a much more challenging task than the measurement of mixed gas permeability, for which several data have been reported [7–12]. In our previous work we have presented in detail the experimental apparatus used for binary gas solubility [19], that was inspired by the one designed by Sanders et al. [20–22]. The present system relies on a similar layout, which consisted of a pressure decay system combined with chromatographic analysis of the equilibrium gaseous mixture, but applies a novel procedure which makes the system more flexible. In particular, the method allows measurements of the solubility of each component with two different protocols: (i) at constant fugacity (or partial pressure) of one component and variable fugacity of the second component, or (ii) at constant equilibrium composition of the gaseous phase and variable total pressure. The latter set of conditions is more suitable to study the gas separation process, in which the composition of the gas mixture is fixed, and the total pressure of the mixture can be increased by compression.

It must also be mentioned that the values of pure and multicomponent solubility can be properly calculated in a predictive way using the existing models, thus allowing the extension of the observed mixed gas behavior to a range of operating conditions greater than the one investigated experimentally, thereby avoiding or limiting as much as possible delicate and time consuming mixed gas measurements. The experimental data collected in part I and part II of this work will later be used, in part III of this work, to test, validate and compare the performance of two models for multicomponent solubility in glassy polymeric membranes, namely, the dual mode model [23,24] and the Nonequilibrium Lattice Fluid (NELF) model [25–27].

2. Experimental

2.1. Membrane and chemicals

PIM-1 was prepared by polycondensation of monomers 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (Sigma-Aldrich, purified by crystallization from methanol) and tetrafluoroterephthalonitrile (Matrix scientific, purified by vacuum sublimation at 150 °C), following a reported high temperature procedure at 160 °C [28]. The resulting PIM-1 had $M_n = 53{,}000$ Da, measured by GPC, and a polydispersity of 2.2.

PIM-1 membranes were prepared from ca. 2.0 wt% filtered chloroform solutions, which were poured into a fluoropolymer-coated Petri dish and partially covered. Chloroform (Riedel de Haen, stabilised, 99.0–99.4%) was allowed to evaporate slowly from the solution over ca. 3 days under ambient air conditions; the membrane was then placed into a vacuum oven (70 °C) for 24 h. Afterward, the mass of the membrane was checked over time and

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