Journal of Membrane Science 318 (2008) 373–378

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Permeation selectivity of gaseous isotopes through dense polymers: Peculiar behavior of the hydrogen isotopes

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ARTICLE INFO

Article history:
Received 13 October 2007
Received in revised form 28 February 2008
Accepted 2 March 2008
Available online 15 March 2008

Keywords:
Permeability
Isotopes
Gases
Polymers
Selectivity

ABSTRACT

The small but significant difference in permeation rates of gaseous isotopes through dense polymers has been previously reported in several studies. Most results remain, however, restricted to hydrogen isotopes. In this study, the steady-state permeation selectivity of a series of seven different gaseous isotopes pairs (D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{17}O/^{16}O$, and $^{36}Ar/^{40}Ar$), covering a broad range of molecular weights (H_2, N_2, Ar, O_2, and CO_2), has been investigated through two dense polymeric structures (PDMS and PTFE). It is shown that, with the notable exception of the H_2/HD pair, isotope permeation selectivity can be described for each polymer type through a single expression as a function of the relative molecular weight difference. We show, for the first time, that this behavior is consistent with Frisch and Rogers (1964) model. More interestingly, it suggests that the peculiarities of the H_2/D_2 pair, such as the high-relative mass difference or small size, may explain the inadequacy of the gas in a box quantum approach for this case.

1. Introduction

The phenomenon of permeation of gases through dense polymers, given its key implications in numerous industrial sectors, is abundantly documented, both from the experimental and theoretical point of views [1,2]. For gaseous species, the permeability coefficient, defined as a pressure and thickness normalized flux, is best described according to the solution diffusion model [3]. Constant permeability is often observed for permanent gases in rubbery polymers, while a more refined analysis, namely the dual-mode model, is required for the interpretation of permeability variation with high pressure conditions in glassy polymers [4,5]. Several predictive models have been proposed in order to estimate the permeability of a given gas/polymer pair. Expressions making use of the Lennard–Jones potential of the gas are classically proposed for the sorption step, while the kinetic diameter of the gas has been proposed as a key variable for the estimation of the diffusion contribution for permanent gases only. An approach based on this theoretical framework has been shown to give remarkable predictions of the trade-off selectivity (α_P) of permanent gases through rubbery and glassy polymers [6]. A combination of sorption selectivity (α_S) and diffusion selectivity (α_D) is logically necessary in order to achieve that purpose:

$$\alpha_P = \alpha_{2/1} = \frac{P_2}{P_1} = \left(\frac{S_2}{S_1}\right)\left(\frac{D_2}{D_1}\right) \tag{1}$$

While the distinct features, in terms of permeation, of two different gases have been intensively investigated, the permeation of different isotopes in dense polymers is an almost unexplored situation. A large majority of studies in this field remain restricted to the hydrogen isotopes (i.e., a comparison of permeation of hydrogen and deuterium). Moreover, a single polymeric matrix is most often considered for each of these studies [7–15]. A more general comparative study, with different isotopes and different polymeric matrices is lacking. Such a piece of work would be of interest for three main reasons:

(i) To estimate the potential applicability of polymeric membranes for industrial processes which aim at isotope separation (isotope enrichment and production, detritiation, fission or fusion technology, etc.) [16–18].
(ii) To evaluate the incidence of membrane concentration devices for isotope analysis with sampling systems, for instance, for trace elements analysis making use of membrane concentration systems coupled to mass spectrometers [19].
(iii) For fundamental purposes, taking advantage of the fact that isotopes, in some cases radiolabelled, can be used as molecular probes in order to estimate polymer structure or to interpret permeability mechanisms [7–10,14,15].

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0376-7388/$ – see front matter
doi:10.1016/j.memsci.2008.03.011

From the fundamental point of view, isotope effects in dense polymers have been analyzed, to our knowledge, through a single theoretical framework developed by Frisch and Rogers in 1964 [7]. The single quantum particle (i.e., molecule) in a box approach was assumed in order to achieve that purpose. For sake of simplicity, a single cavity size, which can be seen as the average cavity diameter, and infinitely high, non-interacting walls are postulated, in order to take into account the distribution of free volume in the polymeric matrix. The predictions of this approach to the H_2/D_2 pair in numerous polymers show considerable discrepancies with experimental results [8,10,13,14]. Various tentative explanations have been proposed in order to explain these inconsistencies.

(i) An oversimplified expression of the partition function proposed by Frisch and Rogers (square well approximation, inconsistent averaging of the cavity size or non-interacting wall hypothesis).
(ii) A possible difference in size between deuterium and hydrogen, which is not taken into account in the model.
(iii) The necessity to take into account subtle factors involving both size and mass differences in the computation of the diffusional velocities in polymers [14].

Surprisingly, the validity of Frisch model for other gaseous isotopes, including large ones, has not been explored. This type of experiment has, to our knowledge, never been reported, probably because differences between large isotopes are expected to be too small to be experimentally determined [14]. We report hereafter a series of experimental results of permeation of hydrogen, deuterium and larger gaseous isotopes species through two different dense polymeric films. A set of experimental data including the permeation selectivity of seven different isotopes pairs will be reported and discussed.

2. Materials and methods

The experimental set-up used for the experiments is shown in Fig. 1. It consists of a stainless-steel permeation cell where a dense polymer (membrane) film can be inserted using a Viton seal to ensure the air tightness. The polymer film is mechanically supported by an Inox frit (Poral) sufficiently porous in order to assert that its mass transfer resistance is negligible with respect to the experimental conditions. Two different membranes, which correspond to two classical polymeric films, have been used for this work: a polydimethysiloxane (PDMS) film, of 175-μm thickness, provided by Dow Corning (Silastic), and a polytetrafluoroethylene (PTFE, Teflon) film, of 15-μm thickness, provided by Aldrich (Fluorofilm).

Table 1
Isotope pairs investigated in this study and permeation selectivities in PDMS and PTFE

Isotope pair	Relative mass difference $(1 - m_2/m_1)$	α_P at 20 °C in PDMS	αP at 20 °C in PTFE
$^{13}C/^{12}C$ in CO_2	0.0222	1.0029 ± 0.0001	1.0038 ± 0.0001
$^{17}O/^{16}O$ in O_2	0.0303	1.0042 ± 0.0003	1.0063 ± 0.0002
$^{15}N/^{14}N_2$ in N_2	0.0345	1.0040 ± 0.0003	1.0066 ± 0.0001
$^{18}O/^{16}O$ in CO_2	0.0435	1.0061 ± 0.0002	1.0087 ± 0.0001
$^{18}O/^{16}O$ in O_2	0.0588	1.0081 ± 0.0005	1.0124 ± 0.0004
$^{40}Ar/^{36}Ar$ in Ar	0.1000	1.0131 ± 0.0005	1.0200 ± 0.0004
D/H in H_2	0.5000	1.0440 ± 0.0003	1.0535 ± 0.0014

The experimental error which is shown for α_P corresponds to three different measurements.

The isotopes pairs which have been analyzed are summarized in Table 1. Analytical grade gases (H_2, N_2, Ar, O_2, and CO_2 with natural isotope abundances), supplied in cylinders by Air Liquide, were used as model permeants. The experimental protocol was as follows:

- The two compartments of the module, namely the high pressure side (HPS = 36.13 cm^3) and the low pressure side volume (LPS = 29.95 cm^3) and the two sample gas tubes (SHP and SLP) were first evacuated by vacuum pumping for at least 24 h down to a pressure lower than 0.1 Pa. Temperature was maintained around 20 ± 1 °C.

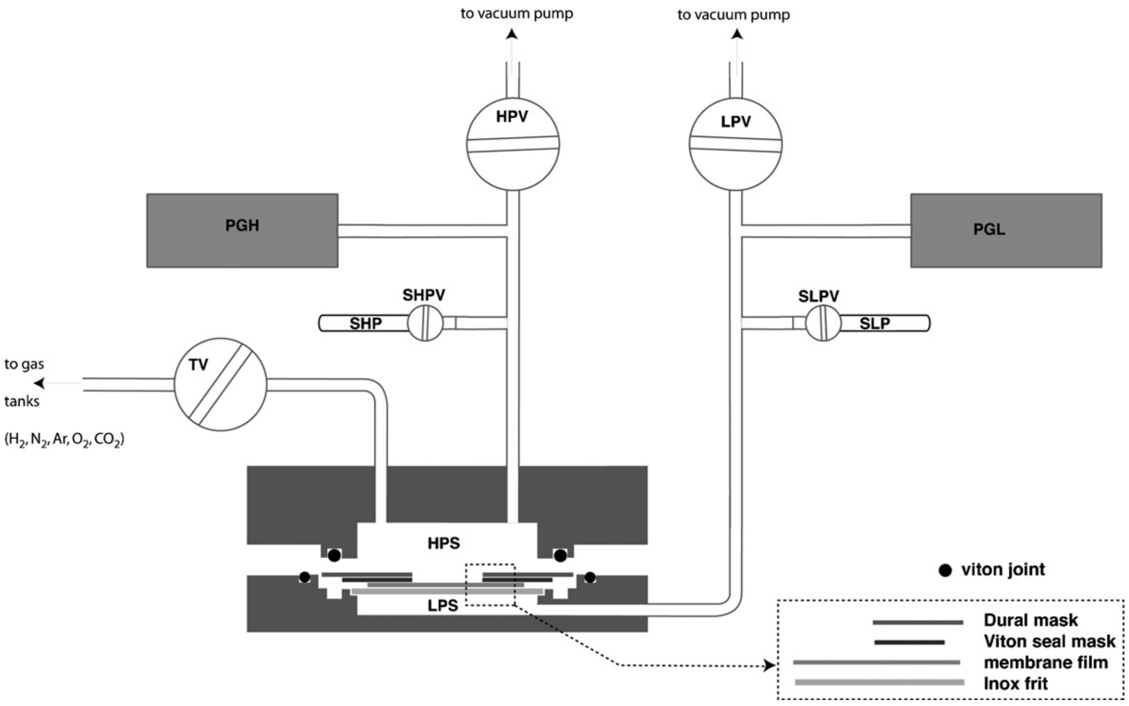

Fig. 1. Experimental set-up.