Journal of Physics: Conference Series **751** (2016) 012042 doi:10.1088/1742-6596/751/1/012042

Regularities of asymmetric gas transfer in PVTMS-membranes

I E Skuridin[1], I M Kurchatov[2] and N I Laguntsov[2]

[1] JSC Aquaservice, Kashirskoe highway 31, Moscow, 115409, Russia
[2] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway 31, Moscow, 115409, Russia

E-mail: aquaserv@mail.ru

Abstract. In this work the dependence of permeability of the polymer asymmetric gas-separation membrane on its orientation relative to the areas of high and low pressure was investigated. It is shown that under different directions of gas supply, permeability values are not the same due to the characteristics of the asymmetry of the object.

1. Introduction

Membrane permeability measured for various gas flow directions may be the same only in the case of identical left and right borders, that is, for symmetric membranes. For asymmetric membranes is commonly observed phenomenon of direct asymmetry, when the flow from the diffusion layer exceeds the flow from the porous support. Typically, the direct effect of permeability asymmetry was observed in ceramic SHS and asymmetric gas separation nonporous polymeric membranes [1]. However, there are objects, where the phenomenon of reverse asymmetry is observed, one of which we discuss in detail in this article. For example, the asymmetry of the gas transfer through PVTMS-membrane has a reverse direction. The phenomenon of reverse anisotropy was firstly observed in [2].

In general, it follows that the measured values of permeability are higher in the case of the gas supply from the side, characterized by a high value of the kinetic factor, i.e. constants ratio of sorption and desorption speeds. The increase of kinetic factor will mean the increase of stationary surface concentration of transported molecules through asymmetric membrane. In turn, the increase of surface concentration due to the sorption differences of the porous support and the film.

2. Main text

Investigated object, on which reverse asymmetry is observed, is an asymmetric gas separation membrane PVTMS. PVTMS is conventionally expressed by three layers: a non-porous diffusion (selective) with a thickness of 70 ÷ 100 nm, fine-pored layer with the thickness 10 ÷ 15 micron and a pore size of 300 nm and a layer with a large (up to 4 mm) transport pores [3]. Thus PVTMS membrane is a gradient porous structure, i.e. medium consisting of a porous layer – support with a thickness change of pore radius and porosity, and non-porous diffusion layer. Diffusion layer and porous support made of the same material. (See. Figure 1).

Journal of Physics: Conference Series **751** (2016) 012042 doi:10.1088/1742-6596/751/1/012042

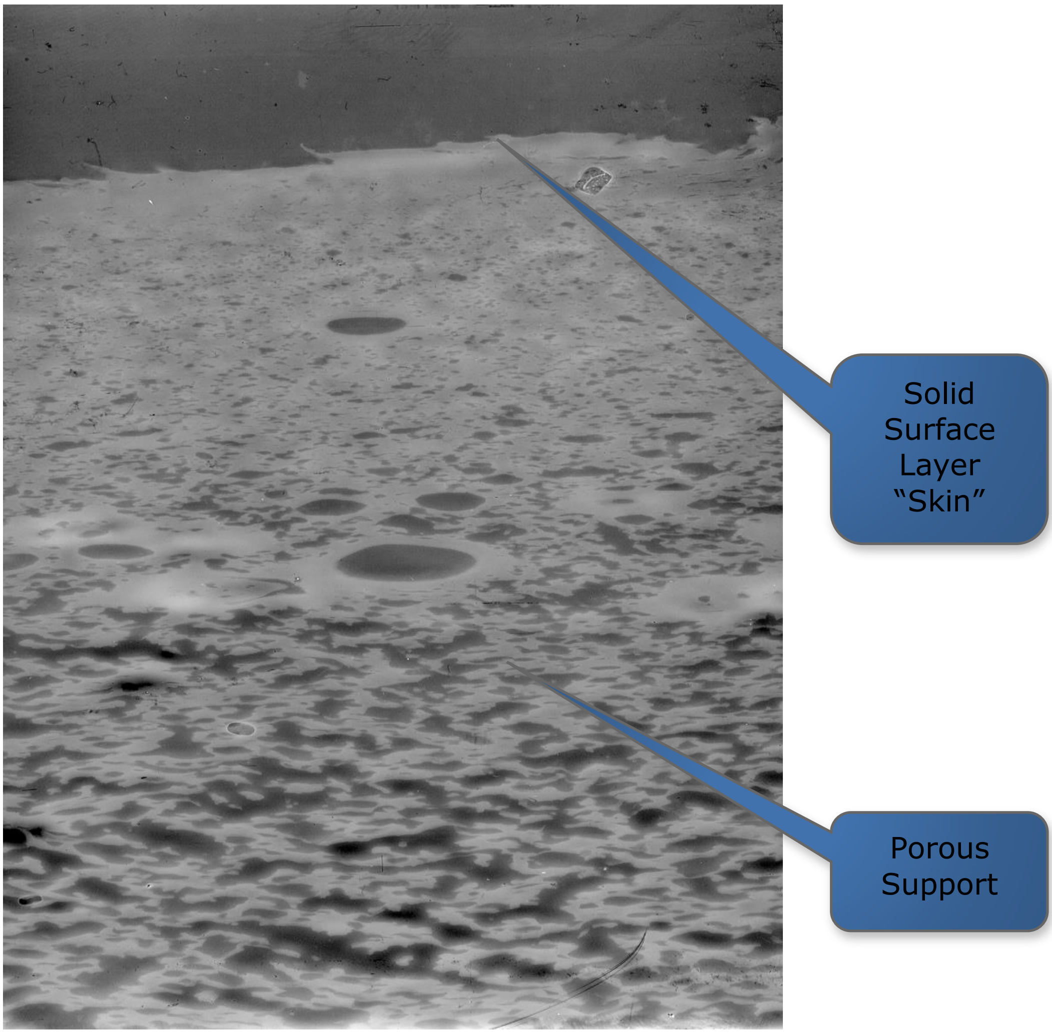

Figure 1. Cross-section view that illustrates the structure of an asymmetric gas separation membrane, made of PVTMS.

This article is devoted to the description of the statistical data of the experimental results using the phenomenological parameters characterizing the process of the transmembrane transport of gases through PVTMS structure.

Test bench in order to determine the permeability of the flat membrane was designed for the experiment. The cell with the flat asymmetric membrane is attached through the gas transportation system of channels with a gas balloons. Cell construction allows performing a series of straight and reverse permeability measurements at different pressures without orientation change of the membrane, that is, the direction of the gas flow, by the use of the electromagnetic valve. For determining the output flow of the membrane system the mass flow sensor with automatic switching depending on the flow is used. Membrane permeability at its different orientation and for different gases can be calculated from the flow values. This method for measuring of permeability is called a differential.

Reverse asymmetry gas transport effect in PVTMS membrane was detected and verified for all gases: N_2, O_2, CO_2, and He, in the pressure range [0.03 - 0.96] MPa, namely. Figure (2) shows the measured values in differential mode for various gas permeability in their forward and reverse feed.

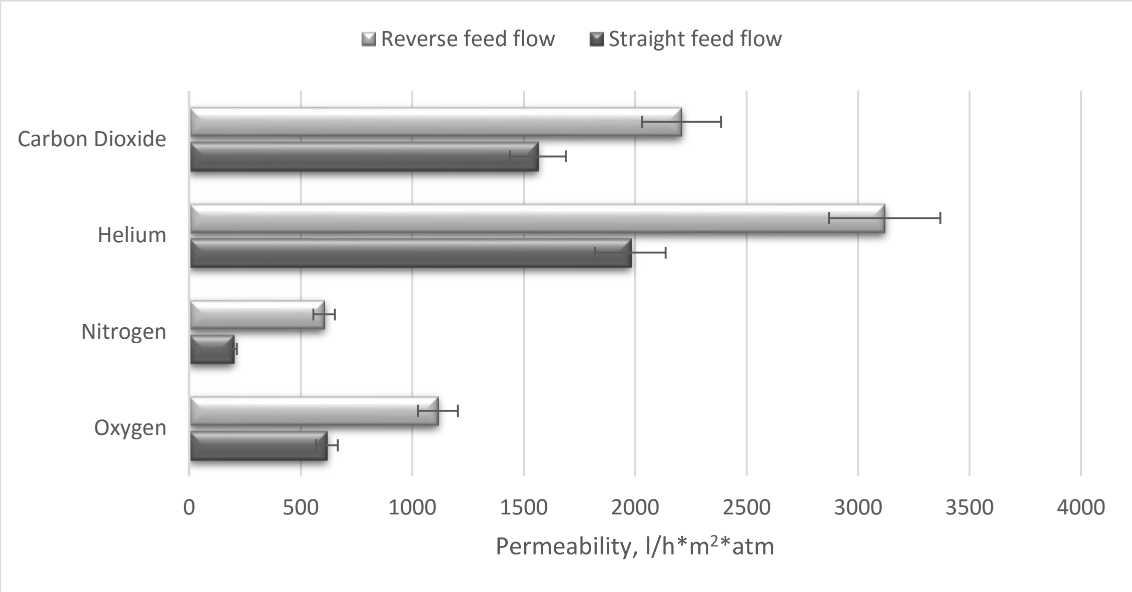

Figure2. Gas permeability values depending on the orientation of the membrane

It should be noted that most clearly reverse asymmetry transport effect appears during the investigation of N_2 transport through the membrane. Gas permeability is essentially independent of the pressure drop generated over a wide range, but for small values of P <2 kPa permeability increases up to a certain value. This change can be attributed to the change of permeability mode, since a transition from a quasi-equilibrium state to disequilibrium with increasing of the pressure drop. The concentration ceases to be determined by its corresponding Henry constant and begins to depend on the state of the polymer surface of the structure [4]. The following Table. (1) shows the calculated values of asymmetry for the transport of gases, ASV, (asymmetry value):

Table. 1 The asymmetry values of selected gases

Gas	O_2	N_2	He	CO_2
Asymmetry value	1,80	3,05	1,57	1,41

Values of selectivity under straight and reverse gas supply to the membrane were also calculated. Results are shown in Table. (2, 3)

Table. 2. Selectivity values under the straight direction of the gas flow (gas is supplied on the diffusion layer).

a (O_2/N_2)	a(O_2/He)	a(O_2/CO_2)	a(N_2/He)	a(N_2/CO_2)	a(He/CO_2)
3,11	0,312	0,394	0,1	0,12	1,266

Table. 3. Selectivity values under the reverse direction of the gas flow (gas is supplied on the porous support).

a (O_2/N_2)	a(O_2/He)	a(O_2/CO_2)	a(N_2/He)	a(N_2/CO_2)	a(He/CO_2)
1,84	0,358	0,504	0,193	0,274	1,412

Using specialized software environment MGS, the initial parameters of the process were set, such as the feed stream F = 1000 l(stp)/h, the optimal division ratio = 0.5 which is corresponded to the extraction degree of oxygen in the flow of permeate FrP = 65%. Concentrations and the extraction degree of air components for a single element of a membrane module used in oxygen concentrators were calculated. The calculation results are shown in Table. 4, from which it can be seen that with a slight degradation of the separation parameters, membrane area decreases by half due to the greater permeability, hence the use of the reverse supply with the same effective membrane area can improve the performance twice of the single element in the membrane module.

Table. 4 Separation parameters association with effective membrane area, depending on its orientation. (calculation data)

	Straight feed, P, l(stp)/h – 395.750 FrP(O_2), % - 65.07; S, m^2 – 1.682E-01		Reverse feed, P, l(stp)/h – 500.500 FrP(O2), % - 65.05; S, m2 – 7.987E-02	
Gas	Pi, l(stp)/h	Cp, %	Pi, l(stp)/h	Cp, %
CO_2	1563.00	2.19	2208.00	1.67
O_2	617.00	32.88	1115.00	26.00
N_2	198.00	64.92	605.00	72.33

One way to describe the transfer of gas through the polymer membrane is dissolution-diffusion model [5]. Apparently, in identical conditions, the amount of adsorbed molecules in the surface layer from the side of porous support is greater than in the outer selective layer. Molecules of gas dissolve in a whole volume of the porous support, wherein the inner side of the selective layer has a well-developed surface area that requires a larger number of sorption centres than at the surface. Obviously, if we compare the sorption surface area at the interface between diffusion layer and porous layer to the surface of the film, they will be different.

Conclusion

Based on this effect, in particular, on the data of permeability, selectivity, and asymmetry value of the various components of the gas mixture it becomes possible to create an apparatus for producing of artificial atmosphere with the possibility of changing CO_2 level. In this work permeability of gases through the polymer membrane depending on its orientation to the high-pressure area was investigated experimentally. The phenomenon of asymmetric gas transfer is detected, and it is shown that the reverse effect of asymmetry is observed, when the flow value from the side of the porous support is greater than flow value from the selective layer: the change of the flow value, depending on selected gas can vary up to three times. Permeability, selectivity and asymmetry values were also represented for these gases.

Acknowledgements

The work was financially supported by the Ministry of Education and Science, agreement № 14.579.21.0046. Unique project identifier RFMEFI57914X0046.

References

[1] Kurchatov I M, Krjukov A V, Laguncov N I 2012 *Membr. Membr. Technol.* **2** 124-229
[2] Kurchatov I M and Laguntsov N I 2010 *Proc. of the XXV International symposium on physico-chemical methods of separation* ARS Separatoria (Torun, Poland) p 286
[3] Dytnerskij J I, Brykov V P and Kagramanov G G 1991 *Membrannoe razdelenie gazov* (Moscow: Chemistry) p 307
[4] Timashev S V *Fiziko-himija membrannyh processov* (Moscow: Chemistry)
[5] Mulder M 1991 *Basic Principles of Membrane Technology* (Kluwer Dordrecht) p 372.