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"SMOLUCHOWSKI TYPE" EQUATIONS FOR MODELLING OF AIR SEPARATION BY MEMBRANES WITH VARIOUS STRUCTURE*

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The problem of a membrane air separation in the presence of a magnetic field, is considered. Paramagnetism of oxygen and diamagnetic behaviour of nitrogen form the basis for air separation. A new concept of polymer membranes filled with neodymium powder and magnetized ("magnetic membranes"), was applied. The Smoluchowski equation for oxygen, and simple diffusion equation for nitrogen behaviour in the air have been used. Multifractal analysis of structure and morphology of membranes were applied to optical microscopy images.

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1. Introduction

Much research at industrial and university laboratories is carried out to improve membrane performance to make air separation by membranes more competitive to conventional techniques like pressure swing adsorption and cryogenics [1, 2]. The interest in membrane separation of gases is still growing and expectations for the future are high. Membrane materials are developed in order to increase membrane selectivity and permeability [2–13]. We propose a new concept of air separation by polymer membranes filled with neodymium powder and magnetized ("magnetic membranes") [14, 16]. The idea of implementing some external fields as a principal reason for gas mixtures separation (air in our case) is very promissing. Since oxygen is

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paramagnetic, while nitrogen is diamagnetic, the use of magnetic field, gives a real chance for their separation. From mathematical point of view we consider one-dimensional model of the diffusional system consisted of one or two gases, permeating through a planar membrane of thickness l. In a most standard case, to describe a permeation process of one gas component we use II Fick's law with constant diffusion coefficient.

$$\frac{\partial c(x,t)}{\partial t} = D\,\frac{\partial^2 c(x,t)}{\partial x^2}\,, \tag{1}$$

where $c(x,t)$ — concentration (probability density) at position x, and time t; D — constant diffusion coefficient.

Sometimes equation (1) is getting insufficient to describe the mass transport through membrane. It happens when other processes accompany diffusion or when molecules of penetrant react with each other or with molecules of surrounding. We have to modify equation (1) also when an external fields affect a permeation process. Different types of interactions can imply functional dependence of the diffusion coefficient on position $D(x)$, time $D(t)$ or concentration $D(c)$. If a potential field act on a system, we add a "drift term" to the equation (1), and finally we get Smoluchowski equation

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(\cdot)\frac{\partial c(x,t)}{\partial x} - wc(x,t)\right], \tag{2}$$

where $D(\cdot)$ — is a diffusion coefficient, to dependent on position, time or concentration, w — a drift coefficient, which can be used for describing the transport of gases in polymeric membranes. Explanation for such implementation of equation (2) is that from physics point of view polymer is a liquid, glassy or semi crystalline medium of a very high viscosity. On the other hand Smoluchowski equation can be generated by simplified equation of motion *i.e.* Langevin equation at high viscosity limit [18].

2. Formulation of the problem

In our experiment we cast the ethylcellulose membranes with neodymium magnetic powder (granulation 20–32 μm). The membranes are cast in coil with stable magnetic field, and then magnetized in field magnet. An APG-1 tester described precisely in [21], is used for the measurements of nitrogen, oxygen and air permeability. Permeate flow rate is measured by flowmeter. The apparatus is supplemented additionally by gas chromatograph used for detection of oxygen in permeate. After measuring the permeated mass $Q^a(l,t)$ or flux $J(l,t)$, a corresponding experimental curve is being plotted to allow the determination of transport coefficients *i.e.* diffusion and drift coefficients, permeability and selectivity. The transport of two gases in polymeric membranes, while external field act on one component, is mostly described by the system:

$$\frac{\partial c_1}{\partial t} = D_{11}\frac{\partial^2 c_1}{\partial x^2} + D_{12}\frac{\partial^2 c_2}{\partial x^2} - w\frac{\partial c_1}{\partial x}\,, \tag{3}$$

$$\frac{\partial c_2}{\partial t} = D_{21}\frac{\partial^2 c_1}{\partial x^2} + D_{22}\frac{\partial^2 c_2}{\partial x^2}\,, \tag{4}$$

with initial and boundary conditions:

$$\begin{aligned} c_1(0,t) &= 1\,, & c_2(0,t) &= 1\,,\\ c_1(l,t) &= 0\,, & c_2(l,t) &= 0\,,\\ c_1(x,0) &= 0\,, & c_2(x,0) &= 0\,, \end{aligned}$$

where D_{ij} transport coefficients, $i,j = 1$ (oxygen), 2 (nitrogen). Since our system (4) is weakly coupled, we can use equation (1) and (2) separately for nitrogen and oxygen, respectively [14].

In our experiment we measure the magnetic induction of membranes before and after magnetization in magnetic field, what corresponds to the drift.

3. Theoretical and experimental results

The experimental details are presented elsewhere [16]. Here, we show permeation results (Table I) for some chosen membranes. Main analysis based on the time lag method [15, 19] and D1–D8 system, that is provided in [16, 17].

TABLE I

Magnetic membranes for oxygen enrichment — experimental results.

Membrane	B [mT]	Time lag for O_2 [s]	Oxygen and nitrogen in permeate
EC (M1)	0	1.17 ± 0.01	$O_2 : 23.8 \pm 1.0\%$ $N_2 : 76.2 \pm 1.3\%$
EC + 1.23g of Nd (M2)	0.50	0.45 ± 0.01	$O_2 : 30.7 \pm 1.1\%$ $N_2 : 69.3 \pm 1.5\%$
EC + 1.38g of Nd (M3)	0.79	0.32 ± 0.01	$O_2 : 40.7 \pm 1.1\%$ $N_2 : 59.3 \pm 1.5\%$
EC + 1.49g of Nd (M4)	1.25	0.23 ± 0.01	$O_2 : 43.8 \pm 1.1\%$ $N_2 : 56.2 \pm 1.5\%$

TABLE II

Comparison of calculated and measured oxygen content in permeate.

Magnetic induction B [mT]	Oxygen content in permeate [%] calculated	measured
0	25	23.8
0.5	33.3	30.7
0.79	38.2	40.7
1.25	45.8	43.8

Calculated oxygen content in permeate originate from theoretical consideration in [14] and is presented in Table II. As can we see theoretical expectations are in really good agreement with experimental data. However, if we present the measured oxygen content in permeate as a function of the magnetic induction we can see, more clearly, tendency of deviation from the straight line relationship (Fig. 1).

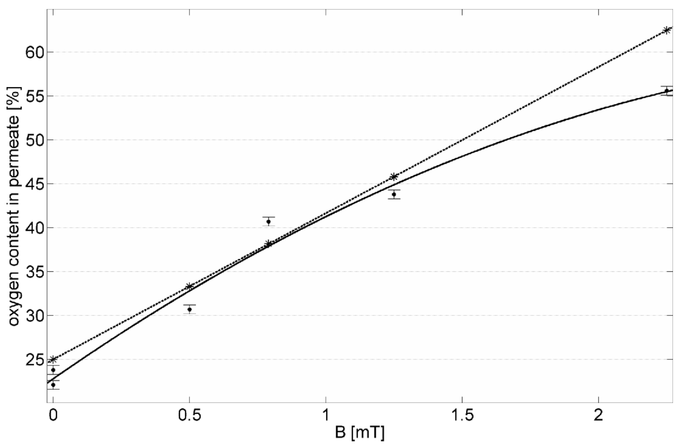


Fig. 1. Dependence of oxygen content in permeate *versus* magnetic field induction. Points marked as stars were predicted by the theory and points marked as circles were obtained in experiment.

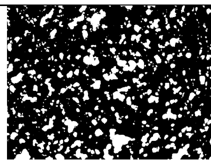
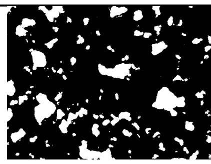
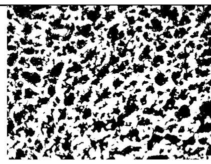
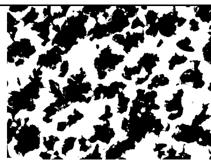
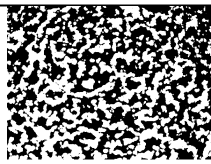
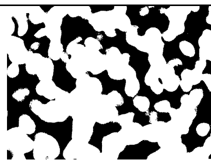
It might be that due to the strong magnetic field nitrogen and oxygen form aggregates which carry more nitrogen, and spoil the separation process. As it was discovered by Tagirov *et al.* [25] for sufficiently strong magnetic field, the molecular clusters are to be formed. For the case of air the clusters $N_2-O_2-O_2$ are preferable. It means that magnetic field, when sufficiently strong, can affect also the transport of N_2 by means of dragging its clusters along with O_2. This leads to a conclusion that the mechanism of a transport has no diffusion character but for a stronger field rather drift dominates.

4. Multifractal analysis of structure and morphology of membranes surface

We decided to check if there are any connections between the structure of membranes and magnetic properties. Our membranes are inhomogeneous, there are molecular clusters so the structure and morphology of membranes definitely have influence on transport properties. We used optical microscopy to our experiment. Table III shows images from optical

TABLE III

Different membranes by optical microscopy: M2 EC+1,23 g Nd M3 EC+1,38 g Nd, M4 EC+1,49 g (powder granulation: 20–32 μ m.)

M4 (with 40× magnification)	
M4 (with 100× magnification)	
M3 (with 40× magnification)	
M3 (with 100× magnification)	
M2 (with 40× magnification)	
M2 (with 100× magnification)	

microscopy of membranes with different amount of magnetic powder. Texture making by magnetic powder was observed by optical microscopy with 40× and 100× magnification and analysed by fractal analysis. We used generalised fractal dimension given by the formula [22]:

$$D_q = \frac{1}{q-1} \lim_{\epsilon \to 0} \frac{\ln \sum_{i=1}^{M(\epsilon)} P_i^q}{\ln \epsilon}\,, \tag{5}$$

where D_q — generalized dimension q — real number, dimension index, P_i — probability of finding a point in a given element of covering, ϵ — size of the covering element, $M(\epsilon)$ — number of covering elements and $f(\alpha)$ formalism:

$$f(\alpha) = \alpha q - \lim_{\epsilon \to 0} \frac{\ln \sum_{i=1}^{M(\epsilon)} P_i^q}{\ln \epsilon}\,, \tag{6}$$

where α — a new dimension index (obtained after Legendre's transform of D_q(1-q)). Properties of $D_q/f(\alpha)$ spectra used in our analysis have been described in papers [22–24]. The results of fractal analysis for membranes (with 40× magnification) are presented in Fig. 2 and Fig. 3 and Table IV.

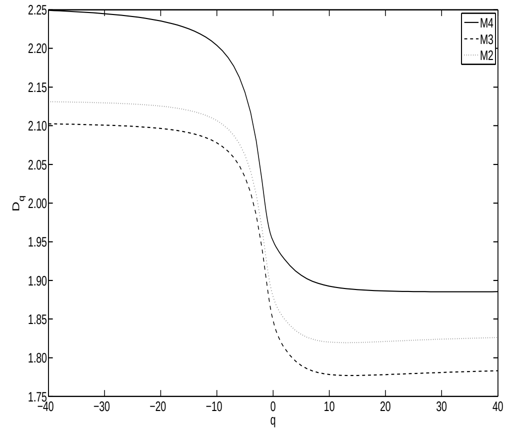


Fig. 2. D_q corresponding to membranes: M2 EC+1.23 g Nd M3 EC+1.38 g Nd, M4 EC+1.49 g shown in Table. III.

We have observed increase of dimension D_0, D_1 and D_2 values, increase of the distance between arms and no zero points for $f(\alpha)$ graph (ΔD) for membranes with increasing amount of magnetic powder. It is connected with increasing of space filling and larger homogeneity of our membranes.

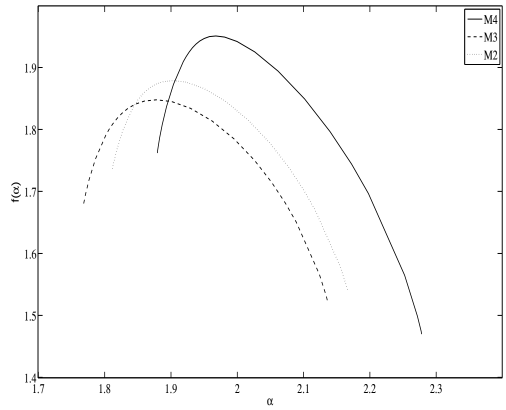


Fig. 3. $f(\alpha)$ spectra corresponding to membranes: M2 EC+1.23 g Nd, M3 EC+1.38 g Nd, M4 EC+1.49 g shown in Table III.

TABLE IV

Generalised fractal dimension for different membranes.

Type of membrane	M4	M3	M2
$D_{-\infty}$	2.25 ± 0.05	2.10 ± 0.05	2.13 ± 0.05
D_{-2}	2.03 ± 0.05	1.94 ± 0.05	1.97 ± 0.05
D_{-1}	1.98 ± 0.05	1.89 ± 0.05	1.92 ± 0.05
D_0	1.95 ± 0.05	1.85 ± 0.05	1.88 ± 0.05
D_1	1.94 ± 0.05	1.83 ± 0.05	1.86 ± 0.05
D_2	1.93 ± 0.05	1.81 ± 0.05	1.85 ± 0.05
$D_{+\infty}$	1.89 ± 0.05	1.79 ± 0.05	1.83 ± 0.05
ΔD	0.36 ± 0.05	0.32 ± 0.05	0.30 ± 0.05

5. Conclusions

The idea of implementing some external fields as a principal reason for gas mixtures separation (air in our case) is very promissing. Due to differences between the oxygen and nitrogen in response to the magnetic field (oxygen is paramagnetic) there exists a real chance for their separation. We have got an oxygen enrichment up to the 43.8% in permeate. In the previous paper [16] we observed that application of the coil in membrane casting process gives rise to much better magnetic properties of the membrane. We stated also that enrichment of air in oxygen depends on magnetic field direction and rises with the increase of magnetic induction. In this paper we decided to make fractal analysis of the texture of magnetic membranes. We wanted to check if there are any connections between the structure of membranes and magnetic properties especially as creation of $N_2{-}O_2{-}O_2$ clusters modify the air enrichment leading to less effective process. We have observed increase of dimension D_0, D_1 and D_2 values, increase of the distance between arms and non zero points for $f(\alpha)$ graph for membranes with larger amount of magnetic powder. It is a consequence of larger space filling and homogeneity of our membranes. Differences between theoretical and experimental data could be a result of molecular clusters forming and resulting functional dependence of the diffusion coefficient.

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