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MATHEMATICAL MODELS OF THE AIR SEPARATION THROUGH POLYMER MEMBRANES AT MAGNETIC FIELD

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ABSTRACT

This paper is addressed to the membrane air separation i.e. the gas mixture of quite similar gases in many respects, except one: oxygen is paramagnetic whereas nitrogen is diamagnetic. This fact forms the basis for their separation. The numerical studies and theoretical predictions concerning the air membrane separation in the presence of a magnetic field are discussed. Some experimental data concerning the „magnetic membranes" i.e. ethylcellulose membranes with neodymium powder, are also presented.

Key words: Diffusion; Membrane, Time-lags, Gas mixtures, Air separation

INTRODUCTION

Air separation or its oxygen enrichment is a problem of a great importance both in industry and everyday life. Nowadays, several different separation techniques for air and other gases are known. All of them belong to one of two general categories:

- cryogenic methods – these methods are based on using very low temperature distillation to separate air components and achieve desired product purities;

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- noncryogenic methods – these processes use physical properties other than boiling point to separate gases; there are two major process categories: adsorption and membrane separation processes.

The most popular among the latter are membrane separation techniques [1,2,3,4]. Especially widely accepted, and used for producing oxygen, are polymeric membranes [2,4,5,6]. The success of polymeric membranes has been largely based on their mechanical and thermal stability, along with good gas separation properties. The process is continuous, has a low capital cost, low power consumption, and the membranes do not require regeneration [3].

In this work we consider a one-dimensional model of a diffusional system consisting of two gases, permeating through a planar membrane of thickness *l*. At the membrane boundaries, for $x = 0$ and $x = l$, concentrations C_0 and 0 are posed, respectively.

A permeation process of a one component gas (N_2, O_2 or H_2) through a dense polymeric membrane can be described by the simplest transport equation i.e. the second Fick's law with a constant diffusion coefficient or with a diffusion coefficient dependent on position, time or concentration, when other processes accompany diffusion [17]:

$$\frac{\partial C(x,t)}{\partial t} = div\left(D(\cdot)\ gradC\right) \tag{1}$$

where: $C(x,t)$ – concentration, $D(\bullet)$ - diffusion coefficient (constant D, dependent on position $D(x)$, time $D(t)$, or concentration $D(C)$).

If the membrane is made of a dense polymer, and a potential field acts on a system, then Eq. (1) may be replaced by the Smoluchowski one [9,10]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - k\frac{\partial C}{\partial x} \tag{2}$$

where: k – drift coefficient (constant).

An analytical description for a mixture of two gases transported through a polymeric membrane has a form of a set of two partial differential equations:

$$\begin{cases} \dfrac{\partial C_1}{\partial t} = D_{11}\dfrac{\partial^2 C_1}{\partial x^2} + D_{12}\dfrac{\partial^2 C_2}{\partial x^2} - k\dfrac{\partial C_1}{\partial x} \\ \dfrac{\partial C_2}{\partial t} = D_{21}\dfrac{\partial^2 C_1}{\partial x^2} + D_{22}\dfrac{\partial^2 C_2}{\partial x^2} \end{cases} \quad 0 < x < 1,\ t \in R^+ \tag{3}$$

where: D_{ij} – diffusion coefficient for component i,j
i,j =1,2

ONE COMPONENT PERMEATION PROCESS

First, we analyse a single equation addressed to a particular air component i.e. Fick's equation for nitrogen, and the Smoluchowski equation for oxygen, respectively.

To provide a coherent frame for such an approach we reuse several formulas for Fick's permeation, and present some original solutions for the Smoluchowski one.

If the membrane is initially free of the diffusing substance, the diffusion equation with the initial and boundary conditions can be expressed in the following form:

$$\begin{cases} \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \quad x \in (0,l), \quad t \in R^+ \\ C(x,0) = 0 \\ C(0,t) = C_0 \\ C(l,t) = 0 \end{cases} \tag{4}$$

The analytical solution of Eq. (6) can be obtained using Laplace transform or separation of variables, which is discussed by Crank [19]. The solution in the form of the Fourier series is given by:

$$C(x,t) = C_0\left(1 - \frac{x}{l}\right) - \frac{2C_0}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\frac{n\pi x}{l}\exp\left(-\frac{n^2\pi^2}{l^2}Dt\right) \tag{5}$$

The diffusive flux $J(x,t)$ can be obtained from Eq. (5), by using the definition of a flux:

$$J(x,t) = -D\frac{\partial C}{\partial x}, \tag{6}$$

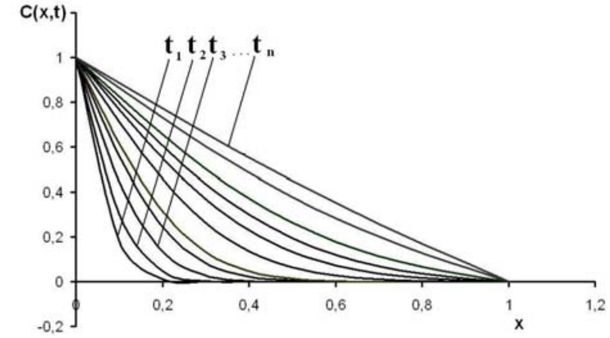
to get a form

$$J(x,t) = \frac{DC_0}{l} + \frac{2DC_0}{l}\sum_{n=1}^{\infty}\cos\frac{n\pi x}{l}\exp\left(-\frac{n^2\pi^2}{l^2}Dt\right) \tag{7}$$

It goes without saying that the flux at the right boundary of the membrane can be obtained by setting $x = l$.

A numerical solution of Eq. (4) was obtained by the finite-difference method [7, 12]. Fig. 1a) presents the solutions of Eq. (4) i.e. concentration profiles C, as a function of x and t; Fig. 1b) presents the flux at the right boundary of the membrane as a function of t.

a)



b)

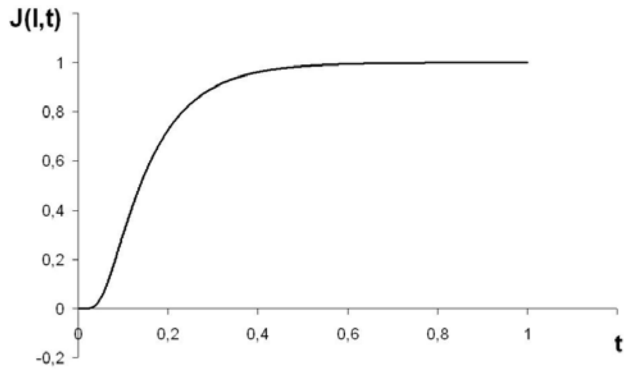


Fig. 1. a) Concentration profiles – solution of equation (4) for constatnt diffusion coefficient, and various times from t_1= 0.002, t_2= 0.004, up to t_n= 0.9, b) flux $J(l,t)$ at the right boundary (Eq. (7)).

When the membrane is made of dense polymers, and an external field (electric, magnetic, etc.) act upon the system, then the permeation process can be described by the Smoluchowski equation (8).

$$\begin{cases} \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - k\frac{\partial C}{\partial x}, x \in (0,l), t \in R^+ \\ C(x,0) = 0 \\ C(0,t) = C_0 \\ C(l,t) = 0 \end{cases} \tag{8}$$

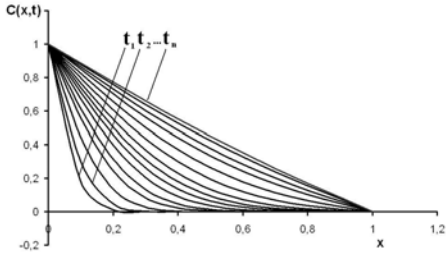
The additional term $k\frac{\partial C}{\partial x}$ in the Smoluchowski equation, as compared with the Fick's one, represents the presence of an external field [10,13]. One of the ways to get an analytical solution of the Smoluchowski equation is to use transformations which reduce the Smoluchowski equation into the Fick's one [16, 20]. There are two possibilities:

- Fürth substitution: $C(x,t) = C^{*}(x,t)\exp\left(\dfrac{k}{2D}x - \dfrac{k^2}{4D}t\right)$,
- travelling wave: $\begin{cases} \hat{x} = x - kt \\ \hat{t} = t \end{cases}$

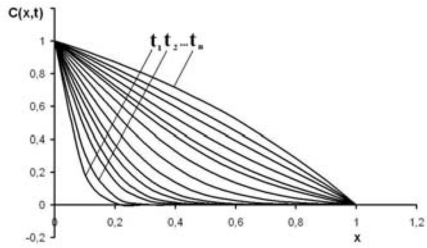
used both for the equation and for the initial and boundary conditions.
The final analytical solution of Eq. (8), after the application of Fürth substitution, has a form [14,20]:

$$C(x,t) = \sum_{n=1}^{\infty} \frac{2n\pi D C_0}{l^2\left(\dfrac{k^2}{4D} + \dfrac{n^2\pi^2 D}{l^2}\right)} Exp\left[\frac{k}{2D}x\right]\left(1 - Exp\left[-\left(\frac{k^2}{4D} + \frac{n^2\pi^2 D}{l^2}\right)t\right]\right)\sin\left[\frac{n\pi x}{l}\right] \quad (9)$$

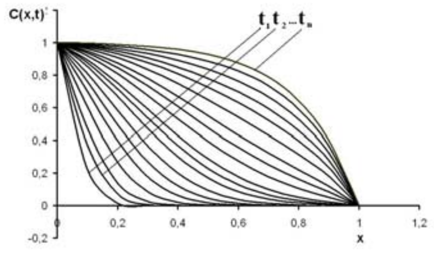
a) k = 0.1



b) k = 1



c) k = 5



d) k = 10

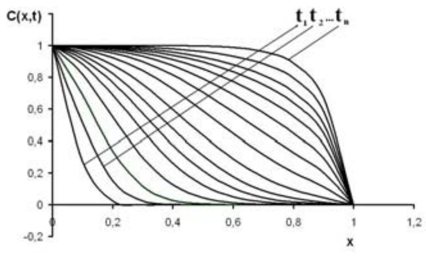


Fig. 2. Transient concentration profiles –solution of Smoluchowski equation for permeation process for different times from t_1= 0.002 up to t_n = 0.9 , diffusion and drift coefficients are constant, a)k = 0.1, b) k=1, c) k=5 and d) k=10.

The diffusive flux has a form:

$$J(x,t) = -D\frac{\partial C}{\partial x} + kC \tag{10}$$

Figure 2 presents the solution of Eq. (8) i.e. concentration profiles as a function of x and t for different drift coefficients. It is interesting to observe that for sufficiently large k the solution of Eq. (8) behaves like the „travelling wave". The numerical solution can be obtained by the finite-difference method.

DIFFUSION EQUATION FOR TWO-COMPONENT GAS MIXTURE

A multicomponent diffusion process, in the simplest case described by the Fick's law, is described by its generalization to an n-component system [8, 11].

The transport equation for a binary mixture (in this case O_2 /N_2) transported by the dense membrane is represented by Eq. (11):

$$\begin{cases} \dfrac{\partial C_1}{\partial t} = D_{11}\dfrac{\partial^2 C_1}{\partial x^2} + D_{12}\dfrac{\partial^2 C_2}{\partial x^2} \\ \dfrac{\partial C_2}{\partial t} = D_{21}\dfrac{\partial^2 C_1}{\partial x^2} + D_{22}\dfrac{\partial^2 C_2}{\partial x^2} \end{cases} \quad x \in (0,l)\,,\; t \in \mathrm{R}^+ \tag{11}$$

The initial and boundary conditions:

$$\begin{array}{ll} C_1(0,t) = C_{01} & C_2(0,t) = C_{02} \\ C_1(1,t) = 0 & C_2(1,t) = 0 \\ C_1(x,0) = 0 & C_2(x,0) = 0 \end{array} \tag{12}$$

where:

c_1 – oxygen concentration in the membrane;
c_2 – nitrogen concentration in the membrane;
D_{11} – main transport coefficient of pure oxygen in the membrane;
D_{12} – cross transport coefficient of oxygen in mixture with nitrogen;
D_{21} – cross transport coefficient of nitrogen in mixture with oxygen;
D_{22} – main transport coefficient of pure nitrogen in the membrane;

The concentration profiles of $C_1(x,t)$ and $C_2(x,t)$ presented in figures 3 a) and b) were obtained numerically.

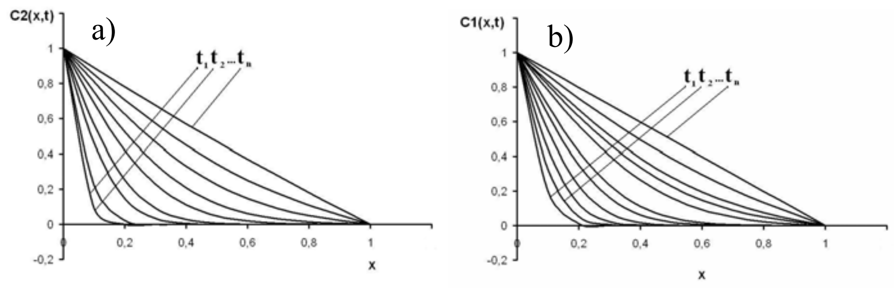


Fig. 3. Concentration profiles – solutions of equation (11) for constant diffusion coefficients D_{11}=1, D_{12}=0.13, D_{21}=0.14, D_{22}=1.1, for different times:
a) concentration profiles for component 1 of the mixture $C_1(x,t)$,
b) concentration profiles for component 2 of the mixture $C_2(x,t)$.

In the case when an additional force acts upon the system, the permeation process for the binary mixture (O_2/N_2) can be described by the set (13). In the first equation of the set, there is an additional $k\frac{\partial C}{\partial x}$ term representing an external force present in the system.

$$\begin{cases} \frac{\partial C_1}{\partial t} = D_{11}\frac{\partial^2 C_1}{\partial x^2} + D_{12}\frac{\partial^2 C_2}{\partial x^2} - k\frac{\partial C_1}{\partial x} \\ \frac{\partial C_2}{\partial t} = D_{21}\frac{\partial^2 C_1}{\partial x^2} + D_{22}\frac{\partial^2 C_2}{\partial x^2} \end{cases} \quad x \in (0,1),\ t \in \mathrm{R}^+ \qquad (13)$$

Along with the initial and boundary conditions:

$$\begin{array}{ll} C_1(0,t) = C_{01} & C_2(0,t) = C_{02} \\ C_1(1,t) = 0 & C_2(1,t) = 0 \\ C_1(x,0) = 0 & C_2(x,0) = 0 \end{array} \qquad (14)$$

where: k – drift coefficient

To solve the system (13) with the conditions (14) the method applied for the system (11) with conditions (12) were used. The concentration profiles are presented in Fig. 4a) and b).

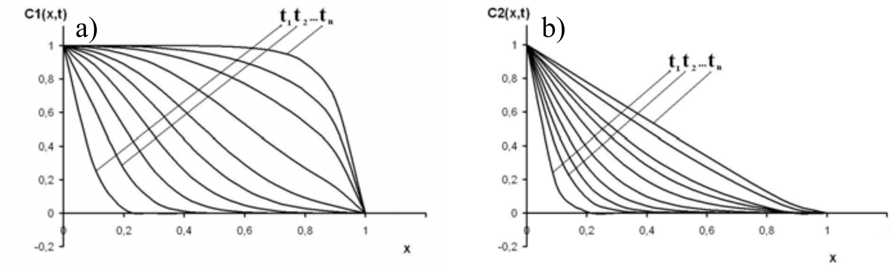


Fig. 4. Concentration profiles – solutions of equation (13) with conditions (14) for constant diffusion coefficients D_{11}=1, D_{12}=0.13, D_{21}=0.14, D_{22}=1.1, and drift coefficient k=10, for different times:
a) concentration profiles for component 1of the mixture $C_1(x,t)$,
b) concentration profiles for component 2 of the mixture $C_2(x,t)$.

EXPERIMENTAL

We cast the ethylcellulose membranes with and without neodyme powder. The membrane filled with neodyme powder was prepared, and then magnetized with the field magnet (magnetic induction of about 0.3 mT which corresponds to the drift coefficient k = 0.7). An APG-1 tester described precisely in [23], was used for the measurement of nitrogen, oxygen and air permeability. The permeant flow rate was measured by a flowmeter. The apparatus was modified additionally by a chromatograph used for the detection of oxygen air enrichment. To analyse the output data, the D1-D8 system described in [22] was used. The results of the analytical calculations are presented in Tab. 1.

Tab. 1. Results of analytical calculations

Membrane	Pure components $\overline{D}[cm^2/s]$		Air $\overline{D}[cm^2/s]$		O_2 and N_2 concentrations in the output
	N_2	O_2	N_2	O_2	
Ethyl-cellulose p=4 bar l=28μm	$\overline{D}=1.63$ $\pm 0.24\cdot 10^{-6}$	$\overline{D}=1.11$ $\pm 0.07\cdot 10^{-6}$	$\overline{D}=1.31$ $\pm 0.25\cdot 10^{-6}$	$\overline{D}=1.33$ $\pm 0.23\cdot 10^{-6}$	O_2:25.20±1.55% N_2:74.80±1.31%
Ethyl-cellulose + magnet p=0.5 bar l=35μm	$\overline{D}=1.09$ $\pm 0.18\cdot 10^{-6}$	$\overline{D}=0.99$ $\pm 0.07\cdot 10^{-6}$	$\overline{D}=1.00$ $\pm 0.03\cdot 10^{-6}$	$\overline{D}=0.99$ $\pm 0.03\cdot 10^{-6}$	O_2:29.90±1.8% N_2:70.10±1.51%

The oxygen air enrichment for the ethylcellulose membrane and the ethylcellulose with magnet membrane is presented in Fig. 5.

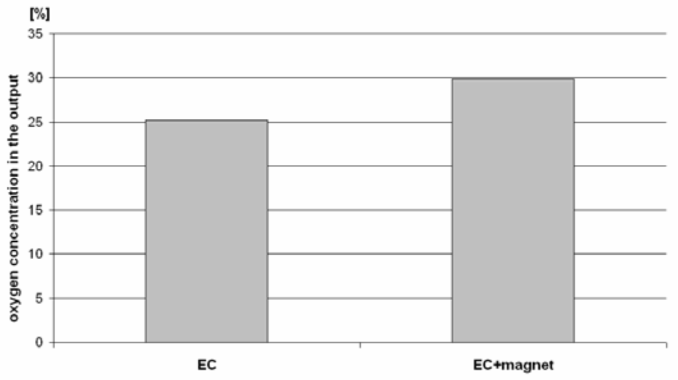


Fig. 5. The oxygen air enrichment for ethylcellulose membrane and ethylcellulose with magnet membrane.

RESULTS AND DISCUSSION

It often happens that a promising difference in transport parameters of the single components, drops dramatically in the mixture making the separation process far less efficient or even useless. One of the reasons may be the coupling of components. The coupling effects then reflect interactions between the components of the multicomponent system, but also an interactions between the membrane matrix and each of the components. The degree of coupling in the case considered here, is represented by the transport coefficients D_{ij} (see Eq. (11) and (13)). Each of the off diagonal terms (i.e. $D_{ij,\ i \neq j}$) gives a measure of the flux of one component that is engendered by the concentration gradient of the second component.

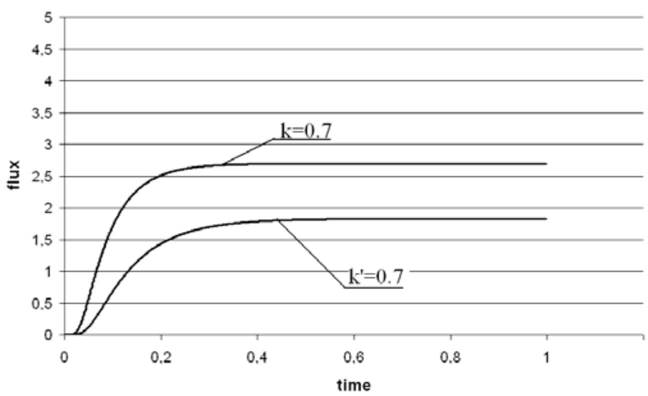


Fig. 6. Comparision of the fluxes of oxygen at right boundary of the membrane for Smoluchowski equation (with drift coefficient k'=0.7), and for the system (13) (drift coefficient k=0.7).

Our preliminary experimental data compared with the numerical calculations show that the system describing the air separation (13) is weakly coupled. Predictions for the separation effectiveness from equation (13) are almost identical with these based on the individual equations i.e. Eq. (4) and (8) (see Fig. 6).
As it can be seen from Fig.7, the linear relationship between the oxygen air enrichment and the strength of magnetic field of the membrane was obtained.

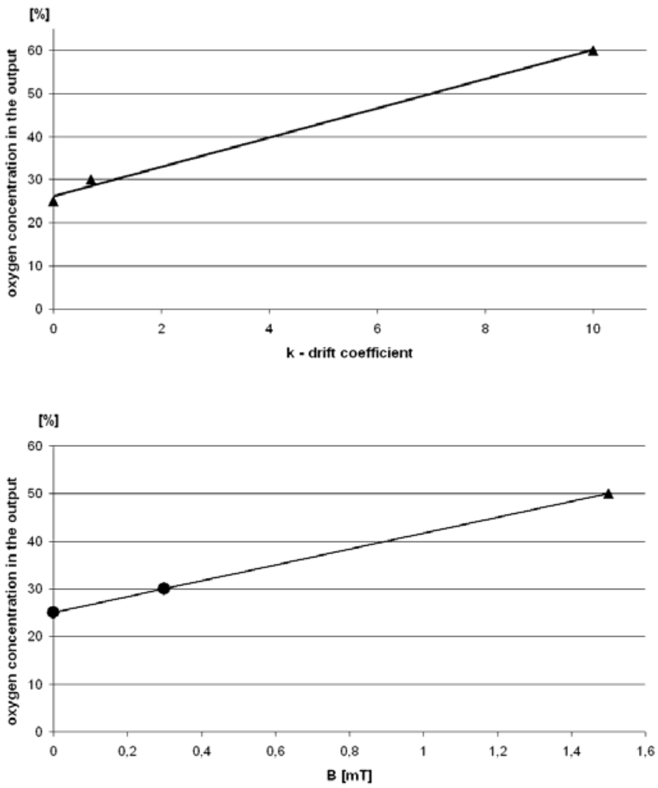


Fig. 7. Relationship between the oxygen air enrichment and a) drift coefficient, b) the strength of magnetic field of the membrane. Points marked as circles were obtained in experiment and points marked as triangles were predicted by the theory.

Taking into account that the value of k can be directly mapped into the strength of the magnetic field, we can see a possibility of a real break through in the air separation, by using this concept.

CONCLUSIONS

It seems that a new, and promising way of an effective and cheap air separation has been opened. We would like to strongly emphasize the preliminary character of our report, especially its experimental part. The idea of implementing certain external fields (in this case – magnetic) as a principal reason for gas mixtures separation sounds solid.

The main task of this paper was to present a theoretical and numerical analysis of a multicomponent mass transport through membranes and preliminary predictions for air separation. Due to the substantial differences between oxygen and nitrogen in response to the magnetic field (oxygen is paramagnetic whereas nitrogen -diamagnetic) there exists a real chance for their separation. In our opinion, the „magnetic membranes" could give an opportunity to control air separation.

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