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Membrane separation of gas mixtures under the influence of resonance radiation

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ABSTRACT

The model is considered for the transfer of gas molecules through dense membranes (including polymeric and supported ionic liquid membranes), allowing for taking into account the surface processes on the feed and permeate membrane sides, as well as the external impacts on the above-mentioned processes. The conditions under which the presented approach reduces to the solution-diffusion model are discussed. The influence of resonance (e.g. laser) radiation on the passage of gas molecules through membranes is studied theoretically. The membrane separation of gas mixtures under the effect of resonance radiation on the gas-membrane system is analyzed.

1. Introduction

In the present time, different kinds of membranes are used in many branches of modern technology (e.g. separation of gas and liquid mixtures, purification of a gas phase from an impurity component, vacuum technology, micro- and nanotechnologies).

It is known that the electric and magnetic fields can affect the gas transport through the membranes that leads to the possibility of managing the membrane separation of gas mixtures. In particular, the influence of the magnetic field on the membrane separation of gas mixtures is studied in [1–4]. The magnetic membranes were used for air enrichment in oxygen. Studies were based on the difference between the magnetic properties of paramagnetic oxygen and diamagnetic nitrogen. It was shown that magnetic particles (e.g. the neodymium powder) embedded into the polymeric matrix can substantially affect the gas transport through the membranes and the membrane separation of gas mixtures.

The possible effects of electromagnetic radiation (including microwave radiation) on the transfer processes and chemical reactions that occur in heterogeneous systems (e.g. aerosols and porous bodies) are discussed in [5,6]. The papers [7,8] provide an overview of the works related to the impact of laser radiation on the processes at the interface between gas and condensed phases. The problems related to the influence of resonance (e.g. laser) radiation on gas flow through thin capillaries and porous bodies are considered in [9,10]. The influence of resonance radiation on the diffusion and separation of gas mixtures in the microporous membrane, transparent in respect to resonance radiation, related to the difference in the sticking coefficients of excited and non-excited gas molecules on the pore walls is studied in [9]. The effect of resonance radiation on the surface diffusion of adsorbed gas molecules and, accordingly, on mass transfer through thin (nanoscale) capillaries is considered in [10].

Recently, supported ionic liquid membranes (SILM) have attracted the increasing attention of researchers due to their specific physicochemical properties [11], in particular, such as the negligible saturated vapor pressure of ionic liquids and their good thermal stability. These properties of supported ionic liquid membranes can be useful, for example, in the case when membranes are used in processes which occur at sufficiently high temperatures. The solution-diffusion model is commonly used to describe transfer of gas molecules through the polymeric and supported ionic liquid membranes [12–14]. It is worth noting that this model does not include parameters describing the interaction of gas molecules with the membrane surface, in particular, the sticking coefficient of gas molecules on the membrane surface and the rate coefficient for desorption of the adsorbed gas molecules from the membrane surface. The mentioned parameters can be changed under the influence of external impacts (in particular, resonance laser radiation). Below, we consider the influence of the surface processes on the side surfaces of the dense membrane, as well as the effect of resonance radiation on the passage of gas molecules through the membrane and the membrane separation of gas mixtures.

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2. Mathematical model

2.1. Influence of processes on the membrane sides on the transfer of gas molecules through membranes

To describe the passage of gas molecules through membranes (including polymeric and supported ionic liquid membranes), it is generally necessary to consider transfer phenomena in the external environment and in the membranes themselves, taking into account the surface processes on the sides of the membranes. Further we will consider the case when the both sides of the flat dense membrane are in contact with a gas which is assumed to be ideal. For simplicity, we assume that the complete gas mixing at the sides of the membrane takes place and that the transport of gas molecules dissolved in the membrane occurs by diffusion. The gas-membrane system is assumed to be isothermal and, for simplicity, the membrane is considered to be homogeneous. The concentration of gas molecules dissolved in the membrane c in the absence of the direct implantation of gas particles into the membrane and chemical reactions in it under the above-mentioned assumptions is described by the equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial X}\left(D\frac{\partial c}{\partial X}\right) \tag{1}$$

where X is the coordinate directed perpendicularly to the membrane side surface, t is the time, D is the diffusivity of gas molecules in the membrane which is given by [12]

$$D = D' \exp\left(-\frac{E_d}{kT}\right) \tag{2}$$

where D' is the pre-exponential factor that is usually assumed to be constant, E_d is the activation energy for diffusion, k is the Boltzmann constant, T is the temperature.

It is worth noting that, in general, the case of the supported ionic liquid membrane the transfer of gas molecules through the membrane depends on parameters characterizing the transfer of gas molecules through the ionic liquid and the polymeric support as well as on the ratio of volumes in the membrane filled by the ionic liquid and the polymer. It should be noted that the porous polymeric support can also affect the entry of gas molecules into the membrane due to the possible difference in parameters, such as the sticking coefficient and the adsorption time of gas molecules for the surface of the ionic liquid and the polymer. In some cases, the transfer of gas molecules through the polymeric support can be neglected and the effective diffusion coefficient D_{eff} for gas molecules in the membrane can be written as $D_{eff} = \varepsilon D_0/\tau$, where ε is the porosity of the support, D_0 is the diffusion coefficient of gas molecules in the pure ionic liquid, τ is the tortuosity factor [13].

The solution of Eq. (1) is often found under the following boundary conditions at the feed side of the membrane ($X = 0$) and at the permeate side of the membrane ($X = L$, where L is the membrane thickness) [14]:

$$c(X = 0) = c_0 \tag{3}$$

$$c(X = L) = c_L \tag{4}$$

Taking into account the foregoing, in a steady state the flux density of molecules passing through the membrane is given by

$$j = D\frac{c_0 - c_L}{L} \tag{5}$$

The values of c_0 and c_L are related to the gas pressure p near membrane sides at $X = 0$ and $X = L$ (p_0 and p_L, respectively) and the solubility coefficient S as [12–14]

$$c_0 = p_0 S \tag{6}$$

$$c_L = p_L S \tag{7}$$

Taking into account Eqs. (5)–(7), the value of j is given by (the so-called solution-diffusion model for mass transfer in the membranes) [12,13])

$$j = P\frac{p_0 - p_L}{L} \tag{8}$$

where $P = DS$ is the permeability coefficient.

The values of P and S depend on the temperature and activation energies of the considered processes similar to Eq. (2) [12]. As noted above, the solution-diffusion model does not include parameters describing the interaction of gas molecules with the membrane surface. The above-mentioned problem does not arise in the case when the boundary conditions for Eq. (1) are written similarly to [15] for the flux densities of molecules but not for their concentrations at $X = 0$ and $X = L$. These boundary conditions can be written as

$$-D\left.\frac{dc}{dX}\right|_{X=0} = J_0^+ - J_0^- = k_0^+ p_0 - k_0^- c(0) \tag{9}$$

$$-D\left.\frac{dc}{dX}\right|_{X=L} = J_L^- - J_L^+ = k_L^- c(L) - k_0^+ p_L \tag{10}$$

Here J_0^+ and J_L^+ are the flux densities of gas molecules entering the membrane from the gas phase at $X = 0$ and $X = L$, respectively, J_0^- and J_L^- are the flux densities of gas molecules escaping from the membrane at $X = 0$ and $X = L$, k_0^+ and k_L^+ are the rate coefficients for the transition of gas molecules from the gas phase into the membrane at $X = 0$ and $X = L$, k_0^- and k_L^- are the rate coefficients for the transition of gas molecules from the membrane to the gas phase at $X = 0$ and $X = L$, the values of $c(0)$ and $c(L)$ are found by solving the boundary value problem. Let us assume, for simplicity, that the rate coefficients for the transition of molecules from the membrane to the gas phase are equal for both sides of the membrane (i.e. $k_0^- = k_L^- = k^-$). Taking into account the above-mentioned, in a steady state we can write the following equations for the concentration of gas molecules in the membrane and the flux density of the molecules passing through the membrane:

$$c = \frac{k_0^+ p_0}{k^-} - \left(\frac{D}{k^-}\right)\left(\frac{k_0^+ p_0 - k_L^+ p_L}{2D + k^- L}\right) - \left(\frac{k_0^+ p_0 - k_L^+ p_L}{2D + k^- L}\right)X \tag{11}$$

$$j = \frac{k_0^+ p_0 - k_L^+ p_L}{2 + \frac{k^- L}{D}} \tag{12}$$

Eq. (12) allows us to assess the conditions under which the solution-diffusion model can be used for the description of mass transfer in membranes. Fig. 1 shows the dependence of the dimensionless flux density $j^* = j/k_0^+ p_0$ on the value of $g = k^- L/D$ at $p_L/p_0 = 0.1$ and different values of $\delta = k_L^+/k_0^+$.

It is seen from Fig. 1 that the value of j^* is positive for $\delta p_L/p_0 < 1$ and decreases with increase in g and δ. As $\delta p_L/p_0 > 1$ the value of j^* is negative and tends to zero with increase in g. The influence of external impacts (in particular, resonance radiation) on the rate coefficient for the transition of molecules from the gas phase into the membrane and, accordingly, on mass transfer through the membrane, will be discussed below in more detail.

Eq. (12) for the value of j at $k^- L/D \gg 1$ can be written as

$$j = D\frac{k_0^+ p_0 - k_L^+ p_L}{k^- L} \tag{13}$$

In the case when parameters describing the interaction of gas molecules incident on the side surfaces of the membrane are the same ($k_0^+ = k_L^+ = k^+$) Eq. (13) is reduced to