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Semi-empirical model of toluene transport in polyethylene membranes based on the data using a new type of apparatus for determining gas permeability, diffusivity and solubility

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ABSTRACT

Solubility, diffusivity and permeability of toluene vapors in low-density polyethylene (LDPE) membranes of various thicknesses (approximately 48, 93, 138 and 187 μm) at different temperatures 30, 40 and 50 °C in the range of relative vapor pressure p/p^0=(0.05; 0.95) were measured using new type of permeation apparatus. Moreover, special construction of the new cell enables determination of the permeant amount sorbed in the membrane in the steady state operation of vapor permeation.

The simple semi-empirical model of toluene transport in a polyethylene membrane based on relation between experimentally obtained effective diffusion coefficients and concentration dependent diffusion coefficients evaluated from experiments on a new permeation apparatus was proposed. The model enables estimation of toluene fluxes, sorption in the steady state of vapor permeation and concentration profiles in a polyethylene membrane from equilibrium sorption isotherms and effective diffusion coefficients. Very good agreement between experimental and calculated values from the proposed model was obtained.

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1. Introduction

Separation efficiency of polymeric membranes is controlled by vapor transport processes occurring inside them and assessment of character and parameters of these processes is very desirable. Numerous papers dealing with evaluation of permeation flux and equilibrium sorption measurements in different polymeric membranes separately are available in literature (Lutzow et al., 1999; Kao et al., 2002; Kumazawa et al., 1993; Favre et al., 1994; Villaluenga et al., 2003). However, experimental studies in which transport processes and sorption of permeating substances in the membrane have been investigated simultaneously are missing. We have recently proposed and constructed the novel apparatus for such measurements (Petrychovych et al., 2011). It makes possible to perform all standard types of transport experiments without the need of manipulation with the membrane. The main advantage of the new cell is its ability to provide information about the amount of the permeant absorbed in the membrane both at the steady state of the vapor permeation process and at equilibrium conditions. Comparison of the steady state and equilibrium sorption data could provide supplemental information helpful for assessment of the possible occurrence of concentration polarization in the studied systems.

The solution-diffusion model (Wijmans and Baker, 1995; Mulder, 1991) is the most frequently used approach to the description of vapor permeation through dense polymeric membranes. It is assumed that the transport proceeds in three steps: sorption of vapor molecules at the upstream membrane surface, their diffusion through the membrane and desorption of the permeated species at the downstream membrane side. The diffusion through the membrane is considered to be the rate-determining step of the process.

Equilibrium sorption data are frequently used as supplemental information improving characterization of vapor transport through a polymeric membrane. However, the concentration polarization in the boundary membrane layer can occur and the permeant concentration on the feed membrane surface in permeation or pervaporation process of mixtures is lower than the bulk concentration of the feed. This results in lower sorption and consequently lower flux than the expected based on the bulk concentration. This means that application of equilibrium sorption data could lead to great errors in the transport description.

The polarization effect can be assessed by comparison of the sorption data in the equilibrium and the steady state of process.

In this paper we report the application of the novel permeation cell design in the apparatus for investigation of toluene vapor transport through the polyethylene membrane. The new apparatus allows one to determine transport parameters as flux, diffusion coefficient, equilibrium sorption and sorption in the steady state of

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vapor permeation from independent measurements. On the basis of obtained sorption data and effective diffusion coefficients a semi-empirical model for toluene transport in a polyethylene membrane was proposed. The simple model enables one to predict flux, concentration gradient and amount of the permeate absorbed in the membrane at the steady state of the permeation process.

2. Experimental

The membrane used in this work was a low density linear polyethylene, Bralen FB2-30, purchased from Slovnaft Bratislava, Slovakia. The polyethylene density was $\rho=919\ \mathrm{kg\ m^{-3}}$ at 25 °C, the volume fraction of crystalline phase was $\phi=0.455$ and glass transition temperature $T_g=-120$ °C.

Toluene used in this study as a permeating substance was of analytical grade with 99% purity purchased from Lachema Neratovice, Czech Republic. Nitrogen used for vapor dilution and as sweeping gas was purchased from Linde Technoplyn, Czech Republic, in 99.99% purity.

The apparatus equipped with the novel cell as well as the experimental procedures were described in detail in previous paper (Petrychovych et al., 2011). The main advantage of the new permeation cell in comparison to a common classical cell is its special construction (two pistons serving as valves adjusting the cell geometry according to the needs of different types of experiments) allowing a great versatility applications—the flux permeation measurements, determination of permeant diffusion coefficient in membranes, measurements of permeant sorption in the equilibrium state and in addition the unique measurement of the permeating substance sorption in a membrane during the vapor permeation process, in steady state (see Fig. 1).

The experiments were carried out for a wide range of toluene vapor concentrations in the feed ($p/p^0=0.05$–0.95) using membranes of different thicknesses (approximately 48, 93, 138 and 187 μm) at temperatures 30, 40 and 50 °C.

3. Results

3.1. Vapor permeation measurements—determination of flux and diffusion coefficient

Experimental toluene fluxes through polyethylene membranes and effective diffusion coefficient D_{eff} evaluated by fitting the experimental time dependences of the permeate flux with the numerical solution of Fick's second law (Eq. (1)) for initial and boundary conditions (Eqs. (2)–(4)) according to (Carslaw and Jaeger, 1959)

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

where c is concentration of permeant in the polymer at the x plane at time t

$$0<x<L \quad t=0 \quad c=0 \tag{2}$$

$$x=0 \quad t\geq 0 \quad c=c_1 \tag{3}$$

$$x=L \quad t\geq 0 \quad c=c_2=0 \tag{4}$$

are given in Tables 1–3 and presented in Figs. 2 and 3.

The stepwise concentration change of the feed at the start of the experiment ($x=0$, $t\geq 0$, $c=c_1$) and very low concentration on the membrane permeate side ($x=L$, $t\geq 0$, $c_2=0$) are assumed.

D_{eff} is exponentially dependent on the feed relative vapor pressure (see Fig. 3). It means that evaluated values represent the mean integral values of concentration dependent diffusion coefficient D (see Eq. (5)):

$$\boldsymbol{D}_{\mathrm{eff}}=\frac{\int_{c_1}^{c_2} D(c)}{c_2-c_1} \tag{5}$$

The values of fluxes and D_{eff} as shown in Tables 1–3 determined from vapor permeation measurements are in reasonable agreement with similar data published by the other authors (Friess et al., 2009; Sipek et al., 2002).

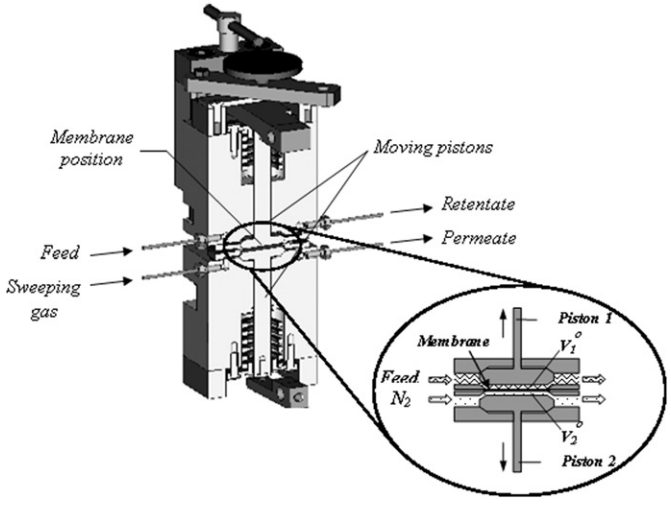

Fig. 1. Construction of a novel cell and in detail the set up of pistons during permeation experiment.

3.2. Sorption measurements

The novel feature of the cell is its special construction, which enables the measurement of the permeant amount sorbed in the membrane at the steady state of vapor permeation process.

This type of sorption data was for the first time published in our previous paper (Fialova et al., 2006) but these data are measured with relatively high error. The reason was that the results were produced by a more complicated way in two steps: (1) a fast removal of the membrane from the permeation cell and (2) the membrane transfer into the desorption cell. In the case of this permeation cell set up it was necessary to correct the permeant concentration sorbed in membrane for error caused by the permeant desorption during membrane transfer time from the permeation into the desorption cell (5–12% for steady state sorption and 10–18% for equilibrium sorption).

The cell used for the measurements is a new arrangement due to its special construction (two moving pistons, see Fig. 1), which allows performing the desorption and determination of the sorbed permeate amount directly within the permeation cell without the need of any manipulation with the membrane; it significantly reduces the experimental error that seldom exceed 7%.

Toluene sorption in the steady state of its vapor permeation in polyethylene membranes was measured after the permeation experiment was performed and the obtained data could be seen in Tables 1–3.

The equilibrium toluene sorption isotherms (30, 40 and 50 °C) were determined for the membrane of the thickness 48 μm (see Table 4). The measured isotherms have exponential shape (Fig. 4) and are in good agreement with previously published data (Friess et al., 2009).

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