EXPERIMENTAL DETERMINATION OF DIFFUSION COEFFICIENTS IN SEMICONDUCTOR POLYMER MEMBRANES

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Abstract

An experimental determination of the diffusion coefficient in polymer membranes is carried out. The advantages of using semipermeable membranes are given. The main aspects and advantages of pervaporation are clarified. The rate of solvent absorption by the polymer was determined. The equilibrium conditions of the solvent on polymer supports are revealed.

Keywords. *Semipermeable membrane, pervaporation, polymer carriers.*

Introduction. In polymers, internal mass transfer is determined by the patterns of migration of molecules of a substance that is distributed between the molecules of a solid body. Diffusion in the polymer matrix can be classified into three categories. The third category includes anomalous diffusion, which refers to processes when the level of diffusion and relaxation of the polymer is comparable. Sorption and transfer of molecules occur due to the presence of microcavities in the polymer matrix. The movement of the permeate depends on the geometrical structure of the polymer.

The aim of our work was the experimental determination of the diffusion coefficient in semipermeable membranes [1,2].

Materials and methods. The experiments were carried out on the installation (Fig. 1), which consists of a tubular pervaporation membrane 1, the lower part of which is closed with a plug 2, and the upper part is connected to a tared container 3, which is closed with a plug 4. Container 3 is glass and has measurable divisions (price divisions of 0.1 ml). Membrane 1 is placed in a hermetic glass case 5.

The sequence of the experiment is as follows. A liquid of organic origin was poured into container 3, which completely filled the inner cavity of membrane 1 and also filled container 3 to a certain extent. The stopwatch was turned on and the time during which the liquid diffused into the membrane wall was measured. The amount of absorbed liquid was determined by the difference of the divisions in the container 3.

The working surface of the pervaporation membrane can be calculated based on the main one kinetic equation of mass transfer:

$$F = \frac{M}{k\Delta_{\text{cp}}\tau}, \tag{1}$$

where M – mass flow of matter that passes through the membrane; k – mass transfer coefficient; Δ_{cp} - average the driving force of the primordial process; τ – duration of the pervaporation process.

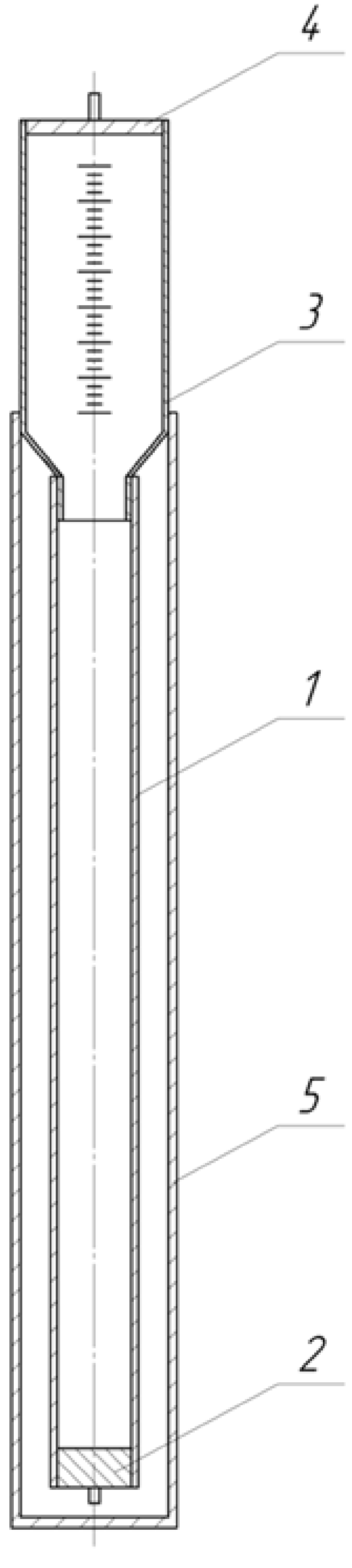

Fig. 1. Laboratory cell for determination of diffusion coefficients: 1 – primary porous membrane; 2, 4 – plugs; 3 – capacity; 5 – housing

The quantity M can be determined from the material balance equation. Determining the average driving force is also not particularly difficult – it is the difference in the concentration of the substance on the surface of the membrane and the flow of the steam-gas mixture.

But the mass transfer coefficient when the substance is transferred through the membrane is equal to:

$$k = \frac{1}{1/\beta_1 + \delta/\lambda_M + 1/\beta_2}, \tag{2}$$

where β_1 - mass transfer coefficient from the flow of the separated mixture to the membrane surface; β_2 -mass transfer coefficient from the membrane surface to the permeate flow; λ_M – membrane mass conductivity coefficient; δ - is the membrane thickness.

The mass transfer coefficients β_1 and β_2 can be calculated according to the criterion equations.

Difficulties arise at the calculation of the coefficient of mass conductivity of the membrane, which depends on the coefficient of diffusion of substance through a membrane. Calculation of coefficient of diffusion for results of empirical equalization [3] in large errors, that is why most effective is experimental determination of coefficient of diffusion. It is considered therefore to one of important aspects of pervaporation.

Dependence of coefficient of diffusion in semi-permeable polymeric membranes from a temperature well approximated by equalization of Arrhenius [4]:

$$D = D_o exp(-E/RT), \tag{3}$$

where D_o - diffusion coefficient at a temperature of 20 °C; E- activation energy; $T -$ is the absolute temperature, R – is the universal gas constant.

The diffusion coefficient was calculated using the formula:

$$D = \frac{V}{F \cdot \Delta\tau} \cdot \delta_M, \tag{4}$$

where $V -$ is the volume of liquid absorbed by the membrane, m^3; F –is the area of the inner surface of the membrane, m^2; $\Delta\tau$ – the time of the experiment, seconds; δ_M – is the thickness of the membrane wall, m.

Results and discussion. Of the many methods of determining the diffusion coefficient, we chose the method of determining the rate of absorption of the solvent by the polymer. If a polymer film of uniform thickness is placed in a solvent, after some time an equilibrium will be established, in which the solvent will be evenly distributed over the entire volume of the film. If the sorption of the solvent on the surface of the film is faster than the diffusion inside the film, then the speed of the dissolution process is determined only by the diffusion coefficient, which can be calculated from the change in the mass of the film depending on time. The results of the conducted experiment are presented in Table 1.

Table 1. Indicators of diffusion coefficients for some organic liquids

№ п/п	Substance	δ_M, м	t, °C	D, м^2/c
1	Methylene chloride	$1{,}3\cdot10^{-3}$	20	$5{,}882\cdot10^{-6}$
2	Triethylamine	$1{,}3\cdot10^{-3}$	20	$8{,}94\cdot10^{-6}$
3	Chloroform	$1{,}3\cdot10^{-3}$	20	$3{,}931\cdot10^{-6}$
4	Tetrachloromethane	$1{,}3\cdot10^{-3}$	20	$3{,}545\cdot10^{-6}$
5	Chlorobenzene	$1{,}3\cdot10^{-3}$	20	$4{,}697\cdot10^{-6}$
6	Styrene	$1{,}3\cdot10^{-3}$	20	$4{,}305\cdot10^{-6}$
7	Ethylbenzene	$1{,}3\cdot10^{-3}$	20	$3{,}299\cdot10^{-6}$
8	Toluene	$1{,}3\cdot10^{-3}$	20	$1{,}951\cdot10^{-6}$
9	Acetone	$1{,}3\cdot10^{-3}$	20	$0{,}822\cdot10^{-6}$
10	Dimethyl sulfoxide	$1{,}3\cdot10^{-3}$	20	$0{,}236\cdot10^{-6}$
11	Phenol (from aqueous solution)	$1{,}3\cdot10^{-3}$	20	$0{,}049\cdot10^{-6}$

Conclusions. An experimental setup was designed and manufactured to determine the diffusion coefficient of organic liquids in polymer membranes. The conducted experiment made it possible to find out the rate of solvent absorption by the polymer.

An approximation was made for semipermeable polymer membranes for various solvents at a temperature of 20°C. The conducted experiment allows us to introduce the basic principles for pervaporation processes in the separation of polymer membranes.

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