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The influence of temperature and pressure of the feed on physical and chemical parameters of the membrane made of PEBA copolymer

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ABSTRACT

Nowadays, one of the main environmental problem is how to remove carbon dioxide from gaseous streams. One of the methods solving that problem could be membrane gas separation. For this purpose, the membrane made of commercially available copolymer Pebax could be used. In this paper, the authors examined the influence of the process parameters, that is, temperature and pressure, on the solubility coefficient, diffusion coefficient and permeability of the membrane in the process of gas permeation through the nonporous membrane made of Pebax. The increased temperature made the solubility coefficient drop and the diffusion coefficient values as well as the membrane permeability values grow for all tested gases. On the other hand, the increased pressure made the solubility coefficient value grow and the diffusion coefficient value drop, but it did not significantly affect the permeability value. This paper provides data concerning operational parameters of the process conducted with Pebax membrane.

Keywords: Pebax 2533; Membrane gas separation; Time-lag; Diffusion; Solubility

1. Introduction

One of the problems related to the separation of gas components is removing CO_2 from the gas streams, for example, a synthesis gas, a mixture created in the reforming process, natural gas or exhaust gases. The presence of CO_2 in the mixtures worsens the incineration process efficiency by decreasing the calorific value and also increases costs related to the process performance and operation of the system. CO_2 is an additional volume of gas during its transferring and storage and, along with humidity, causes corrosion of pipes and devices. Additionally, the industry standards limit the CO_2 content in particular gas streams [1].

Absorption and adsorption can be recognized as classic processes of CO_2 removal. However, these methods involve high investment costs and a high energy demand as well as the necessity to use additional substances. Membrane processes, which have many economic and technological advantages, are an alternative to conventional methods [2].

In order to prepare an efficient process of removing CO_2 with the membrane methods, materials with CO_2 permeability higher than for gaseous components of a system such as CH_4, O_2, N_2 and H_2 are searched for. A group of commercially available PEBA copolymers, of which nonporous membranes can be made, is one of such materials [3].

The molar flux of gas component i transported through the nonporous membrane can be described by the following equation:

$$J_i = P_i \times \frac{p_{in} - p_{ip}}{l} \tag{1}$$

where P_i means permeability (1 Barrer = 3.35×10^{-16} mol m/(Pa s m^2)), p_{in} means partial pressure of component i in the

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feed channel (Pa), p_{ip} means partial pressure of component *i* in the permeate (Pa) and *l* means thickness of the membrane (m).

The permeation coefficient determines the velocity of gas permeating through the membrane and its value is typical for a particular gas–polymer pair. According to the generally accepted model of gas transport through the nonporous membrane, that is, a solution-diffusion model, the permeation coefficient can be expressed as the product of the solubility coefficient and the diffusion coefficient [4]:

$$P_i = S_i \times D_i \tag{2}$$

where S_i means solubility coefficient of component *i* on the membrane surface (mol/(m^3 Pa)) and D_i means diffusion coefficient of component *i* through the membrane (m^2/s).

Values of solubility and diffusion coefficients depend on both, physical and chemical properties of the gas particles and on physical and chemical properties of the membrane material. For rubbery polymers, which include PEBA polymers, the value of the solubility coefficient depends mainly on the molecule condensability [5,6], and the value of the diffusion coefficient depends mainly on the kinetic diameter of the molecule [7]. Gases that condense better, that is, gases with a higher critical temperature, dissolve easier in polymers [8]. Smaller gas molecules, on the other hand, diffuse easier through the polymer material. Additionally, the diffusion coefficient is affected by the properties of gas, such as its polarity and decomposition of electric charge in a molecule. The latter two properties of gas influence the mutual interaction of gas particles with polymer chains that form the membrane. The selected physical parameters of the tested gases are presented in Table 1.

Conditions, in which the phenomenon takes place, in particular the gas temperature and its pressure determine how gas solubility and diffusion proceed. This paper is dedicated to the influence of these two process parameters on the gas solubility and diffusion in the membrane made of Pebax 2533 polymer.

2. Membranes manufacturing and testing

The commercially available Pebax 2533 material (Arkema Group, France) was used to produce the tested membranes. It is a block polyetherimide copolymer (poly(ether-*block*-amide) – PEBA), the structure of which can be divided into two groups of polymers: polyether (PE), which consists of materials in the amorphous form and with high mobility of polymer chains causing a high permeability of the membrane, and polyamides (PA) characterized by a crystalline structure that affects the strength of the created layer, being to small extent responsible for the transport of the components [14]. In the case of Pebax 2533, poly tetramethylene oxide is included in the polyether group, while nylon 12 (PA 12) is included in the polyamide group, with a mass ratio of 80/20 [15].

Flat membranes made of Pebax 2533 were produced by a dry phase inversion method based on the evaporation of a solvent from the membrane-producing solution in controlled atmospheric conditions. 2-Butanol (Sigma-Aldrich, Poland) was used as the solvent. The membrane itself was formed with the casting by a knife technique. In order to provide the same conditions during the casting of the membranes and the evaporation of the solvent, the film of the polymer solution of a specified thickness was applied on thermostatic tables.

The membrane-producing solution containing 10% of mass polymer was prepared by intensive stirring in the temperature of 70°C for 24 h. Next, the solution was cooled to the temperature of 40°C and flat membranes were formed. Such prepared membranes were left for 3 h under cover that provided controlled conditions for solvent evaporation. Next, the membranes were placed in the vacuum heater in the temperature of 50°C for 24 h.

To determine parameters characteristic of the membrane, that is, solubility coefficient, diffusion coefficient and permeability, a modified method of a time-lag was used. This method consists of the measurement of changes in the permeate pressure during the process. An earlier removal of gas from the membrane and the permeate space as well as starting the measurement in the initial conditions of vacuum in the measurement system are the main purposes of this method. The result of the measurement in this method is the curve of the permeate pressure change in time.

On the basis of the obtained curve, with the use of the first and second Fick's laws, the diffusion coefficient is determined with the following dependence:

$$D = \frac{l^2}{6 \times \theta} \tag{3}$$

where *l* means thickness of the membrane (m) and θ means so-called time-lag read out from the measurement curve accordingly (s).

Moreover, the value of the membrane permeability can be determined from the curve of pressure changes on the basis of the following dependence:

$$P = \frac{V \times l}{\left(p_n - p_p\right) \times F \times R \times T} \times \frac{dp_p}{dt} \tag{4}$$

where *V* means volume of permeate space (m^3), *F* means membrane surface area (m^2), *R* means gas constant (J/(mol K)),

Table 1
Selected physicochemical properties of gases

Gas	Kinetic diameter (Å)	Critical temperature (K)	Quadrapole moment (10^{-40} C m^2)	Polarizability (10^{-31} m^3)
CO_2	3.30 [9]	304.12 [10]	–14.3 [11]	26.5 [9]
CH_4	3.80 [9]	190.56 [10]	0.0 [12]	26.0 [15]
O_2	3.46 [9]	154.58 [10]	–1.3 [13]	15.9 [9]
N_2	3.64 [9]	126.20 [10]	–5.0 [13]	17.6 [9]

T means temperature (K) and dp_p/dt means increase of permeate pressure in time determined in steady-state gas permeation through the membrane.

Determining the diffusion and permeability coefficients from Eqs. (3) and (4), respectively, allows for the calculation of the solubility coefficient with the use of Eq. (2) [16,17].

It should be strongly emphasized that coefficients S, D and P determined in this manner refer to the current conditions of temperature and pressure only.

To carry out tests with the use of the time-lag method, devices of the authors' own design were used. The diagram of the system is presented in Fig. 1. The system comprises of a module with a flat membrane placed inside, which separates the feed space from the permeate space, the set of cutting-off valves, a vacuum pump, two pressure transmitters on both sides of the membrane and containers for the feed and the permeate. The system is located in the thermostatic chamber.

Prior to the measurement, the system should undergo the vacuum process in order to remove gas from the system and desorb gas from the membrane. This stage is repeated before each measurement. The space in front of and behind the membrane remains under pressure, that is almost the same as the vacuum until the measurement is started.

The feed in the tests carried out included the following pure gases: CO_2, CH_4, O_2 and N_2. Each gas was tested under pressure of 2, 4, 8 and 10 bar as well as in the temperatures of 25°C, 45°C and 55°C. The surface area of the tested membranes was 29 cm^2.

3. Results and discussion

The results of the measurements and calculations obtained from the tests are presented in Figs. 2–6.

Figs. 2 and 3 present results obtained for gases tested in the temperature of 45°C and under pressure of 4 bar. Fig. 2 presents the dependence of the solubility coefficient on the critical temperature of gas. The obtained results confirmed the above-mentioned dependence that gases condense better, that is, characterized by a higher critical temperature, dissolve better in the membrane. Fig. 3, on the other hand, presents the dependence of the diffusion coefficient on the kinetic diameter of a gas particle. The chart presents a noticeable tendency for decrease in the diffusion coefficient with an increasing kinetic diameter of a gas particle. However, the value of the diffusion coefficient obtained for CH_4 was higher than for particles of O_2 and N_2 that were smaller than

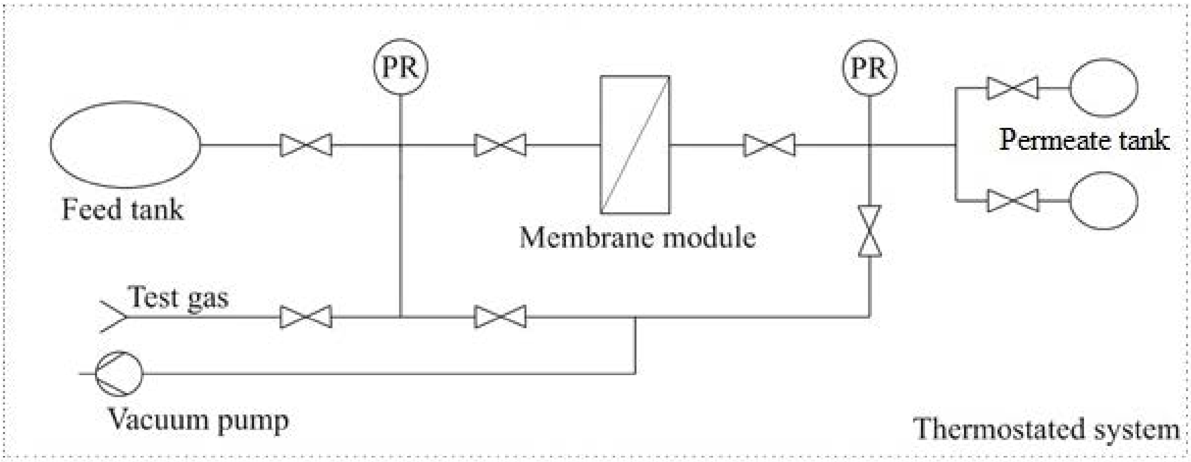

Fig. 1. The scheme of the installation for permeation and diffusion coefficients determination with the time-lag method.

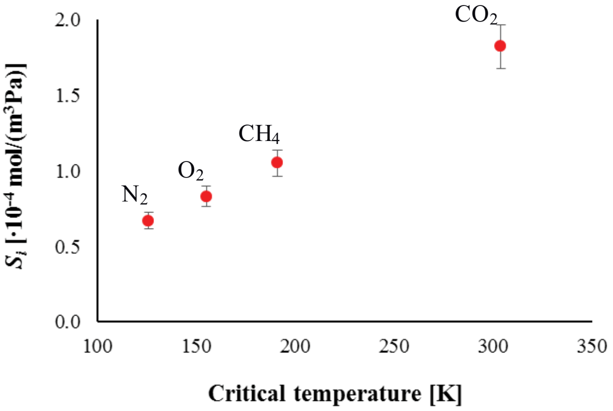

Fig. 2. Solubility coefficients for tested gases.

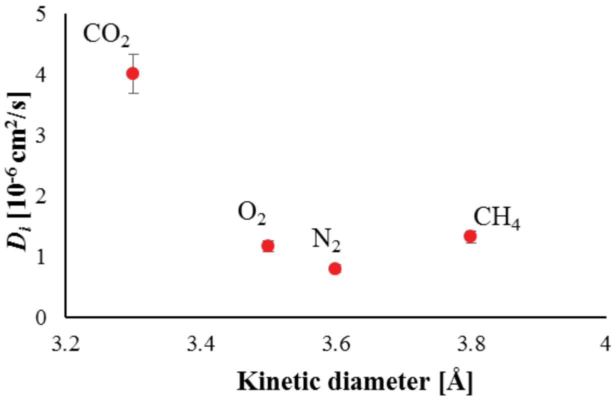

Fig. 3. Diffusion coefficients for tested gases.

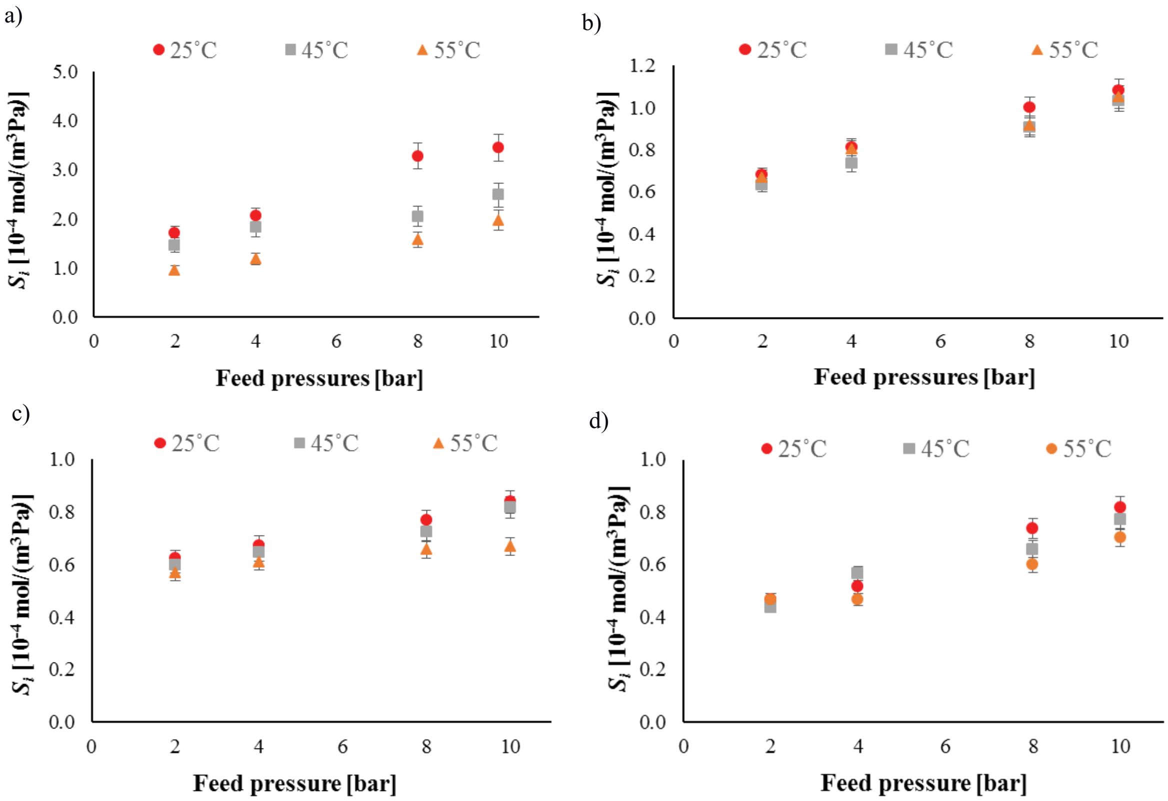

Fig. 4. The change of solubility coefficients for various feed pressures and temperatures: (a) CO_2, (b) CH_4, (c) O_2 and (d) N_2.

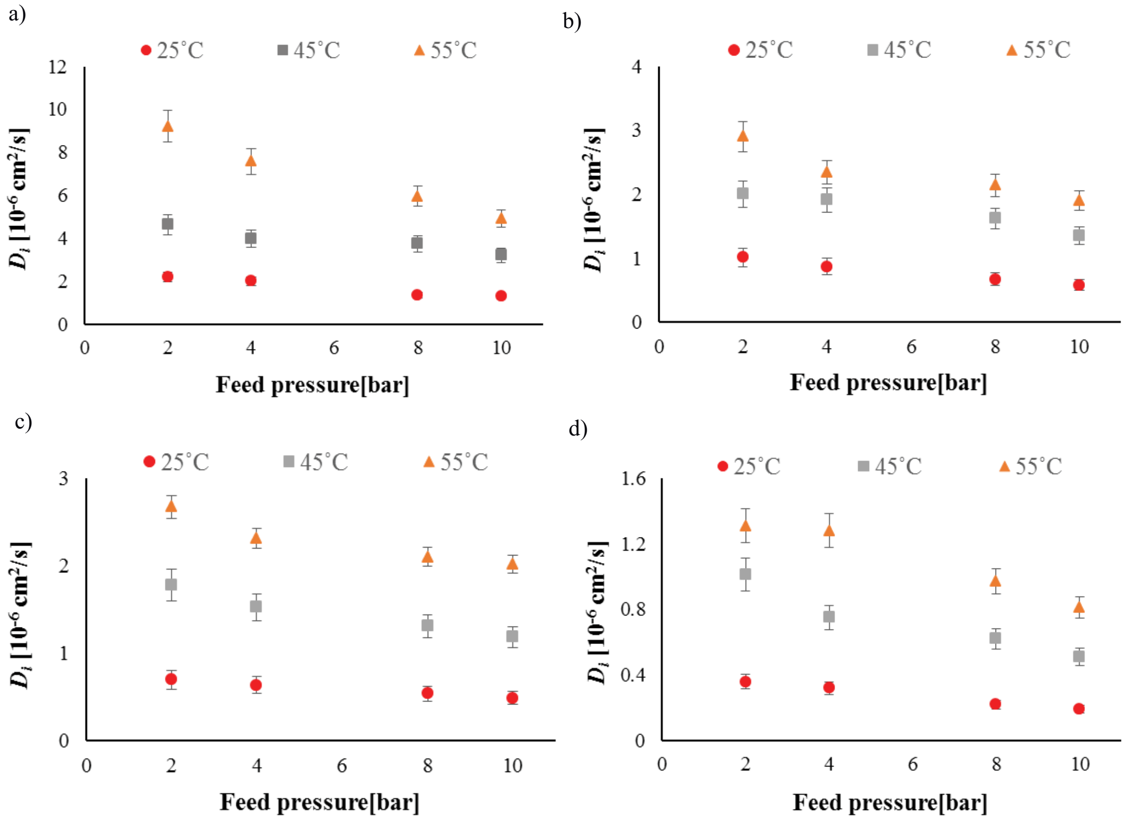

Fig. 5. The change of diffusion coefficients for various feed pressures and temperatures: (a) CO_2, (b) CH_4, (c) O_2 and (d) N_2.

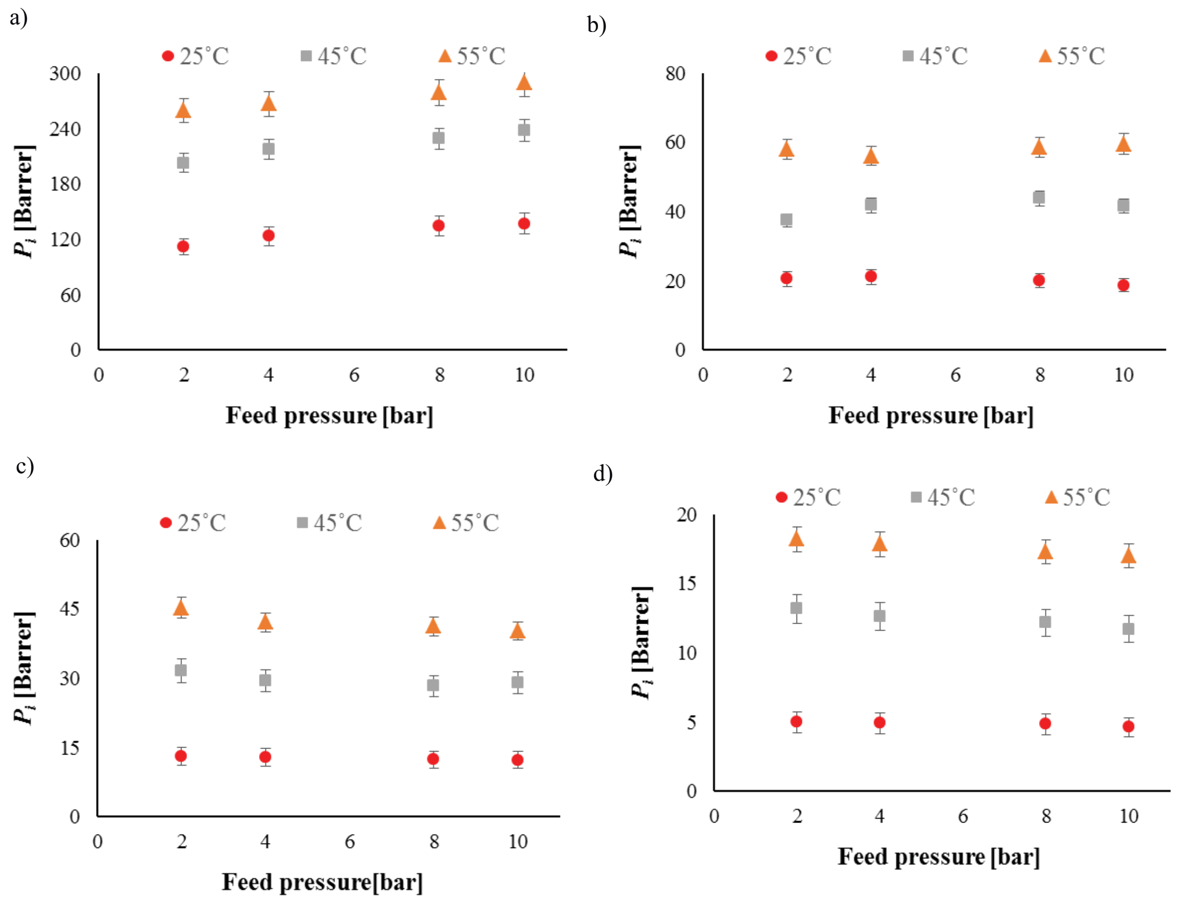

Fig. 6. The change of permeation coefficients for various feed temperatures and pressures: (a) CO_2, (b) CH_4, (c) O_2 and (d) N_2.

the coefficient. The value of the diffusion coefficient for CH_4 higher than expected was sought in the polarity value higher than for O_2 and N_2 (see Table 1). This property of CH_4 made the transport between the polar chains of PEBAX 2533 copolymer easier [18]. The same property affected the high value of the CO_2 diffusion coefficient through the membrane.

The product of the solubility and diffusion coefficients, Eq. (2), is the permeability. This allowed for the following arrangement of membrane permeability for the tested gases: $P_{CO_2} > P_{CH_4} > P_{O_2} > P_{N_2}$. These results confirmed the thesis proposed in this paper on the usefulness of the membrane made of Pebax 2533 polymer to remove CO_2 from the gas streams. The value of CO_2 diffusion coefficient that was several times higher than for the other tested gases made the value of permeability coefficient of the membrane for this gas higher.

Figs. 4–6 present results of tests of the influence of the temperature and pressure on the solubility coefficient, diffusion coefficient and permeability of the membrane for individual tested gases.

Fig. 4 presents values of the solubility coefficient obtained for various gases during tests in various temperatures and under various pressures. The analysis of the figure allows for the conclusion that the solubility coefficient for all gases increased with the drop of temperature and the rise of pressure. The influence of the temperature on the solubility coefficient was as expected. Such an influence of temperature is assumed in the van't Hoff's equation for the dissolution of gases, while the sorption enthalpy is negative [9]. On the other hand, the increased solubility coefficient value with the increase of pressure proved the nonlinearity of the sorption isotherm. The nonlinearity, which departs from the Henry's law, is confirmed for many gas-polymer systems [7].

Fig. 5 presents values of the diffusion coefficient obtained for various gases during tests in various temperatures and under various pressures. The analysis of this figure allows for the conclusion that the value of the diffusion coefficient rose with the increase of temperature and decreased with the increase of pressure. The influence of temperature on the value of the coefficient was as expected and supported by Arrhenius–van't Hoff's equation [19]. On the other hand, the effect of the decreased diffusion coefficient with the rising pressure may be explained by two phenomena. The first one is the compression of the membrane material under higher pressure [20]. Such compression makes the polymer chains less active and close to each other, which renders the movement of gas molecules among the polymer chains more difficult. The second phenomenon is the formation of permeating molecule clusters, described in the literature. The increased pressure leads to a better dissolution of gas in the membrane material. Large accumulation of gas particles in the membrane material is conducive to formations of the above-mentioned clusters. Larger particles, on the other hand, diffuse slower, which is manifested by the decrease in the efficient value of the diffusion coefficient [21].

Fig. 6 presents values of the membrane permeability obtained for various gases during tests in various temperatures and under various pressures. The analysis of this figure allows for the conclusion that the value of permeability increased with the rise of temperature and remained practically unchanged with the rise of pressure.

The influence of temperature on the value of permeability can be, just like in the case of diffusion, explained by Arrhenius–van't Hoff's equation. In this case, however, the energy of permeation activation is the sum of the diffusion activation and the sorption enthalpy. While the activation energy is always positive, the ultimate symbol permeation energy activation depends on mutual dependence of absolute values of the diffusion activation and the sorption enthalpy [19]. In the tested polymer-gas systems, the absolute value of the diffusion activation was higher than the absolute value of the sorption enthalpy. This made the permeability value increased with the rise of temperature. Such dependence applies to most polymer-gas systems. On the other hand, the influence of pressure on the permeability was reduced by the opposite effects, having an impact on the change with the pressure of the solubility and diffusion coefficients.

4. Summary

The authors examined the influence of process parameters, that is, temperature and pressure, on the solubility coefficient, diffusion coefficient and permeability in the process of gas permeation through the nonporous membrane.

From the process point of view, the analysis of the influence of the process parameters on the permeability of the membrane with regard to specific gases is the most significant. It was proven that the membrane permeability increased with the rise of temperature of the process. On the other hand, there were no significant changes in the value of permeability related to the pressure.

The thesis proposed in this paper that membranes made of Pebax 2533 polymer may be useful in the processes aiming at removing CO_2 from the gas streams, for example, biogas (mixture of CO_2 and CH_4) or waste gases (CO_2 and N_2), was confirmed. The high value of the membrane permeability for CO_2 was influenced by the high value of the solubility coefficient resulting from the high critical temperature of CO_2 as well as by the high value of the diffusion coefficient resulting simultaneously from the smaller kinetic diameter of CO_2 particle as compared with other gases and from polarizing properties of this gas particle.

Symbols

D_i	—	Diffusion coefficient of component *i* through the membrane, m^2/s
F	—	Membrane surface area, m^2
l	—	Thickness of the membrane, m
P_i	—	Permeability of component *i*, mol m/(Pa s m^2)
p_{in}	—	Partial pressure of component *i* in the feed channel, Pa
p_{ip}	—	Partial pressure of component *i* in the permeate, Pa
R	—	Gas constant, J/(mol K)
S_i	—	Solubility coefficient of component *i* on the membrane surface, mol/(m^3 Pa)
T	—	Temperature, K
t	—	Time, s
V	—	Volume of permeate space, m^3
θ	—	time-lag, s

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