



The influence of surfactant Pluronic P123 addition on the mixed matrix membrane PEBA[®] 2533 – ZIF-8 separation properties

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ABSTRACT

The membrane gas separation process is frequently employed to remove H₂S from biogas and to enrich it with methane. This process could be conducted using polymeric membranes, that is, made from PEBA[®] 2533 copolymer. The mixed matrix membranes prepared using PEBA[®] 2533 and metallic-organic framework fillers were tested in this paper. The presence of the dispersion phase could lead to the formation of defects in the composite structure. This is, in particular, the result of the agglomerates formation and the formation of void spaces between filler particles and polymeric chains. In order to decrease the probability of negative phenomena, the influence of Pluronic P123 surfactant addition on the membrane properties was also tested in this work. In the tests of the membranes with ZIF-8 filler, for CO₂, CH₄ and N₂, there was noticed an improvement of permeability of about 20%–50% after the addition of Pluronic P123 surfactant, as well as an increase of membrane selectivity of about 10%–30%.

Keywords: Membrane gas separation; Mixed matrix membrane; PEBA[®] 2533; Modification; ZIF-8; Surfactant

1. Introduction

The application of membrane techniques to separate gaseous mixtures is becoming increasingly more important in the industrial implementation of this process. Over the past decades, these techniques have become an alternative to conventional ways of industrial separation of gases. Membrane techniques compared to other commonly used techniques such as absorption, adsorption and cryogenic distillation demonstrate several advantages such as lack of phase change, high performance, low energy consumption, user-friendly operation and relatively low operating costs [1].

One of the areas in which membranes could be applied is enriching biogas in methane as well as drying and removing H₂S of it [2,3]. What can be used in this type of process are Polyether Block Amide (PEBA) copolymers. Structures made of this type of polymers have better permeability

for the gases, organic vapors and water vapor in relation to methane and components of the air [4–6]. In addition, they can be used to make capillary composite membranes, which can be applied on an industrial scale [7,8].

Unfortunately, polymer membranes have natural limitations that result from the properties of the polymer and the gas. It is connected with the principle that as the permeability of the membrane increases, its selectivity decreases, and vice versa. The dependence of permeation P_i and selectivity α_{ij} for a pair of gases is presented on the graph $\log P_i - \log \alpha_{ij}$ (where P_i refers to the gas with a higher coefficient of permeation). The border-line that is formed in the graph is referred to in the literature as the Robeson limit [10]. The mathematical dependence that describes its course is described by Freeman [9] in his paper, which confirmed the analysis based on the literature data presented by Robeson [10].

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One of the solutions that make it possible to achieve higher parameters that are typical of the separation properties of the membranes and thus cross the Robeson [10] line is to add a filler to the polymer matrix [11]. To improve the separation of CO₂ from mixtures containing CH₄, N₂ and O₂ metallic-organic framework (MOF) type compounds are used such as MIL-53, ZIF-7, ZIF-8, ZIF-90 or Cu₃(BTC)₂ [12–15]. MOF material has a spatial structure consisting of metallic cations coordinatively connected with organic ligands. The presence of MOF particles in the polymer matrix enlarges the distances between the polymer chains and increases their movement, which improves the permeation properties of the membrane. The improved selectivity, on the other hand, may result from two effects. Firstly, the shape and diameter of the pores allow for the transport of only such gases that have a smaller kinetic diameter of the molecule, so a selective transport based on a sieving mechanism occurs. Secondly, between MOF particles and gas particles there may be a guest–host interactions [16] or acceptor–donor interactions [17], which improve gas transport through the membrane.

However, the presence of a new phase generates defects at the border of the filler – polymer, among which one may include sieve in a cage, matrix rigidification, plugged sieves. These phenomena could degrade the separation or mechanical properties of the membrane [18,19]. Another of the negative phenomena that may appear, is the emergence of agglomerates with sufficiently high concentrations of the filler. Both around the agglomerate and in its interior free spaces are formed which do not cause resistance to the permeating gas, and this results in a reduction in the selectivity of the membrane and its increased permeability [20]. The intensity of the above described adverse phenomena can be reduced by improved interaction between the filler particle and the polymer chain. In this aim, surfactants could be used. The properties of surfactants result from the characteristic structure form of the surfactant particle, which includes both hydrophilic and hydrophobic groups. In the filler particles – polar solvent system, hydrophobic segments are surrounded by particles and the hydrophilic part is positioned toward the solvent. This phenomenon is used to reduce the degree of particle agglomeration [21,22]. A similar effect occurs in the additives particles – polymer system; in this case the hydrophilic part interacts by hydrogen bonds with hydrophilic polymer chains [23,24], which increases the interaction between the two phases. In addition, the formation of the polymer – surfactant complex increases the mobility of the polymer chains and reduces their packing, which improves the diffusion of gases [25,26].

The aim of the study is to examine the effects of the additive of surfactant Pluronic P123 on the separation properties of heterogeneous membranes made of copolymer PEBAX® 2533 and filler – ZIF-8.

2. Experimental

2.1. Materials

To make flat polymer membranes a block copolymer was used, with the trade name PEBAX® 2533 (Arkema Group, France). The compound used in the study consists of 80%

mass polyether (PTMO – polyphenylene oxide/tetramethylene) and 20% mass polyamide (PA12 – nylon 12). The vast content of PTMO makes the above copolymer classified as a thermoplastic elastomer.

In the presented study, a metal-organic compound with the trade name Basolite® Z1200 (Sigma-Aldrich, Germany) classified as ZIF-8 was used as the filler of the polymer matrix. This structure consists of zinc cations connected with 2-methylimidazole ligands. This compound is characterized by high porosity and thus a large specific surface area. What is special about this compound is a relatively high chemical and thermal resistance [27,28]. The specific surface area of Basolite® Z1200 is 1,300–1,800 m²/g and the diameter of the particles (D50) is 4.9 μm [29]. In the presented tests, a non-ionic, block copolymer Pluronic P123 (Sigma-Aldrich, Germany) was used as a surfactant. Its structure is composed of a hydrophilic group of poly(ethylene oxide) (PEO) and a hydrophobic group of poly(propylene oxide) (PPO). The mass ratio of PEO/PPO is 70/30 [30].

2.2. Preparation of membranes

A process of dry phase inversion was used to make membranes. The method is based on the evaporation of the solvent from the casting solution. Flat membranes were prepared in the tests. The casting solution film was formed with a casting knife, and the film was 500 μm thick. Both the temperature of the solution and the temperature of the surface on which the layer was formed were 50°C. The surface temperature was maintained throughout the evaporation of the solvent. After 4 h of the solvent evaporation, the membranes were placed in a vacuum oven for 24 h in order to remove traces of the solvent.

The thickness of the membranes after the evaporation of the solvent was between 40–50 μm. For the preparation of the membranes PEBAX® 2533 in 2-butanol with mass concentration of 7% was used. In the case of heterogeneous membranes or those containing a surfactant first a 2-butanol was prepared with a specific quantity of the polymer additionally after appropriate stirring/dissolving. In order to achieve a high degree of ZIF-8 particle dispersal, mechanical stirring and ultrasound were used alternately. In the case of solutions containing ZIF-8 and Pluronic P123, first the surfactant was dissolved, then ZIF-8 was added, and the resulting mixture was stirred mechanically and with ultrasound. After obtaining a homogeneous mixture, PEBAX® 2533 was added. After each component was added, the mixture was stirred for 24 h in a fixed temperature. The compositions of casting solutions are presented in Table 1. ZIF-8 concentration and Pluronic P123 concentration are given in relation to PEBAX® 2533 mass.

2.3. Test methods

To determine the coefficient of diffusion, solubility and permeation of the membranes being made a time-lag method was used [31], with the system proposed by the authors in the paper [32]. The method consists of measuring the pressure on the permeate side as a function of time. Based on the obtained function, the so-called parameter of time lag₀ (s) is determined, which enables the diffusion

Table 1
Casting solutions composition

Sample	1	2	4	4	5	6	7	8	9	10	11	12	13
Solvent						2-butanol							
PEBAX® 2533 concentration (%)	7												
Pluronic P123 concentration (%)	0					2.5				5			
ZIF-8 concentration (%)	0	2	5	8	10	0	2	5	10	0	2	5	10

coefficient D (m²/s) to be determined, when the membrane thickness l (m) is known (Eq. (1)).

$$D = \frac{l^2}{6\theta} \quad (1)$$

In turn, the angle of inclination of the straight section of the obtained function enables the permeation coefficient P (barrer) to be determined (Eq. (2)).

$$P = \frac{V \cdot l}{(p_n - p_p) \cdot F \cdot R \cdot T} \frac{dp}{dt} \quad (2)$$

where V is the volume of gas on the permeate side (m³), p_n is the gas pressure on the feed side (Pa), p_p is the gas pressure on the permeate side (Pa), F is the membrane surface (m²), R is the gas constant 8.314 (J/(mol K)), T is the temperature (K).

Then using the basic relationship related to the solution-diffusion model (Eq. (3)), it is possible to determine the solubility coefficient S (mol/(m³ Pa)) [33].

$$P = D \cdot S \quad (3)$$

It should be noted that the unit of membrane permeability coefficient commonly used while considering the process of gas permeation is 1 (barrer). This results from the fact that the use of the corresponding SI unit leads to very low values of the permeability coefficient.

The tests were conducted at a temperature of 45°C and under the pressure of the feed of 4 bar. Before the measurements, the gases were removed from the plant by the use of a vacuum pump. The change in pressure on the permeate side during the measurement was recorded by the computer.

To test the changes in the surface properties of the membranes a microscopic analysis, the contact angle test and the Fourier-transform infrared spectroscopy (FTIR) method were used. The microscopic analysis was conducted using a microscope scanning electron microscopy (SEM) Phenom Pro. In order to evaluate the structure of the membrane photos of the surface and cross-section of the membrane were taken. The photos of the cross-section were additionally used to determine the thickness of the membrane. With the use of the 3D Roughness Reconstruction application, the surface roughness was determined. In order to evaluate it, the average roughness (R_a) and roughness height (R_z) parameters were used. For SEM analysis, the Charge Reduction Sample Holder was used. This holder makes it possible to take photos of non-conductive

samples, such as polymers, glass, paper, without sputtering. The contact angle was tested with the sessile drop method using the goniometer OCA 25 Dataphysics. The test of the contact angle shows changes in the surface properties of the membranes connected with the appearance of particles ZIF-8 or the presence of surfactant Pluronic P123. The contact angle was tested with the use of reverse osmosis water (conductivity 15 µS/cm), the drop volume was 2 µl. Additionally, the changes in the structure in the surface layer were tested using the FTIR analysis with the attenuated total reflectance method. The tests were conducted with the Nicolet iS10 (Thermo Scientific). The sample was scanned 32 times within the wavenumbers 4,000–800 cm⁻¹.

3. Results and discussion

In the first part of the test, the concentration effects of ZIF-8 C_{mZIF-8} on the separation properties of the membrane were identified. Membranes with ZIF-8 concentration amounting to 1%, 2%, 5%, 8% and 10% were prepared (samples 1–5). The obtained permeability coefficients of $CO_2 \cdot P_{CO_2}$ and selectivity coefficients of CO_2 in relation to $CH_4 \cdot \alpha_{CO_2/CH_4}$ and $N_2 \cdot \alpha_{CO_2/N_2}$ for the tested membranes are shown in Fig. 1. In addition, the results of permeation coefficients for $CO_2 \cdot P_{CO_2}$, $CH_4 \cdot P_{CH_4}$ and $N_2 \cdot P_{N_2}$ obtained for the membranes with ZIF-8 concentrations, which were selected for further tests are shown in Table 2.

On the basis of the results, it is possible to conclude that the membranes made with PEBAX® 2533 are characterized by preferential transport of CO_2 compared to other tested gases. This is due to the presence of polar polyether chains in the polymer structure, which interact with CO_2 molecules [34].

In turn, the permeation coefficient for all gases increases with the increase in ZIF-8 concentration. However, it should be noted that above the specified concentration, there is a decrease in the selectivity of CO_2 in relation to other gases, particularly in relation to N_2 . This effect can be seen for membranes containing 5%, 8% and 10% of ZIF-8. The decreased selectivity of the membrane and increased permeability reflect the formation of free spaces around the particles and agglomerates of the filler. The increase in both the permeation coefficient of CO_2 and selectivity occurs only for the membranes with the concentration of ZIF-8 amounting to 1% and 2%. Later in the study, the following membranes will be analyzed: a membrane which has the highest coefficient of selectivity ($C_{mZIF-8} = 2\%$), a membrane with the concentration of ZIF-8 amounting to 5%, for which a clear decrease in selectivity was observed and a membrane with the highest ZIF-8 concentration ($C_{mZIF-8} = 10\%$).

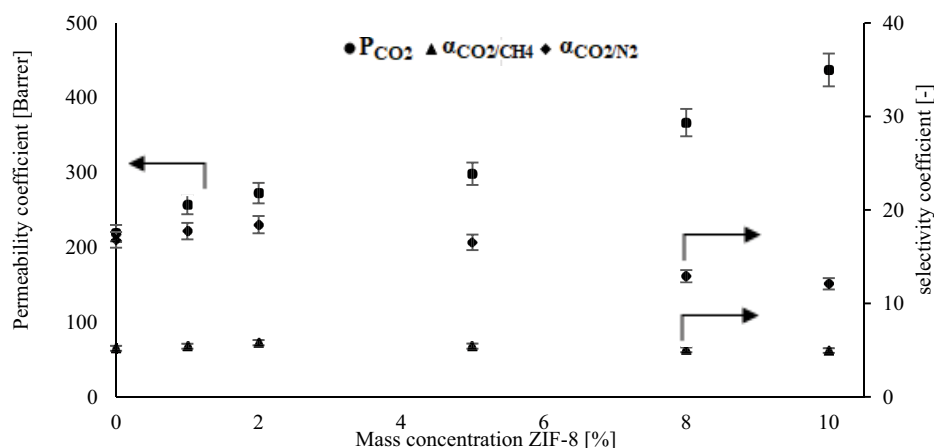


Fig. 1. Effects of ZIF-8 concentration on the permeability and selectivity of the membrane.

Table 2

Permeation P_i of the test gases for different concentrations of ZIF-8

C_{mZIF-8} (%)	0	2	5	10
P_{CO_2} (barrer)	218.9	272.5	298.4	437.2
P_{CH_4} (barrer)	42.1	47.0	55.0	88.1
P_{N_2} (barrer)	13.0	14.8	18.0	36.1

Next, the effects of surfactant Pluronic P123 on the separation properties of membranes containing ZIF-8 were tested. For this purpose, membranes with a concentration of 2%, 5% and 10% of ZIF-8 without Pluronic addition (samples 6 and 10) and with the additive of 2.5% or 5% surfactant were prepared (samples 7–9 and 11–13). The results of the permeation coefficients of CO_2 are shown in Fig. 2.

On the basis of the above results, it is possible to observe improved permeability of CO_2 for membranes containing 2% and 5% ZIF-8 with the additive of 2.5% surfactant. In the case of the membrane containing 10% ZIF-8 and 2.5% Pluronic P123 as well as heterogeneous membranes containing 5% surfactant, there is a drop in the permeation coefficient of CO_2 in relation to the membranes without a surfactant. Nevertheless, for both concentrations of the surfactant, the selectivity of the membranes improves in relation to heterogeneous membranes without the additive of surfactant (Fig. 3).

The tests also covered homogeneous membranes, that is, made of the copolymer PEBAX® 2533 only, with the additive of 2.5% and 5% of surfactant (samples 6 and 10). This will eliminate the phenomena connected with the effects of the surfactant on the sole polymer and make it possible to determine the effects on the filler. The obtained permeation coefficients of the test gases and the selectivity coefficients are shown in Tables 3 and 4, respectively.

With regard to the results, it can be concluded that the obtained permeation coefficients for membranes containing only a surfactant are lower than for membranes containing ZIF-8 and Pluronic P123 and higher than for the homogeneous membrane. This shows that the improved

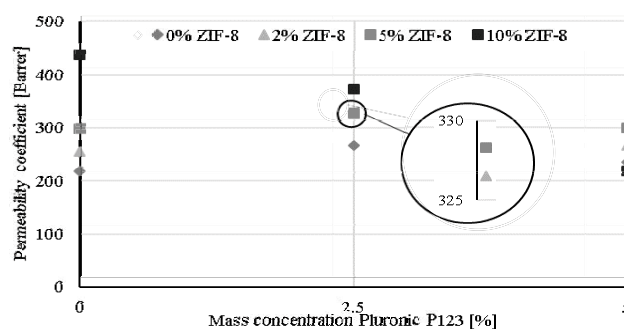


Fig. 2. Permeation coefficient of CO_2 for membranes containing ZIF-8 and Pluronic P123.

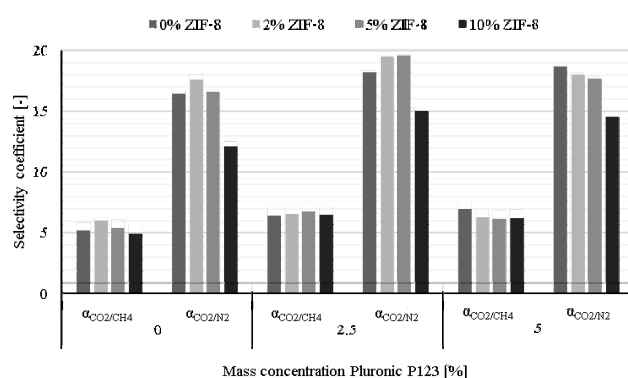


Fig. 3. Selectivity coefficient for membranes containing ZIF-8 and Pluronic P123.

permeation properties result both from the presence of Pluronic P123 and ZIF-8, while the increase in the permeability for membranes containing 2% or 5% ZIF-8 and 2.5% Pluronic P123 in relation to the corresponding membranes without the additive of a surfactant as well as the membrane containing only 2.5% surfactant reflects its influence on the filler particles. Also, the value of selectivity coefficients that describe the membrane containing Pluronic P123 is higher than for the homogeneous membrane.

Table 3
Permeation coefficients P_i of the test gases for membranes with different concentrations Pluronic P123

Permeation coefficient P_i (barrer)	Pluronic P123 Concentration		
	0	2.5%	5%
P_{CO_2}	218.6	267.1	235.2
P_{CH_4}	42.1	41.7	33.6
P_{N_2}	13.3	14.7	12.6

Table 4
Selectivity coefficients α_{ij} typical of membranes with different Pluronic P123 concentrations

Selectivity coefficient α_{ij}	Pluronic P123 concentration		
	0	2.5%	5%
$\alpha_{\text{CO}_2/\text{CH}_4}$	5.2	6.4	7.0
$\alpha_{\text{CO}_2/\text{N}_2}$	16.4	18.2	18.6

In addition, for heterogeneous membranes containing 2.5% surfactant, there is an improvement in selectivity in relation to both homogeneous membranes containing 2.5% surfactant and heterogeneous membranes without the additive of Pluronic P123. This confirms that the surfactant also affects the separation properties of heterogeneous membranes.

3.1. Material analysis of the membranes

The presence of ZIF-8 in the structure of the membrane can be observed in photomicrographs of the surface and cross-section of the membranes, shown in Figs. 4 and 5.

What can also be observed in the photos are agglomerates that emerge with the increase of the filler concentration. However, the structure of the membranes keeps having a solid form, there are no clear pores or free spaces.

In the case of membranes with the additive of surfactant, there are no clear changes in the structure of the membrane or defects, which can be seen in Fig. 6. The reason for this is that the Pluronic P123 is a polymer with similar chemical groups as PEBAX® 2533.

The presence of ZIF-8 or surfactant Pluronic P123 on the surface of the membrane affects the wettability of the surface and its roughness, which confirm the results in Tables 5 and 6.

The increased hydrophobicity of the membrane surface results from the relatively hydrophobic nature of the particles of ZIF-8 [35]. A slight decrease in the contact angle for membranes containing 10% ZIF-8 results from a significant increase in roughness, because for a surface with a contact angle below 90°, the increased roughness reduces the contact angle [36]. On the other hand, the increased roughness is connected with the appearance of filler particles and tiny cracks on the surface of the membrane. The second defect is due to the difference between the thermal expansion of the polymer matrix and the filler particles, which during the evaporation of the solvent leads to cracking of the membrane surface.

The increased wettability of the membrane surface is due to the appearance of hydrophilic groups PEO present in the structure of Pluronic P123 [37]. In addition, the appearance of new groups on the surface of the membrane affected the rate of evaporation of the solvent and the formation of the membrane surface, which is reflected by the change in the roughness of the membrane.

The presence of new chemical groups on the surface of the membrane connected with particles of the used

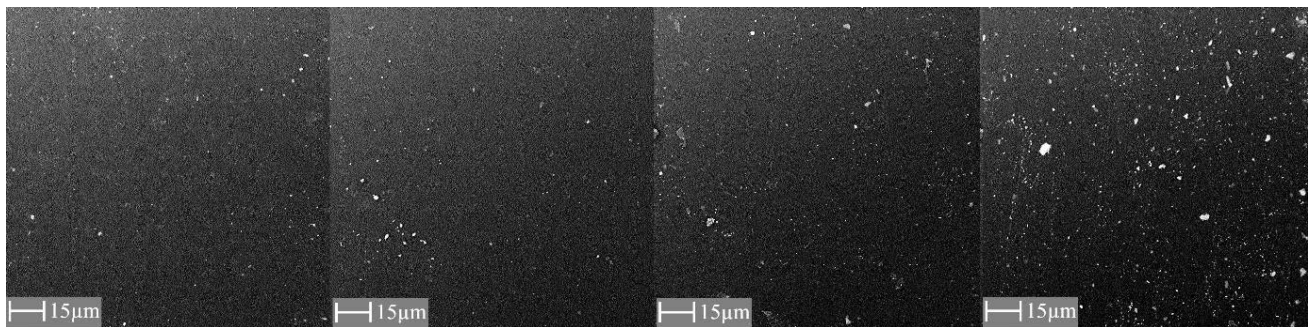


Fig. 4. Photomicrographs of the surface of the membranes. The membranes presented with the following composition: PEBAx® 2533, PEBAx® 2533 + 2%/5%/10% ZIF-8, respectively.

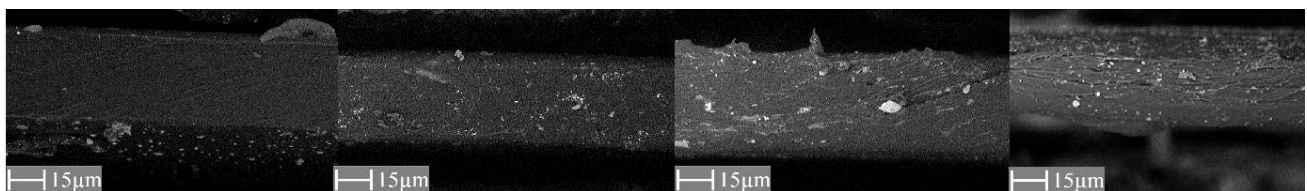


Fig. 5. Photomicrographs of the cross-section of the membranes. The membranes presented with the following composition: PEBAx® 2533, PEBAx® 2533 + 2%/5%/10% ZIF-8, respectively.

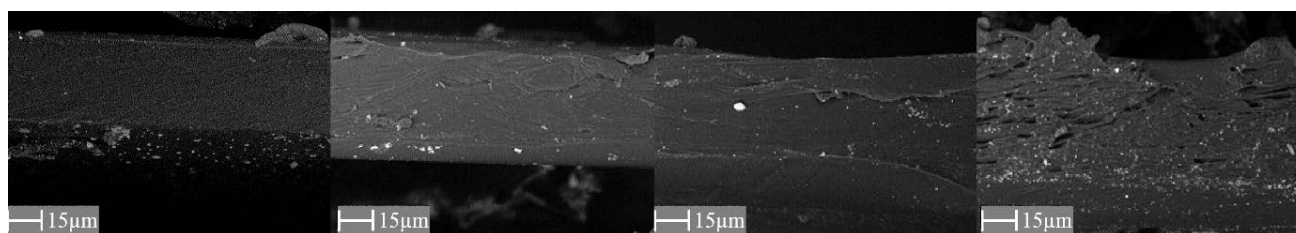


Fig. 6. Photomicrographs of the cross-section of the membranes. The membranes presented with the following composition: PEBAX[®] 2533, PEBAX[®] 2533 + 2%/5%/5% Pluronic P123, respectively.

Table 5
Change in the surface properties of the membranes for different ZIF-8 concentrations

C_{mZIF-8} (%)	0	2	5	10
θ (°)	82.83	88.27	89.06	87.10
R_a (μm)	1.07	1.11	1.28	1.43
R_s (nm)	167.6	178	203.6	229.0

Table 6
Change in the surface properties of the membranes for different Pluronic P123 concentrations

C_{mP123} (%)	0	2.5	5
θ (°)	82.83	80.18	53.15
R_a (μm)	1.07	1.25	1.31
R_s (μm)	167.6	206.2	207.6

additives was confirmed by the FTIR analysis. The obtained spectra of the modified membranes using ZIF-8 are shown in Fig. 7.

The absorption bands that are typical of ZIF-8 correspond to the vibrations: bonds Zn–N (421 cm^{-1}) and bonds that occur in an imidazole ligand in the range of wavenumbers $500\text{--}1500\text{ cm}^{-1}$. The intense peak occurring with the wavenumber 1146 cm^{-1} corresponds to the vibrations of bond C–N [38]. In the figure, two characteristic peaks for particles ZIF-8 corresponding to bonds Zn–N and C–N are marked. For membranes with the content of 2% and 5% of ZIF-8, the peak corresponding to bond C–N is invisible, which results from the insufficiently low intensity of adsorption (too small ZIF-8 concentration) or overlapping with the spectrum characteristic of the material PEBAX[®] 2533. However, there is a clearly visible peak corresponding to bond Zn–N, the intensity of which increases with

the concentration and for the concentration of 10% ZIF-8 there appears a peak corresponding to bond C–N.

In the case of membranes containing Pluronic P123, the FTIR analysis did not reveal any appearance of new peaks, not connected with the material PEBAX[®] 2533. The reason for this is that a surfactant has chemical groups that also occur in the structure of a copolymer, only the intensity of the peaks changed.

3.2. Analysis of coefficients of diffusion and solubility

The presence of ZIF-8 and Pluronic P123 affects the solubility of gases on the surface of the membrane, which is indicated by the results of the solubility coefficients S_i presented in Tables 7 and 8.

Based on the results it can be concluded that there is an increase in the solubility of the gases with the increase

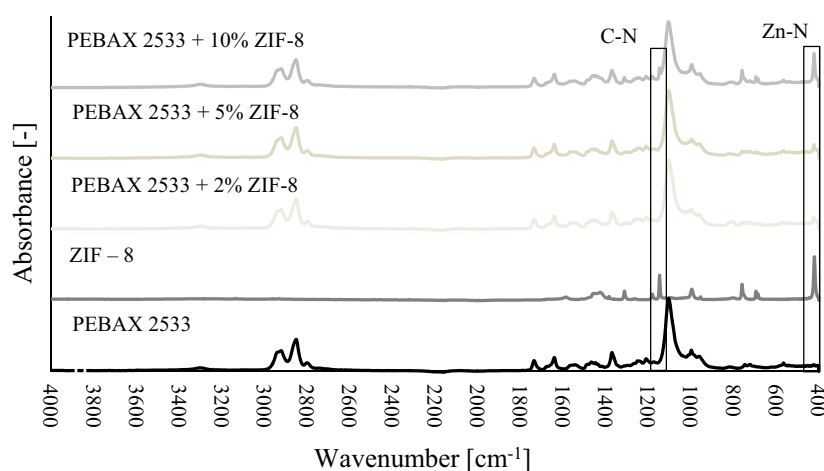


Fig. 7. FTIR analysis of a non-modified membrane (PEBAX[®] 2533), particle ZIF-8 (ZIF-8) and membranes containing different ZIF-8 concentrations (PEBAX[®] 2533 + 2%/5%/10% ZIF-8).

Table 7
Coefficient of solubility S_i for membranes of different ZIF-8 concentrations

C_{mZIF-8} (%)	0	2	5	10
$S_{CO_2}^a$	0.385	0.412	0.459	0.520
$S_{CH_4}^a$	0.281	0.288	0.306	0.310
$S_{N_2}^a$	0.145	0.145	0.148	0.158

^a S (10^{-3} mol/(m³ Pa)).

Table 8
Coefficient of solubility S_i of the test gases for different Pluronic P123 concentrations

C_{mP123} (%)	0	2.5	5
$S_{CO_2}^a$	0.385	0.437	0.522
$S_{CH_4}^a$	0.281	0.294	0.320
$S_{N_2}^a$	0.145	0.159	0.165

^a S (10^{-3} mol/(m³ Pa)).

in ZIF-8 concentration. The increased solubility of gases results from the expansion of the membrane surface, which affects the increase in the contact area between the gas and the membrane. The expansion of the membrane surface is confirmed by the results of roughness. However, the increase in solubility selectivity of CO₂, the results obtained are shown in Table 9 in relation to the remaining gases, suggests that the additive of the filler improves the solubility of CO₂ more intensely than N₂ or CH₄. Between particles CO₂ and organic heterocyclic particles containing an atom of nitrogen such as imidazole ligands [39], there may arise proton–donor interactions, which improve the solubility of CO₂ on the surface of the membrane. The presence of new chemical groups is confirmed with the use of the FTIR analysis.

On the basis of the results it can be concluded that with the increase in the concentration of the surfactant, there is an increase in the solubility coefficient for all gases. This is due to the occurrence of hydrophilic chains of PEO on the surface of the membrane. In addition, it is possible to see an increased solubility selectivity (Table 10) of CO₂ in relation to CH₄ and N₂, which reflects a more intense increase in the solubility of CO₂. It is related to a higher degree of interaction between the molecule CO₂ and the chains of PEO than between other gases and the group PEO. The increase in the solubility of gases may also be due to the increased roughness of the surface.

The heterogeneous membranes additionally containing Pluronic P123 have a higher coefficient of solubility both than membranes not containing surfactant and homogeneous membranes with the surfactant additive (Fig. 8).

On the basis of the increased solubility selectivity (Fig. 9) it can be concluded that the improvement of the increase in the solubility of CO₂ is more intense than for other gases also in the case of heterogeneous membranes with the additive of Pluronic P123.

Table 9
Solubility selectivity α_{ij}^S for membranes with different ZIF-8 concentrations

C_{mZIF-8} (%)	0	2	5	10
α_{CO_2/CH_4}^S (-)	1.37	1.43	1.50	1.68
α_{CO_2/N_2}^S (-)	2.66	2.83	3.09	3.30

Table 10
Coefficients of solubility selectivity and α_{ij}^S of the test gases for different Pluronic P123 concentrations

C_{mP123} (%)	0	2.5	5
α_{CO_2/CH_4}^S (-)	1.37	1.49	1.63
α_{CO_2/N_2}^S (-)	2.66	2.61	2.96

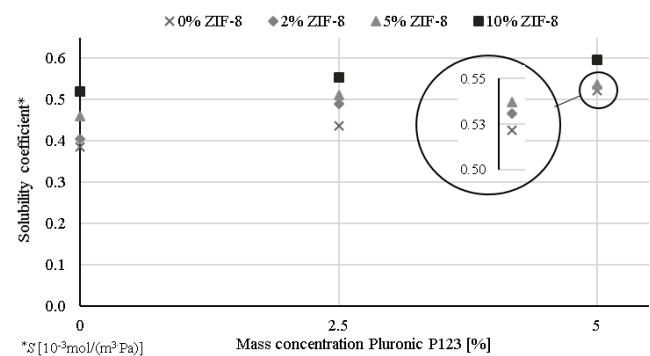


Fig. 8. Solubility coefficient of CO₂ for membranes containing ZIF-8 and Pluronic P123.

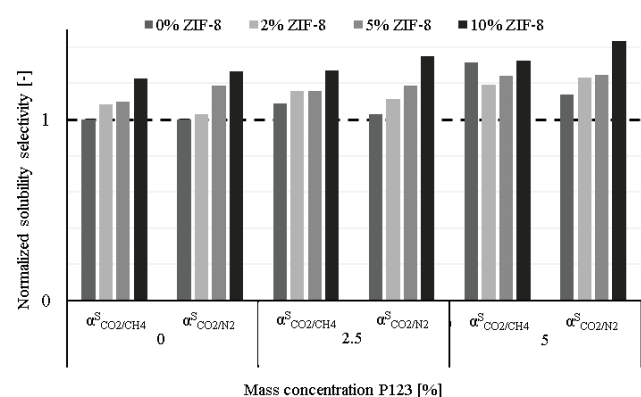


Fig. 9. Normalized solubility selectivity coefficient for membranes containing ZIF-8 and Pluronic P123.

The presence of ZIF-8 and Pluronic P123 also affects the diffusion of gases through the membrane. Tables 11 and 12 present the obtained coefficients of diffusion of the test gases D_i and diffusivity selectivity α_{ij}^D for membranes with different ZIF-8 concentrations C_{mZIF-8} .

Table 11
Diffusion coefficient of D_i of the test gases for different ZIF-8 concentrations

C_{mZIF-8}	0	2	5	10
$D_{CO_2}^a$	1.91	2.15	2.18	2.82
$D_{CH_4}^a$	0.50	0.55	0.60	0.95
$D_{N_2}^a$	0.29	0.34	0.41	0.77

^a D (10^{-10} m²/s).

Table 12
Diffusivity selectivity α_{ij}^D for membranes with different ZIF-8 concentrations

C_{mZIF-8} (%)	0	2	5	10
α_{CO_2/CH_4}^D (-)	3.80	3.92	3.62	2.96
α_{CO_2/N_2}^D (-)	6.55	6.29	5.34	3.37
α_{CH_4/N_2}^D (-)	1.72	1.60	1.47	1.24

With regard to the results, it can be concluded that there is an increase in the diffusion coefficients with the increase in ZIF-8 concentration. The initial increase in the diffusion coefficients and the slight decrease in α_{CO_2/N_2}^D and α_{CH_4/N_2}^D probably result from free spaces being formed around the filler particles, which reduce the resistance of gas permeation. With higher ZIF-8 concentration ($C_{mZIF-8} = 5\%$) there is a decrease in both α_{CO_2/CH_4}^D and α_{CO_2/N_2}^D which is due to a more intense phenomenon of the formation of free spaces around the filler particles and the appearance of agglomerates which do not constitute resistance to gas molecules. The presence of agglomerates in the membrane structure can be seen in photomicrographs, while the high ZIF-8 concentration ($C_{mZIF-8} = 10\%$) causes a significant increase in the diffusion of all gases and a large drop in the diffusivity selectivity coefficients. This reflects an intense overlap of the phenomena leading to defects, in particular the formation of agglomerates. The formation of free spaces around the filler and increased intensity of this phenomenon together with the concentration of the filler are also confirmed by the drop in α_{CH_4/N_2}^D that is, the diffusion of smaller particles of nitrogen (3.6 Å) increases faster than in the case of larger particles of methane (3.8 Å).

Next, Tables 13 and 14 present the obtained diffusion coefficients of test gases D_i and diffusivity selectivity α_{ij}^D for membranes with different Pluronic P123 concentrations

$C_{mPluronicP123}$.
Based on the results, for the concentration of 2.5% Pluronic P123 an increased diffusion of CO_2 , CH_4 , N_2 and improved diffusivity selectivity coefficients can be observed. This is due to the presence of new groups PEO, which increases the transport of gases through the membrane, CO_2 in particular. However, with a more concentrated surfactant (5%) reduced diffusion coefficients of the test cases as well as slight changes in diffusivity selectivity in relation to the non-modified membrane can be observed. The drop in the diffusion results from the rigidity of the polymer chains,

Table 13
Diffusion coefficient of D_i of the test gases for different Pluronic P123 concentrations

$C_{mPluronicP123}$ (%)	0	2.5	5
$D_{CO_2}^a$	1.91	2.05	1.51
$D_{CH_4}^a$	0.50	0.53	0.39
$D_{N_2}^a$	0.29	0.29	0.24

^a D (10^{-10} m²/s).

Table 14
Diffusivity selectivity α_{ij}^D for membranes of different Pluronic P123 concentrations

$C_{mPluronicP123}$ (%)	0	2.5	5
α_{CO_2/CH_4}^D (-)	3.80	3.88	3.90
α_{CO_2/N_2}^D (-)	6.55	6.95	6.29

which makes the transport of gases difficult. The drop in the coefficient α_{CO_2/N_2}^D may reflect the formation of free spaces in the structure of the membrane.

With low concentrations, there are interactions of the polymer with free monomers of the surfactant, which causes the development of chains of the polymer. However, after the micellar concentration is exceeded, interactions of the polymer with micelles occur, which makes the chains rigid [40,41].

In addition, the diffusion coefficients for membranes containing both ZIF-8 and Pluronic P123 were determined. The results of the diffusion are shown in Fig. 10.

On the basis of the results a slight improvement in the diffusion of CO_2 for the membrane containing 2% and 5% of ZIF-8 with the additive of 2.5% Pluronic P123 in relation to the membranes without the additive of surfactant can be observed. In the event of a concentration of 10% ZIF-8, there is a drop in the diffusion coefficient, both for the membranes containing 2.5% and 5% surfactant in relation to the membrane without the surfactant additive. A large drop in the diffusion coefficient for membranes containing 10% ZIF-8

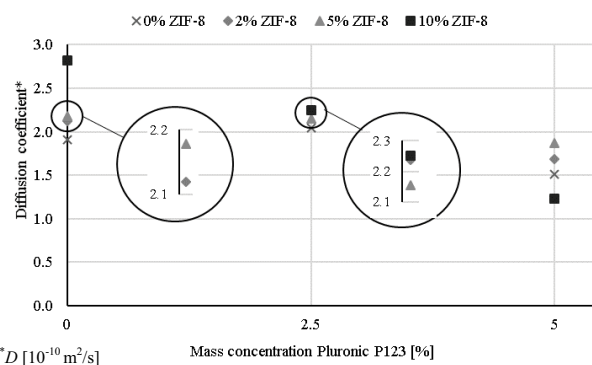


Fig. 10. Diffusion coefficient of CO_2 for membranes containing ZIF-8 and Pluronic P123.

results from a reduction in the agglomeration degree of the particles ZIF-8, which prevents the occurrence of negative phenomena. A smaller quantity of agglomerates enlarges the membrane resistance as a result of the reduction in free space between particles forming agglomerates and around them. However, the large concentration of the better-deployed filler in the structure of the membrane increases the way of the diffusion of the gas molecules and rigidifies a greater number of polymer chains, as a result of which there is a decrease in the diffusion coefficient of CO₂ (as well as other gases). A large decrease in the diffusion coefficient for the membrane with 10% ZIF-8 and 5% Pluronic P123 is the cause of the reduced permeation coefficient of CO₂ for this membrane (Fig. 2). The decreased diffusion for the membrane containing a 5% surfactant is described in the section on the effects of surfactant concentration on the separation properties of membranes.

The reduction of the agglomeration degree is also confirmed by the obtained coefficients of diffusivity selectivity (Fig. 11). The increased diffusivity selectivity of CO₂ in relation to other gases shows that the transport of CH₄ and N₂ in relation to CO₂ was limited, which is particularly visible in the case of membranes containing 2.5% surfactant. Both in relation to nitrogen and methane, the obtained coefficients of diffusivity selectivity were higher than for membranes without the surfactant additive. In the case of membranes containing 5% surfactant, this effect is visible only in relation to CH₄. In the case of N₂, there was a drop in α_{ij}^D . This may result from the above-mentioned phenomenon of the formation of the system of polymer – micelles in the case of this concentration of the surfactant, which still distorts the formation of the membrane structure.

4. Conclusion

The results confirm that surfactant Pluronic P123 affects the properties of both the homogeneous membrane made of PEBA[®] 2533 and the heterogeneous membranes containing ZIF-8. The surfactant addition influences both the CO₂ diffusion and the CO₂ solubility at the membrane surface. These effects are related to the presence of the PEO group in the Pluronic P123 structure. The presence of the hydrophilic PEO groups at the membrane surface has been confirmed by contact angle measurements. Nevertheless,

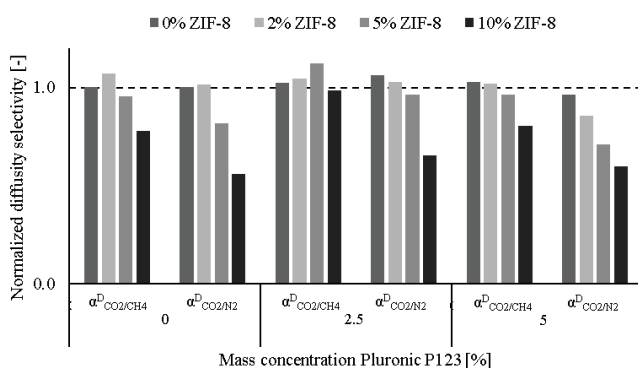


Fig. 11. Normalized diffusivity selectivity coefficient for membranes containing ZIF-8 and Pluronic P123.

the separation properties of membranes can be improved up to a specific concentration of the surfactant.

In case of ZIF-8, the increase in gas diffusion is the consequence of the formation of free spaces around the filler. This is due to weak interactions between the filler particle and the polymer rather than a specific interaction of ZIF-8 with one of the gases or polymer chains, or the interactions are so weak that their effects on the transport properties of the membrane are negligible.

The addition of the surfactant reduces the agglomeration degree of ZIF-8 particles; this effect is particularly visible at higher concentrations of the filler. For such concentrations, the presence of the surfactant influences the decrease of the gas diffusion coefficient, but the selectivity of the membrane made with the surfactant is higher than for the membrane without the surfactant.

Based on the results it can be concluded that the improvement in the solubility selectivity of CO₂ in the ratio of N₂ and CH₄ results both from the presence of ZIF-8 and Pluronic P123. The increase of CO₂ solubility is related to the presence of new chemical groups at the membrane surface: imidazole ligands (from ZIF-8 particles) and PEO groups (from Pluronic P123). The presence of new chemical groups at the membrane surface has been confirmed by contact angle measurements and FTIR analyses. Additionally, the increase of solubility of all tested gases is related to the expansion of the membrane surface, which makes the gas – membrane contact area greater. This effect has been confirmed by the increase of surface roughness.

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