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Research Article

Natural Gas Sweetening via Membrane-Assisted Gas Absorption. Part 2: A Hollow-Fiber Unit with Dimethyl Diethanolammonium Glycinate-based Absorbent

Abstract: The present study deals with continuation of the development, enhancement and optimization of novel hybrid separation method – membrane assisted gas absorption, which is designed for natural gas processing, namely for acid gases removal. The second part is focused on the design of absorbent solutions and their application in the proposed technique in order to increase the acid gases removal efficiency and decrease losses of the hydrocarbons. Absorbent systems based on the methyldiethanolamine aqueous solutions and containing novel ionic liquid - dimethyl diethanolammonium glycinate were proposed and studied comprehensively in terms of properties, which affect the mass transfer rate: sorption capacity, viscosity and density. As a result of that complex absorbents study, its optimal composition was determined for further separation tests in membrane-assisted gas absorption unit. On the example of model ternary gas mixture and quasi-real natural gas separation it was found that proposed technique provides efficient separation. It not only reduces the concentration of acid gases up to 0.75 mol.% but allows to recovery 99% of hydrocarbons as a product flow.

Keywords: Gas separation; Hollow fibers; Ionic liquids; Membrane-assisted gas absorption; Natural gas sweetening.

1. Introduction

Natural gas produced from different deposits varies considerably in composition (Flores, 2014). The main component of natural gas is methane and its content varies from 75 to 90 %. It also includes ethane, propane, butane and 1-3 % of other higher hydrocarbons. In addition, natural gas contains undesirable impurities (water, mercury, nitrogen, carbon dioxide and hydrogen sulphide) (Duval, 2023). Although the composition of produced gas is variable, the content of the main components, and especially of impurities, in commercial natural gas is strictly regulated (Mokhatab et al., 2019). Therefore, before being fed into the pipeline, natural gas undergoes treatment, including condensate and free water removal, acid gas removal, water vapour removal, mercury removal, nitrogen capture, as well as liquid hydrocarbon recovery, fractionation and purification (Baker and Lokhandwala, 2008; Poe and Mokhatab, 2017). Natural gas processing is by far the largest area of industrial gas treatment and purification.

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One of the most energy-intensive steps in the natural gas treatment process route is the removal of acid gas impurities (CO_2 and H_2S) (Banat et al., 2014; Kusrini et al., 2017). Currently, the widely used technology in the industry is chemical absorption using aqueous solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA), diglycolamine (DGA) and methyldiethanolamine (MDEA) (Aghel et al., 2022; Bahadori, 2014; Barth et al., 1981; K. Li et al., 2016; Nozaeim et al., 2020; Shohrat et al., 2022). Although this is a widely used method, it has a number of disadvantages, such as absorbent loss, which is one of the most important indicators of amine plant performance, since absorbent costs are a significant part of operating costs. The main causes of absorbent loss are gas entrainment (amine loss value reaches 100 $mg \cdot m^{-3}$ of processing gas), mechanical losses and thermochemical destruction of amines, which leads to formation of persistent nitrogen-containing compounds (Hatchell et al., 2014; Islam et al., 2011). Accumulation of hard-to-regenerate products in the system leads to increased viscosity of the solution, which leads to increased load on pumps, increased corrosion activity and, as a consequence, reduced efficiency of the gas cleaning process as a whole. Another disadvantage of amine processes is high energy costs, mainly due to the stage of regeneration of saturated solutions, as well as significant capital costs due to the need to use expensive pumping equipment and the size of the plants (Anselmi et al., 2019; Baker*, 2002; Merkel et al., 2010a).

One of the ways to enhance the process of natural gas sweetening is to carry out absorption using new absorbents, for example, solutions based on MDEA and additional agents that increase their sorption capacity. MDEA, in comparison with other amines, is characterised by lower heat of reaction with CO_2. Reaction enthalpies of absorption process at maximum capacity α ($mol_{CO_2} \cdot mol^{-1}_{amine}$) 30% aqueous solutions at 313.15 K are -85.1 and -52.5 $kJ \cdot mol^{-1}_{CO_2}$ for MEA and MDEA respectively, which allows to reduce heat consumption for absorbent regeneration in desorption process (Hadri et al., 2015).

To overcome the reactivity limitations of MDEA solutions and to increase the carbon dioxide absorption capacity, new absorption solutions can be developed. Ionic liquids (ILs) can be used as additives in MDEA solutions (Akhmetshina et al., 2019, 2017b, 2017a; Atlaskina et al., 2025, 2021; Cheng Sun , Shujing Wen , Jingkai Zhao , Chongjian Zhao , Wei Li, Sujing Li, 2017; Feng et al., 2012, 2010; Fu et al., 2016b, 2016a; Li et al., 2023; Mechergui et al., 2020) as they have unique properties: low saturated vapour pressure, thermal stability and high sorption capacity towards acid gases. By combining different cations and anions or introducing functional groups, it is possible to tune their physicochemical properties. For instance, there are studies describing the addition of ionic liquids to absorbing solutions as additional agents to increase the reaction rate, leading to an increase in the CO_2 absorption rate by adding a limited amount of [bmim][BF_4] to an aqueous solution of MDEA (Ahmady et al., 2010). It has also been shown that systems containing ILs as a component are characterised by increased CO_2 solubility and their viscosities are lower than those of pure ILs. It has been shown that 1 kg of absorbent can absorb 3.6 mol of CO_2, demonstrating the potential of such combined systems (Anggerta et al., 2025; Zhao et al., 2010; Kartohardjono et al., 2017).

However, most of the ILs with high CO_2 sorption capacity have an anion containing fluorine atoms that are prone to hydrolysis, which can yield hydrogen fluoride. This increases the hazard class of the productions and is a limiting factor for their application (Swatloski et al., 2003). In this regard, in order to effectively remove acid gases, the main attention should be paid to the development of new environment friendly ionic liquids, for example, based on amino acids. In addition, the initial components for the synthesis of such ionic liquids have relatively low cost, which can significantly reduce capital and operating costs and, consequently, the cost of the whole process of gas purification as a whole.

Along with the development of new sorption materials, new approaches to avoid energy-intensive chemical absorption methods are of great interest. Membrane methods, being reactionless processes, appear to be a promising way to reduce energy consumption and increase economic efficiency of natural gas purification (Belaissaoui et al., 2012; Bernardo et al., 2009; Ibrahim et al., 2018; Merkel et al., 2010b; Muharam et al., 2018; Sanaeepur et al., 2019; V. M. Vorotyntsev et al., 2006). A unique hybrid method - membrane-assisted gas absorption (MAGA) was proposed to overcome the above-mentioned limitations. It is a hybrid pressure-driven separation method combining membrane gas separation and absorption in a single volume mass exchange unit, where selective absorption of acid gases takes place in a specific absorbent followed by permeation through the high-permeable membrane. Because of that, the separation occurs without any phase transition and does not require heat supply or removal (Atlaskin et al., 2021, 2020; Kryuchkov et al., 2021; Petukhov et al., 2021, 2020; Vorotyntsev et al., 2017; I. V. Vorotyntsev et al., 2006). The use of liquid absorbents in this process increases selectivity, while the gas separation membrane provides absorbent regeneration in a continuous stationary mode.

2. Materials and Methods

2.1 Materials

The materials used during the study are presented in Table 1.

Table 1 Viscosities of MDEA-AAILs aqueous solutions at 313.15 K and 0.1 MPa (ωMDEA = 30%).

Product name	Purity	Manufacturer
2-chloroethanol	99 wt%	Sigma-Aldrich (Darmstadt, Germany)
Aminoacetic acid	99%	
Potassium hydroxide	>99.5 vol.%	JSC Vekos (Nizhny Novgorod, Russia)
Ethanol	>99.5 vol.%	
Diethyl ether	>99.5 vol.%	
N-Ethyldimethylamine	99 wt%	«Oka- Sintez» Ltd. (Dzerzhinsk, Russia)
N,N-Bis (2-hydroxyethyl) methylamine	99 wt%	
Nitrogen	≥99.999 %	LLC «NII KM», LLC «Voessen» and LLC «Firma Horst»
Methane	≥99.99 %	
Xenon	≥99.999 %	
Ethane	≥99.94 %	
Propane	≥99.98 %	
Butane	≥99.97 %	
Carbon dioxide	≥99.99 %	
Hydrogen sulphide	≥99.5 %	
Helium	≥99.995 %	

2.2 Synthesis

A detailed description of the synthesis methodology is given in (Atlaskina et al., 2023). Briefly: Equimolar amounts of ethylene chlorohydrin were added to N-ethyl dimethylamine to give the chloride ion compound. Then, a 10% molar excess of KOH (0.1 mol) dissolved in absolute ethanol (0.4 mol) was added to the chloride-anion compound (0.09 mol) to give the hydroxide-anion ionic compound. Next, an aqueous solution of glycine (0.1 mol) was added to the resulting ionic compound and the mixture was stirred for 24 h at room temperature. The product is a light-yellow liquid and the yield was 90 %.

Moisture content was determined using a Fischer titrator by coulometric titration. To determine the amount of moisture in the synthesized IL, a sample weighing up to 50 mg was introduced directly into the measuring module. The moisture content in IL was 0.2 wt. %.

Sorption capacity of solutions was determined using gravimetric analysis using analytical balance SHIMADZU AUW-220D (measurement accuracy: $1{\cdot}10^{-4}/1{\cdot}10^{-5}$ g). The aqueous solutions were loaded into a glass cuvette with holes for gas inlet and outlet. The mass fraction of MDEA in the solutions remained constant – 30 wt.%, The mass fraction of [M_2E_2A][Gly]in the solutions was 0, 5, 10, 20 and 30 wt. %. The cell was placed in a thermostat and maintained at a constant temperature. The experiment was carried out at atmospheric pressure. The gas flow rate was kept constant using a gas mass flow controller and was 20 cm^3 min^{-1}. Figure 2 shows the results of gravimetric analysis of absorbent solutions with different mass content of [M_2E_2A][Gly]at 313.15 K. The rheological characteristics of sorption solutions were studied on a modular compact rheometer MCR 702e MultiDrive (Anton Paar, Austria). Measurements were carried out at a temperature of 313.15 K.

2.3 Membrane permeance test

One of the main challenges in the design of membrane-assisted gas absorption unit is to choose a suitable membrane material, taking into account its permeance, selectivity and stability in the presence of acidic carbon dioxide and hydrogen sulphide, which are plasticizers. The membrane must be highly permeable with regard to carbon dioxide and hydrogen sulfide, meanwhile the high selectivity is provided by the absorbent system.

In the present study, a new membrane-assisted gas absorption unit based on hollow fibers is considered. Previously, it was shown, that polysulfone (PSF) hollow fibers provide suitable permeance [1] comparing to polyetherimide (PEI) and polyetherimide/polyimide blend (PEI +PI) hollow fibers. In this regard, and taking into account the aging effect of polymers the additional experimental study of the gas transport properties of PSF (polysulfone) membranes was carried out using pure gases (methane, ethane, carbon dioxide, propane, nitrogen, butane, hydrogen sulphide and xenon) and a gas mixture in the ratio of these components as examples: 75.68/7.41/5.40/4.53/3.01/2.47/1.39/0.11 mol.%, respectively. The experimental results are summarized in Figure 5. The ideal gas transport characteristics of the hollow fibers were determined by the time-lag method (Daines-Barrer method). The study of membrane materials was carried out on an experimental setup, which is equipped with quadrupole mass spectrometer. The principal diagram of the setup is presented in Figure S1 and the description is given in Supplementary Materials.

2.4 Membrane-assisted gas absorption separation performance test

The efficiency of the membrane-assisted gas absorption process (on the example of a gas separation module on hollow fibers) was evaluated during the separation of two gas mixtures: a three-component model mixture containing methane, carbon dioxide and xenon in the ratio of 94.50/5.35/0.15 mol.% and an quasi-real natural gas, which is consists of methane, ethane, carbon dioxide, propane, nitrogen, butane, hydrogen sulphide and xenon in the ratio: 75.68/7.41/5.40/4.53/3.01/2.47/1.39/0.11 mol.%. The efficiency of the separation technique was evaluated by means of removing impurities of acid gases and recovering the hydrocarbons. A pure 30 wt.% aqueous solution of the amino alcohol, methyldiethanolamine, containing no ionic component was used as a reference and a solution containing 20 wt.% [M2E2A][Gly]was used as the absorbent. The scheme of the cell, technical data, procedure description and photos of the cell are given in Supplementary Materials (Table S1, Figures S2 and S3).

The results obtained for the process of separation of a model gas mixture are presented in Figure 5 (a-c), and also Figure 5 contain data on the dependences of the content of components of that mixture in the retentate stream on the stage cut. Figure 6 demonstrates the change in the flows composition in the result of the separation process. Figures 7 and 8 shows the dependence of the gas content of a quasi-real natural gas in the permeate stream on the stage cut. Figure 7 contains data without acid gases (CO_2 and H_2S) and Figure 8 contains data on acid gases.

The dependence of xenon content in the permeate stream on the stage cut is not shown, because in the whole range of values of the stage cut its content was below the detection limit of the gas chromatograph equipped with a thermal conductivity detector with increased sensitivity, which allows us to conclude that the xenon content in the permeate stream did not exceed 10 ppm.

3. Results and Discussion

3.1 Determination of sorption properties of MDEA-IL solutions

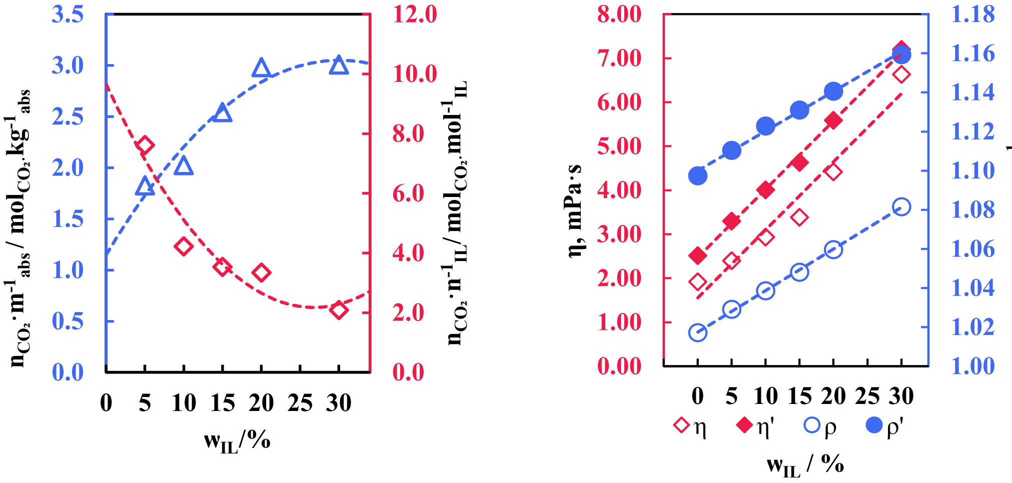
Present Sorption properties of the prepared solutions were evaluated gravimetrically at a temperature of 313.15K. This temperature was determined as the most convenient for the experiment under room conditions. The sorption capacity of pure 30 wt.% aqueous solution of MDEA is 1.54 $mol_{CO_2}.kg^{-1}$abs. According to the proposed reaction mechanism, in the present aqueous solution systems, the amino group of glycine amino acid can react rapidly with CO_2 to form zwitterions, which will transfer protons to MDEA. Accordingly, as the proportion of ILs in the solutions increases, their sorption capacity ($n_{CO_2}·m^{-1}CO_2$ / $mol_{CO_2}·kg^{-1}{}_{abs}$) increases significantly compared with the aqueous MDEA solution, which is confirmed by the experimental results. The proposed mechanism of the reaction is given below in Section 3.3 Theoretical basis: Proposed mechanism.

Compared to pure ones, in solutions containing [M_2E_2A][Gly]the sorption capacity increased by 18 % for 5 wt.% solution and was 1.83 $mol_{CO_2}·kg^{-1}{}_{abs}$, increased by 32 % for 10 wt.% solution (2.03 $mol_{CO_2}·kg^{-1}{}_{abs}$), increased by 94 % for 20 wt.% solution (2.98 $mol_{CO_2}·kg^{-1}{}_{abs}$) and by 95 % for 30 wt.% solution (3.01 $mol_{CO_2}·kg^{-1}{}_{abs}$). However, an increase in the mass fraction of ILs in the solutions is accompanied by a 73 % decrease in the sorption efficiency ($n_{CO_2}·n^{-1}{}_{IL}$ / $mol_{CO_2}·mol^{-1}{}_{IL}$) на 73% (с 7.62 до 2.09 $mol_{CO_2}·mol^{-1}{}_{IL}$) Figure 2 (a)). This trend is explained by the difference between a slight increase in sorbed gas moles and a significant increase in IL moles. The carbon dioxide saturation reaction rate estimated from the linear plot f(t) = $n_{CO_2}·n^{-1}{}_{IL}$ decreases from 220.63 mmol·min-1 (5 wt.% IL) to 54.91 mmol·min^{-1} (30 wt.% IL).

3.2 Viscosity, Density and Sorption Capacity Measurements

The rheological characteristics of absorption solutions are important parameters for real industrial gas processing processes. Viscosity has a significant influence on the kinetics of absorption and desorption processes and, in some cases, can be a determining factor in the choice of absorbent. As the gas molecules diffusion in liquid is a function of viscosity, the lower viscosity provides higher diffusion of gas in the volume of liquid. Because of that, it is important to find compromise between absorption capacity and viscosity of an absorbent. Figure 1 shows the dependences of absorption capacity, viscosity and density of absorption solutions on the mass content of [M_2E_2A][Gly] at temperature 313.15 K and pressure 0.1 MPa.

As expected, the density and viscosity of the absorption solutions increase with increasing mass fraction of the ionic liquid. It is worth noting that these values are much lower than in the case of aqueous solutions of MDEA with other Amino Acid Ionic Liquid, which, from this point of view, makes [M_2E_2A][Gly] a much more attractive ionic agent in such sorption solutions (Table 2). After CO_2 saturation, both viscosity and density of the solutions increase linearly from (η – c 2.51 mPa·s (0 wt.% IL) to 7.20 mPa·s (30 wt.% IL); ρ – from 1.10 g·cm^{-1} (0 wt.% IL) to 1.16 g·cm^{-1} (30 wt.% IL)).



a) b)

Figure 1. Dependence of sorption and rheological parameters on the mass fraction of [M_2E_2A][Gly] in solution (w). Symbols - experimental data, lines - linear correlation result:
(a) Sorption capacity (left y-axis) and sorption efficiency (right y-axis) of solutions
(b) Viscosity η (left) and density ρ (right) of solutions (at 313.15 K). Empty symbols (ρ, η) - initial values, shaded symbols (ρ', η')- values after CO_2 saturation.

Table 2 Viscosities (mPa·s) of MDEA-AAILs aqueous solutions at 313.15 K and 0.1 MPa (w_{MDEA} = 30%).

w_{AAILs} / %	[Bmim][Gly] [2]	[Bmim][Lys] [2]	[N_{1111}][Gly] [2]	[M_2E_2A][Gly] (This work)
5	2.55	3.25	2.60	2.40
10	3.03	3.36	3.15	2.94
15	3.69	5.03	3.77	3.39
20	-	-	-	4.42
30	-	-	-	6.63

Although the highest value of CO_2 sorption capacity under the investigated conditions was achieved for the solution containing 30 wt.% [M_2E_2A][Gly] (3.01 $mol_{CO_2}\cdot kg^{-1}_{abs}$), this value is not significantly different from the value for the solution with 20 wt.% of this IL (2.98 $mol_{CO_2}\cdot kg^{-1}_{abs}$). However, the viscosity value for the solution with 30 wt.% [M_2E_2A][Gly] (6.63 mPa·s) is 1.5 times higher than that for the solution with 20 wt.% of this IL. The advantage of adding the IL in the absorbent composition is a rapid increase in the absorption capacity with regard to acid gases. The disadvantage of adding IL - sharp increase in viscosity, which limits the diffusion of gases in the volume of the absorbent. Because of that, it is important to find compromise between these two characteristics of absorbent. In view of the above, the solution H_2O (50 wt.%)-MDEA (30 wt.%)- [M_2E_2A][Gly] (20 wt.%) is determined to be the more promising of those investigated for CO_2 absorption applications at T = 313.15 K and P = 0.1 MPa.

3.3 Theoretical basis: Proposed mechanism.

Tertiary amines, such as MDEA, do not form carbamates because they have no hydrogen atom to substitute for CO_2. However, in aqueous solutions, amines are weak bases, and CO_2 directly combines with the free OH^- formed when the amines are protonated. If an alcohol radical is present in the amine, the formation of monoalkyl carbonate will occur at high pH values.

The reaction mechanism of MDEA (tertiary amines) and CO_2 was proposed by Donaldson and Nguyen [3] (Eq. 1):

$$MDEA + CO_2 + H_2O = MDEAH^+ + HCO_3^- \tag{1}$$

Since this reaction is a base-catalysed hydrolysis of CO_2, i.e. no CO_2 addition takes place, the absorption process is relatively slow. For pure amino acid-based ILs, one molecule of CO_2 combines with two molecules of ILs [4], thus the theoretical maximum of CO_2 absorption capacity is 0.5 mol mol^{-1} IL.

The zwitterionic mechanism is commonly used to model the absorption of carbon dioxide by amino acid solutions [5–7]. Initially, the zwitterion is formed as a result of the reaction of CO2 with an amino acid (Eq. 2). The zwitterion is then deprotonated by bases in solution (bases include RNH_2, H_2O, OH^- and MDEA) (Eq. 3):

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \tag{2}$$

$$RNH_2{+}COO^- \leftrightarrow B = RNHCOO^- + BH^+ \tag{3}$$

The process of CO_2 absorption by mixtures of MDEA and amine additives can be represented as a shuttle mechanism: along the diffusion path from the interface to the bulk liquid, CO_2 first reacts with the reactive amine to form carbamate, then dissociates to carbonate, and the released H^+ reacts with MDEA. The released additive can react again with CO_2 (Figure 2).

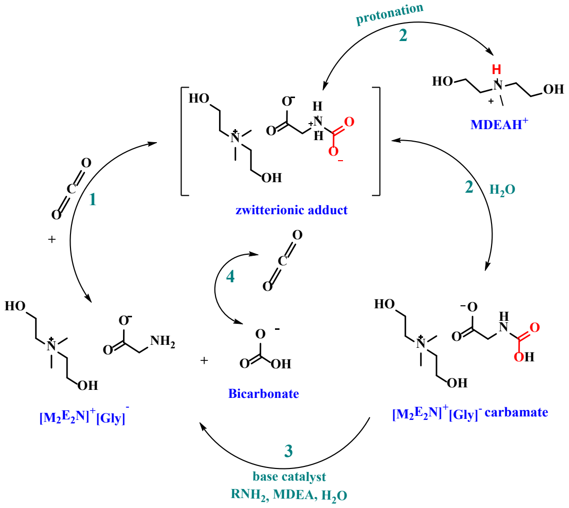


Figure 2. Proposed reaction mechanism of CO_2 absorption by H_2O/MDEA/[M_2E_2A][Gly] solution

3.4 Membrane permeability determination

The results of the PSF permeance study are given in Figure 4. According to the results of the study, the permeability values for a number of gases included in the considered gas mixtures were determined. It was determined that the polysulfone hollow fibre has high permeability values for all gases considered. Thus, for the selected membrane, the permeability of individual gases decreases in the series $H_2S > CO_2 > CH_4 > C_2H_6 > C_3H_8 > C_4H_{10} > N_2 > Xe$ and is 244.3, 220.4, 30, 22.9, 18.9, 17.4, 13.2 and 6.2 GPU, respectively.

During the study of gas transport characteristics of gas mixture components, a sharp increase in permeability values compared to these values for individual gases is observed, which is most likely caused by plasticisation of the membrane under the influence of carbon dioxide and hydrogen sulphide. It generally leads to an increase in the fractional free volume of the membrane. In turn this increases the diffusion of all gas species through the membrane and there is thus an increase in permeability but a loss of selectivity. Plasticisation also tends to lead to a loss of mechanical strength and this can result in total membrane failure due to the collapse of the support structure.

At the same time, there is a change in the membrane selectivity for all the considered gas pairs. However, such values are preserved at long-term operation of the membrane. The results of the study of gas transport characteristics of the membrane are presented in Figure 3 (a,b). The additional results are given in Supplementary Materials (Tables S2-S5).

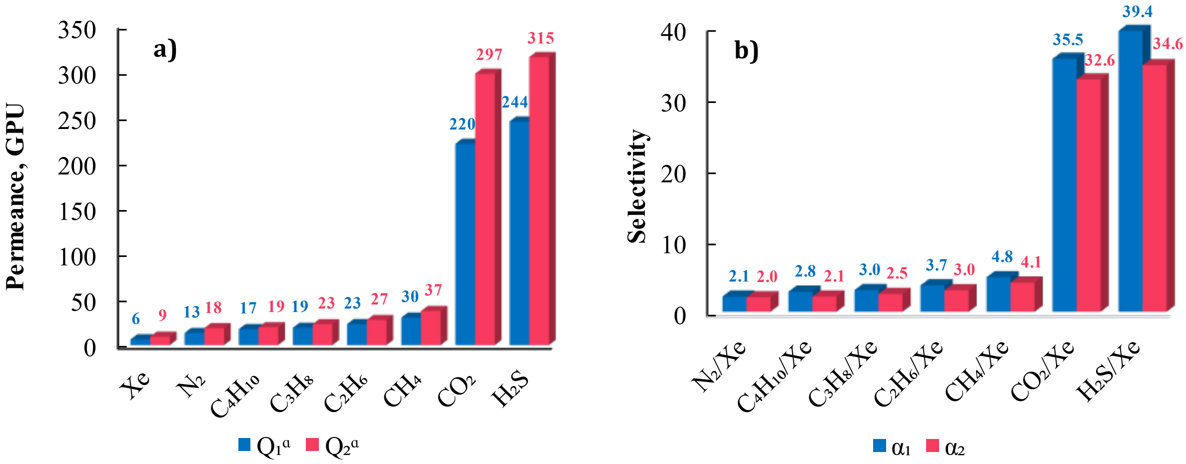


Figure 3 Gas transport characteristics of polysulfone membrane:
(a) Permeability, GPU (Q_1^a) of membrane for individual gases, permeability (Q_2^a) of membrane for gas mixture components;
(b) ideal selectivity (α_1) of the membrane for individual gases and selectivity (α_2) of the membrane for components of the gas mixture
(a) pressure drop across the membrane 101 kPa, 293.15 K; 1 GPU = 1 × 10^{-6} $cm^3\ cm^{-2}s^{-1}\ cmHg^{-1}$)

3.5 Experimental evaluation of the efficiency of the membrane-absorption method of gas separation

3.5.1 Model gas mixture separation

The efficiency of the membrane-assisted gas absorption process (on the example of a gas separation module on hollow fibers) was evaluated during the separation of two gas mixtures: a three-component model mixture containing methane, carbon dioxide and xenon in the ratio of 94.50/5.35/0.15 mol.% and an quasi-real natural gas, which is consists of methane, ethane, carbon dioxide, propane, nitrogen, butane, hydrogen sulphide and xenon in the ratio: 75.68/7.41/5.40/4.53/3.01/2.47/1.39/0.11 mol.%. The efficiency of the separation technique was evaluated by means of removing impurities of acid gases and recovering the hydrocarbons. A pure 30 wt.% aqueous solution of the amino alcohol, methyldiethanolamine, containing no ionic component was used as a reference and a solution containing 20 wt.% [M_2E_2A][Gly] was used as the absorbent.

The results obtained for the process of separation of the ternary gas mixture are presented in Figure 4, where the dependence of the content of components of this gas mixture in the retentate stream on the stage cut is shown. It can be seen from the presented dependence that for the solution MDEA - water, not containing IL, when carrying out the process with the minimum value of stage cut equal to 0.001, practically no change in the concentration of methane in the retentate stream (94.59

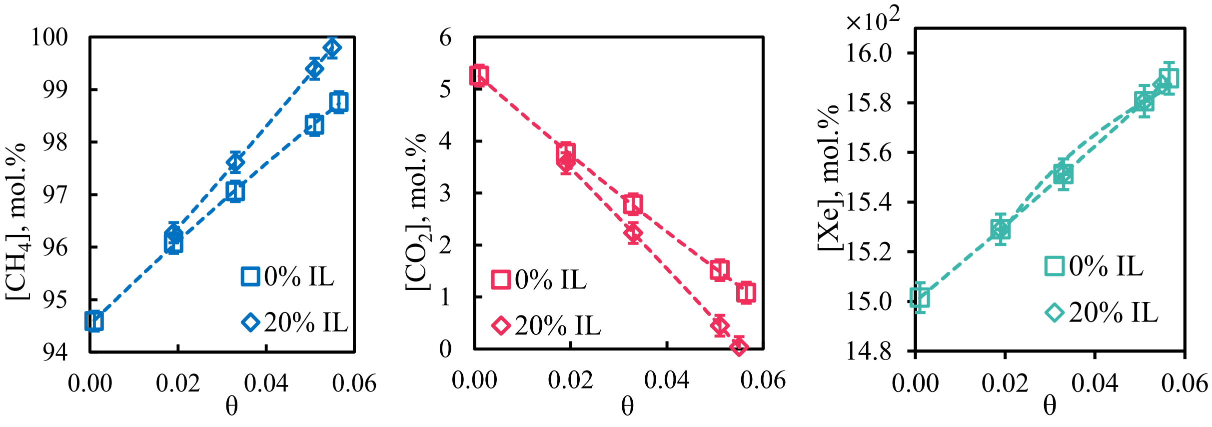
mol.%) is observed, while its initial concentration in the mixture was equal to 94.50 mol.%. However, the maximum achieved concentration of this component in the retentate stream is 98.76 mol.%.

In the case of the solution containing IL, when carrying out the process with the minimum value of stage cut equal to 0.020, an increase in the concentration of methane in the retentate stream was observed - the concentration was 96.27 mol %. The maximum achieved concentration of this component in the retentate stream is 99.80 mol %. Thus, when 20 wt.% [M_2E_2A][Gly] was added to the absorbent, the concentration of methane in the retentate stream increased by 6 % compared to the initial concentration of this component in the mixture, and by 1 % compared to the pure MDEA solution.

The presented dependence shows that the growth of stage cut is accompanied by a significant increase in the methane content in the retentate stream. Such dependence is explained by the fact that methane is a low-soluble component in the used absorption system, as well as by the fact that the permeance value of the used membrane for this component is significantly lower than the same value for carbon dioxide. Since the stage cut value is determined by the ratio of the permeate stream rate to the feed stream rate, an increase in the proportion of the stage cut value means an increase in the permeate stream (with the feed mixture stream rate constant). Thus, when the stage cut increases, a more soluble component - carbon dioxide - penetrates into the submembrane space, which allows obtaining more concentrated methane in the retentate stream.

The dependence of carbon dioxide concentration in the retentate stream on stage cut, presented in Figure 4, is in good agreement with the conclusions described above. It can be seen that the growth of stage cut is accompanied by a sharp decrease in the carbon dioxide content in the retentate stream. Thus, in the case of the solution not containing IL, at the minimum value of stage cut, the concentration of carbon dioxide practically did not change and was equal to 5.26 mol.%. At the same time, carrying out the process at the maximum value of stage cut (0.055) allows to reduce the concentration of carbon dioxide in the withdrawn retentate stream to 1.08 mol.%.

In the case of the solution containing ionic liquid, when carrying out the process with the minimum value of stage cut, a sharp decrease in the concentration of carbon dioxide (3.57 mol.%) in the retentate stream is observed. The minimum concentration of this component in the retentate stream is observed at the maximum stage cut value (0.055) and is 0.04 mol.%.



a) b) c)

Figure 4 Dependence of CH_4 (a), CO_2 (b) and H_2S (c) content in the retentate stream on the stage cut value during separation of a three-component gas mixture (marks - experimental data (squares - solutions without IL, rhombuses - solutions with 20% IL), dotted line - trend line).

Thus, when 20 wt% [M_2E_2A][Gly] was added to the absorbent, the concentration of CO_2 in the retentate stream decreased by 99 % with respect to the initial concentration of this component in the mixture, and by 96 % with respect to the pure MDEA solution. Such dependence is explained by the fact that carbon dioxide is well dissolved in the used absorption system, and its effective removal from the system at a higher value of the permeate stream rate allows to remove most of it from the separated gas mixture. As is seen from Figure 2, the IL containing absorbents characterized with higher absorption capacity with regard to CO_2 up to 5 times, meanwhile the viscosity of IL containing absorbents increases comparing with pure MDEA aqueous solution too. Considering both the results described in Sections 3.2 and given here, it is possible to conclude that IL containing system provides higher selectivity, due to higher absorption capacity and, presumably, higher acid gases normalized flux, due to much higher absorption capacity of IL containing absorbent compared to pure MDEA aqueous solution.

As for xenon (Figure 4), the increase in the stage cut value is accompanied by a slight increase in the concentration of this component in the withdrawn stream. Thus, when carrying out the process with the maximum stage cut equal to 0.055, the concentration of xenon in the case of using both aqueous MDEA solution without IL and with 20 wt.% IL is 0.16 mol.%. This dependence is explained by several factors: the inability of xenon to dissolve in such an absorbent, the low permeability of the membrane used for this gas, and the relatively large kinetic diameter of the xenon molecule. The low permeability of the membrane for this component and the large size of the molecule do not allow xenon to pass through the combined membrane-absorbent system, which explains the fact that the xenon content in the permeate stream was below the detection limit of the gas chromatograph. Xenon is not transferred to the submembrane space, which indicates that there is no loss of such a valuable product. This effect should be taken into account in further optimization of the proposed method.

As a result of cumulative analysis (Table 3) of the obtained results on the example of separation of the model three-component gas mixture it can be concluded that the proposed method is promising for the removal of acid gases from the natural gas stream. Thus, in case of application of 30 wt.% aqueous solution of methyldiethanolamine, the maximum concentration of methane extracted in the form of retentate stream is 98.76 mol.% with its content in the permeate stream at the level of ~ 24 mol.%. In case of application of MDEA solution containing IL, the maximum concentration of methane in the retentate stream is 99.80 mol.% at its content in the permeate stream at the level of 3.40 mol.%. The obtained results show that the addition of synthesised ionic liquid [M_2E_2A][Gly] as an agent increasing the efficiency of carbon dioxide absorption by aqueous MDEA solution is a promising approach to improve the efficiency of methane concentration in the retentate stream, as well as to reduce methane losses in the permeate stream. Besides, the dependence of xenon content in the permeate stream on the stage cut value is not given, because in the whole considered range of stage cut values its content was below the detection limit of the gas chromatograph equipped with a thermal conductivity detector with increased sensitivity, which allows us to conclude that the xenon content in the permeate stream did not exceed 10 ppm. This means that xenon is not transferred to the submembrane space, and therefore there is no loss of such a valuable product.

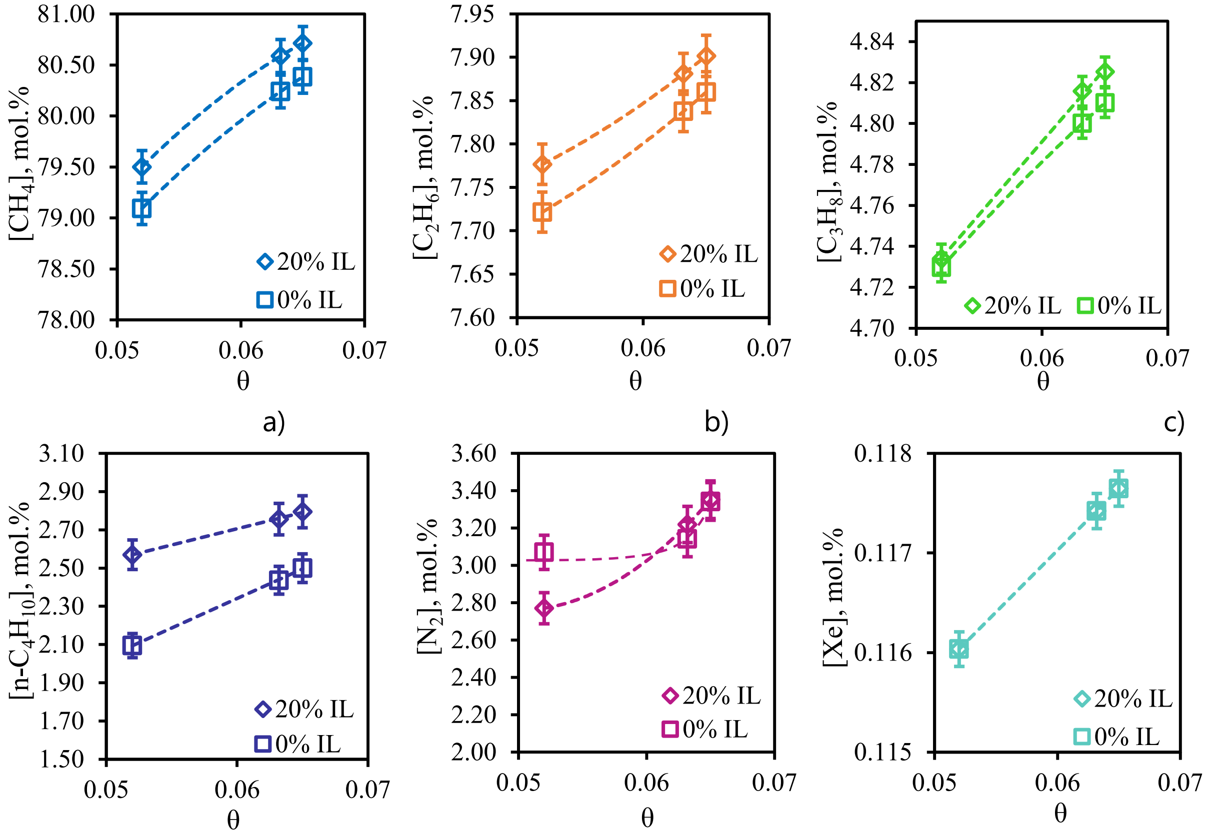
Table 3 Result flows composition over the separation of a model gas mixture using membrane-assisted gas absorption technique

SC	Retentate			Permeate		Retentate			Permeate	
	MDEA-H_2O					MDEA-H_2O-[M_2E_2A][Gly]				
	Concentration, mol.%									
	CH_4	CO_2	Xe	CH_4	CO_2	CH_4	CO_2	Xe	CH_4	CO_2
0.001	94.59	5.26	0.15	3.6	96.4	-	-	-	-	-
0.02	96.08	3.77	0.15	13.17	86.83	96.27	3.57	0.15	2.91	97.09
0.03	97.06	2.78	0.16	19.46	80.54	97.61	2.23	0.16	3.26	96.74
0.05	98.33	1.52	0.16	23.32	76.68	99.39	0.45	0.16	3.45	96.55

0.06	98.76	1.08	0.16	23.37	76.63	99.80	0.04	0.16	3.4	96.6

3.6 3.5.2 Quasi-real natural gas separation

For more detailed study of the proposed method, a similar study was carried out for an eight-component gas mixture containing methane, ethane, carbon dioxide, propane, nitrogen, butane, hydrogen sulfide and xenon in the ratio: 75.68/7.41/5.40/4.53/3.01/2.47/1.39/0.11 mol.%. The results obtained for the process of separation of eight-component gas mixture are presented in Figures 5 – 6, Figure 5 contains data on the dependences of the content of insoluble components of the gas mixture in the retentate stream on the stage cut, and Figure 5 shows the dependences of the content of carbon dioxide and hydrogen sulfide in the retentate stream on the stage cut.



a) b) c)

d) e) f)

Figure 5 Dependence of CH_4 (a), C_2H_6 (b), C_3H_8 (c), C_4H_{10} (d), N_2 (e) and Xe (f) content in the retentate stream on the value of stage cut during separation of an 8-component gas mixture ((marks - experimental data (squares - solutions without IL, rhombuses - solutions with 20% IL), dotted line - trend line).

From the presented curve for methane (Figure 5, (a)) it can be seen that the change in the content of this component is in the range from 79.10 to 80.38 mol.%, in the case of application of aqueous solution of MDEA. This indicates an insignificant change in this value when changing the stage cut at which the process is carried out. In case of application of aqueous solution of MDEA containing ionic liquid $[M_2E_2A][Gly]$, the change of methane content in the retentate stream is in the range from 79.50 to 80.71 mol.%, which also indicates insignificant change of this value from the stage cut at which the process is carried out. Taking into account the initial content of this component in the mixture (75.68 mol.%), it can be concluded that carrying out the process of membrane-assisted gas absorption with the use of aqueous solution of MDEA promotes insignificant concentration of methane in the withdrawn stream, however, when adding 20 wt.% $[M_2E_2A][Gly]$ to the solution, the maximum achieved purity of methane in the retentate increased by 7 % in comparison with the initial content of this component in the mixture.

At the same time, the growth of stage cut is accompanied by the growth of methane concentration value, which is in good agreement with the data obtained earlier for a three-component gas mixture. The obtained dependence is explained by the fact that the growth of stage cut is caused by the increase of permeate stream rate, which in turn promotes more efficient removal of highly soluble components to the permeate side, and since methane is practically insoluble in the absorbent, its accumulation in the retentate stream occurs.

Figure 5 (b) shows the dependence of the ethane content in the retentate stream on the stage cut value at which the gas separation process is realised. From the presented dependence we can see that the concentration of ethane, as well as in the case with methane, practically does not depend on the value of stage cut. At the same time, as the stage cut increases, there is a very insignificant increase in the content of this component in the retentate stream, namely, when changing the value of stage cut from 0.05 to 0.07, the concentration of ethane increases from 7.72 to 7.86 mol.% in the case of using MDEA solution as an absorbent, and from 7.78 to 7.90 mol.% in the case of using the solution with IL. Since ethane is also a low soluble component, its concentration has little dependence on the gas flow rate through the combined membrane-absorbent system. Comparing the concentration of ethane in the withdrawn stream with its initial content in the mixture (7.41 mol.%), it can be seen that a slight increase in the concentration of this component is observed.

Figure 5 (c) shows the dependence of propane content in the retentate stream on the stage cut value. From the obtained curves of this dependence, we can see that for the propane concentration the tendency described above is also observed, namely, the growth of stage cut is accompanied by an extremely low change in the propane concentration. Thus, in case of application of aqueous MDEA solution with stage cut value 0.05 the propane content in the permeate stream is at the level of 4.72 mol.%, while at the maximum value of stage cut (0.06) its concentration is 4.81 mol.%. In the case of the solution containing an ionic component, at the minimum stage cut value the propane content in the permeate stream is 4.73 mol.%, while at the maximum stage cut value its concentration is 4.83 mol.%.

Here it should be noted that as a result of the process even at the lowest value of stage cut, which favours the lowest concentration of low permeating and low soluble components, an increase in propane content of 0.2 mol.% compared to its initial content is observed.

Figure 5 (d) illustrates the dependence of n-butane concentration in the retentate stream on the stage cut value. The obtained dependence shows that in case of application of aqueous MDEA solution, change of stage cut causes insignificant change in the content of this component in the retentate stream. Thus, carrying out the process at the stage cut equal to 0.05 a decrease of n-butane concentration value to 2.09 mol.% with its initial content in the mixture (2.47 mol.%) is observed. However, increase of stage cut value up to 0.07 is accompanied by growth of n-butane concentration up to 2.50 mol.%, which already exceeds its initial content by 0.03 mol.%.

In case of application of MDEA-water-IL solution as an absorbent, the dependence of n-butane concentration in the retentate stream on the stage cut value is also linear and practically does not change. Thus, conducting the process at stage cut equal to 0.05 a slight increase of n-butane concentration value (2.57 mol.%) in comparison with its initial content in the mixture (2.47 mol.%) is observed. Increase of stage cut value up to 0.07 is accompanied by growth of n-butane concentration up to 2.80 mol.%, which exceeds its initial content in the mixture by 0.33 mol.%.

Thus, the cumulative analysis of dependences of hydrocarbon concentrations on the value of stage cut shows that for all these components insignificant concentration is observed at carrying out the process with stage cut ≥ 0.06. Such character of the obtained dependences is explained by the fact that all these components, firstly, are poorly soluble in the applied liquid absorbent, and secondly, the used membrane is characterised by low values of permeability for these gases. Thus, the use of a hybrid method - membrane-assisted gas absorption allows to slightly concentrate these components in the withdrawn retentate stream.

Figure 5 (e) shows the dependence of nitrogen content in the retentate stream on the stage cut value. From the obtained dependence for aqueous MDEA solution it is seen that the nitrogen content in the withdrawn retentate stream depends little on the value of stage cut, at which the gas separation process is realised. Thus, nitrogen concentration in the whole considered range of stage cut values varies from 3.07 to 3.42 mol.%. At that, comparing the achieved average nitrogen concentration with its initial content in the separated gas mixture, we can see that its content increased by 0.4 mol.%. However, in case of application of MDEA-water-IL solution the nitrogen concentration in the retentate stream at stage cut value 0.05 slightly decreases from 3.01 to 2.77 mol.%. At the same time, with increase of stage cut up to 0.07 the achieved nitrogen concentration in the retentate stream still increased up to 3.52 mol.%, which is 17% more in comparison with its initial content in the separated gas mixture.

Thus, it can be concluded that the implementation of the membrane-assisted gas absorption process allows to slightly concentrate nitrogen, which is also a poorly soluble component, which does not allow it to penetrate and concentrate in the submembrane space.

Figure 5 (f) illustrates the dependence of the xenon content in the retentate stream on the stage cut value. In general, in the case of aqueous MDEA solution, the dependence for xenon is similar to nitrogen. In the whole considered stage cut range, the value of xenon concentration varies from 0.116 to 0.118 mol.%. However, there is a weakly pronounced tendency to increase the xenon concentration in the retentate stream with increasing stage cut, at which the gas separation process is realised. Thus, at stage cut equal to 0.05 the concentration of xenon is equal to 0.116 mol.%, and at stage cut equal to 0.07 the concentration of xenon increased up to 0.118 mol.%. In the whole considered range of stage cut values it was found that in the process of separation of the mixture, xenon concentration in the retentate stream occurs. Thus, the maximum increase of xenon concentration is equal to 0.018 mol.% in case of application of aqueous MDEA solution.

In the case of MDEA solution containing 20 wt.% [M2E2A][Gly] in the whole considered range of stage cut from 0.05 to 0.07, the value of xenon concentration changes also from 0.116 to 0.118 mol.%, respectively. The nature of the dependences of xenon concentration on stage cut for the pure solution and the solution with ILs does not differ, and the maximum increase in xenon concentration for both solutions is equal. The dependence obtained for the eight-component mixture differs from the same dependence obtained for the triple mixture. Although xenon is able to dissolve in water, this does not occur in the aqueous solution of MDEA.

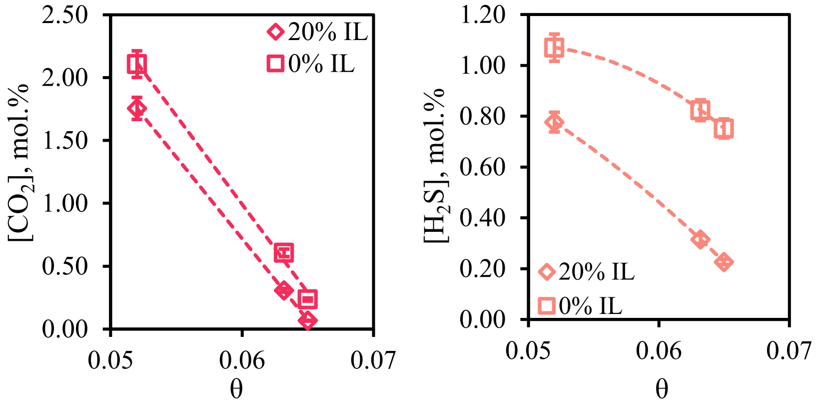
Figure 6 (a,b) shows the dependences of carbon dioxide and hydrogen sulphide content in the retentate stream on the stage cut value. Increase of stage cut is accompanied by decrease of the content of these components in the retentate stream taken from the membrane-absorption gas separation module in case of application of both absorption solutions. So, at stage cut equal to 0.05, the maximum concentration of carbon dioxide is reached, which makes 2.11 mol.% for pure solution of MDEA and 1.76 mol.% for solution containing IL. And the concentration of hydrogen sulphide is 1.07 mol.% in case of solution without IL, and 0.78 mol.% in case of solution with IL.

Carrying out of process at value stage cut 0.07 both in case of application of solution MDEA-water, and solution MDEA-water-IJ, has allowed to reduce the content of carbon dioxide to 0.24 mol.% and 0.07 mol.%, accordingly. At the same time, a significant decrease in the concentration of carbon dioxide was observed compared to its initial content in the mixture (5.40 mol.%). Thus, when carrying out the process with stage cut equal to 0.07, the concentration of carbon dioxide decreases by 82%

(aqueous MDEA solution) and by 99% (MDEA-water-IL solution). The obtained dependence is explained by the fact that carbon dioxide, is a well-soluble gas in the aqueous solution of methyldiethanolamine, and the addition of 20 wt.% [M2E2A][Gly] to the solution increases the efficiency of CO_2 absorption. In addition, the membrane is characterised by the highest permeability for this component (among those considered). Thus, in the considered process, carbon dioxide is able to effectively dissolve in the liquid absorbent layer and move into the submembrane space of the membrane-absorption gas separation module.

At a stage cut equal to 0.05 and at a stage cut equal to 0.07, the concentration of hydrogen sulfide decreased to 0.75 mol.% and 0.23 mol.%, respectively. Thus, as a result of this process, a 46% reduction in hydrogen sulphide content was observed compared to its initial concentration in the mixture for the MDEA-water solution. Addition of 20 wt.% of the synthesised ionic liquid to the absorbent reduced the concentration of hydrogen sulphide in the retentate stream compared to its concentration in the initial mixture by 83%.

As well as in the case with carbon dioxide, the received dependence is explained by ability of the absorbent to effectively dissolve this component and comparatively high permeability of a membrane on hydrogen sulphide that provides effective transfer of this gas in submembrane space. The composition of the gas stream extracted as retentate as a result of the MAGA process for the example of separation of an 8-component gas mixture is presented in Table 4.



a) b)

Figure 6 Dependence of CO_2 (a) and H_2S (b) content in the retentate stream on the stage cut value during separation of an 8-component gas mixture (marks - experimental data (squares - solutions without IL, rhombuses - solutions with 20% IL), dotted line - trend line).

Table 4 Result flows composition over the separation of a quasi-real natural gas using membrane-assisted gas absorption technique

Absorbent		C, mol.%							
		CH_4	C_2H_6	CO_2	C_3H_8	N_2	C_4H_{10}	H_2S	Xe
$MDEA/H_2O$	Retentate	79.69	7.81	0.98	4.77	3.27	2.61	0.75	0.12
	Permeate	8.02	0.94	79.70	0.50	1.06	0.23	9.55	-
$MDEA/H_2O/IL$	Retentate	80.85	7.77	0.53	4.77	3.11	2.62	0.23	0.12
	Permeate	3.26	0.34	82.11	0.28	1.98	0.27	11.76	-

It is also possible to compare the results of the present study with previous works (Atlaskin et al., 2021, 2020). The only issue is that these studies deal with two model binary mixtures of methane/carbon dioxide and methane/hydrogen sulfide. It was shown that, imidazolium-based ILs provides the removal of acid gases, so the methane content in the retentate stream is up to 90.2 and 99.87 vol.% during CO_2 and H_2S removal, respectively. Appliance of trihexyltetradecylphosphonium indazolide IL provides more efficient separation, where the methane content is 93.34 and 99.98 vol.% as a result of processing same binary gas mixtures. The present study shows, that it is possible to increase the methane content in product flow up to 99.8 mol.% separating the ternary gas mixture and maintain 99.24 mol.% CH_4 concentration in retentate.

4. Conclusions

In order to enhance the gas separation process and overcome the limitation of reactivity of MDEA solutions, absorption solutions based on MDEA with $[M_2E_2A][Gly]$ as an additional agent were prepared. An analysis of the effect of the IL addition on the sorption capacity of MDEA solutions is presented. The most effective ratio of components in the obtained solutions for CO_2 absorption has been determined experimentally. Experimental evaluation of the efficiency of MDEA solutions application (with and without IL addition) in the process of membrane-assisted gas absorption has been carried out. The IL addition allowed to reduce CO_2 concentration in the retentate stream by 3.5 times in comparison with the solution without IL. Carrying out the process using aqueous solution of MDEA containing 20 wt.% $[M_2E_2A][Gly]$ provides reduction of CO_2 concentration in the withdrawn retentate stream almost 134 times (from 5.35 to 0.04 mol.%) at separation of three-component gas mixture, and also 77 times (from 5.40 to 0.07 mol.%) at separation of eight-component gas mixture. The process of membrane-assisted gas absorption carried out at stage cut equal to 0.07 provides significant reduction of concentration of impurities of acid gases (CO_2 and H_2S) with increase of methane concentration and preservation of other components in the retentate stream, which indicates high selectivity of the process and high degree of hydrocarbons recovery (up to 99 %). It is important to note that the use of a new absorbent containing $[M_2E_2A][Gly]$ provides more efficient removal of impurities of acid gases. The present technology can be applied in the gas processing industry to reduce energy consumption and capital cost. It is also was shown, that implementation of MAGA process allows to easily meet the requirements of pipeline gas specifications in terms of CO_2 content, N_2 content and sum of inerts (Mokhatab et al., 2019).

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Author Contributions

The authors declare no conflicts of interest.

Conflict of Interest

Disclose any conflicts of interest, or explicitly state "The authors declare no conflicts of interest." Authors are required to disclose and acknowledge any personal circumstances or interests that may be perceived as inappropriately influencing the representation or interpretation of the research results.

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