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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

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Abstract: The present study deals with the continuation of the development, enhancement, and optimization of a novel hybrid separation method – membrane assisted gas absorption, which is designed for the removal of acid gases from natural gas processing. The second part focuses on the design of absorbent solutions and their application in the proposed technique to increase the efficiency of acid gas removal and decrease the losses of hydrocarbons. Absorbent systems based on methyldiethanolamine aqueous solutions and containing a novel ionic liquid, dimethyl diethanolammonium glycinate, were proposed and comprehensively studied in terms of the properties that 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 a membrane-assisted gas absorption unit. On the example of the model ternary gas mixture and quasi-real natural gas separation, the proposed technique provides efficient separation. It not only reduces the concentration of acid gases up to 0.75 mol% but also allows the recovery of 99% of hydrocarbons as a product flow.

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

1. Introduction[1]

The composition of natural gas produced from different deposits varies considerably (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 (e.g., water, mercury, nitrogen, carbon dioxide, and hydrogen sulfide) (Duval, 2023). Although the composition of the produced gas is variable, the content of the main components, especially impurities, in commercial natural gas is strictly regulated (Mokhatab et al., 2019). Therefore, before being fed into the pipeline, natural gas is treated, including condensate and free water removal, acid gas removal, water vapor removal, mercury removal, nitrogen capture, and liquid hydrocarbon recovery, fractionation, and purification (Poe and Mokhatab, 2017; Baker and Lokhandwala, 2008). 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) (Kusrini et al., 2017; Banat et al., 2014). Chemical absorption using aqueous solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA), diglycolamine (DGA), and methyldiethanolamine (MDEA) is currently the most widely used technology in the industry (Aghel et al., 2022; Shohrat et al., 2022; Nozaeim et al., 2020; K. Li et al., 2016; Bahadori, 2014). Although this is a widely used method, it has several disadvantages, such as absorbent loss, which is one of the most important indicators of amine plant performance, because 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 the formation of persistent nitrogen-containing compounds (Hatchell et al., 2014; Islam et al., 2011). The accumulation of hard-to-regenerate products in the system leads to an increased viscosity of the solution, which leads to an increased load on the pumps, increased corrosion activity, and reduced efficiency of the overall gas cleaning process. Another disadvantage of amine processes is high energy costs, mainly due to the regeneration stage 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; Merkel et al., 2010a; Baker, 2002).

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 characterized by a lower heat of reaction with CO_2. The reaction enthalpies of the absorption process at maximum capacity α ($molCO_2 \cdot mol^{-1}_{amine}$) 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 the reduction of heat consumption for the regeneration of the absorbent during the desorption process (Hadri et al., 2015).

New absorption solutions can be developed to overcome the reactivity limitations of MDEA solutions and increase the carbon dioxide absorption capacity. Ionic liquids (ILs) can be used as additives in MDEA solutions (Atlaskina et al., 2025; M. Li et al., 2023; Atlaskina et al., 2021; Mechergui et al., 2020; Akhmetshina, Gumerova, et al., 2017, Akhmetshina, Petukhov, et al., 2017, Akhmetshina et al., 2019; Cheng et al., 2017; Fu et al., 2016; Feng et al., 2010, Feng et al., 2012) as they have unique properties: low saturated vapor pressure, thermal stability, and high sorption capacity toward acid gases. Combining different cations and anions or introducing functional groups makes it possible to tune their physicochemical properties. For instance, some studies have described 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 are characterized by increased CO_2 solubility and lower viscosities than those of pure ILs. It has been shown that 1 kg of absorbent can absorb 3.6 mol of CO_2, demonstrating the actantial of such combined systems (Anggerta et al., 2025; Kartohardjono et al., 2017; Zhao et al., 2010).

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

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 the economic efficiency of natural gas purification (Sanaeepur et al., 2019; Ibrahim et al., 2018;

Muharam et al., 2018; Belaissaoui et al., 2012; Merkel et al., 2010b; Bernardo et al., 2009). V. Vorotyntsev et al., 2006 A unique hybrid method, membrane-assisted gas absorption (MAGA), was proposed to overcome the limitations mentioned above. It is a hybrid pressure-driven separation method that combines membrane gas separation and absorption in a single volume mass exchange unit, where acid gases are selectively absorbed in a specific absorbent, followed by permeation through the high-permeable membrane. Therefore, the separation occurs without any phase transition and does not require heat supply or removal (Kryuchkov et al., 2021; Atlaskin et al., 2021, Atlaskin et al., 2020; Petukhov et al., 2021, Petukhov et al., 2020; I. Vorotyntsev et al., 2017, I. Vorotyntsev et al., 2006). The use of liquid absorbents in this process increases selectivity, while the gas separation membrane provides absorbent regeneration in a stationary mode.

2. Materials and Methods

2.1 Materials

The study materials are presented in Table 1.

Table 1 Viscosities of MDEA-AAILs aqueous solutions at 313.15 K and 0.1 MPa ($_w$MDEA = 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 wt%	LLC ≪NII KM≫, LLC ≪Voessen≫ and LLC ≪Firma Horst≫
Methane	99 wt%	
Xenon	99 wt%	
Ethane	99 wt%	
Propane	99 wt%	
Butane	99 wt%	
Carbon dioxide	99 wt%	
Hydrogen sulphide	99 wt%	
Helium	99 wt%	

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 produce 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 with a yield of 90%.

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

The sorption capacity of the solutions was determined by gravimetric analysis using an 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 gas inlet and outlet holes. The

mass fraction of MDEA in the solutions remained constant at 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 conducted 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 the gravimetric analysis of the absorbent solutions with different mass content of $[M_2E_2A][Gly]$at 313.15 K. The sorption solutions' rheological characteristics were studied on a modular compact rheometer MCR 702e MultiDrive (Anton Paar, Austria). Measurements were performed at a temperature of 313.15 K.

2.3 The membrane permeance test

One of the main challenges in designing a membrane-assisted gas absorption unit is selecting a suitable membrane material that considers its permeance, selectivity, and stability in the presence of acidic carbon dioxide and hydrogen sulfide, which are plasticizers. The membrane must be highly permeable about carbon dioxide and hydrogen sulfide, while the absorbent system provides high selectivity.

In this study, a new membrane-assisted gas absorption unit based on hollow fibers is considered. Previously, it was shown that polysulfone (PSF) hollow fibers provide a suitable permeance (Kryuchkov et al., 2024) compared with polyetherimide (PEI) and polyetherimide/polyimide blend (PEI+PI) hollow fibers. Considering the aging effect of polymers, an additional experimental study of the gas transport properties of PSF membranes was conducted using pure gases (methane, ethane, carbon dioxide, propane, nitrogen, butane, hydrogen sulfide, 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. Figure 5 summarizes the experimental results. 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 conducted on an experimental setup equipped with a quadrupole mass spectrometer. Figure S1 presents the principal diagram of the setup, and the description is given in Supplementary Materials.

2.4 Membrane-assisted gas absorption separation 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 a quasi-real natural gas, consisting of 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 efficiency of the separation technique was evaluated by removing acid gas impurities 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 cell scheme, 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 separation process of a model gas mixture are presented in Figure 5 (a-c), and Figure 5 also contains data on the dependence of the content of components of that mixture in the retentate stream on the stage cut. Figure 6 demonstrates the change in the composition of the flow in the separation process. Figures 7 and 8 show the dependence of the stage cut on the gas composition of a quasi-real natural gas in the permeate stream. Figure 7 contains data without acid gases (CO_2 and H_2S) and Figure 8 contains data on acid gases.

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

3. Results and Discussion

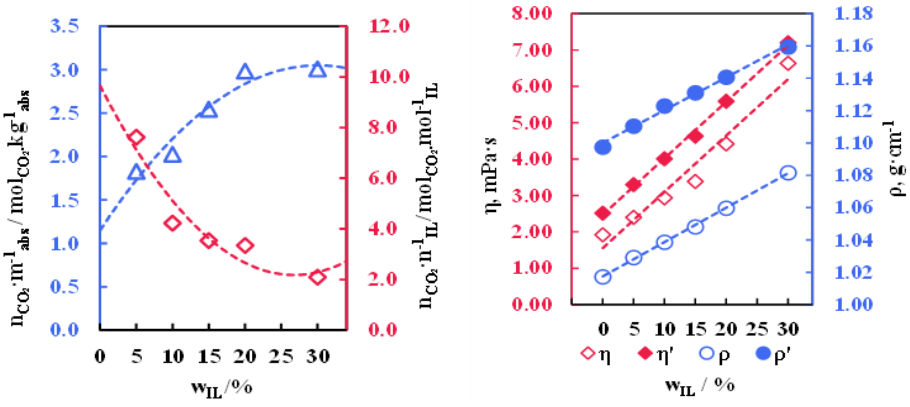
3.1 Determination of the sorption properties of the MDEA-IL solutions

Sorption properties of the prepared solutions were gravimetrically evaluated at a temperature of 313.15 K. This temperature was determined to be the most convenient for the experiment under room conditions. The sorption capacity of pure 30 wt% aqueous MDEA solution is 1.54 $molCO_2 \cdot kg^{-1}abs$. 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 ($nCO_2 \cdot m^{-1}CO_2$ / $molCO_2 \cdot kg^{-1}abs$) increases significantly compared with that of the aqueous MDEA solution, as 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 solutions, in solutions containing $[M_2E_2A][Gly]$the sorption capacity increased by 18% for 5 wt% solution and was 1.83 $molCO_2 \cdot kg^{-1}abs$, increased by 32% for 10 wt% solution (2.03 $molCO_2 \cdot kg^{-1}abs$), by 94% for 20 wt% solution (2.98 $molCO_2 \cdot kg^{-1}abs$) and by 95% for 30 wt% solution (3.01 $molCO_2 \cdot kg^{-1}abs$). However, an increase in the mass fraction of ILs in the solutions is accompanied decrease in the sorption efficiency ($nCO_2 \cdot n^{-1}IL$ / $molCO_2 \cdot mol^{-1}IL$) by α 73% (from 7.62 to 2.09 $molCO_2 \cdot mol^{-1}IL$) 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 $f(t) = nCO_2 \cdot n^{-1}IL$ decreases from 220.63 $mmol \cdot min^{-1}$ (5 wt% IL) to 54.91 $mmol \cdot min^{-1}$ (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 the absorption and desorption processes and, in some cases, can be a determining factor in the choice of the absorbent. As the diffusion of gas molecules in liquid is a function of viscosity, a lower viscosity provides a higher diffusion of gas in the liquid volume. Therefore, it is important to find a compromise between the absorption capacity and viscosity of an absorbent. Figure 1 shows the dependence of the absorption capacity, viscosity, and density of the absorption solutions on the mass content of $[M_2E_2A][Gly]$ at a temperature of 313.15 K and a pressure of 0.1 MPa.



(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

As expected, the density and viscosity of the absorption solutions increase with the mass fraction of the IL. These values are much lower than those in the case of aqueous solutions of MDEA with other amino acid ionic liquids, which makes $[M_2E_2A][Gly]$ a much more attractive ionic agent in such sorption solutions (Table 2). After CO_2 saturation, both the viscosity and density of the solutions increased linearly - from 2.51 mPas (0 wt% IL) to 7.20 mPas (30 wt% IL); ρ – from 1.10 $g \cdot cm^{-1}$ (0 wt% IL) to 1.16 $g \cdot cm^{-1}$ (30 wt% IL)).

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 $molCO_2 \cdot kg^{-1}$abs), this value was not significantly different from that of the solution containing 20 wt% of this IL (2.98 $molCO_2 \cdot kg^{-1}$abs). However, the viscosity value of the solution with 30 wt% $[M_2E_2A][Gly]$ (6.63 mPas) is 1.5 times higher than that of 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 about acid gases. The disadvantage of adding IL is the sharp increase in viscosity, which limits the diffusion of gases in the absorbent volume. Therefore, it is important to find a compromise between these two characteristics of the 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: The proposed mechanism

Tertiary amines, such as MDEA, do not form carbamates because they do not have a hydrogen atom to substitute for CO_2. However, amines are weak bases in aqueous solutions, and CO_2 directly combines with the free OH^- formed when the amines are protonated. If an alcohol radical is present in the amine, monoalkyl carbonate will form at high pH values.

The reaction mechanism of MDEA (tertiary amines) and CO_2 was proposed by Donaldson and Nguyen, 1980 (Eq. 1):

$$MDEA + CO_2 + H_2O = MDEAH^+ + HCO_3^- \quad (1)$$

Since this reaction is a base-catalyzed hydrolysis of CO_2, i.e., no CO_2 addition occurs, 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 carbon dioxide absorption by amino acid solutions [5–7]. The zwitterion is formed because of the reaction of CO_2 with an amino acid (Eq. 2). Then, bases in solution such as RNH_2, H_2O, OH^- and MDEA deprotonate the zwitterion (Eq. 3):

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \quad (2)$$

$$RNH_2 + COO^- \leftrightarrow B = RNHCOO^- + BH^+ \quad (3)$$

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).

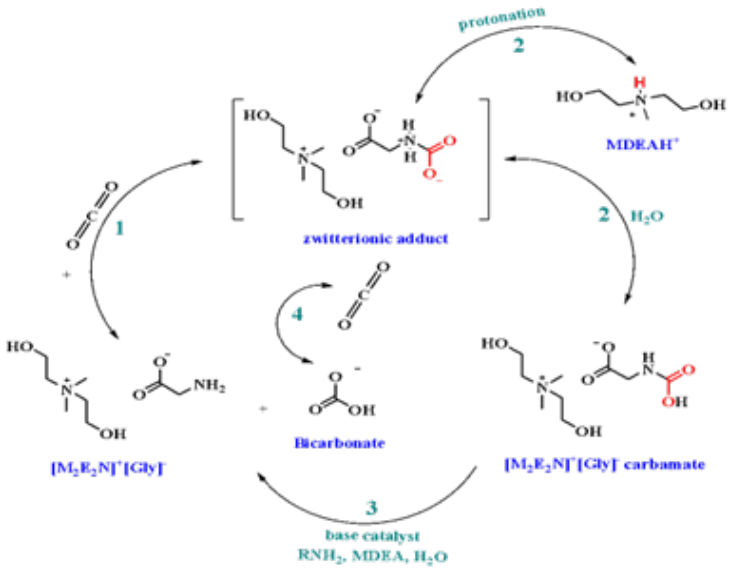


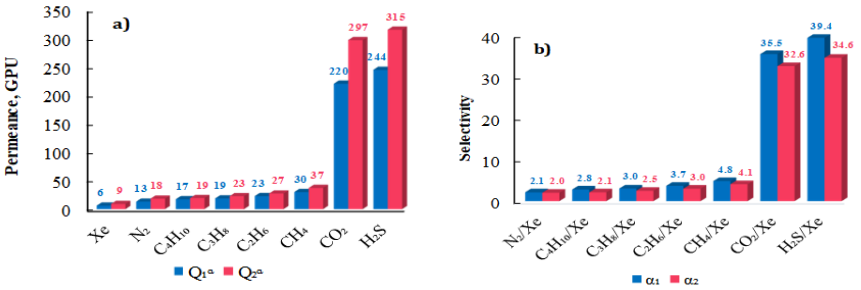
Figure 2 Proposed reaction mechanism of CO_2 absorption by H_2O/MDEA/[M_2E_2A][Gly] solution

3.4 Determination of membrane permeability

Figure 4 shows the results of the PSF permeance study. The permeability values for a number of gases included in the considered gas mixtures were determined according to the results of the study. The polysulfone hollow fiber was determined to have 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 membrane plasticization under the influence of carbon dioxide and hydrogen sulfide. It generally increases the membrane's fractional free volume. In turn, this increases the diffusion of all gas species through the membrane, resulting in an increase in permeability but a loss of selectivity. Plasticization also leads to a loss of mechanical strength, which can result in total membrane failure due to the support structure's collapse.

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



(a) (b)

Figure 3 Gas transport characteristics of polysulfone membrane: (a) Permeability, GPU ($Q1^a$) of membrane for individual gases, permeability ($Q2^a$) of membrane for gas mixture components; (b) ideal selectivity ($\alpha 1$) of the membrane for individual gases and selectivity ($\alpha 2$) 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-assisted gas absorption method

3.5.1 Model of 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 a quasi-real natural gas, consisting of 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 efficiency of the separation technique was evaluated by removing acid gas impurities 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.

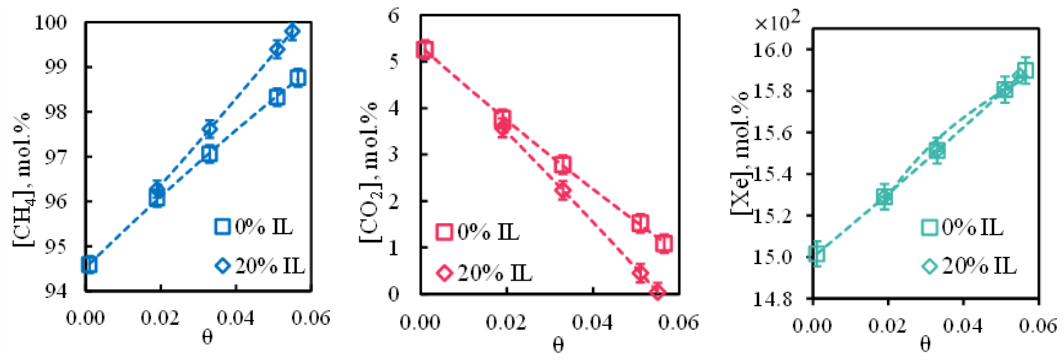
Figure 4 presents the results obtained for the separation process of the ternary gas mixture, where the dependence of the content of components of this gas mixture in the retentate stream on the stage cut is shown. It can be seen from the presented dependence that for the solution MDEA - water, not containing IL, when carrying out the process with the minimum stage cut value of 0.001, practically no change in the methane concentration 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 the minimum value of the stage cut was equal to 0.020, an increase in the concentration of methane in the retentate stream was observed (96.27 mol%). The maximum achieved concentration of this component in the retentate stream was 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 retentate stream methane content. 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 membrane's permeance value for this component is significantly lower than that 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 indicates an increase in the permeate stream (with the feed mixture stream rate constant). Thus, when the stage cut increases, a more soluble component, i.e., carbon dioxide, penetrates into the submembrane space, allowing the retentate stream to obtain more concentrated methane.

The dependence of the carbon dioxide concentration in the retentate stream on the stage cut (Figure 4) is in good agreement with the conclusions described above. The growth of the 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 stage cut value, the carbon dioxide concentration practically did not change and was equal to 5.26 mol%. Simultaneously, conducting the process at the maximum value of stage cut (0.055) allows the reduction of the concentration of carbon dioxide in the withdrawn retentate stream to 1.08 mol%.

In the case of the ionic liquid-containing solution, when the process is conducted 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 0.04 mol% at the maximum cut-off stage value (0.055).



(a) (b) (c)

Figure 4 Dependence of CH_4 (a), CO_2 (b), and H_2S (c) contents in the retentate stream on the stage cut value during the 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 permeate stream rate allows it to be removed from the separated gas mixture. As shown in Figure 2, the IL-containing absorbents exhibited a higher absorption capacity with regard to CO_2 up to 5 times, meanwhile the viscosity of the IL-containing absorbents increased compared with that of the pure MDEA aqueous solution. Considering the results described in Sections 3.2 and given here, it is possible to conclude that the IL-containing system provides higher selectivity due to higher absorption capacity and, presumably, higher acid gas normalized flux due to the much higher absorption capacity of the IL-containing absorbent compared to the pure MDEA aqueous solution.

The increase in the stage cut value for xenon (Figure 4) 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 xenon concentration 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 why the xenon content in the permeate stream was below the detection limit of the gas chromatograph. Xenon is not transferred to the submembrane space, indicating that such a valuable product is not lost. This effect should be considered in the further optimization of the proposed method.

As a result of the cumulative analysis (Table 3) of the obtained results on the example of separation of the model three-component gas mixture, the proposed method is promising for the removal of acid gases from the natural gas stream. Thus, in the case of the application of a 30 wt% aqueous solution of methyldiethanolamine, the maximum concentration of methane extracted in the form of the retentate stream is 98.76 mol%, with its content in the permeate stream at the level of 24 mol%. In the case of the application of MDEA solution containing IL, the maximum concentration of methane in the retentate stream is 99.80 mol%, and its content in the permeate stream is 3.40 mol%. The results show that the addition of synthesized ionic liquid $[M_2E_2A][Gly]$ as an agent to increase 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 and to reduce methane losses in the permeate stream. Moreover, the dependence of the xenon content in the permeate stream on the stage cut value is not given

because its content was below the detection limit of the gas chromatograph equipped with a thermal conductivity detector with increased sensitivity in the whole considered range of stage cut values, 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, such a valuable product is not lost.

Table 3 Flow composition over the separation of a model gas mixture using the 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

3.5.2 Quasi-real separation of natural gas

A similar study was conducted 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 dependence of the content of insoluble components of the gas mixture in the retentate stream on the stage cut, and Figure 5 shows the dependence of the content of carbon dioxide and hydrogen sulfide in the retentate stream on the stage cut.

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 of 79.10–80.38 mol% in the case of the application of an aqueous solution of MDEA. This indicates an insignificant change in this value when the cut-off stage at which the process is carried out is changed. In the case of the application of an aqueous solution of MDEA containing ionic liquid [M_2E_2A][Gly], the change in the CH_4 content in the retentate stream is in the range of 79.50–80.71 mol%, which also indicates an insignificant change in this value from the stage cut at which the process is carried out. Considering the initial content of this component in the mixture (75.68 mol%), it can be concluded that the membrane-assisted gas absorption process with the use of an aqueous solution of MDEA promotes an 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% compared with the initial content of this component in the mixture.

Simultaneously, 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 the stage cut is caused by the increase in the permeate stream rate, which in turn promotes the efficient removal of highly soluble components to the permeate side, and its accumulation in the retentate stream occurs because methane is practically insoluble in the absorbent.

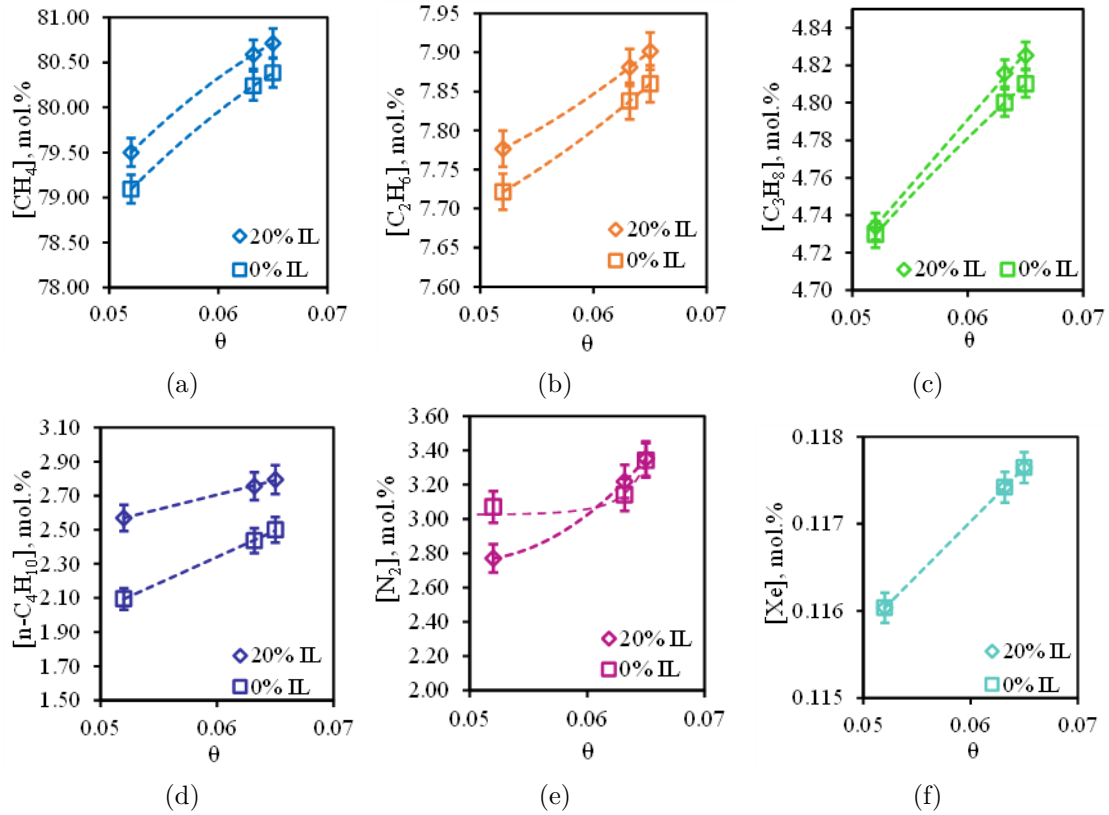


Figure 5 Dependence of CH_4 (a), C_2H_6 (b), C_3H_8 (c), C_4H_{10} (d), N_2 (e), and Xe (f) contents in the retentate stream on the stage cut value during the separation of an 8-component gas mixture ((marks - experimental data (squares - solutions without IL, rhombuses - solutions with 20% IL, dotted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

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 realized. From the presented dependence, we can see that the concentration of ethane, as well as in the case with methane, does not depend on the stage cut value. Simultaneously, as the stage cut increases, there is a very insignificant increase in the content of this component in the retentate stream. When the value of stage cut is changed from 0.05 to 0.07, the concentration of ethane increases from 7.72 to 7.86 mol% when using MDEA solution as an absorbent and from 7.78 to 7.90 mol% when 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%), a slight increase in the concentration of this component was observed.

Figure 5 (c) shows the dependence of the stage cut value on the propane content in the retentate stream. From the obtained curves of this dependence, we can see that the tendency described above is also observed for the propane concentration, namely, the growth of stage cut is accompanied by an extremely low change in the propane concentration. Thus, in the case of the application of an aqueous MDEA solution with a stage cut value of 0.05, the propane content in the permeate stream is at the level of 4.72 mol%, while its concentration is 4.81 mol% at the maximum stage cut value of 0.06%. In the case of the solution containing an ionic component, the propane content in the permeate stream is 4.73 mol% at the minimum stage cut value, while its concentration is 4.83 mol% at the maximum stage cut value. Here, it should be noted that even at the lowest value of the stage cut, which favors the lowest concentration of low permeating and low soluble components, an increase in the propane content of 0.2 mol% compared to its initial content is observed as a result of the process.

Figure 5 (d) shows the dependence of the n-butane concentration in the retentate stream on the stage cut value. The obtained dependence shows that in the case of the application

of an aqueous MDEA solution, a change in the stage cut causes an insignificant change in the content of this component in the retentate stream. Thus, performing 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, an increase of stage cut value up to 0.07 is accompanied by an increase in the n-butane concentration up to 2.50 mol%, which exceeds its initial content by 0.03 mol%.

In case of application of MDEA-water-IL solution as an absorbent, the dependence of the 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 the stage cut equal to 0.05, a slight increase in the n-butane concentration value (2.57 mol%) in comparison with its initial content in the mixture (2.47 mol%) is observed. An increase of stage cut value up to 0.07 is accompanied by an increase in the 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 the dependence of hydrocarbon concentrations on the value of the 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 are poorly soluble in the applied liquid absorbent, and the used membrane is characterized by low permeability values for these gases. Thus, the use of a hybrid method, membrane-assisted gas absorption, allows the slight concentration of these components in the withdrawn retentate stream.

Figure 5 (e) shows the dependence of the stage cut value on the nitrogen content in the retentate stream. From the obtained dependence for the aqueous MDEA solution, it is seen that the nitrogen content in the withdrawn retentate stream depends little on the stage cut value, at which the gas separation process is realized. Thus, the nitrogen concentration in the whole considered range of stage cut values varies from 3.07 to 3.42 mol%. Comparing the achieved average nitrogen concentration with its initial content in the separated gas mixture, 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%. Simultaneously, with an increase in the stage cut up to 0.07, the achieved nitrogen concentration in the retentate stream increased to 3.52 mol%, which is 17% more than its initial content in the separated gas mixture.

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

Figure 5 (f) shows the dependence of the xenon content in the retentate stream on the stage cut value. In general, in the case of an aqueous MDEA solution, the xenon dependence is similar to that of nitrogen. In the whole considered stage cut range, the 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 as the stage cut increases, at which the gas separation process is realized. Thus, at stage cut equal to 0.05 the concentration of xenon is equal to 0.116 mol%, and at a stage cut of 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 xenon concentration in the retentate stream occurs during the separation of the mixture. Thus, the maximum increase in xenon concentration is equal to 0.018 mol% in the case of the application of an aqueous MDEA solution.

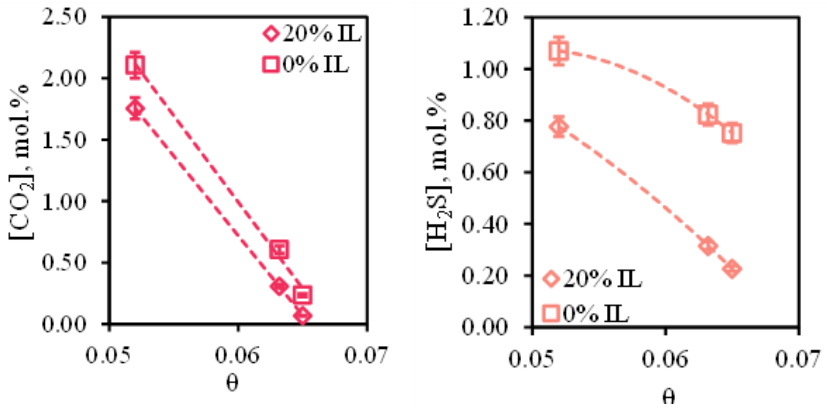
In the case of MDEA solution containing 20 wt% $[M_2E_2A][Gly]$ in the whole considered range of stage cut from 0.05 to 0.07, the xenon concentration also changes from 0.116 to 0.118 mol%. The nature of the dependence of xenon concentration on stage cut for the pure solution and the solution with ILs does not differ, and the maximum increase in xenon concentration is equal for both solutions. The dependence obtained for the eight-component mixture differs from that obtained for the triple mixture. Although xenon can dissolve in water, this does not occur in the aqueous solution of MDEA.

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

Carrying out the process at the value stage cut 0.07 both in the case of the application of solution MDEA-water and solution MDEA-water-IJ, which allowed the reduction of the carbon dioxide content to 0.24 mol% and 0.07 mol%, respectively. At the same time, a significant decrease in the carbon dioxide concentration was observed compared with its initial content in the mixture (5.40 mol%). Thus, when the stage cut is equal to 0.07, the carbon dioxide concentration decreases by 82% (aqueous MDEA solution) and 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% $[M_2E_2A][Gly]$ to the solution increases the efficiency of CO_2 absorption. In addition, the membrane has 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 of 0.05 and 0.07, the concentration of hydrogen sulfide decreased to 0.75 and 0.23 mol%, respectively. Thus, a 46% reduction in hydrogen sulfide content was observed compared to its initial concentration in the MDEA-water solution mixture. The addition of 20 wt% of the synthesized ionic liquid to the absorbent reduced the concentration of hydrogen sulfide in the retentate stream by 83% compared to its initial concentration in the mixture.

As well as in the case with carbon dioxide, the received dependence is explained by the ability of the absorbent to effectively dissolve this component and the comparatively high permeability of a membrane on hydrogen sulfide that provides effective transfer of this gas in the submembrane space. Table 4 presents 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.



(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	Stream	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 this study with those of previous studies (Atlaskin et al., 2021; Atlaskin et al., 2020). The only issue is that these studies discuss two model binary mixtures of methane/carbon dioxide and methane/hydrogen sulfide. It was shown that imidazolium-based ILs can remove acid gases; thus, the methane content in the retentate stream is up to 90.2 and 99.87 vol% during CO_2 and H_2S removal, respectively. The application of trihexyltetradecylphosphonium indazolide IL provides more efficient separation, with methane contents of 93.34 and 99.98 vol% because of processing the same binary gas mixtures. The present study shows that it is possible to increase the CH_4 content in the product flow up to 99.8 mol% separating the ternary gas mixture and maintain CH_4 concentration in the retentate at 99.24 mol%.

4. Conclusion

To enhance the gas separation process and overcome the reactivity limitation 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 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 solution application (with and without IL addition) in membrane-assisted gas absorption was experimentally evaluated. The addition of IL reduced the CO_2 concentration in the retentate stream by 3.5 times compared with the solution without IL. The process using an aqueous solution of MDEA containing 20 wt% $[M_2E_2A][Gly]$ reduces the CO_2 concentration in the withdrawn retentate stream almost 134 times (from 5.35 to 0.04 mol%) at the separation of the three-component gas mixture and 77 times (from 5.40 to 0.07 mol%) at the separation of the eight-component gas mixture. The process of membrane-assisted gas absorption carried out at a stage cut of 0.07 significantly reduces the concentration of impurities of acid gases (CO_2 and H_2S) with an increase in methane concentration and preserves other components in the retentate stream, indicating high selectivity of the process and high degree of hydrocarbon recovery (up to 99%). Notably, the use of a new absorbent containing $[M_2E_2A][Gly]$ provides a more efficient removal of acid gas impurities. This technology can be applied in the gas processing industry to reduce energy consumption and capital costs. The implementation of the 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

Conceptualization, M.E. Atlaskina;; Software, D.M. Zarubin; Formal analysis, S.S. Suvorov; Investigation, K.A. Smorodin.; Data curation, A.N. Petukhov, and E.A. Stepanova.; Methodology, A.A. Atlaskin, O.V. Kazarina; Writing—original draft, S.S. Kryuchkov and A.A. Atlaskin.; Visualization, A.N. Stepakova.; Validation, A.V. Vorotyntsev; Supervision, I.V. Vorotyntsev. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare no conflicts of interest.

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