

ANALYZES OF PURIFICATION OF HYDROGEN SULFIDE GAS USING METHYLDIETHANOLAMINE

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Abstract. For the first time the comprehensive study of a unique hybrid technique – membrane-assisted gas absorption (MAGA) for the acid gases removal was performed. As a case study, the influences of the presence of imidazolium ionic liquids in the methyl diethanolamine (MDEA) absorbent solutions on process separation efficiency were evaluated on the example of separation of two binary methane-based gases mixtures containing impurities of carbon dioxide or hydrogen sulfide. The achieved purity of target component (methane) using absorbent solutions containing imidazolium ionic liquids exceeds the pure MDEA results more when 6 vol% and equals to 90.2 vol% in case of CH₄/CO₂ separation. In case of hydrogen sulfide removal (the initial content in the mixture is 5 vol%) using a sorbent containing an ionic liquid, the methane purity is 99.87 vol%, which exceeds the purity of methane achieved by using pure MDEA by 1.8 vol%. Moreover, as an important part of process study the dynamics of establishing the steady state under a closed-mode operation was studied and the most efficient operational time regions and ultimate separation performance of a process was observed.

Keywords: membrane-assisted gas absorption, ionic liquid, carbon dioxide, hydrogen sulfide, natural gas.

Introduction. Natural gas purification from its associated impurities, particularly CO₂ and H₂S is one of the major operations encountered in a typical natural gas treatment application [1]. These impurity components negatively affect the produced gas quality, its market competency and thus its price [2]. A number of conventional techniques such as physical and chemical absorption, solid adsorption and batch units were proven effective in CO₂ and H₂S removal from raw gas [1,3]. Among them favorably stand out the membrane-based gas separation techniques [4–9], which have proven to be the affordable and energy-effective technology characterized by a small footprint, flexible design and operational simplicity.

Abbreviations	
MAG	membrane-assisted gas absorption
A	poly(vinyltrimethylsilane)
PVTM	polypropylene
SPP	polyphenylene oxide
PPO	polyetheretherketone
PEEK	polytetrafluoroethylene
PTFE	monoethanolamine
MEA	methyldiethanolamine ionic
MDEA	liquid
IL	[bmim][Tf ₂ N] 1-butyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl)imide
	[bmim][PF ₆] 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][BF ₄] 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][doc] 1-butyl-3-methylimidazolium 1,4-bis(2-ethylhex-yloxy)-1,4-dioxobutane-2- sulfonate
	[bmim][FEP] 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
	TCD thermal conductivity detector
	GC gas chromatograph

The major part of researches is devoted to physicochemical properties, particularly to the study of the membrane's structure, composition and properties [10–14]. Another approach to optimize and intensify the acidic gases removal from the raw gas process is the design of a membrane-based process, such as membrane contactors, which have received considerable attention due to their high performance and a high ratio of membrane area per unit volume [15–20]. Nevertheless, due to the presence of membrane, the main drawbacks of conventional gas-liquid contactors (tray towers, spray towers, packed bed columns and also bubble columns) such as liquid flooding, foam formation, channeling and entrainment do not occur in hollow fiber membrane contactors [21]. Moreover, it requires two elements (absorber and desorber) and where is a necessity to regenerate the liquid absorbent due to its degradation.

In current work the unique gas separation technique – membrane assisted gas absorption (MAGA), which previously was invented by authors and called absorbing pervaporation [22–26] was proposed for acid gases removal from raw natural gas and biogas applications. That hybrid separation technique is a combination of gas absorption by liquid absorbent displaced on the membrane and further permeance through the membrane. Additionally, this process provides separation without any phase transition, in a single-volume mass-exchange apparatus and with a liquid absorbent-membrane system, which provides higher selectivity compared to conventional membrane process. Important to note, that during the separation process, the continuous sorbent solution regeneration occurs (desorption of gases and permeance through the membrane) due to the pressure gradient across the combined liquid-membrane system. Because of that, apparatus does not require any heat supply/removal. Moreover, device characterized with scalable design and may be applied individually and as a final stage in technology route or in point-of-use operation. To be competitive and provide high separation efficiency membrane assisted gas absorption technique requires a sorbent, which characterized with high acid gases capacity and a membrane with high permeability, which allows continuous desorption i.e. regeneration of liquid sorbent displaced on its surface. Choosing the most suitable for the process membrane, attention was paid to its performance rather than selectivity, since the main separation action takes place in a liquid absorbent and the membrane mostly acts as a mechanical support and slightly affects the process selectivity. Moreover, it is necessary for the membrane surface to be lyophobic to the sorbent solution to prevent solution permeance through the membrane. Among the conventionally applied and commercially available gas separation membranes (cellulose acetate, polyimide, perfluoro polymers [27,28]), the polyvinyltrimethylsilane (PVTMS) membrane is the most suitable for the membrane-assisted gas separation technique.

Different absorbents have been used as liquid phase to absorb acid gases from gas mixtures. The list of possible absorbents includes amino acid salts, amine solutions, ionic liquids, ammonia solutions, enzyme solutions, alkaline solutions, deep eutectic solvents [29,30]. Amines (monoethanolamide, diethanolamine, triethanolamine, methyl diethanolamine etc.) are the most widely used media that is employed for capturing H_2S and especially CO_2 . They are able to form weakly bound complexes with CO_2 to produce effluent streams with very low CO_2 concentrations. However, the presence of amines leads to corrosion of industrial equipment materials, and foam production. The combination of ionic liquids (IL) with conventional sorbents provides an opportunity to make sorption-based separation technologies more competitive in the field of CO_2 and H_2S capture. Many studies have been conducted for improving the acid gases absorption capacities by taking advantage of the tunable properties of these substances. They are neat salts

that are liquids at temperatures ≤ 100 °C, and have a unique combination of material properties that include negligible volatility, high thermal stability, no flammability, good ion conductivity, and high intrinsic solubility of CO₂ and H₂S compared with such gases as CH₄, N₂ and others [31,32]. Since their discovery, ionic liquids have piqued the interest of many researchers, resulting in an expansion of the many chemical technologies field, and as well as analytical chemistry [33], biochemistry [34], catalysis [35–38], electrochemistry [39], separation technology [40,41]. Blanchard et al. [42] were the first to observe that significant amounts of CO₂ could be dissolved in imidazolium-based ionic liquids to facilitate the extraction of dissolved carbon dioxide, without contaminating from the ionic liquid, due to its insolubility in CO₂. It is known that the solubility of CO₂ increases in the following order of the anions: [NO₃] < [SCN] < [MeSO₄] < [BF₄] < [DCA] < [PF₆] < [Tf₂N] < [Methide] < [C₇F₁₅CO₂] [43]. The paired [Tf₂N] anion with different cations demonstrates the following trend in CO₂ solubility: [omim] > [hmim] > [pmim] > [bmim] > [emim] [44,45]. Among the wide range of ILs a number of commercially available imidazolium-based ionic liquids ([bmim][Tf₂N], [bmim][BF₄] and [bmim][PF₆]) have shown high solubility for carbon dioxide and hydrogen sulfide [46,47]. Moreover, in the work [46] authors concluded, that ILs containing anions such as the doc (1,4-bis(2-ethylhexyloxy)-1,4-dioxobutane-2-sulfonate), FEP (tris(pentafluoroethyl)trifluoro phosphate) and Tf₂N were estimated to have the highest CO₂ and H₂S capacity.

2. Materials and methods

2.1. Materials

In order to study and optimize the system it is of interest to perform the experimental study using two binary methane-based gas mixtures containing attendant impurities – carbon dioxide or hydrogen sulfide. According to that purpose the CH₄/CO₂ and CH₄/H₂S gas mixtures with CH₄ content of 80 and 95 vol%, respectively, were prepared by a static volumetric method and pressurized up to 2 MPa (20 bar) in 10 L cylinders. Methane (99.9 vol%), carbon dioxide (99.99 vol%), hydrogen sulfide (99.5 vol%) and helium (99.9999 vol%) were purchased from Monitoring Ltd. (Tashkent, Uzbekistan).

The membrane inside the separation cell was covered with uniform layer of a solution consisting of methyldiethanolamine (MDEA) and ionic liquid (IL). Ionic liquids: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) were purchased from Sigma Aldrich Group (Germany). Methyldiethanolamine was purchased from «Oka-Sintez» Ltd (Karshi, Uzbekistan).

The operating conditions of the GC system.

2.2. Experimental setup

As a preliminary study, the pure component permeability, diffusivity and solubility through different membrane-absorbent systems were measured according to Dynes-Barrer technique [48,49] in a constant volume variable-pressure apparatus for gas permeability measurements at the initial transmembrane pressure of 110 kPa and at the temperature equals to 25 °C. The experimental procedure is well - illustrated in our previous works [50,51].

The gas mixture is continuously supplied from the cylinder to the feed side of the membrane module through a pressure regulator (1) and a filter (2) with a constant pressure maintained at 0.5 MPa. Permeated components removed from the cell by a diaphragm vacuum pump (6), model MZ 2C NT (Vacuubrand, Germany). The pressure of the feed side is monitored by pressure gauge (4)

with an accuracy of 0.4% of full scale. The detailed GC-analysis conditions are presented in Table 1.

Component of the GC	Characteristic
Detector	TCD, 120 °C
Chromatographic column	Porapak Q, 80/100 mesh, 50 °C (CH ₄ /CO ₂) and 100 °C (CH ₄ /H ₂ S) 3 m × 2 mm i.d. stainless steel tube
Sample loop	1 ml, 100 °C
Carrier gas	He 99.9999 vol%, 30 ml/min

GC methods for gas analyses using Porapak Q column is also presented in details in [52–55]. All measurements were performed at least 5 times. the error value of measurement did not exceed 5%.

The key component of the setup is a radial membrane module specially designed for membrane-assisted gas absorption technique made of AISI 316 stainless steel with PTFE sealing. The mathematical model and experimental investigation of gas purification process in membrane module of this type were presented by Vorotyntsev et al. in [53,56]. Fig. 2 shows the schematic design and the principle flow scheme of the membrane module used.

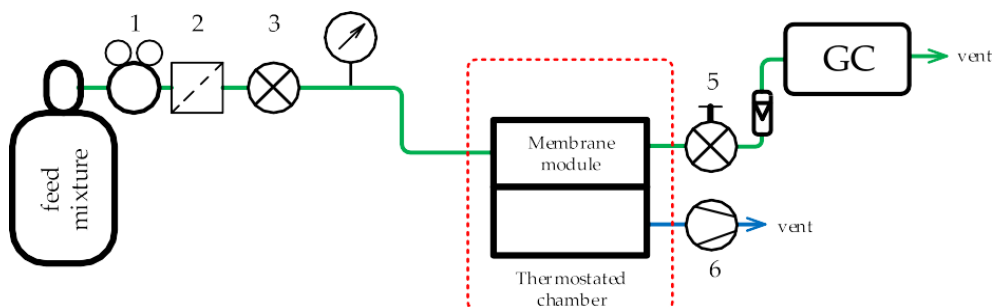


Fig. 1. The principal scheme of the experimental setup. 1 – pressure regulator; 2 – filter; 3 – valve; 4 – pressure gauge 5 – needle valve; 6 – vacuum pump.

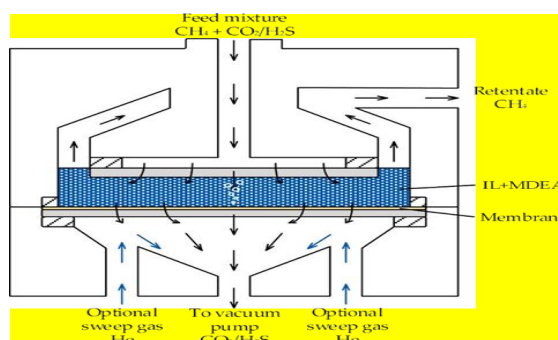


Fig. 2. Principle flow scheme of the radial MAGA membrane module.

Absorbent solution

Ionic liquids are physical absorbents, and may not be appropriate for some applications, for example, when the partial pressure of CO₂ in feed gas is low. In such cases, chemical absorbents such as amine solutions are usually preferred. Mixing ionic liquids with chemical absorbents such as amines can be a suitable strategy to increase the absorption ability. Here, the MDEA was selected, because it has high acid gas loading.

However, its efficiency is not high for CO₂ separation because of its low CO₂ solubility compared to ionic liquids and relatively low reaction rate. Addition of various imidazolium-based ionic liquids to MDEA may improve its absorption performance, and the influence of ionic liquids presence in MDEA-based solution on overall process separation performance will be studied in the following sections.

MDEA + IL solutions were prepared by mass, using analytical balance AUW220D (Shimadzu, Japan) with sensitivity ± 0.01 mg, in quantities of 30 g. In order to evaluate the influence of ionic liquids presence on overall sorption ability the 5 vol% content of IL was chosen. This value was chosen due to the study purpose – to determine the influence of IL presence in absorbent solution on overall process separation efficiency.

Moreover, the higher concentrations of IL decrease the diffusion coefficient of CO₂ in solution, and it may negatively affect the process separation performance.

3. Results and discussion

During the experimental comparison of influence of different imidazolium-based ionic liquids used as an absorbent for acid gases removal efficiency the permeability of pure components (methane, carbon dioxide and hydrogen sulfide) was determined through the PVTMS membrane and combined system of PVTMS covered with liquid absorbent which were MDEA + IL solutions. An experimental efficiency comparison and the process dynamic study under a closed mode operation was performed using the laboratory setup, which was described above.

Pure gases permeation test

The CH₄, CO₂ and H₂S pure gases permeability, diffusivity and solubility were measured through the different PVTMS membrane-liquid sorbent systems: MDEA and MDEA with 5 vol% of three different imidazolium-based ILs ([bmim][Tf₂N], [bmim][BF₄] and [bmim][PF₆]) to obtain and compare the values of mass transfer properties. The results shown in [Table 2](#).

The measurement of the membrane permeability for the chosen gases was carried out in the steady-state system operational mode. It was shown that both acid gases permeabilities exceed the permeability of methane by an order of magnitude. In the case of the PVTMS-MDEA + IL absorbent system, as is seen from the data presented in the [Table 3](#), CO₂ permeability increases with the increase of CO₂ solubility in the following order [bmim][BF₄] < [bmim][PF₆] < [bmim][Tf₂N], and H₂S permeability increase in order [bmim][PF₆] < [bmim][BF₄] < [bmim][Tf₂N].

Important to note, that increase in acid gases permeability for the IL containing systems is not accompanied by an increase in CH₄ permeability and its value remains nearly constant, because of that the selectivity ([Table 4](#)) increases.

System behaviour study

Moreover, from the process optimization point of view, comprehensively studied process dynamics allows to choose the most efficient regions (operational time) to perform withdrawals containing the purest target component, as it is indicated in [\[57\]](#).

Permeate flow is continuously evacuated by the vacuum pump, and a small retentate flow (~1.5 cm³/min) starts going to the GC. Each experimental run was repeated at least three times. All measurements were performed in thermostatic chamber at 25 °C.

Table 2.

Single gases permeability through PVTMS membrane covered with different liquid absorbents.

Permeability coefficient, Barrer					
	PVTMS	PVTMS-MDEA	PVTMS-MDEA + [bmim][Tf ₂ N]	PVTMS-MDEA + [bmim][PF ₆]	PVTMS-MDEA + [bmim][BF ₄]
CH ₄	51.3	1.1	0.06	0.06	0.06
CO ₂	117.4	4.8	2.2	2.1	2.1
H ₂ S	234.4	6.3	3.6	3.3	3.4

Measured 25 °C, 110 kPa. 1 Barrer = $3.346 \times 10^{-16} \text{ mol} \cdot \text{m} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$.

Table 3.

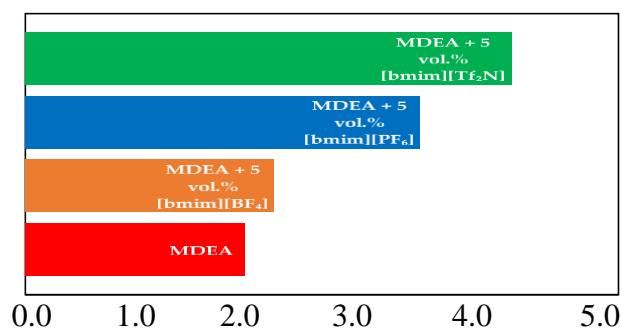
Single gases diffusivity (D) and solubility (S) in PVTMS membrane covered with different liquid absorbents.

	PVTMS-MDEA	PVTMS-MDEA + [bmim][Tf ₂ N]	PVTMS-MDEA + [bmim][PF ₆]	PVTMS-MDEA + [bmim][BF ₄]
$D \times 10^{10}, \text{m}^2 \cdot \text{s}^{-1}$				
CH ₄	1.21	0.92	0.64	0.92
CO ₂	0.65	0.44	0.43	0.43
H ₂ S	0.37	0.28	0.27	0.27
$S \times 10^5, \text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$				
CH ₄	0.31	0.02	0.03	0.02
CO ₂	2.48	1.68	1.62	1.64
H ₂ S	5.72	4.33	4.21	4.10

retentate flow rate was checked by a glass bubble flow meters. The experimental results obtained for establishing the steady state under a closed mode operational conditions during the separation of CH₄/CO₂ and CH₄/H₂S gas mixtures are presented in Figs. 3 and 4 respectively. As is seen from the graphs, for both cases – CH₄/CO₂ and CH₄/H₂S separation, the pure MDEA usage as a sorbent requires less time to establish steady state in a comparison with MDEA + 5 vol% IL.

3.3. Separation performance

The separation efficiency of the proposed method – membrane-assisted gas absorption for acid gases removal was evaluated during the separation of two custom-made gas mixtures: CH₄/CO₂ and CH₄/H₂S using three MDEA-based absorbents with 5 vol% of imidazolium ionic liquids. The separation performance of PVTMS-MDEA system was taken



Operational time, h

Fig. 3. The operational time required to establish steady state during the separation of CH₄/CO₂ gas mixture under closed mode operation for different sorbent solution.

as a reference to determine the influence of IL presence in absorbent solution and evaluate the evolution degree in separation efficiency. MAGA cell separation performance is represented as methane content

$$\theta = \frac{l_{perm}}{l_{feed}}$$

where l_{perm} – volume permeate flow (cm³/min), l_{feed} – volume feed flow (cm³/min).

The experimental data is shown in Figs. 7 and 8.

Table 4.

Ideal selectivity of PVTMS membrane covered with different liquid absorbents for CO₂/CH₄ and H₂S/CH₄ gases pairs.

		<i>Ideal select a</i>			
PVTMS		PVTMS-MDEA	PVTMS-MDEA + [bmim][Tf ₂ N]	PVTMS-MDEA + [bmim][PF ₆]	PVTMS-MDEA + [bmim][BF ₄]
CO ₂ /CH ₄	2.3	4.3	36.8	35.2	34.3
H ₂ S/CH ₄	4.6	5.6	60.5	54.2	57.0

Fig 4.

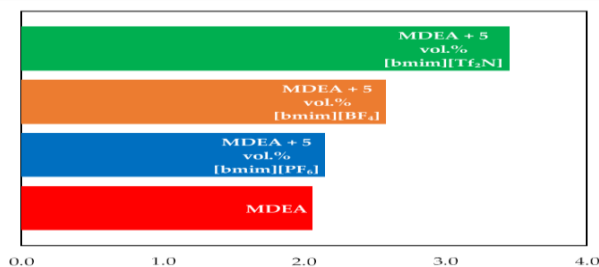


Fig 6.

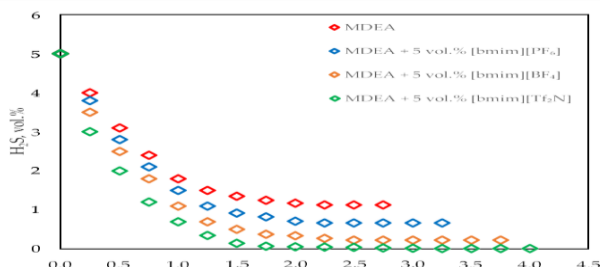


Fig. 4. The operational time required to establish steady state during the separation of CH₄/H₂S gas mixture under closed mode operation for different sorbent solution.

Fig. 6. Experimentally obtained dynamics of the separation process performed under closed mode operation in case of removal H₂S from CH₄/H₂S gas mixture.

Fig 5.

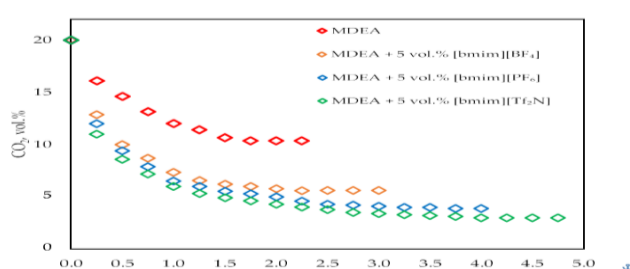


Fig 7.

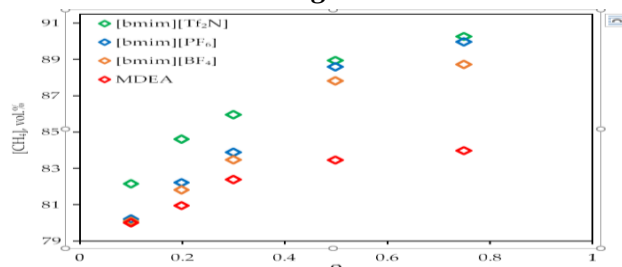


Fig. 5. Experimentally obtained dynamics of the separation process performed under closed mode operation in case of removal CO₂ from CH₄/CO₂ gas mixture.

Fig. 7. CH_4 concentration in the retentate flow in dependence on stage-cut during the separation of binary gas mixture CH_4/CO_2 with 20 vol% of CO_2 using three IL-containing absorbents and pure MDEA as a reference.

Generally, the separation performance test has confirmed the order, observed in single gases permeation test and results obtained by other scientific groups [58–60]. As it was mentioned in [58,59], the solubilities of CO_2 in [bmim][Tf₂N] are higher than those in [bmim][BF₄] and [bmim][PF₆], compared at a similar conditions. The solubilities of CO_2 in [bmim][BF₄] and [bmim][PF₆] are almost the same. According to [61], where the empirical estimation of the heat of absorption was performed, the enthalpy of the CO_2 sorption is typically –10 to –20 kJ/mol, that is mean that sorption process is characterized by physical interactions between CO_2 and ionic liquid. ATR-IR spectroscopy data obtained by Kazarian et al. [62] showed the favorable interaction between the anions ([BF₄] and [PF₆]) and CO_2 . For instance, in the works [63–65] has been shown, that the free volume mechanism where CO_2 molecules are hosted in the free spaces (cavities) of the liquid is not unlikely since the liquid volumes of ILs do not change significantly upon dissolution of large amounts of CO_2 . In addition, Kanakubo et al. [66] performed X-ray diffraction measurements on the [bmim][PF₆]- CO_2 system and showed that CO_2 preferentially organizes around the [PF₆] anion.

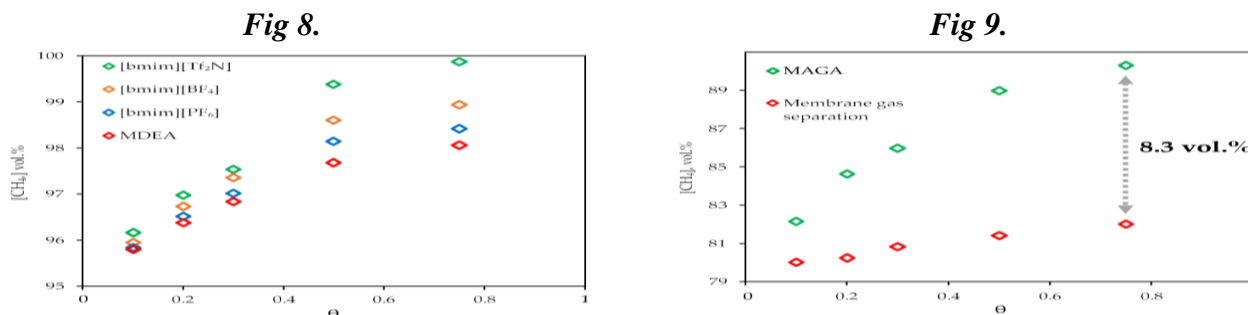


Fig. 8. CH_4 concentration in the retentate flow in dependence on stage-cut during the separation of binary gas mixture CH_4/H_2S with 5 vol% of H_2S using three IL-containing absorbents and pure MDEA as a reference.

Fig. 9. CH_4 concentration in the retentate flow in dependence on stage-cut during the separation of binary gas mixture CH_4/CO_2 with 5 vol% of CO_2 using membrane-assisted gas absorption technique with MDEA + [bmim][Tf₂N] (5 vol%) in a comparison with conventional single-module membrane gas separation technique.

Moreover, the effect of the presence of anion fluorine groups on the CO_2 solubility was studied [64,67,68], and it was shown, that increase in their number increase the ionic liquid capacity. Further, the intermolecular interactions (electrostatic, hydrogen bonding, and van der Waals) between the species in the fluid phase were computed. The contribution of each of these interactions to the solubility of CO_2 in ILs was determined, and the results indicate that the attractive van der Waals forces dominate the behavior of CO_2 dissolution in ILs. The electrostatic interactions had a secondary contribution to the excess enthalpy of dissolution, whereas the contribution of hydrogen bonds was found insignificant [69].

Conclusion

In the current study, for the first time the comprehensive study of a novel membrane-assisted gas absorption technique in process of acid gases removal was performed experimentally including evaluation of process separation performance and study of the steady-state establishing

dynamic taking into account the engineering aspects (separation cell configuration, technological scheme, analytical support etc.).

The achieved purity of methane using absorbent solutions containing imidazolium ionic liquids exceeds the pure MDEA results more when 6 vol% and equals to 90.2 vol% in case of CH₄/CO₂ separation with initial 20 vol% of CO₂. In case of hydrogen sulfide removal (initial content in the mixture is 5 vol%) using a sorbent containing an ionic liquid, the methane purity is 99.87 vol%, which exceeds the purity of methane achieved by using pure MDEA by 1.8 vol%. The comparison of proposed MAGA technique with conventional single-stage membrane gas separation demonstrates, that MAGA provides higher separation efficiency in an entire considered range and the highest methane purity exceeds the results achieved membrane gas separation more than 8 vol% and 2.5 vol% for CO₂ and H₂S removal respectively.

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