MEMBRANE CONTACTORS WITH POLYMER MEMBRANES FOR AMINE CO_2 SOLVENT DEOXYGENATION

Stepan Bazhenov*, Denis Kalmykov, and Sergey Shirokikh

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Abstract

Anthropogenic CO_2 emissions into the atmosphere are one of the unsolved problems of the modern world. A significant contribution to the increase in the concentration of CO_2 in the atmosphere is made by the flue gases of the energy production industry. The most mature technology for post-combustion CO_2 capture is absorption using amine solvents. The disadvantage of this technology is the oxidative degradation of amines due to the presence of dissolved oxygen in the solvent. A promising solution to control the cause of amine degradation is oxygen concentration maintenance. In this work, membrane contactors were developed for dissolved oxygen removal (deoxygenation) from model alkanolamine CO_2 solvents. Composite and flat sheet membranes based on highly permeable glassy polymers poly[1-(trimethylsilyl)-1-propyne] and poly[vinyltrimethylsilane] were obtained. Gas-liquid and liquid-liquid membrane contactors based on the fabricated membranes were developed. A deoxygenation process was implemented using a vacuum to create a driving force in the case of a gas-liquid contactor, while a liquid-liquid membrane contactor was tested using aqueous solutions of oxygen scavengers. The various types of alkanolamines were used to test the deoxygenation process. It has been shown that 5-37% of dissolved oxygen can be removed from amine solution using the developed membrane contactors. The process efficiency was evaluated with a resistance-in-series model.

Keywords: Amine CO_2 solvent; composite membrane; deoxygenation; membrane contactor

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Introduction

In recent years, increasing attention has been paid to the problems of carbon dioxide emissions. The world's main suppliers and consumers of fossil fuels make a significant contribution to the process of increasing the concentration of CO_2 in the atmosphere. According to this, for further safe technological and economic development, subject to restrictions to avoid potential changes in climatic conditions, it is necessary to research and develop carbon capture, storage, and utilisation (CCUS) technologies (Bazhenov *et al*., 2022; Chen *et al*., 2022; Gür, 2022). One of the major sources of CO_2 emissions is flue gases from the energy sector. Absorption using aqueous solutions of alkanolamines can be used as the most mature technology for purifying such gas mixtures from carbon dioxide (Wu *et al*., 2020; Ochedi *et al*., 2021). At the same time, this technology has a significant drawback associated with the oxidative degradation of CO_2 solvents. This process leads to the formation of products (heat-stable salts of alkanolammonium and anions of organic/mineral acids), which contribute to a decrease in the sorption capacity of alkanolamine CO_2 solvents, foaming, and the organisation of an autocatalytic degradation process in the presence of equipment corrosion products (Gouedard *et al*., 2012; Ooi *et al*., 2020).

Modern industrial approaches to solving this problem, such as electrodialysis, ion exchange and distillation, are mainly aimed at combating the consequences of oxidative degradation of alkanolamines, that is, by removing heat-stable salts and reusing regenerated solvents (Wang *et al*., 2015; Bazhenov *et al*., 2019). However, a more promising approach may be the removal of dissolved oxygen from amine solvents (deoxygenation) (Bazhenov, 2022). A decrease in the concentration of O_2 in solutions of alkanolamines leads to a sharp decrease in the rate of oxidative degradation of solvents and the prevention of intensive formation of heat-stable salts (Figueiredo *et al*., 2021).

Deoxygenation of alkanolamine solvents can be implemented with high efficiency using membrane contactors with compactness, modularity and controlled mass transfer surface area (Gabelman and Hwang, 1999; Li *et al*., 2020; Kim *et al*., 2021; de Cunha *et al*., 2022). At the same time, the creation of a driving force for transmembrane oxygen transfer can be implemented by evacuating the gas part of the contactor using gas-liquid types of contactors (Lee *et al*., 2020) and liquid-liquid membrane contactors using aqueous solutions of oxygen scavengers (Saeed *et al*., 2018). The effectiveness of membrane contactors for dissolved oxygen removal from the liquid phase has been previously demonstrated in the production of ultrapure water for the biotechnology industry (Kishi *et al*., 2020), as well as for water treatment in the energy industry (Lee *et al*., 2020).

In addition, a group of researchers from TNO, Norway, successfully applied a membrane contactor approach for deoxygenation of aqueous solutions of alkanolamines, which led to a decrease in the rate of formation of amine degradation products-heat-stable salts (Figueiredo *et al*., 2021). In general, the initial strategy of using porous membranes for the oxygenation process may be successful, since dense polymer membranes contribute to high resistance to mass transfer (Al-Saffar *et al*., 1997; Ozturk and Hugles, 2012). However, for the tasks of deoxygenation of amine solvents, porous membranes are limitedly applicable and significantly lose their effectiveness over time as a result of the gradual wetting of membrane pores and changes in their structure. Thus, in the case of dissolved oxygen removal from alkanolamine solvents, it is more rational to use non-porous polymer films or composite membranes with a thin, non-porous selective layer on a porous substrate to reduce the resistance to mass transfer in comparison with thick polymer films. The barrier properties of non-porous films will prevent the wetting of membranes by solvents and contribute to a longer operation of various types of membrane contactors.

The deoxygenation process of alkanolamine solvents can be successfully implemented using membranes based on highly permeable glassy polymers of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and its mixtures with polyvinyltrimethylsilane (PVTMS). These polymeric materials have previously demonstrated the prospect of their use in membrane absorption/ desorption of carbon dioxide due to high gas transport characteristics and stability after exposure to alkanolamines (Bazhenov *et al*., 2014; Dibrov *et al*., 2014; Volkov *et al*., 2015). Thus, this work aimed to study the membrane deoxygenation process of carbon dioxide alkanolamine solvents using non-porous polymer films and composite membranes with a thin, non-porous selective layer based on PTMSP and PVTMS. At the same time, it is supposed to use membrane contactors of the gas-liquid type (vacuum to create the driving force of the process) and liquid-liquid (use of aqueous solutions of oxygen scavengers to create the driving force of the process).

Materials and Methods

Materials and Chemicals

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP; Gelest Inc., USA; $M_w = 250 \cdot 10^3$ g/mol) and polyvinyltrimethylsilane (PVTMS; resolubilised membranes manufactured by the Kuskovsky Chemical Plant, USSR; $M_w = 800 \cdot 10^3$ g/mol) were used to produce flat non-porous polymer films and a selective layer of composite membranes. As support for the composite membranes obtained, polysulfone (PSF) hollow fibres with an outer thin, porous layer made of polysulfone (Ultrason® S 6010, BASF, Germany) were used. To prepare polymer solutions, n-hexane and chloroform were used as solvents (KHIMMED, Moscow, Russia).

As model alkanolamine solvents, we used monoethanolamine (MEA, KHIMMED, Moscow, Russia), diethanolamine (DEA, Sintez-OKA, Russia), N-methyldiethanolamine (MDEA, Sintez-OKA, Russia), 2-amino-2-methylpropanol-1 (AMP, Sigma Aldrich) and piperazine (PZ, Sigma Aldrich). Na_2SO_3 (KHIMMED, Moscow, Russia) was used as a model oxygen scavenger. Aqueous solutions of amines and an oxygen scavenger were prepared gravimetrically using distilled water as a solvent. Detailed data on the used model alkanolamine carbon dioxide solvents are presented in Table 1. It should be noted that when studying the process of membrane deoxygenation at room temperature, the alkanolamine solutions had a concentration of 30 wt%, with the exception of PZ, the concentration of which was 10 wt%. This is due to the low solubility of PZ at room temperature due to the formation of piperazine hexahydrate (Fosbøl *et al*., 2011).

Pure gases carbon dioxide, nitrogen, and oxygen (MGPZ, Moscow, Russia) were used to measure the gas permeance of the obtained membranes. All reagents were used without further purification.

Fabrication of Flat Sheet Polymeric Non-Porous Membranes

Homogeneous flat sheet polymeric membranes were obtained by pouring a 1 wt% solution of a mixture of PTMSP and PVTMS in a mass ratio of 7/3 (Kalmykov *et al*., 2022) in chloroform onto cellophane in a metal frame. The poured solution was covered to allow gradual evaporation of the chloroform over a period of se days at room temperature. As a result, non-porous films were obtained, which were then dried and treated with n-butanol, ethanol and water-ethanol mixtures. All polymer films were visually transparent. The film thickness determined by a Mitutoyo® 273 Quick Step electronic micrometer was 30±2 μm.

Fabrication of Hollow Fibre Composite Membranes

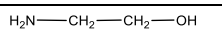
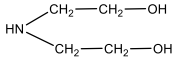
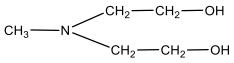
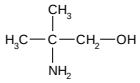
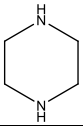
Composite membranes were obtained by applying a polymer solution to the surface of a porous PSF hollow fibre support. PSF support was obtained by wet spinning from a PSF spinning solution in N-methylpyrrolidone (Matveev *et al*., 2022).

A 1 wt% solution of a mixture of PTMSP/ PVTMS polymers with a mass ratio of 7/3 in hexane were also applied to the surface of a thin, porous layer of membrane supports and dried until the solvent completely evaporated in an oven.

The Study of Membrane Properties

The transport properties of non-porous polymer films were determined by the barometric method of gas permeability using an automatic high-precision installation for determining the gas transport properties of polymeric materials HZG

Table 1. Shows the CO_2 amine solvents used in the work

Amine	Designation	Structural formula of amine	Concentration in solution, wt%	Comment
Monoethanolamine	**MEA**		30	Primary
Diethanolamine	**DEA**		30	Secondary
N-methyldiethanolamine	**MDEA**		30	Tertiary
2-Amino-2-methylpropanol-1	**AMP**		30	Primary, sterically hindered
Piperazine	**PZ**		10	Cyclic

Gas and Vapor Permeability Test Unit, Germany, at a gas pressure supplied to the membrane of 0.2-0.8 bar using individual gases N_2, O_2, and CO_2. Before measurement, the films were held for at least 2 h to stabilise the transport properties.

The transport characteristics of the obtained composite membranes were also studied using the volumetric method using individual gases N_2, O_2, and CO_2. The gas volume passing through the membrane was measured using a Shinagawa dry gas meter (Tokyo, Japan) at room temperature (23±2°C) at a transmembrane pressure of 0.5 to 2 bar, while the permeate pressure was kept constant at 1 bar.

As the main transport characteristics of the membranes, their gas permeance and ideal selectivity were used.

The gas permeance was calculated according to the formula:

$$P/l = \frac{Q}{\Delta p \cdot S}, \quad (1)$$

where (P/l) is the individual gas permeance, $m^3/(m^2 \cdot h \cdot atm)$; Q is the volumetric flow rate of the passed through the membrane gas, m^3/h; Δp is the transmembrane pressure bar; and S is the membrane active surface area, m^2.

The ideal selectivity α for the gas pair was calculated using the equation:

$$\alpha = \frac{(P/l)_1}{(P/l)_2}, \quad (2)$$

where $(P/l)_i$ is the membrane permeance for the individual gas, $m^2/(m^2 \cdot h \cdot atm)$.

The membrane surface morphology was studied by scanning electron microscopy (SEM, Thermo Fisher Phenom XL G2, USA). Membrane cleavages were obtained in liquid nitrogen after preliminary impregnation of the samples with isopropanol. After that, a thin (5-10 nm) layer of gold was deposited on the surface of the membranes in a vacuum chamber (~0.01 mbar) using a desktop magnetron sputterer (Cressington 108 auto Sputter Coater, UK). The accelerating voltage during imaging was 15 kV. Image analysis and determination of the thickness of the selective membrane layer were performed using the Gwyddion software (version 2.53).

Membrane Deoxygenation of Model CO_2 Solvents

To study the membrane deoxygenation process of model amine carbon dioxide solvents, laboratory facilities were developed and built, containing a flat-frame and hollow fibre membrane module. Figures 1-3 present, respectively, schemes of a facility with a flat-frame membrane module containing non-porous polymer films (Figures 1 and 2) and a hollow fibre membrane module based on the obtained composite hollow fibre membranes (Figure 3). Vacuum has been used as the process driving force in gas-liquid membrane contactors

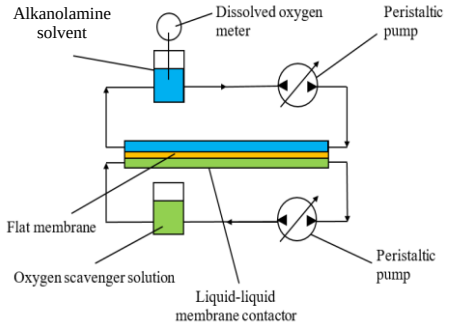


Figure 1. A scheme of a membrane deoxygenation process using a flat sheet membrane module and an oxygen scavenger solution to generate the driving force

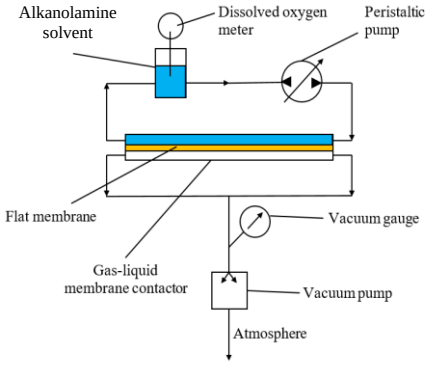


Figure 2. A scheme of a membrane deoxygenation process using a flat sheet membrane module and vacuuming to generate the driving force

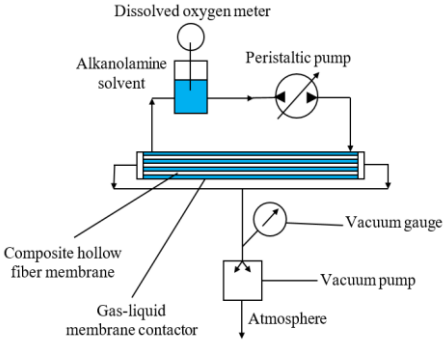


Figure 3. A scheme of a membrane deoxygenation process using a hollow fibre membrane module and vacuuming to generate the driving force

(Figures 2 and 3). In a liquid-liquid membrane contactor, an aqueous solution of Na_2SO_3 at a concentration of 50 g/l as a model oxygen scavenger was used to create the driving force (Figure 1).

In the case of a flat-frame liquid-liquid and gas-liquid contactor, the main working element was a flat sheet membrane module with a rectangular geometry of liquid channels containing turbulent grids. The area of the membrane in the contactor was 21.2 cm^2. The vertical arrangement of the contactor made it possible to avoid the formation of gas bubbles and stagnant zones during the flow of liquids in the internal channels of the module. The supply of liquids (a model solution of a carbon dioxide solvent and an oxygen scavenger) to the membrane contactor was carried out in a countercurrent mode with the recirculation of liquids using peristaltic pumps. The operating parameters of the system were: linear feed rates of absorbent and antioxidant solutions were ~4.5 cm/s; transmembrane pressure was 0±2 kPa; the volume of each of the supplied liquids was 400 ml. In the case of evacuation of the gas part of the flat-frame module, a residual pressure of 100 mbar was maintained using a vacuum pump.

In the case of a hollow fibre membrane gas-liquid contactor, a model solution of carbon dioxide solvents with a volume of 400 ml was also pumped through the membrane module using a peristaltic pump from the shell side of the selective layer of the resulting composite membranes in the absorbent recirculation mode. The area of the membranes in the hollow fibre contactor was 37.7 cm^2, with a packing density of membranes in the module of 664 m^2/m^3. The liquid flow was carried out with a linear phase flow rate of ~4.5 cm/s. A vacuum pump maintained a residual pressure of 100 mbar in the gas space of the membrane module.

The concentration of dissolved oxygen was measured in all cases using an electrochemical dissolved oxygen sensor HI9146N (HANNA Instruments, USA). The content of O_2 in the solution before the start of deoxygenation, if necessary, was preliminarily increased to values close to the limiting solubility (Buvik *et al*., 2021) by bubbling with gaseous oxygen. Deoxygenation experiments were carried out at room temperature 23±2°C.

Results and Discussion

Structure and Transport Properties of Obtained Polymeric Membranes

A scanning electron microscope was used to study the membrane structure and determine the thickness of the selective layer of composite membranes. Figure 4 shows SEM images of a cross-section and surface of a flat sheet polymeric

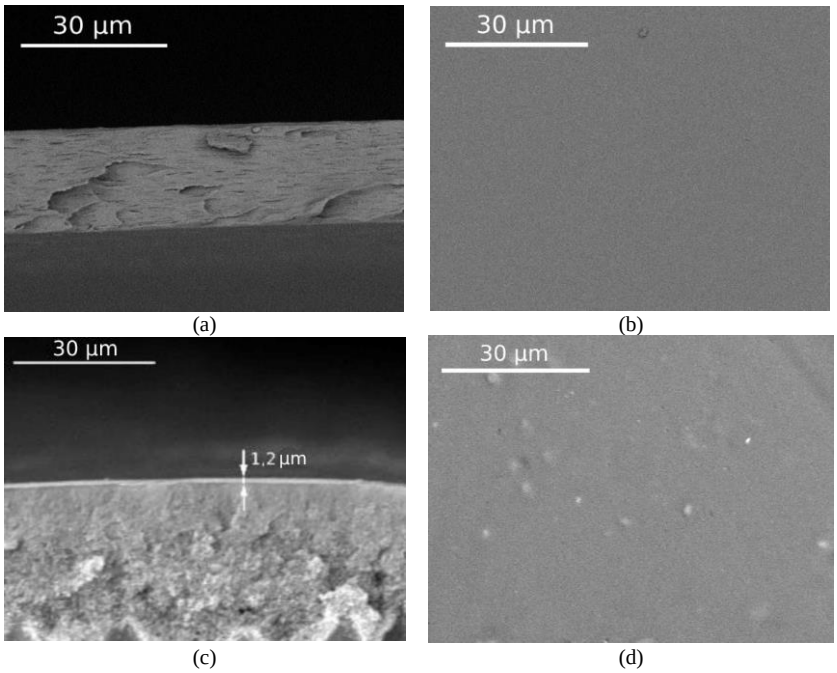


Figure 4. SEM images of a cross-section (a) and surface (b) of a flat sheet polymeric membrane and a cross-section (c) and surface of a selective layer (d) of a composite membrane on a PSF support

membrane and a composite membrane on a PSF support.

From the images presented in Figure 4, it can be seen that the polymer film from a mixture of PTMSP and PVTMS does not have a porous structure and defects and inclusions are not observed on its surface. The average film thickness was 30±2 μm. It can also be seen that a defect-free thin selective layer of a PTMSP/PVTMS mixture with a thickness of 1.2±0.3 μm was successfully deposited on the surface of the porous PSF support.

Also, the transport characteristics of all obtained membranes were determined (Table 2). It should be noted that the transport properties of membranes in gas-liquid and liquid-liquid contactors in contact with aggressive media, which include alkanolamine solutions, may change due to swelling and contamination of selective membrane layers. Therefore, in order to assess the resistance of the resulting membranes to the action of model solutions of CO_2 solvents, as well as a more correct description of the mass transfer of oxygen through these membranes during deoxygenation, the transport characteristics of the membranes after their exposure to aqueous solutions of alkanolamines were evaluated. To do this, samples of the obtained flat non-porous polymer films and hollow fibre composite membranes were placed in sealed vessels with 30 wt% solutions of monoethanolamine and kept at 100°C for at least 14 days. After that, the membranes were removed from the solutions, kept at room temperature in ethanol (2 h) and water (2 h) to remove residual model absorbents, dried in air to constant weight, and their transport characteristics were studied. The results of an evaluation of the transport characteristics of membranes after their exposure to alkanolamine solvents are also presented in Table 2. It can be seen that in the case of flat, non-porous polymer films and composite hollow fibre membranes, the permeance for individual gases (N_2, O_2, CO_2) turned out to be close in value. For example, the oxygen permeability of flat polymer films was 0.17 $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$, and the oxygen permeability of composite hollow fibre membranes was 0.12 $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$. The decrease in the permeance of a composite membrane with a significantly thinner selective layer in comparison with the permeance of a sufficiently thick flat film can be explained by the contribution of a PSF support with a relatively low surface porosity, which can contribute to resistance to mass transfer (Matveev *et al*., 2022). At the same time, the differences between the values of ideal selectivities (for example, for the gas pair O_2/N_2 1.7 and 2.0 for flat and hollow fibre membranes, respectively) indicate their greater potential efficiency in the release of oxygen from alkanolamine solvents.

It should also be noted that keeping samples of the obtained membranes in an alkanolamine medium for 14 days at 100°C leads to a decrease in their transport characteristics. Thus, in the case of flat non-porous polymer films, a decrease in oxygen permeability from 0.17 to $7.6\cdot10^{-4}$ $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$ was observed, and in the case of composite hollow fibre membranes, a decrease in oxygen permeability from 0.12 to $5.7\cdot10^{-4}$ $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$ was also observed. The results indicate the presence of the effect of 'physical ageing' of polymer materials of non-porous polymer films, as well as a selective layer of composite membranes, which consists in the relaxation of free volume elements in the structure of membranes based on glassy highly permeable PTMSP and PVTMS. This effect can lead to a decrease in the rate of oxygen mass transfer in the membrane contactor and a gradual decrease in the efficiency of the process.

At the same time, the selectivity values for the O_2/N_2 gas pair decrease insignificantly for both types of membranes. For example, in the case of non-porous polymer films, the ideal selectivity for

Table 2. Membranes transport properties before and after exposure to 30 wt% solutions of MEA

Membrane type		Flat sheet	Composite hollow fiber membrane
Before exposure to amine solvents			
Permeance·10^1, $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$	N_2	1.0±0.2	0.6±0.2
	O_2	1.7±0.2	1.2±0.2
	CO_2	6.7±0.2	2.0±0.2
Ideal selectivity	CO_2/N_2	6.7±0.1	3.3±0.1
	O_2/CO_2	0.3±0.1	0.6±0.1
	O_2/N_2	1.7±0.1	2.0±0.1
After exposure to amine solvents			
Permeance 10^4, $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$	N_2	5.2±0.2	3.1±0.2
	O_2	7.6±0.2	5.7±0.2
	CO_2	28.1±0.2	8.7±0.2
Ideal selectivity	CO_2/N_2	5.4±0.1	2.8±0.1
	O_2/CO_2	0.3±0.1	0.5±0.1
	O_2/N_2	1.5±0.1	1.5±0.1

the O_2/N_2 pair decreased from 1.7 to 1.5, while in the case of hollow fibre composite membranes, the ideal selectivity for the O_2/N_2 decreased from 2.0 to 1.5. This indicates a slight degradation of the obtained membranes and their potential applicability in gas-liquid and liquid-liquid membrane contactors for the deoxygenation of alkanolamine CO_2 solvents.

Deoxygenation of Alkanolamine CO_2 Solvents in a Flat Sheet and Hollow Fibre Membrane Contactor

Using the obtaining membranes, deoxygenation of an aqueous solution of MEA 30 wt% was carried out using a flat-frame gas-liquid and liquid-liquid membrane contactors and using a vacuum and an oxygen scavenger solution to create the driving force of the process, respectively (Figure 5).

It can be seen that the concentration of dissolved oxygen in the MEA solution of 30 wt% gradually decreases with time. In this case, when using a vacuum to create the driving force of the process, a large degree of dissolved oxygen removal of 10.2% was achieved, compared to 5.6% in the case of using a Na_2SO_3 solution.

To increase the efficiency of the deoxygenation process, a hollow fibre membrane gas-liquid contactor with a smaller thickness of the non-porous selective layer and a larger mass transfer surface area was used. Vacuum was used to create the driving force of the process due to the higher degree of dissolved oxygen removal achieved. Also, the influence of the type of alkanolamine on the efficiency of the membrane deoxygenation process using MEA (primary), DEA (secondary), MDEA (tertiary), AMP (primary sterically hindered) and PZ (cyclic) was additionally investigated. The results of studying the deoxygenation process with the used alkanolamines are shown in Figure 6.

It can be seen that in the case of using a hollow fibre membrane contactor and vacuuming, the concentration of dissolved oxygen gradually decreases over time as a result of a decrease in the driving force of the process in a closed system with absorbent recirculation and then reaches a plateau at a level of 5-7 mg/l for all alkanolamines used. It can also be seen that, after 60 min. of the process, the degree of extraction of dissolved oxygen from alkanolamine solutions increases in the series AMP ≈ MDEA < DEA < PZ ≈ MEA from 19 to 37%, which may be due to the greater mass transfer resistance of more viscous amine solutions.

Based on the data obtained on the deoxygenation of various types of alkanolamine absorbents using a vacuum and a hollow fibre membrane contactor more efficient than a flat-frame contactor, the main characteristics of oxygen mass transfer were determined. Thus, the transmembrane oxygen flux J, m^3/h, was calculated during the deoxygenation process:

$$J = \frac{(V_t - V_0)}{t}, \quad (3)$$

where V_0 and V_t are the volume of oxygen in the liquid phase at the beginning of the process and at time t, respectively, m^3(STP); t is the time from the beginning of the experiment, h.

The overall oxygen mass transfer coefficient K_{ov} during the deoxygenation process was also estimated (Rivero *et al*., 2020; Vadillo *et al*., 2021):

$$K_{ov} = \frac{J}{\Delta C_{ln} \cdot S} \quad (4)$$

where J is the transmembrane oxygen flux, m^3/h, S is the membrane surface area, m^2, ΔC_{ln} is the average logarithmic difference in oxygen

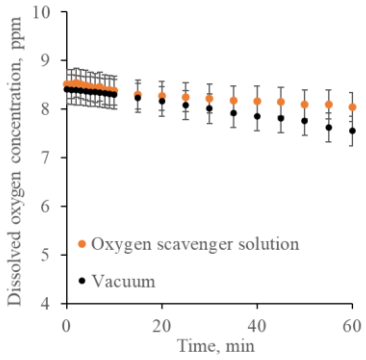


Figure 5. Dissolved oxygen concentration in amine solvent vs deoxygenation process time by using a flat sheet membrane module

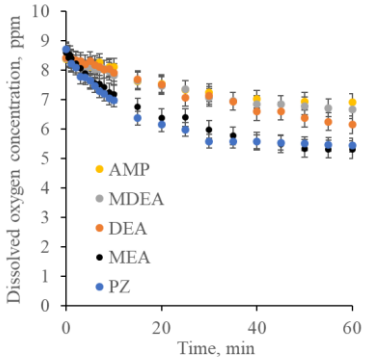


Figure 6. Dissolved oxygen concentration in amine solvent vs deoxygenation process time by using hollow fibre membrane module

Table 3. Oxygen mass transfer parameters through the composite membrane

Amine	MEA	DEA	MDEA	AMP	PZ
Transmembrane oxygen flow $\cdot 10^{-7}$, m^3/h	9.2	6.4	4.9	4.1	9.1
ΔC_{ln}	6.8	7.2	7.5	7.6	7.0
Mass transfer coefficient $K_{ov} \cdot 10^{-7}$, sm/s	10.0	6.5	4.8	4.0	9.7
Mass transfer resistance $1/K_{ov} \cdot 10^{6}$, s/sm	1.0	1.5	2.1	2.5	1.0

concentrations at the initial moment of time and after the completion of the process.

The resistance to oxygen mass transfer during deoxygenation was also calculated as $1/K_{ov}$. The results of calculating the main parameters of oxygen mass transfer are presented in Table 3.

The contribution of various phases to the resistance to oxygen mass transfer during the process of deoxygenation of alkanolamine solvents in a gas-liquid membrane contactor can also be further evaluated. According to the film theory, the resistance to gas mass transfer in processes occurring in gas-liquid membrane contact cores can be defined as the sum of three series resistances: resistance to mass transfer in the boundary layer of the gas part, resistance to mass transfer introduced by the membrane, and resistance to mass transfer in the boundary layer of a liquid. Thus, the total resistance to gas mass transfer in a hollow fibre membrane gas-liquid contactor can be represented in a resistance-in-series model (Mavroudi *et al*., 2006; Khaisri *et al*., 2010; Zhao *et al*., 2016, Rivero *et al*., 2020; Vadillo *et al*.; 2021):

$$\frac{1}{K_{ov}} = \frac{1}{k_g d_i} + \frac{d_i}{k_m d_{ln}} + \frac{H d_i}{k_l d_o}, \quad (5)$$

where K_{ov} is the total mass transfer coefficient, k_g is the mass transfer coefficient in the gas part of the contactor, k_m is the mass transfer coefficient through the membrane, k_l is the mass transfer coefficient in the liquid boundary layer, d_i, d_o, d_{ln} are the inner, outer and average logarithmic diameters of the fibres in the hollow fibre contactor, respectively.

At the same time, in the case of using evacuation and gas-liquid contactors in general, the resistance of the gas part of the contactor can be neglected due to its small values (Al-Saffar *et al*., 1997; Khaisri *et al*., 2010; Rivero *et al*., 2020; Vadillo *et al*., 2021). Thus, the 2nd and 3rd terms on the right side of Equation 5 are significant. The mass transfer coefficient in a membrane is, by definition, the gas permeability of the membrane. In a rather rough approximation, as the resistance to oxygen mass transfer in the membrane, one can use the reciprocal values of the membrane gas permeability, reduced to the driving force, obtained in experiments to determine the gas permeance of membranes (Table 2). At the same time, for greater accuracy of calculations, the values of permeance after contact with solutions of alkanolamines were used.

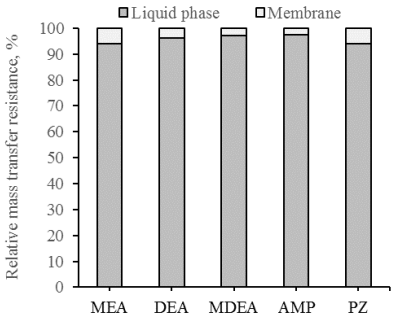


Figure 7. Relative mass transfer resistance of membrane and liquid phase in the deoxygenation process of amine CO_2 solvents

The assessment of the contribution of the membrane and the absorbent boundary layer to the total resistance to oxygen mass transfer in a membrane contactor based on the obtained composite membranes is shown in Figure 7.

It can be seen that the resistance to mass transfer in the boundary layer of solvents makes a decisive contribution to the resistance to mass transfer of oxygen during the deoxygenation process (94-98%) to the total resistance to mass transfer. This fact also indirectly confirms the absence of significant wetting of the membranes with the liquid phase, since, in the case of a high degree of wetting, the resistance to membrane mass transfer can reach high values (Rivero *et al*., 2020).

Conclusions

Thus, flat, non-porous films and composite membranes based on highly permeable glassy polymers PTMSP and PVTMS were obtained. Based on them, flat sheet and hollow fibre membrane contactors were created, and various alkanolamine carbon dioxide solvents were deoxygenated. The maximum degree of oxygen removal achieved was 37%. At the same time, it was found that the main resistance to oxygen mass transfer in the studying process using the obtained

membranes is introduced by the boundary layer of the liquid flowing through the contactor. Thus, to potentially increase the efficiency of the deoxygenation process of carbon dioxide alkanolamine solvents using composite membranes based on porous supports and a mixture of PTMSP and PVTMS glassy polymers and evacuation in a gas-liquid membrane contactor, the linear flow rate of absorbents in the liquid part of the membrane contactor can be increased, and also additional flow turbulence to reduce the thickness of the boundary layer in the liquid.

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