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Dossier

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PART 2

Post Combustion CO_2 Capture

Captage de CO_2 en postcombustion

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Dossier

Post Combustion CO_2 Capture
Captage de CO_2 en postcombustion

Regeneration of Alkanolamine Solutions in Membrane Contactor Based on Novel Polynorbornene

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Résumé — Régénération de solutions d'alcanolamine dans un contacteur à membrane basé sur un nouveau polynorbornène — Un nouveau polymère vitreux à haute perméabilité, le poly[bis (triméthylsilyl)tricyclononene] (PBTMST), est proposé pour la première fois pour une utilisation dans un contacteur gaz-liquide à membrane pour la régénération de liquides d'absorption riches en CO_2 (désorption de CO_2). Ce matériau membranaire possède une bonne stabilité chimique et de bonnes propriétés barrière pour de nombreuses alcanolamines (solutions de 30 % poids de MEA, DEA, MDEA, AMP, DEAE ou AEAE) dans des conditions typiques de régénération (T = 100 °C). Les études des propriétés de transport des gaz du PBTMST (à 100 °C et sous 1 à 40 bar) montrent que les coefficients de perméabilité à l'oxygène, à l'azote et au dioxyde de carbone tendent à diminuer puis à se stabiliser après les 6 à 8 premières heures de mesure. Ce comportement peut être expliqué par une relaxation partielle de la structure de volume libre du PBTMST. Aucune dégradation à haute température du matériau polymère n'a pu être confirmée par analyse IR. De plus, ce matériau membranaire conserve des coefficients de perméabilité aux gaz élevés, supérieurs à ceux des matériaux conventionnels utilisés dans les contacteurs à membrane. Un contacteur gaz-liquide à membrane fabriqué à partir d'une membrane dense de PBTMST présente de performances bonnes et stables. En particulier, le taux de charge en CO_2 d'une solution de diéthanolamine (30 % poids) peut être réduit de 0,05 à 0,34 mole/mole *via* un simple passage à travers le régénérateur à membrane à 100 °C et à pression élevée. Il semble que le taux de désorption soit principalement contrôlé par la phase liquide, une diminution de l'épaisseur membranaire de 50 % (de 31 à 21 μm) n'apportant qu'une amélioration de 1,5 à 8,5 % de la régénération de la DEA.

Abstract — Regeneration of Alkanolamine Solutions in Membrane Contactor Based on Novel Polynorbornene — *For the first time, a novel highly permeable glassy polymer, addition poly[bis (trimethylsilyl)tricyclononene] (PBTMST), was proposed for its use in a gas-liquid membrane contactor for the regeneration of CO_2 absorption liquids (desorption of CO_2). This membrane material possesses a good chemical stability and high barrier properties for a number of alkanolmines (30 wt% solutions of MEA, DEA, MDEA, AMP, DEAE or AEAE) under typical regeneration conditions (T = 100°C). Studies on gas transport properties of PBTMST (100°C and 1-40 bar)* *show that permeability coefficients of oxygen, nitrogen and carbon dioxide initially tend to decrease, and then level off after first 6-8 hours of operation. This behavior can be explained by partial relaxation of the free-volume structure of PBTMST, no chemical degradation of polymer material at high temperature was confirmed by IR analysis. At the same time, this membrane material preserves high gas permeability coefficients which are higher than those of conventional materials used in the membrane contactors. Gas-liquid membrane contactor based on dense PBTMST membrane shows a good, stable performance; particularly,* CO_2 *loading in diethanolamine solution (30 wt%) can be reduced for 0.05-0.34 mole/mole by single pass through the membrane desorber at 100°C and elevated pressure. It seems that desorption rate here is mainly controlled by liquid phase because decreasing of membrane thickness by 50% (from 31 to 21 µm) leads to improvement of DEA regeneration only by 1.5-8.5%.*

INTRODUCTION

In recent years, numerous studies have focused on the advantages of a new promising technology for the purification of different gas streams from carbon dioxide – gas/liquid membrane contactors for absorption and desorption of CO_2. The membrane absorbers/desorbers can be considered as analogues of absorption and desorption columns with the only difference that gas and liquid phases contact each other through a membrane. The feasibility of CO_2 capture by membrane contactors was first been highlighted in 1985 [1, 2]. Noteworthy is that membrane contactors show numerous benefits over conventional industrial processes which are primarily based on packed columns [3]. For example, high specific surface area of membrane contactors (800-3 000 m^2/m^3) and independent control over gas and liquid flows make it possible to provide high mass transfer coefficients, which are several times higher than those of conventional absorption processes; moreover, advantages of this approach are also related to noticeable reduction in weight-dimensional characteristics [3-7]. The most studied application of membrane contactors is CO_2 absorption by using porous hollow-fiber membranes based on hydrophobic polymers such as PolyPropylene (PP), PolyEthylene (PE), Poly[TetraFluoroEthylene] (PTFE) or Poly[VinyliDene Fluoride] (PVDF) [3, 5, 8-12]. This approach allows one to achieve a marked increase in the packing density of the membrane module as well as to reduce the mass-transport resistance.

Recently, it was shown that porous PTFE hollow fibers could be used for high pressure absorption of CO_2 at 50 bar if the pressure difference across the membrane is strictly controlled [13]. Nevertheless, porous membranes have major drawbacks for long-term operation due to pores wetting problems. Even partial wetting of the membrane pores leads to dramatic decrease in mass-transfer coefficients across the membrane and, as a result, a drop in the efficiency of CO_2 removal process [12, 14-17].

The above problems related to unwanted wetting of pores can be solved by using membranes with a non-porous selective layer based on hydrophobic polymers [18-24]. Additional resistance provided by this dense membrane layer can be diminished by the use of polymers with high permeability with respect to CO_2. Obviously, hydrophobic glassy polymers with a high free-volume fraction can be considered as advantageous membrane materials for gas/liquid contactors [21, 24]. For example, a polymer with gas permeability, Poly[1-(TriMethylSilyl)-1-Propyne] (PTMSP), shows good barrier properties towards industrial chemical absorption liquids at a trans-membrane pressure of 40 bar but, at the same time, it is permeable for CO_2 [21, 24]. This combination of good membrane barrier properties and high CO_2 flux offers evident benefits for a gas-liquid membrane contactor, which can be used not only for CO_2 absorption but also for the regeneration of CO_2 absorption liquids. Replacement of desorption column by membrane desorption unit allows to regenerate absorption liquid without its depressurization, *i.e.* the liquid pressure in the desorption unit can be maintained almost at the same level as that in the absorption column due to the independent operation of gas and liquid flow. As a result, electricity consumption for unit operation unit can be noticeably reduced. Lower weight-dimensional characteristics of the desorption unit due to a higher gas-liquid interface area in the membrane module also seem to be beneficial for the high-pressure performance.

Further development of this approach is hindered by the limited assortment of commercially available membranes and membrane materials with high chemical stability in absorbents at high temperatures, good barrier properties towards liquids, and high gas transport characteristics. Therefore, the objective of this work is concerned with the evaluation of a novel polymer, addition Poly[3,4-Bis (TriMethylSilyl)Tricyclononene-7] (PBTMST), as a promising membrane material for the regeneration of CO_2 absorption liquids at high pressures/temperatures. Among all other known glassy polymers, this membrane material shows sufficiently high gas permeability coefficients as well as the high glass transition temperature ($T_g \geq 370°C$) [25-28]. The additional advantage of PBTMST is related to the absence of any double bonds in the polymer structure.

1 EXPERIMENTAL PART

1.1 Polymer

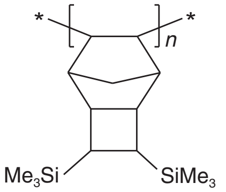
Polymer PBTMST (*Tab. 1*) was synthesized using the catalytic system $(CH_3COO)_2Pd/B(C_6F_5)_3$ according to the protocol developed in TIPS RAS [27]. The experimental procedure was the following (3,4-bis (trimethylsilyl)tricyclononene-7/$Pd(OAc)_2/B(C_6F_5)_3$ ratio = 3 000/1/150): 0.06 M toluene solution of $Pd(OAc)_2$ (0.1 mL, 0.000556 mmol) and monomer (0.48 mL, 1.67 mmol) were added to a pre-evacuated and argon-filled round-bottom glass ampoule (5-10 mL) equipped with a magnetic stirrer. Polymerization was initiated by the addition of 0.09 M toluene solution of $B(C_6F_5)_3$ (0.94 mL, 0.084 mmol). The reaction mixture was continuously stirred for 24 h at the ambient temperature. The polymers were precipitated by acidified ethanol (ethanol: HCl = 10:1); then, the polymer was separated, repeatedly washed with ethanol and dried in vacuum. This mixture was twice re-precipitated by ethanol from toluene solution and dried in vacuum at 80-90°C up until its constant weight was attained.

1.2 Absorption Liquids

As absorption liquids, we selected aqueous solutions of alkanolamines, which are widely used in industry as chemisorbents for the purification of gaseous mixtures from acidic components. 2-(2-AminoEthylAmino) Ethanol (AEAE) was synthesized in the Central laboratory of the JSC Kazanorgsintez (Tatarstan, Russia). As absorbents, we used MonoEthanolAmine (MEA), DiEthanolAmine (DEA), N-MethylDiEthanolAmine (MDEA), 2-Amino-2-Methyl-1-Propanol (AMP), and 2-DiEthylAminoEthanol (DEAE) (*Sigma Aldrich Chemie Gmbh*); their grade of purity was not less than 99%. The absorption liquids were not subjected to any additional purification. For the preparation of 30 wt% aqueous solutions distilled water was used.

TABLE 1

Structural formula of PBTMST

Polymer	Structure	T_g (°C)
Poly [3,4-Bis (TriMethylSilyl) Tricyclononene-7] *Addition-type* (PBTMST)		> 370

1.3 Preparation of Membranes

Homogeneous dense membranes based on PBTMST were prepared by casting polymer solutions in toluene onto a cellophane support and by subsequent drying at room temperature and later in a vacuum chamber. To provide relaxation of tangential stress, the samples were initially soaked in *n*-butanol and later in ethanol; then, the samples were repeatedly washed with water-ethanol solutions with gradually decreasing alcohol concentrations. Thickness of the membranes was measured on a *Mitutoyo*® digital micrometer with an accuracy of 20-40 μm.

1.4 Measurements of Gas Permeability

Gas permeability was measured for individual gases (N_2, O_2, and CO_2) at room temperature and at a transmembrane pressure of 1-40 bar. Membrane active area was 3.79 cm^2. Gas flow J at constant pressure p was measured by the volume method according to the following equation:

$$J = \frac{V}{t \cdot S}$$

where V is the gas volume passed through the membrane with active area S within time t. Permeability coefficients are expressed in Barrers (1 Barrer = 10^{-10} cm^3 (normal conditions).cm/(cm^2.s.Hg cm)).

Gas permeability at high temperature was studied as follows: the sample was fixed in a measuring cell and conditioned in a thermal chamber at 100°C for 32 h. Gas permeability coefficients were measured within prescribed time intervals without any cooling.

1.5 Flotation Method

Microheterogeneity and free-volume fraction of PBTMST were measured by the flotation method, which includes weighing of the sample in air and in different liquids. In the case of a non-wetting liquid (water), the measurements gave geometric density ρ_g, which is the density of the whole sample including microvoids. In the case of a wetting liquid (ethanol), pycnometric density was estimated, which is the density of the densest regions of the microheterogeneous medium because microvoids of the polymer matrix (free volume elements) are filled with the corresponding liquid molecules. As a result, overall microporosity W of the polymer can be given as:

$$W = \frac{\rho_p - \rho_g}{\rho_p}$$

where ρ_p is the pycnometric density of the polymer film, ρ_g is the geometric density of the polymer film.

1.6 Evaluation of Polymer Chemical Stability

Chemical stability of the membrane materials was studied as follows: the PBTMST samples with a thickness of 20-30 μm were immersed in different absorption liquids at a temperature of 100°C; the overall exposure time at high temperatures varies from 255 to 265 hours. To remove the absorbent for further analysis, the samples were allowed to stay in ethanol for several days; then, the samples were repeatedly washed with water-ethanol solutions with gradually decreasing concentrations of ethanol. Then, the samples were stored in distilled water and dried at a temperature of 40°C.

Chemical stability of the membrane materials after their storage in the absorption liquids was studied by the IR spectroscopy. The IR spectra of the films were recorded on an *IFS-Bruker* 66/Vs FTIR spectrometer in the transmission mode (50 scans, resolution is 2 cm^{-1}). The measurements were performed within the spectral region of 4 000-400 cm^{-1} and the collected IR spectra were analyzed using an OPUS 6.0 software (*Bruker*).

1.7 Membrane Leakage Testing

Transport of absorption liquids across the PBTMST membranes was studied at a temperature of 100°C and at a trans-membrane pressure of 40 bar. The experiments were performed according to the following procedure. The sample of the tested membrane was placed in a dome-shaped filtration cell (active surface area is 3.79 cm^2); then, the upper compartment of the cell was partially filled with the selected absorption liquid and pressurized with pure carbon dioxide up to 40 bar. Both cell and permeate collector were kept in the oven in order to prevent any condensation of absorbent vapors.

1.8 Absorption Liquid Regeneration

Figure 1 shows the experimental setup for the regeneration of the absorption liquid (30 wt% aqueous solution of DEA). Saturation of the absorbent with carbon dioxide takes place in the absorber *5*, which is equipped with a high pressure stirrer. Gas absorption was carried out

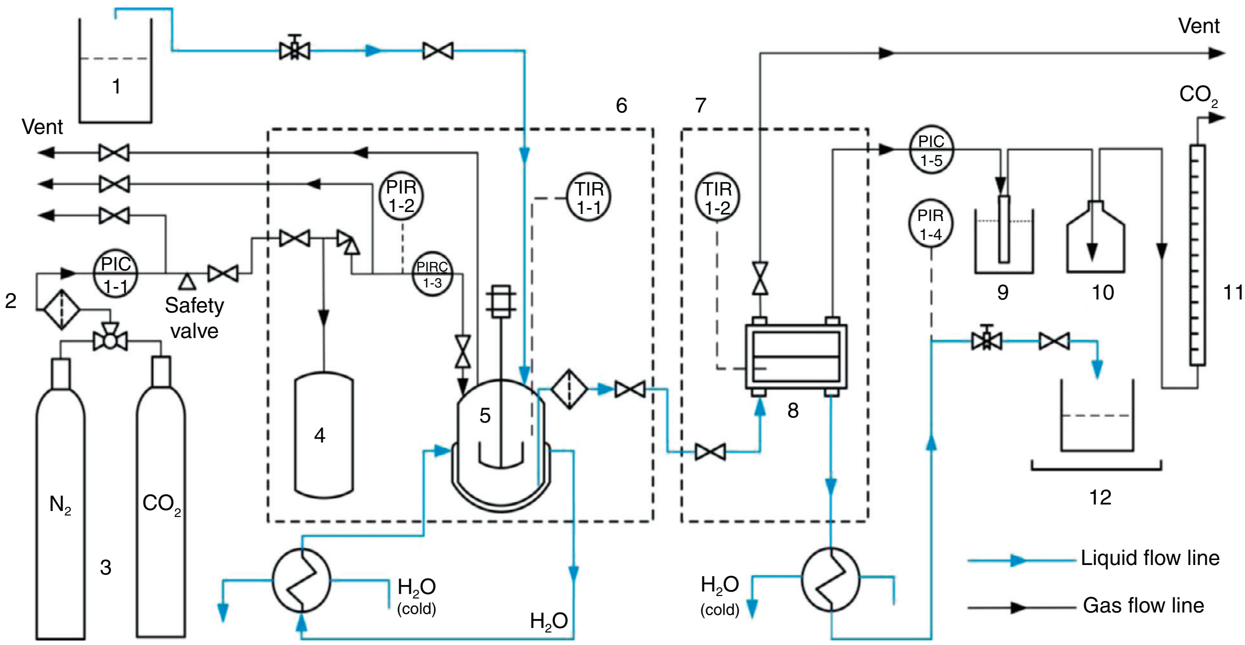


Figure 1

Membrane gas desorption set-up: 1) lean absorbent tank; 2) filter; 3) gas cylinders; 4) gas tank; 5) absorber; 6, 7) thermal ovens; 8) gas-liquid membrane contactor; 9) cold trap; 10) safety flask; 11) gas flow meter; 12) regenerated absorbent tank + microbalance.

under a constant stirring rate at a temperature of 24°C and 10 bar of CO_2 resulting in initial CO_2 loading of 0.98 mole/mole. Then, the saturated liquid under the same pressure was supplied into the liquid flow line of the membrane desorption module *8*, where thermal regeneration of the absorbent takes place at a temperature of 100°C. In the course of the experimental run, CO_2 flow leaves the gas flow line of the contactor at 1 bar, and the CO_2 flow rate is measured with the flow meter *11*. The absorbent loss was measured by weighting of condensate in the cold trap *9* at 0°C. The flow rate of the absorbent in the cell is adjusted with a needle valve. The amount of the regenerated liquid collected in the collector *12* with an electronic microbalance was estimated by weighing. The membrane active area in the desorption module is 16.6 cm^2. Thickness of the liquid layer in the desorption module is equal to 0.1 mm in order to minimize the diffusion resistance.

2 RESULTS AND DISCUSSION

2.1 Gas Permeability

The first stage of this work was focused on the study of gas transport characteristics of the PBTMST membranes (N_2, O_2 and CO_2) at elevated pressures up to 40 bar and at the room temperature (23 ± 2°C); the results of this study are listed in Table 2. One can conclude that, as compared with all known polymeric materials, the selected glassy polymer is characterized by high permeability coefficients [28]. To illustrate this the CO_2 permeability coefficient of Poly[DiMethylSiloxane] (PDMS), Poly[VinylTriMethylSilane] (PVTMS) and Poly[PhenyleneOxide] (PPO), which are traditionally used as a dense layer in membranes for membrane contactors, appear to be much lower: 3 230, 190, and 57 Barrer [28], respectively. High gas transport characteristics of the selected polymer can be attributed to high free-volume fraction, which is equal to nearly 19% for PBTMST (*Tab. 3*).

TABLE 2

Gas permeability coefficients at 25°C

Membrane	P (Barrer)		
	N_2	O_2	CO_2
PBTMST	1 200	2 150	8 500

2.2 Thermal Resistance

In industry, regeneration of chemical absorbents takes place at a temperature of 100°C or higher. In this connection, thermal resistance of the membrane materials is the key parameter, which could secure long-life service operation of the high-pressure/temperature gas-liquid membrane contactor [9, 10].

As follows from the literature data, gas transport characteristics of glassy polymers with the high free-volume fraction tend to decline with time, especially, at elevated temperatures [29, 30]. This decline can be explained by several factors: among them are "physical aging" of polymers (relaxation of non-equilibrium free volume), chemical degradation of polymers, and presence of various admixtures in the materials (adsorption of various substances).

In this connection, we studied changes in the gas transport characteristics of the PBTMST membranes with time at high temperatures which are traditionally used for the regeneration of absorbents. Figure 2 presents the time dependences of permeability coefficients P of the samples for three gases (N_2, O_2, and CO_2) at a temperature of 100°C. As follows from Figure 2, the gas permeability coefficients $P(N_2)$, $P(O_2)$ and $P(CO_2)$ tend to decrease with time when the samples are exposed at 100°C. At the same time, these changes take place within the first 6-8 hours. Taking into account the fact that at later stages gas transport characteristics seem to be unchanged, one can conclude that this phenomenon is primarily attributed by partial relaxation of free volume in polymer (so called "physical aging" of the material) rather than by chemical degradation of polymers.

To prove this assumption, we studied changes in the density of the membrane materials before and after annealing at 100°C for 30 h (*Tab. 3*). Comparing these results with the data for the initial samples, one can

TABLE 3

Geometric density ρ_g, pycnometric density ρ_n and microporosity W of the samples

Membrane	Initial sample			After 30 h at 100°C		
	ρ_g (g/cm^3) (H_2O)	ρ_n (g/cm^3) (EtOH)	W (%)	ρ_g (g/cm^3) (H_2O)	ρ_n (g/cm^3) (EtOH)	W (%)
PBTMST	0.79	0.98	19	0.81	0.98	17

conclude that, upon annealing, geometric density of the membranes (density of the whole sample including microvoids) increases whereas pycnometric density (density of the densest regions of the microheterogeneous medium) remains unchanged. As a consequence, fraction of unrelaxed free volume W decreases from 19 to 17%.

Noteworthy is that annealing does not lead to marked changes in the transport characteristics of PBTMST with only saturated bonds. As was shown in the earlier studies, for PTMSP, $P(O_2)$ decreases by an order of magnitude after heating at 100°C for 15 h [31] and by two orders of magnitude after heating at 120°C for 8 h [32]. At the same time, oxygen permeability of the addition Poly[5-(TriMethylSilyl)Norborn-7-ene] (PTMSN) decreases only from 980 to 900 Barrer after annealing in air at 80°C for 16 h [33].

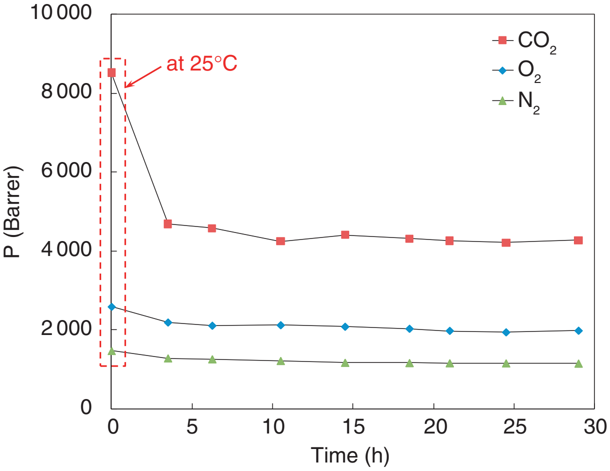


Figure 2

Time dependences of gas permeability coefficient of the membranes at 100°C (as reference, initial data at 25°C are presented).

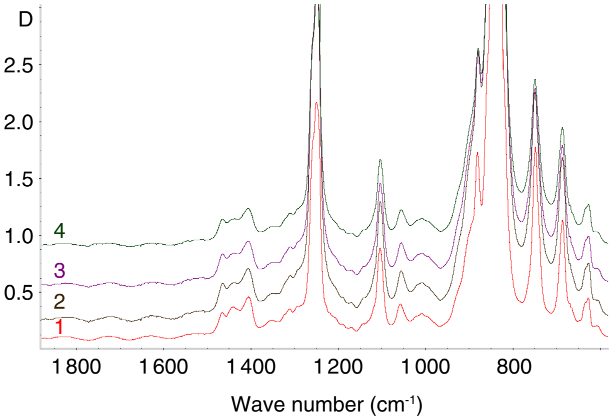


Figure 3

The IR-spectra for the PBTMST samples at 150°C; duration of thermal treatment: 1) initial sample at 23 ± 2°C, 2) 60 min, 3) 120 min, 4) 240 min.

The absence of chemical degradation and oxidation of PBTMST at elevated temperatures has been proved by the IR spectral measurements. Figure 3 features the IR spectra of the membrane samples before annealing (1) and after conditioning in air for 4 h at 150°C (2-4).

As follows from Figure 3, the IR spectra of the PBTMST membranes appear to be virtually the same: in particular, they do not reveal the presence of any oxygen-containing groups (for example, C-O and C = O) in the structure which can attest the occurrence of oxidation and degradation of the polymer at elevated temperatures. Therefore, these results make it possible to conclude that no chemical degradation of the material upon thermal treatment at 150°C for, at least, 4 h takes place.

2.3. Chemical Resistance in Absorbents

The required criterion for materials used in a gas-liquid membrane contactor is concerned with their resistance to the absorption liquids (chemically aggressive media) at elevated temperatures over long operation period.

In this connection, the long-term lab-scale experiments (up to 265 hours) were performed when the PBTMST samples were allowed to stay at 100°C in the medium of various chemisorbents (30 wt% of aqueous solutions of alkanolamines). Table 4 lists the results of the visual inspection of the membranes such as changes in color, morphology, dimensions, and strength characteristics of the samples as well as their possible swelling or dissolution. Noteworthy is that the overall duration of the membrane/absorbent contact is three times higher than the values listed in Table 3 because the test samples were kept in the corresponding liquids overnight at room

TABLE 4

Chemical resistance of membranes in absorbents at 100°C (“+” – the sample is stable in a given absorbent)

	PBTMST
MEA (30%)	+255 h
DEA (30%)	+265 h
MDEA (30%)	+265 h
AMP (30%)	+265 h
DEAE (30%)	+265 h
AEAE (30%)	+265 h

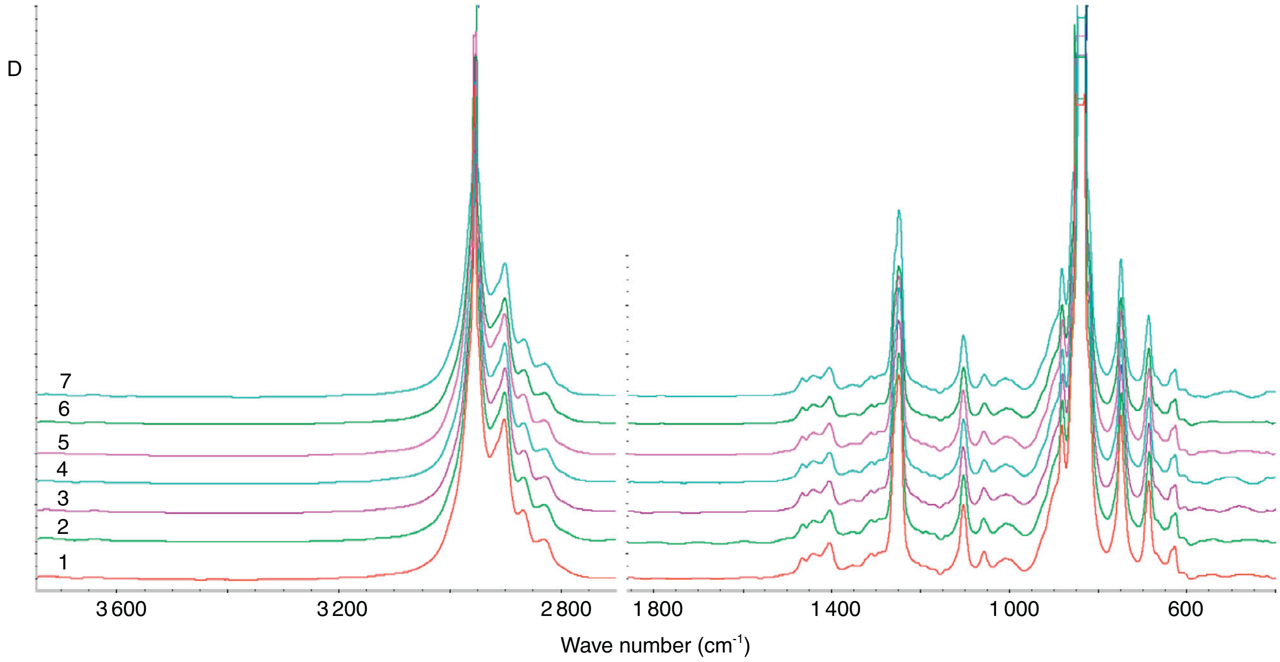


Figure 4

The IR spectra of the samples before 1) and after 2-7) experiments on the chemical resistance at 100°C in aqueous solutions of MEA 2), DEA 3), MDEA 4), DEAE 5), AMP 6) and AEAE 7).

temperature. As follows from Table 4, the membranes show high chemical resistance in the absorption liquids at 100°C, and no marked changes in their macroscopic characteristics were observed.

Chemical resistance of the materials was also proved by the IR spectroscopy. Figure 4 shows the IR spectra of the samples before (1) and after long-term storage in the absorption liquids (2-7) at temperatures below 100°C. According to the data of the IR analysis, the IR spectra of the materials appear to be virtually unchanged. Therefore, our results make it possible to conclude that the long-term contact of the PBTMST membranes with the chemical absorption liquids under the conditions typical of the regeneration process does not entail any marked changes in their chemical structure.

2.4 Liquid Flow across Membranes

Another key requirement providing successful operation of the gas-liquid membrane contactor is concerned with the absence of liquid transport across the membrane at elevated pressures and temperatures. The absence of any flow of absorbents for, at least, 30 hours was proved by the filtration experiments at a trans-membrane pressure of 40 bar and at a temperature of 100°C. The membrane materials are shown to exhibit good barrier properties with respect to the selected absorption liquids – 30 wt% aqueous solutions of different alkanolamines; at the same time PBTMST remains permeable for carbon dioxide.

2.5 Membrane Desorption of CO_2 at Elevated Pressure and Temperature

Figure 5 presents the desorbed flux of carbon dioxide through the dense PBTMST membrane with a thickness of 31 μm plotted as a function of liquid linear velocity of 30 wt% aqueous DEA solution. In this work, CO_2 loading of rich solutions was 0.96 moles of CO_2 per one mole of DEA, and this value corresponds to the equilibrium absorption capacity at 10 bar and 24°C. Desorption was carried out at a pressure of 10 bar in the liquid part of membrane desorber, and the CO_2 pressure in the gas part of 1 bar.

As shown in Figure 5, all curves can be divided into two regions. In the first region corresponding to the low linear velocity, the flux of the gas desorbed through the membrane increases with increasing of liquid linear velocity. Then, the flux of the desorbed carbon dioxide tends to level off but linear velocity of liquid increases.

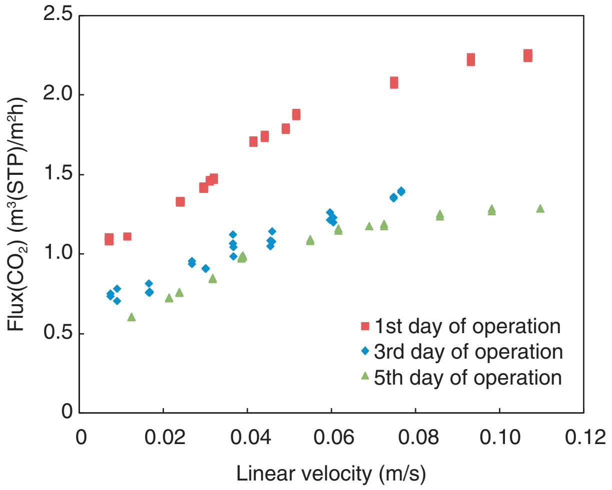


Figure 5

Flux of desorbed CO_2 as a function of linear velocity for 30 wt% of aqueous DEA solution and the dense PBTMST-based film (thickness of 31 µm).

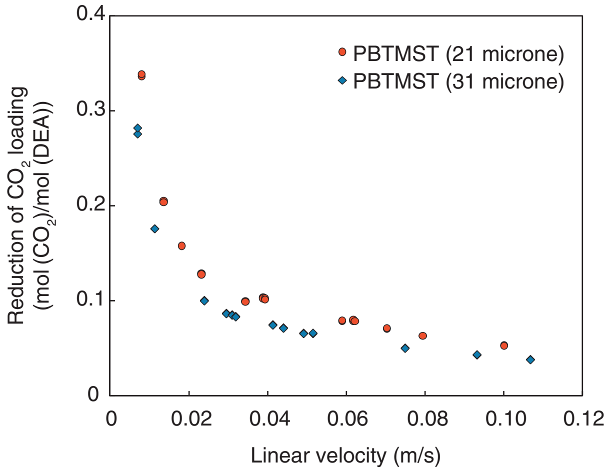


Figure 6

Effect of PBTMST thickness on performance of membrane desorber at elevated pressure: reduction of CO_2 loading in 30 wt% aqueous DEA solution as a function of liquid linear velocity.

This behavior can be explained by finite rates of reversible chemical reactions between CO_2 and DEA as well as by the diffusion resistance to the transport of carbon dioxide from the liquid bulk to the liquid-membrane interface, in the boundary layer and further transport across the membrane. As was shown by Li and Teo [19] and by Simons *et al.* [34], the membranes with the dense selective layer showed noticeable resistance to the mass transfer; as a result, the contribution from the membrane resistance to the overall resistance of the gas-liquid contactor to the transport of CO_2 increases.

As in the case of gas permeability, gas transport characteristics of the membrane tend to decrease with the time due to the partial relaxation of the non-equilibrium free volume (*Fig. 5*). However, the decrease takes place only within the first hours of operation upon membrane gas desorption; then, the gas transport characteristics of the membrane approach their steady-state level. Despite this drawback, the PBTMST membranes still exhibit high carbon dioxide flux. As compared with conventional desorption columns, the advantages of dense membranes based on highly permeable glassy polymers are also related to the absence of absorbent droplet entrainment. The actual loss of the absorbent during regeneration of 30 wt% of DEA through PBTMST at 100°C was estimated on the level of $2\text{-}8.10^{-4}$ kg/m^2.h, which is at least three orders of magnitude lower in contrast to CO_2 flux of 0.6-1.3 kg/m^2.h (see the fifth day of operation, *Fig. 5*). It should be pointed out that such absorbent loss is due to solvent evaporation through the membrane, and no liquid transport takes place across the membrane. Indeed, titrometric analysis of condensate collected from the desorbed CO_2 stream revealed that its composition is correlated to the equilibrium composition of vapor phase over 30% aqueous solution of DEA.

As was mentioned above, the replacement of the conventional porous membranes by the membranes with a dense selective layer leads to additional resistance to the mass transfer, such membrane resistance could play a significant role in overall process resistance. Therefore, performance of the high-pressure membrane contactor can be improved by further reduction in the thickness of the selective layer. As can be shown in Figure 6, decrease of the membrane thickness from 31 down to 21 µm improves regeneration of aqueous DEA at the same linear velocities. As a result, dense PBTMST membrane with a thickness of 21 µm can provide reduction in the CO_2 loading for 0.05-0.34 mole/mole by a single pass of the absorbent through the membrane desorber operated at 100°C. It should be noted that for industrial sweetening processes, the difference in the CO_2 loading between reach and lean solutions usually does not exceed 0.2-0.4 mole/mole.

As follows from Figure 6, desorption process in membrane contactor based on PBTMST is mainly governed by mass-transfer in the liquid phase because decreasing of membrane thickness by 50% (from 31 to 21 µm) leads to improvement of DEA regeneration only by 1.5-8.5%. As was expected, longer contact between a liquid and a membrane provides bigger difference in the performance of the two membranes with different thicknesses. This limitation by liquid phase can be explained by mass-transfer resistance in the liquid and rates of reversible reactions between CO_2 and aqueous solution of DEA [35, 36].

Decrease in the carbon dioxide partial pressure in the gas flow line of the membrane desorber by applying of vacuum or stripping gas allows further improvement of the DEA regeneration; however, this approach is beyond the scope of this work because for transportation and geological storage pure carbon dioxide is required for its further compression. The ongoing study is being focused on the development of the high-flux composite membranes based on PBTMST and a solvent-resistant porous support.

CONCLUSIONS

For the first time, dense membranes based on the addition PBTMST were used for the regeneration of the typical CO_2 absorption liquids (30 wt% DEA in water) in the high-pressure/temperature membrane contactor at 100°C. PBTMST is shown to exhibit high barrier characteristics with respect to aqueous solutions of different alkanolamines at a trans-membrane pressure of 40 bar and at 100°C. Long-term exposure of PBTMST to the above absorbents at 100°C does not entail any chemical degradation (as proved by the IR spectroscopy). Some decline of gas transport characteristics at high temperatures can be attributed by partial relaxation of high free-volume fraction in PBTMST. Dense PBTMST membranes can provide the reduction of CO_2 loading for 0.05-0.34 mole/mole with respect to used liquid linear velocities by a single pass of the absorbent through the membrane desorber operated at 100°C and elevated pressure. It seems that the desorption rate here is mainly controlled by the liquid phase mass-transfer because decreasing of membrane thickness by 50% (from 31 to 21 μm) leads to improvement of DEA regeneration only by 1.5-8.5%. As expected, a longer contact time of the liquid with the membranes is responsible for the bigger difference in the performance of two membranes with different thicknesses.

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