Use of nonporous polymeric flat-sheet gas-separation membranes in a membrane-liquid contactor: experimental studies

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Abstract

Flat-sheet non-porous asymmetric poly(vinyltrimethylsilane) (PVTMS) membranes and composite membranes comprising a dense layer of polydimethylsiloxane/polyphenylsilsesquioxane (PDMS/PPSQ) block copolymer were evaluated for low-temperature bubble-free deoxygenation of water flowing in a two-channel countercurrent liquid-membrane contactor. A novel large-scale three-channel flowing-liquid-membrane module (selective membrane valve), designed for gas separation, is also described. The system comprised PVTMS or PDMS/PPSQ non-porous membranes which acted as gas-permeable barriers. A membrane system (SMV) in which pure water formed a flowing liquid membrane was evaluated to control hydrogen transfer rates. The liquid flowing along the turbulence-promoter spacers between the membranes reduced liquid-film resistance. The overall mass-transfer coefficients were found to be a function of the liquid flow rate. The liquid-film resistance controlled the rate of gas transfer in such membrane contactors.

Keywords: Gas separations; Liquid membranes; Membrane-liquid contactors; Flowing liquid membranes

l. Introduction

Numerous concepts in the design and performance of liquid-membrane systems for gas separation and purification have been proposed; these include: immobilized liquid membranes (ILM) [1-5]; membrane contactors (MC) [6-12]; membrane permabsorbers (MP) [13-19] (these contain non-porous gas-separation membranes); flowing liquid membranes (FLM) [20-25] and hollow-fiber-contained liquid membranes (HFCLM) [26-29]. For a variety of reasons, according to Kimura and Walment [30], liquid membranes which are immobilized inside the pores of polymeric supports are not stable.

In the case of gas separation by means or membrane-contacting systems (MC, MP, HFCLM, etc.), polymeric membranes (porous or non-porous) serve as the contacting media. As the polymeric membrane is either porous and hydrophobic or non-porous, the liquid and gas phases are separated from each other, making it possible for gas absorption by means of membranes to take place. Liquid-membrane contacting systems combine absorption selectivity with the technical advantages of membrane processes. The main advantages of the contacting liquid-membrane systems for gas separation have been summarized elsewhere [6 - 19, 31, 32].

Earlier studies on membrane gas-liquid contactors focused on systems operating with porous membranes in the non-wetted mode (gas-filled pores) and in the wetted mode (absorption liquid-filled pores) [12, 26-29]. It has been shown that the liquid-film resistance controls the mass transfer in gas-separation liquid-membrane systems if the gas component does not react chemically with the liquid-phase [8, 11].

The development of thin gas-permeable polymeric membranes has stimulated research to evaluate their utilization in liquid-membrane contactors. It has been shown [11,18] that the presence of a thin and highly permeable non-porous film, interposed between the gas and liquid phases, does not strongly affect the overall mass-transfer resistance to gas permeation. The advantages of this technique were summarized by Bessarabov et al. [18] who demonstrated also the main disadvantage of such a system, that is, pollution of the gas phase because of the pervaporation of a hot solution of a liquid absorbent through the non-porous membrane.

Where MC was used as a liquid-phase oxygenator, microporous hydrophobic hollow fibers of polypropylene were applied to oxygenate water [33], and the performance of a porous-membrane water

degasser has been demonstrated [34, 35]. Bubble-free aeration of water has been achieved by means of membranes, and a mass-transfer analysis has been presented [36]. In these studies two types of membranes which show useful oxygen-transfer properties have been identified: microporous hydrophobic polymeric membranes and thin silicone rubber films [37].

In this paper, emphasis is placed on the design of flowing-liquid membrane systems comprising non-porous polymeric flat membranes for gas separation, and on the evaluation of such systems in various operations. It is discussed how the modification of the two-channel membrane-liquid contactor, which has been used to deoxygenate water, enables to apply it to gas separation.

2. Experimental

Two types of the membrane contacting modules have been used in this study: a two-channel membrane contactor (MC) and three-channel selective membrane valve (SMV). A detailed description of the large-scale MC module, used in absorption-desorption modes and comprising the PDMS/PPSQ composite gas-separation membrane, was given in an earlier paper describing the separation of an ethylene and ethane gas mixture [18].

Table 1. Permeabilities of oxygen in various polymers

Polymer	Oxygen permeability (cm^3(STP) cm/cm^2 s cmHg)	References
PDMS	$6.0 \cdot 10^{-8}$	[42]
PDMS/PPSQ	$4.5 \cdot 10^{-8}$	This study
PVTMS	$3.6 \cdot 10^{-9}$	[42]

2.1. Deoxygenation of water flowing in a two-channel membrane-liquid contactor

A two-channel membrane cassette and stainless steel frame (MC), as described earlier [18], was used in this study. The multimembrane cassette comprised 24 asymmetric membranes made from PVTMS or PDMS/PPSQ-coated composite membranes. PVTMS asymmetric and PDMS/PPSQ-coated composite membranes were used in the deoxygenating experiments. The use of asymmetric gas separation membranes offers high productivity because of the presence of a very thin diffusion layer in such membranes. Table 1 shows the permeabilities of PDMS, PVTMS and PDMS/PPSQ block copolymer. Table 2 shows the oxygen permeance (P/l) of the asymmetric membranes used in this study and of the silicone rubber film used in previous work [37]. The SEM micrograph illustrates the structure of a PVTMS asymmetric membrane (Fig. 1). A schematic diagram of the deoxygenation of flowing water is shown in Fig. 2.

Distilled water with a conductivity of 4.01 μS/cm was used. A peristaltic pump (Masterflex pump controller, Cole-Parmer Instrument Co.) fed water into the system in a once-through mode (flowing mode) and the flow rates of gases and liquids were measured by rotameters. The oxygen concentration in the water was determined by means of a digital oxygen meter (Scott Gerate‚jCG 867). A vacuum of -1050 mbar was applied to the gas channels in the module. The initial oxygen concentration in water was 8.6 mg/1. The temperature of the water was 21-22°C throughout. Polymeric net-like turbulence promoters similar to those described by Bessarabov et al. [18] were used to enhance the mass transfer. The hydraulic diameter, d_h, of the membrane module was defined by means of the equation derived by Schock and Miquel [39] as:

$$d_h = \frac{4\varepsilon}{2/h + (1-\varepsilon)A_{V,SP}} = 0.031 \qquad (1)$$

where ε is porosity of the spacer and $A_{V,SP}$ is the specific surface area of the spacer [39]:

$$A_{V,SP} = A_{SP}/V_{SP} = 182 \qquad (2)$$

The value for porosity was obtained from its definition [39]:

$$\varepsilon = 1 - V_{SP}/V_{Tol} = 0.73 \qquad (3)$$

All geometric variables of the spacer were determined by means of visual measurements with a microscope.

Table 2. Oxygen permeances of various polymeric membranes

Polymer	Membrane thickness (cm)	Oxygen permeance (cm^3(STP)/cm^2 s cmHg)	Remarks
PDMS	$1.5 \cdot 10^{-2}$	$4.0 \cdot 10^{-6}$	Nonporous film [371
PDMS/PPSQ	$\approx 5.5 \cdot 10^{-4}$ [a]	$8.2 \cdot 10^{-5}$ [b]	Composite membrane
PVTMS	$\approx 2.3 \cdot 10^{-4}$ [a]	$1.9 \cdot 10^{-5}$ [b]	Asymmetric membrane

[a] Thickness of the dense diffusional layer.
[b] "Gas-membrane-gas" experiments to determine the permeances of these membranes showed variations in permeances. This divergence in the data is explained by the non-uniform thickness of the membrane dense layer.

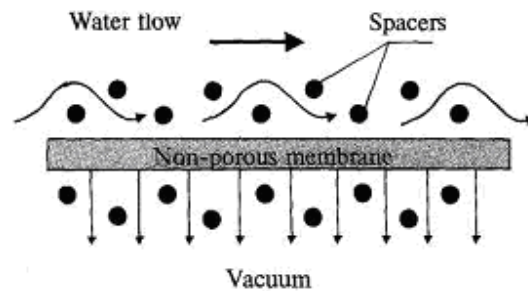Fig.1. Gross-section of the PVTMS asymmetric membrane (view of the sublayer)

Fig. 2. Schematic diagram of the deoxygenation of water flowing in a two-channel membrane contactor.

2.2. *Large-scale three-channel flowing-liquid membrane contactor*

In this study a description of a novel three-channel flowing-liquid-membrane module for ternary gas separation, that is, a selective membrane valve (SMV) is presented. In an SMV a liquid flows between two non-porous membranes (Fig. 3), and a ternary gas mixture can be separated into its components by the membrane valve: the first component which is insoluble in the liquid membrane phase, the second which diffuses through the membrane sandwich, and the third component which reacts chemically with the liquid membrane phase and is pumped to a desorption module for degassing. The selective membrane valve therefore has one inlet for the feed and three outlets for the products.
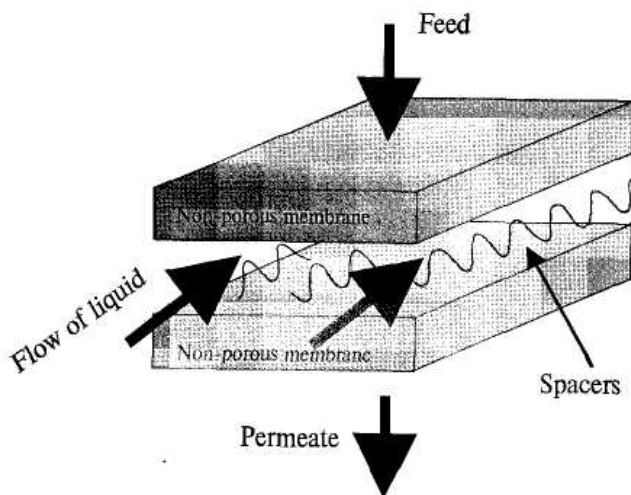

Fig. 3. Schematic diagram of the three-channel membrane "sandwich": the middle layer is a flowing liquid membrane

To obtain the highest efficiency from the SMV with the minimum of equipment a considerably modified two-channel multimembrane module, described earlier [18], was used. The key element of the gas-separation system is the membrane cassette (Fig. 4). The modification comprised addition of a third independent channel into the cassette. Fig. 4 shows that these membrane cassettes have three branch ports (one for the entry of feed-gas; one for the entry of liquid; and one for the entry of sweep-gas). Fig. 5 shows one of these membrane cassettes placed on the surface of the stainless steel block. The membrane cassette is compressed between two blocks of stainless steel. Fig. 6 shows three cassettes between two blocks. The bottom block has two branch pipes (one for the entry and one for exit of gas or liquid) and nine ports, through which gas (or liquid) is fed to contact the membranes. The upper block has three branch pipes (one
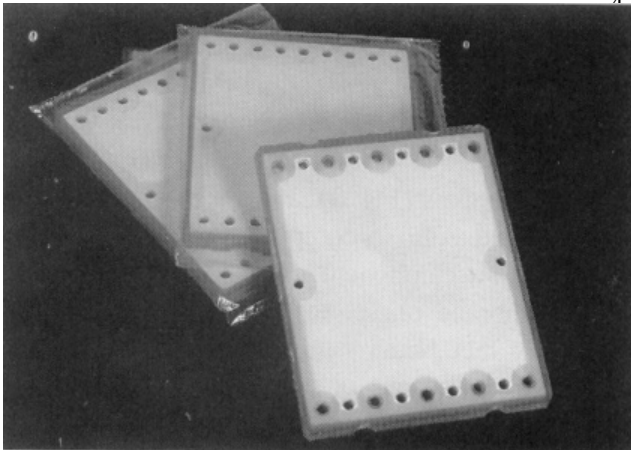
each for feed-gas, for sweep-gas and for liquid). When the upper pipes are locked, the membrane system can operate as a conventional MP (Fig. 7). The same polymeric net-like spacers were used to enhance mass transfer, as described by Bessarabovetal. [18] for the two-channel module. The space between the membranes was 0,045 cm. The total membrane area in one cassette was 0.57 m^2.
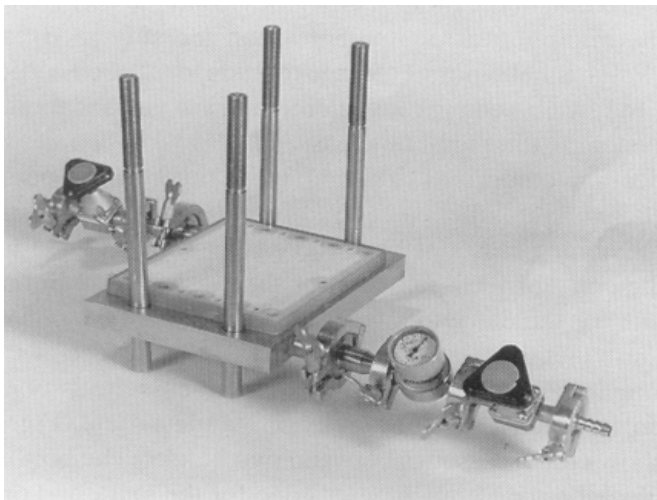
Fig. 4. Three-channel multimembrane cassettes.

Fig. 5. The bottom block of the SMV and a three-channel cassette on it.

Fig. 8 shows clearly the principle of the performance of this cassette. Although this diagram shows only three membranes between the steel blocks, the real cassette contains 24 flat-sheet asymmetric membranes made from PVTMS [17] or PDMS/PPSQ composite membranes [18].
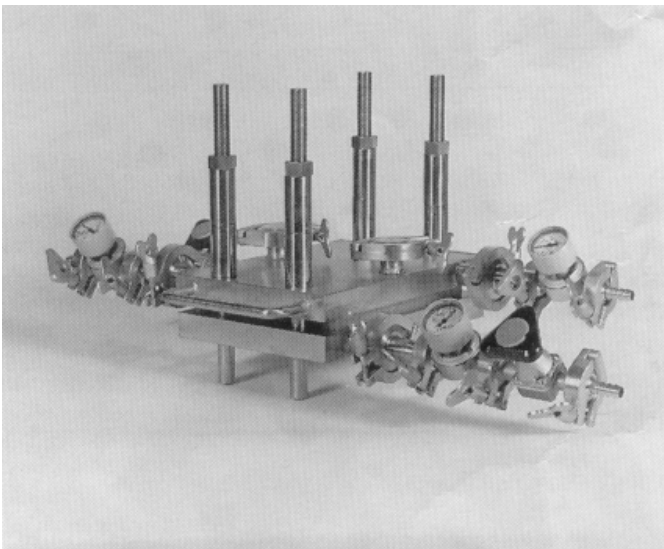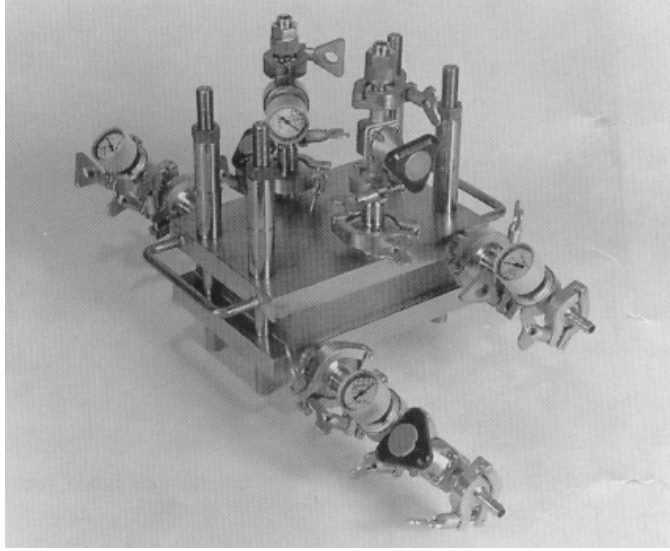

Fig. 6. A three-channel liquid-membrane contacting system for gas separation. The system contains three casettes.

2.3. Hydrogen permeation through the SMV comprising PVTMS membranes in the flowing mode

The purpose of this study was to demonstrate a new design for a liquid-membrane contacting system for gas separation. A peristaltic pump was used to feed water into the system. The flow rates of water were measured by flow-meters. In this study the single SMV module, operating in the flowing mode, was used. The feed-gas was technical-grade hydrogen, and the flowing membrane was distilled water. Hydrogen was fed into the system through the upper port as shown in Fig. 6. The hydrogen concentration in the permeate was determined with a Varian gas chromatograph (model 3700), at room temperature. The carrier gas and the sweep gas were nitrogen. A TCD was used. The flow rate of the sweep gas was 20 ml/s. The separation data were recorded by a Hewlett Packard (3380A) integrator. The steady-state productivity, that is, (permeance, P/l, cm^3/cm^2 s cmHg) was calculated using the same technique as was described in a previous paper [18]. Since nitrogen was used as a sweep gas on the permeate side of the SMV as a model replacement for vacuum stripping, the exiting hydrogen stream

contained nitrogen. The presence of nitrogen and water vapor on the permeate side of the SMV was not taken into account in our calculation of hydrogen permeance.

Fig. 7. A three-channel liquid-membrane contacting system with locked upper ports.

Table 3 Experimental results for water deoxygenation using vacuum stripping

Water flow rate (ml/s)	Concentration of oxygen in water (mg/1)	
	PVTMS membranes	PDMS/PPSQ membranes
0.5	2.3	2.3
1	2.0	2.0
2	1.2	0.9
4	0.7	0.6
5	0.6	0.6
10	0.6	0.5
14	0.6	0.5
20.8	1	1

3. Results and discussion

3.1. Deoxygenating of water

Table 3 shows the oxygen concentration obtained at various water-flow rates. The overall mass transfer coefficient (K_{ov}) for oxygen removal can be calculated by the following equation [38]:

$$K_{OV} = \frac{\Omega}{aL} \ln\left(\frac{[O_2]_{in}}{[O_2]_{aut}} \right)$$ (4)

Where $[O_2]_{in}$ and $[O_2]_{out}$ are the inlet and outlet oxygen concentrations in the liquid, respectively, a is the membrane area per volume of the membrane bed *(a* = 31.7 cm^{-1}), L is the length of the membranes in the direction of flow (L = 20 cm), and Ω is the superficial liquid velocity in the module, that is, the volumetric flow rate divided by cross-section for the flow.

For the deoxygenation experiments the overall transport resistance (1 /K_{ov}) is given by the sum of the membrane resistance (*l*/PH) and the resistance of the boundary liquid layer (l/K_L) [36]:

$$\frac{1}{K_{OV}} = \frac{1}{PH} + \frac{1}{K_L}$$ (5)

where H is Henry's constant, P is the polymer permeability, and l is the thickness of the membrane dense layer.

Table 4 shows the dependence of the overall mass transfer coefficient and liquid film resistance on the liquid flow rate. Fig. 9 shows the relationship between the mass transfer coefficient and water velocity though the following correlation [39]:

$$Sh = 0.065 Re^{0.875} Sc^{0.25}$$ (6)

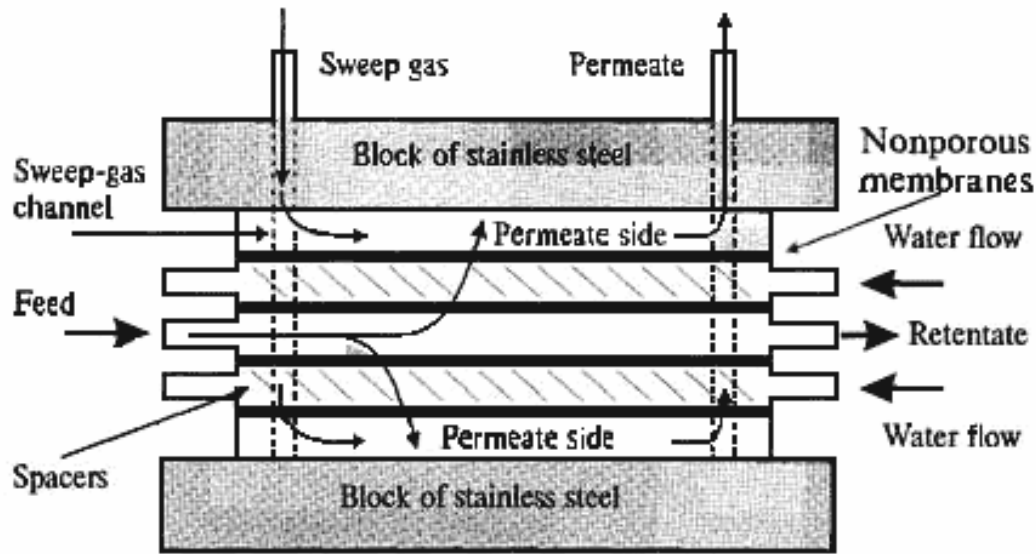where $Sh = K_{QV} h_d/D$; $Re = h_d \Omega/v$; $Sc = v/D$.

Fig. 8. Schematic diagram of the multimembrane three-channel cassette along with a stainless steel frame.

The divergence in correlation between experimental and calculated results can be explained in the light of the sensitivity of the mass transfer coefficient for the prevailing hydraulic conditions when turbulence-promoter spacers were used. It is clear from Table 4 and Fig. 9 that the liquid-film resistance controls oxygen transfer in such a system. As the liquid flow rate increases, the liquid-boundary resistance decreases slightly. The experimental data show that the individual selectivities of the non-porous gas-separation polymeric membranes are not important in such *a* membrane contacting system. For example, selectivity (α) of the PVTMS asymmetric membrane for oxygen and nitrogen (α O_2/N_2) is at least 3.5 and selectivity of a PDMS/PPSQ composite membrane for oxygen and nitrogen is at least 2.1. Membrane selectivity may be important at very high liquid flow rates. In order to obtain such a high liquid flow rate inside a module, it is necessary to apply a rather high pressure at the inlet of the liquid channels; this is not of practical interest here. Where there is a fast chemical reaction between gas and liquid, the selectivity of the separation process is determined by selective absorption. Once again selectivity's of the membranes are not important. Hence, the membranes for such a system should be selected on the basis of their mechanical properties. It is possible, therefore, to predict that the "fast" silicon rubber-based asymmetric gas-separation membranes are the best choice, at this stage, for such a system.

Table 4 Dependence of the oxygen overall mass transfer coefficient and the liquid film resistance on the liquid flow rate in the deoxygenator, operating in the once-through mode

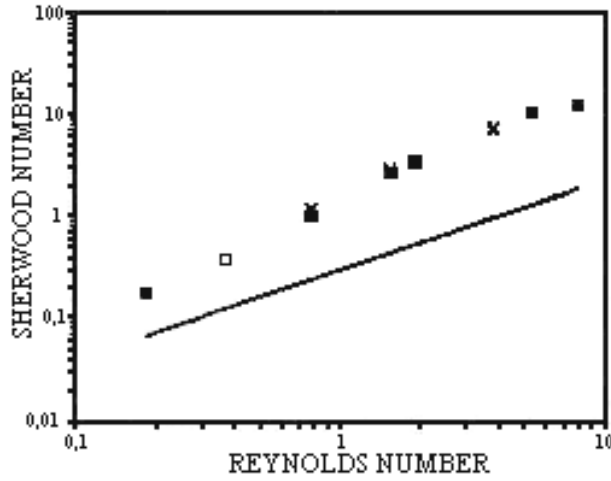| Superficial water velocity (cm/s)	Overall mass transfer coefficient K_{ov} 10^4 (cm/s)		Resistance liquid/total (%)	
	PVTMS membrane	PDMS/PPSQ membrane	PVTMS membrane	PDMS / PPSQ membrane
0.06	1.3	1.3	99.7	99.9
0.12	2.8	2.8	99.3	99.8
0.25	7.8	8.9	98.2	99.5
0.5	19.9	21.1	95.3	99.0
0.62	26.1	26.1	93.9	98.8
1.23	51.8	55.4	87.8	97.5
1.73	72.9	77.9	82.9	96.5
2.57	87.5	87.5	79.4	96.1

Fig. 9. Mass transfer correlation for the deoxygenation of water in a flowing mode. Closed symbols, PVTMS membrane resistance taken into account. Open symbols, ignoring PVTMS membrane resistance contribution. Cross symbols, PDMS/PPSQ composite membrane resistance taken into account.

3.2. Hydrogen permeation

The results of the hydrogen permeation experiments in the three-channel module are presented in the Table 5, which shows that the flux of the hydrogen permeating through the SMV increased in the low range of the liquid flow rate and decreased slightly in its higher range.

The permeability coefficient (P) for hydrogen in PVTMS is $2.0 \cdot 10^{-8}$ (cm^3 cm/cm^2 s cmHg) under 1 atm pressure difference [40]. The permeability coefficient (P) for hydrogen in water under the same conditions can be calculated using the following equation:

$$P = SD \qquad\qquad (7)$$

where S is the solubility coefficient and D is the diffusion coefficient of hydrogen in water. The diffusion coefficient of hydrogen in water is $5.0 \cdot 10^{-5}$ cm^2/s [41]. The solubility coefficient (S) of hydrogen in water at a pressure of 1 atm at 20°C is $2.3 \cdot 10^{-4}$ (cm^3(STP) /cm^3 cmHg). The calculated permeability of hydrogen in water by means of Eq. (7) is $1.2 \cdot 10^{-8}$ (cm^3(STP)cm/cm^2 s cmHg). The permeance (P/l) of hydrogen, that is, the ratio of permeability to thickness, through the liquid layer in our experiments was $1.2 \cdot 10^{-8}/0.045 = 2.7 \cdot 10^{-7}$ (cm^3(STP)/cm^2 s cmHg). Since the thickness of the diffusion layer in the PVTMS membranes was $2.3 \cdot 10^{-4}$ cm [17], the permeance (P/l) of hydrogen in such a membrane was $8.7 \cdot 10^{-5}$ The total resistance of the system to gas permeation ($1/\Omega_{Total}$) was estimated by [37]:

$$\frac{1}{Q_{Total}} = \frac{2}{Q_{Membrane}} + \frac{1}{Q_{Liquid}} \qquad\qquad (8)$$

where $1/Q_{Liquid}$ is the resistance of the liquid layer to gas permeation and $2/ Q_{Membrane}$ is the resistance of the membranes to gas permeation. It is seen from Eq. (8), the calculated value for the hydrogen permeance and experimental data in Table 5, that the mass transfer through the SMV is controlled by the diffusion in the liquid layer. The experimental data for the low range of the liquid flow rates demonstrated that the hydrogen permeance was larger than for stagnant liquid, but less than for the two polymeric membranes. The increase in the permeance at the lower range of the water flow rates can be explained by the increase in the so-called eddy mass diffusivity (E_D) in such a system. It can be assumed that the presence of the turbulence promoters in the liquid channels increased eddy diffusivity of hydrogen with an increase in liquid flow rates. It can be assumed that the mass transfer in the SMV is characterized by two factors acting in opposite directions: an increase in mass transfer with an increase in liquid flow rate due to increasing eddy mass diffusivity; and a decrease in mass transfer with an increase in liquid flow rate due to a convectional drift that takes place in the SMV operating in the flowing mode [23].

Table 5 Experimental results for hydrogen permeation through the SMV comprising PVTMS membranes and operating in the flowing mode

Water flow rate (ml/s)	Hydrogen permeance through SMV [cm^3(STP)/cm^2scmHg]
0.1	$1.1 \cdot 10^{-6}$

0.5	$1.4 \cdot 10^{-6}$
0.6	$1.4 \cdot 10^{-6}$
5.0	$0.8 \cdot 10^{-6 \circ}$

In our experiments we were restricted by the mechanical stability of the membrane three-channel cassette; with an increase in the liquid flow rate the pressure of water was also increased. When the water pressure, measured by manometers at the inlet of the three-channel system, was larger than 2.5 atm, the cassette leaked. This could be explained by the fact that the total number of the channels for liquid in the new type of the «three-channel» cassette decreased in comparison with that number of in the ' 'two-channel" cassette [18].

The two-channel liquid-membrane contactor, which was described above, can be used not only for degassing liquids but also for a reverse process, for example, oxygenation of water. Where liquid circulates between two contactors, gas separation of a binary mixture is possible. In that case, one of the gas components should react reversibly with the liquid phase. This was described earlier for the separation of ethylene/ethane mixture [18].

4. Conclusions

The aim of this article was to demonstrate the use of non-porous polymeric flat-sheet gas-separation membranes in membrane-liquid contactors; the possible modification of the two-channel liquid-membrane contactor was shown. Evaluation of a novel large-scale configuration for an SMV (selective membrane valve) comprising non-porous gas separation membranes and flowing liquid membranes for the control of hydrogen diffusing through the SMV and water-deoxygenating experiments by means of conventional two-channel membrane system led to the following conclusions:

• the flux could be controlled by adjusting the liquid-membrane flow rate;
• the overall mass transfer coefficients were functions of the water flow rate; and
• the liquid-film resistance controlled mass transfer in both the experiments.
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5. List of symbols

A_{SP} wetted area of the spacer (cm^2)
$A_{V,SP}$ specific area of the spacer (cm"^{1})
D diffusion coefficient (cm^2/s)
E_D eddy mass diffusivity (cm^2/s)
K mass transfer coefficient (cm/s)
L membrane length (cm)
H Henry's constant (cm^3(STP) cmHg/cm^3)
P permeability (cm^3(STP)cm/cm^2_s cmHg)
$Q = P/l$ permeance (cm^3(STP)/cm^{2}scmHg)
S solubility coefficient (cm^3(STP) /cm^3 cmHg)
V volume (cm^3)
Ω liquid velocity (cm/s)
a membrane area per volume of the membrane bed (cm""^{1})
h channel height (cm)
h_d hydraulic diameter (cm)
I thickness of the diffusional membrane layer (cm)
α selectivity (-)
ε porosity (-)
v kinematic viscosity (cm^2/s)
Sh Sherwood number, $Sh = Kh_dD$(-)
Re Reynolds number, $Re = h_d\Omega/v$ (-)
Sc Schmidt number, $Sc=v/D$ (-)
Subscripts
OV   overall

Tot   total
SP   spacer
L   liquid

Acknowledgements

References

[1] M. Teramoto, H. Matsuyama, T. Yamashiro and Y. Katayama, Separation of ethylene from ethane by supported liquid membranes contained silver nitrate as a carrier, J. Chem. Eng. Jpn., 19(5) (1986)419.

[2] R.D. Hughes, J.A. Mahoney and E.F. Steigelmann, Olefin Separation by Facilitated Transport Membranes, in N.N. Li and J.M. Calo (Eds.), Recent Developments in Separation Science, Vol. 9, CRC Press, Cleveland, 1986, p. 173.

[3] R.W. Baker, I.C. Roman and H.K. Lonsdale, Liquid membranes for the production of oxygen-enriched air I. Introduction and passive liquid membranes, J. Membrane Sci., 31 (1987) 15.

[4] B.M. Johnson, R.W. Baker, S.L. Matson, K.L. Smith, I.C. Roman, M.E. Tuttle and H.K. Lonsdale, Liquid membranes for the production of oxygen-enriched air II. Facilitated-transport membranes, J. Membrane Sci., 31 (1987) 31.

[5] H. Kreulen, C.A. Smolders, G.F. Versteeg and W.P.M. van Swaaij, Selective removal of H_2S from sour gas with microporous membranes. Part II. A liquid membrane of water-free tertiary amines, J. Membrane Sci., 82 (1993) 82.

[6] Z. Qi and E.L. Cussler, Microporous hollow fibers for gas absorption. I. Mass transfer in the liquid, J. Membrane Sci., 23 (1985) 321.

[7] Z. Qi and E.L. Cussler, Microporous hollow fibers for gas absorption. II. Mass transfer across the membrane, J. Membrane Sci., 23 (1985) 333.

[8] M.-C. Yang and E.L. Cussler, Designing hollow-fiber contactors, AIChEJ., 32(11) (1986) 1910.

[9] M.J. Semmens, D.M. Foster and E.L. Cussler, Ammonia removal from water using microporous hollow fibers, J. Membrane Sci., 51 (1990) 127.

[10] H. Kreulen, G.F. Versteeg, C.A. Smolders and W.P.M. van Swaaij, Selective removal of H_2S from sour gas with microporous membranes. Part 1. Application in a gas-liquid system, J. Membrane Sci., 73 (1992) 293.

[11] H. Kreulen, C.A. Smolders, G.F. Versteeg and W.P.M. van Swaaij, Microporous hollow fiber membrane modules as gas-liquid contactors. Part 2. Mass transfer with chemical reaction, J. Membrane Sci., 78 (1993) 217.

[12] S. Karoor and K.K. Sirkar, Gas Absorption Studies in microporous hollow fiber membrane modules, Ind. Eng. Chem. Res., 32 (1993) 674.

[13] A.B. Shelekhin and I.N. Beckman, Gas separation processes in membrane absorber, J. Membrane Sci., 73 (1992) 73.

[14] D.G. Bessarabov and I.N. Beckman, Model of mass transfer in the integrated liquid-membrane system for gas separation, Vestnik Moskovskogo Universiteta, Ser. 2, Khimia, 34(6) (1993) 604 (in Russian).

[15] D.G. Bessarabov, D.A. Sirtsova, V.V. Teplyakov and I.N. Beckman, Separation of ethylene/methane mixture by membrane/absorption system with flowing liquid selective absorbent, Vestnik Moskovskogo Universiteta, Seria 2, Khimia, 35(4) (1994) 385 (in Russian).

[16 D.G. Bessarabov, R.D. Sanderson, E.P. Jacobs and I.N. Beckman, Mass transfer in absorption/membrane integrated hybrid systems for gas separation, Second Int. Symp., PMST'94, Dinkeldruk, Oldenzaal, The Netherlands, 1994, Abstr., pp. 59-60.

[17] D.G. Bessarabov, R.D. Sanderson, E.P. Jacobs, C.N. Windt and V.S. Gladkov, Asymmetric non-porous flat sheet membranes from polyvinyltrimethylsilane for water oxygenation and deoxygenating, SA J. Chem. Eng., 6(2) (1994)26.

[18] D.G. Bessarabov, R.D. Sanderson, E.P. Jacobs and I.N. Beckman, High-efficiency separation of ethylene/ethane mixture by a large-scale liquid-membrane contactor containing flat-sheet non-porous polymeric gas-separation membranes and a selective flowing-liquid absorbent, Ind. Eng. Chem. Res., 34 (1995) 1769.

[19] D.G. Bessarabov, R.D. Sanderson and E.P. Jacobs, Membrane separation and affinity interaction. A new hybrid gas separation process, Proc. 7th Natl. Meet. South African Inst. Chem. Eng., 22-24 August, Esselen Park, South Africa,

1994, pp. 582-592.

[20] M. Teramoto, H. Matsuyama, T. Yamashiro and S. Okamoto, Separation of ethylene from ethane by a flowing liquid membrane using silver nitrate as a carrier, J. Membrane Sci., 45 (1989) 115.

[21] I.N. Beckman, D.G. Bessarabov and U.R. Dzelme, V.V. Teplyakov, The device for membrane gas separation, Russian Pat. no. 5024663/26, BOID 61/38, 1992 (in Russian).

[22] I.N. Beckman, D.G. Bessarabov, V.V. Teplyakov and A.V. Teplyakov, Integrated membrane systems with moving liquid carriers for multicomponent gas separation, 3rd Int. Conf. Effective Membrane Processes, Mechanical Engineering, London, 1993, pp. 297-306.

[23] I.N. Beckman.D.G. Bessarabov and V.V. Teplyakov, Selective membrane valve for ternary gas mixture separation: model of mass transfer and experimental test, Ind. Eng. Chem. Res., 32 (1993)2017.

[24] D.G. Bessarabov and I.N. Beckman, Phenomenological theory of selective gas permeation in the membrane valve, Vestnik Moskovskogo Universiteta, Seria 2, Khimia, 34(2) (1993) 194 (in Russian).

[25] I.N. Beckman, Unusual membrane processes: non-steady-state regimes, nonhomogeneous and moving membranes, in D.R. Paul and Y.P. Yampolskii (Eds.), Polymeric Gas Separation Membranes, CRC Press, 1994, pp. 301-352.

[26] S. Majumdar, A.K. Guha and K.K. Sirkar, A new liquid membrane technique for gas separation, AIChE J., 34(7) (1988) 1135.

[27] S. Majumdar, A. Sengupta and, K.K. Sirkar, Simultaneous SO_2/NO separation from flue gas in a contained liquid membrane permeator, Ind. Eng. Chem. Res., 33 (1994) 667.

[28] A.K. Guha, S. Majumdar and K.K. Sirkar, Gas separation modes in a hollow fiber contained liquid membrane permeator, Ind. Eng. Chem. Res., 31 (1992) 593. [29] T. Papadopoulos and K.K. Sirkar, A modified hollow fiber contained liquid membrane technique for gas separation at high pressures, J. Membrane Sci., 94 (1994) 163.

[30] S.G. Kimura and G.F. Walmet, Fuel gas purification with permselectivemembranes, Sep. Sci.Technol., 15 (1980) 1115.

[31] A.E. Jansen, R. Klaassen, P.H.M. Feron, J.H. Hanemaaijer and B. Meulen, Membrane gas absorption processes in environmental applications, in Membrane Processes in Separation and Purification, NATO ASI Series, Series E, Vol. 272, Kluwer, Dordrecht, 1994, pp. 343-356.

[32] E.L. Cussler, Hollow fiber contactors, in Membrane Processes in Separation and Purification, NATO ASI Series, Series E, Vol. 272, Kluwer, Dordrecht, 1994, pp. 375-394.

[33] T. Ahmed and M.J. Semmens, Use of sealed end hollow fibers for bubbleless membrane aeration: experimental studies, J. Membrane Sci., 69 (1992) 1. [34] M.S.L. Tai, I. Chua, K. Li, W.J. Ng and W.K. Teo, Removal of dissolved oxygen in ultrapure water production using microporous membrane modules, J. Membrane Sci., 87 (1994) 99.

[35] T. Leiknes, M.J. Semmens and C Gantzer, The Performance of a Membrane Vacuum Degasser, 3rd Int. Conf. Effective Membrane Processes, Mechanical Engineering, London, 1993, pp. 341-351.

[36] P. Cote, J.-L. Bersilon and A. Huyard, Bubble-free aeration using membranes: mass transfer analysis., J. Membrane Sci., 47(1989)91.

[37] H. Yasuda, C.E. Lamaze, Transfer of gas to dissolved oxygen in water via porous and nonporous polymer membranes, J. Appl. Polym. Sci., 16 (1972) 595.

[38] S.R. Wickramasinghe, M.J. Semmens and E.L. Cussler, Hollow fiber modules made with hollow fiber fabric, J. Membrane Sci., 84 (1993) 1.

[39] G. Schock and A. Miquel, Mass transfer and pressure loss in spiral wound modules, Desalination, 64 (1987) 339.

[40] V. Teplyakov and P. Meares, Correlation aspects of the selective gas permeabilities of polymeric materials and membranes, Gas. Sep. Purif., 4 (1990) 66.

[41] D.L. Wise and G. Houghton, The diffusion coefficients often slightly soluble gases in water at 10-60°C, Chem. Eng. Sci., 21 (1966)999.

[42] M. Mulder, Basic Principles of Membrane Technology, Kluwer, Dordrecht, 1991, p. 32.