SEPARATIONS

Selective Membrane Valve for Ternary Gas Mixture Separation: Model of Mass Transfer and Experimental Test

I. N. Beckman

Chemistry Department, Moscow State University, 119899, Moscow, Russia

D. G. Bessarabov and V. V Teplyakov*

A. V. Topchiev Institute of Petrochemical Synthesis, Leninsky Prospect 29,117912, GSP-1, Moscow, Russia

The prospects for the gas separation membrane system with mobile liquid extractants flowing between two membranes (membrane valve) are discussed in this paper. The use of mobile membranes allows separation of multicomponent gas mixtures which are difficult to separate by conventional methods and leads to selectivity factors with the separate extraction of each component. The proposed technique for separation of gases was tested by separation of $CO_2/CH_4/H_2$ gas mixtures on a membrane valve with membranes from poly(vinyltrimethylsilane) (PVTMS) and flowing liquid membranes containing H_2O and monoethanolamine solutions as carrier of CO_2· The initial $CO_2/CH_4/H_2$ gas mixture consisted of 40% CO_2, 30% CH_4, and 30% H_2, respectively. The concentrations of each of the separated gases obtained were more than 90 % on the outlets of the membrane valve. The phenomenological theory of selective gas permeation in a membrane valve in four possible modes is considered. Computer simulation of the separation process in a membrane valve was carried out.
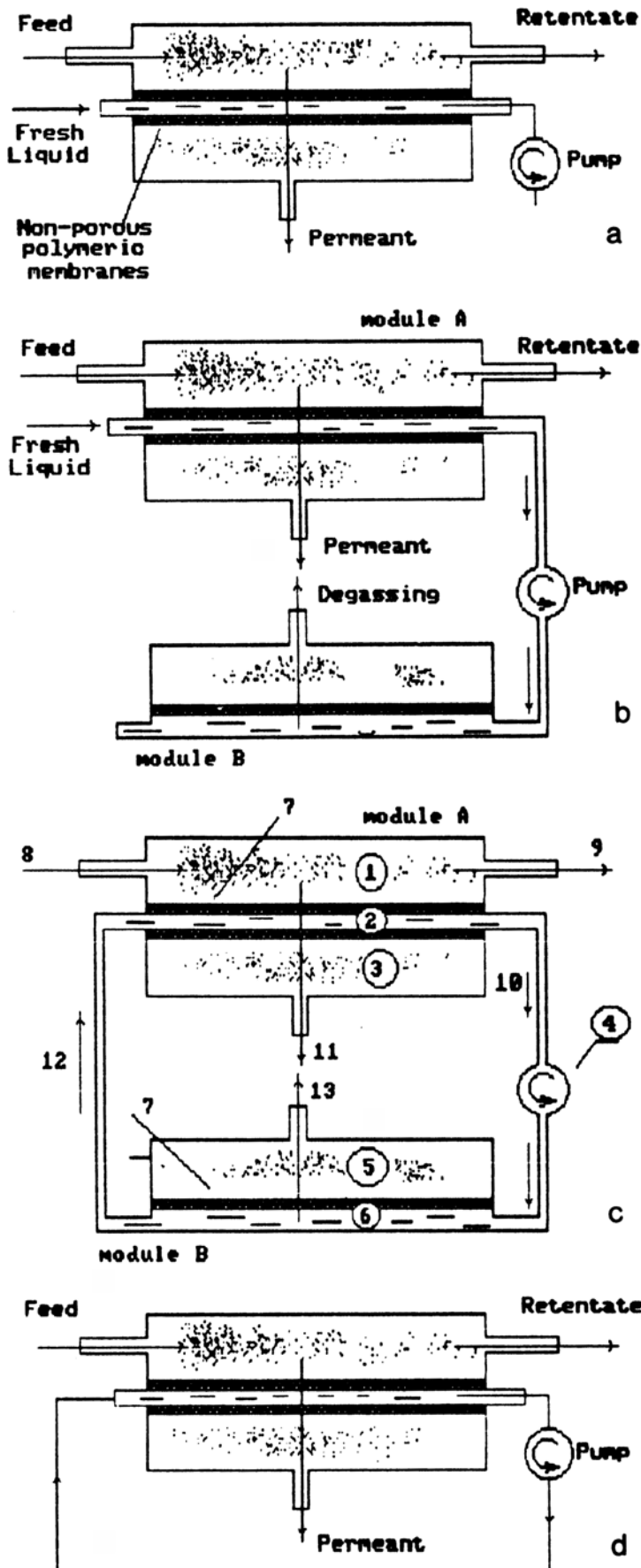
Introduction

An area of membrane technology of continuing interest is the improvement of productivity, selectivity, and flexibility of membrane gas separation systems.

One of the ways for increasing the selectivity of passive gas separation can be the application of unsteady-state boundary conditions at the membrane inlet. Such behavior has been predicted upon passage of a concentration pulse through the membrane (Paul, 1971; Higuchi and Nakagawa, 1989; Beckman, 1991).

Other approaches include immobilized liquid membranes using carriers which can selectively and reversibly bind certain permeant species (Scholander, 1960; Schultz, 1974; Roman, 1985).

Recently, moving solid membranes (Klass and Landahl, 1974) and flowing liquid membranes (Teramoto, 1989), in which a liquid membrane solution flows along a microporous (Ward, 1979) or nonporous membrane (Shelekhin and Beckman, 1989,1990), have been proposed. In this case (Ward, 1979) hydrogen sulfide is removed from a mixture of gases including carbon dioxide by passing the mixture over an immobilized liquid membrane in intimate contact with a hydrophobic, microporous gas permeable barrier and absorbing in a liquid solution hydrogen sulfide passing through the membrane. The use of mobile membranes allows separation of ternary gas mixtures which are difficult to separate by conventional methods.

A ternary mixture separation can be carried out in a two-membrane permeator using inversely selective membranes (Sengupta and Sirkar, 1984). Results of this study have been presented for $H_2/CO_2/N_2$ gas mixtures with a permeator having one cellulose acetate type membrane and one silicone membrane. The ternary separation can be carried out using a single-module two-membrane permeator, or using two

Figure 1. Schematic diagrams of the different versions of the selective membrane valve: (a) flowing mode; (b) flowing mode with desorber; (c) circulation mode; (d) circulation mode without desorber. 1 and 3, gas chambers; 2, sandwich of two membranes and thin liquid layer; 4, pump; 5, desorber gas chamber; 6, liquid layer; 7, polymeric nonporous membranes; 8, feed gases ($CO_2/CH_4/H_2$); 9, retentate (CH_4); 10, dissolved gas (CO_2); 11, permeant (H_2); 12, liquid; 13, degassing (CO_2).

single-membrane permeators in series (Sengupta and Sirkar, 1987,1988). In this case the efficiency of gas separation is restricted by the selectivity of the nonporous membranes being used. The development of permeators combining the membrane and absorption phenomena can enhance the gas separation selectivity.

The integrated membrane system involving a liquid flowing between two nonporous membranes (the selective membrane valve, SMV) is considered in this paper. The liquid may be nonspecific in relation to the components of the gas separation mixture; also, the solubility of the gas components in a liquid can considerably differ; and finally, a liquid can react with one or several gas components. The productivity and selectivity of SMV will depend on gas-transport parameters in polymeric membranes, on gas-transport parameters in a liquid, and on the physical parameters of the process.

Three-component gas mixtures can be separated by a membrane device of this type: the first component (retentate) is insoluble in a liquid; the second one (permeant) diffuses through the membrane sandwich; the third component, which is well dissolved in a liquid layer, is pumped to a degassing in a desorption module. Thus, the SMV has one inlet for the feed gas and three outlets for the products and provides a higher selectivity of separation and flexibility of the gas separation.

Selective Membrane Valve

The selective membrane valve (Figure la) can consist of a permeation module (A) and a desorption module (B). Module (A) contains a sandwich (2) of two nonporous polymeric membranes (they can be from various polymers) between which a thin liquid layer moves. Module (A) is divided by this membrane sandwich into two chambers for gases (1, 3). Desorption module (B) contains a polymeric membrane which is intended for degassing of a liquid.

The possible modes of SMV operation are a flowing mode without a desorber (Figure la), a flowing mode with a desorber (Figure lb), a circulation mode without a desorber (Figure lc), and a circulation mode with a desorber (Figure Id).
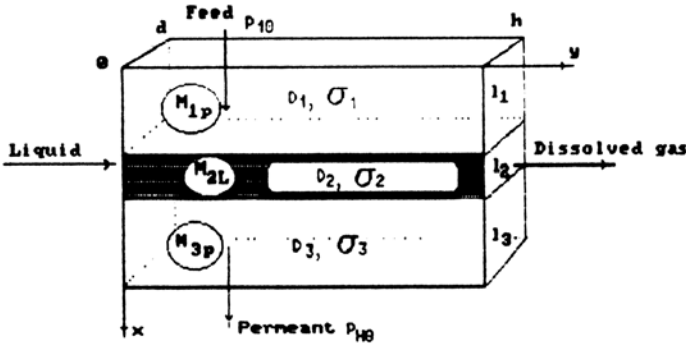

Figure 2. Schematic diagram of the three-layered medium. Mi and M2 are the polymeric membranes; L is the liquid layer.

Mathematical Model

In terms of the phenomenological theory we consider the gas permeability of a three-layered medium (Figure 2) consisting of a polymeric membrane (M_1), a thin layer of a liquid (L) flowing at a linear velocity v(cm/s), and polymeric membrane (M_2).

Here we are going to deal with a cocurrent-type module, in which the ideal mixing mode is maintained in gas phases over the membranes: in a liquid layer the mixing occurs in the transverse direction *(x)* whereas mixing in the *y* direction does not take place.

The three-layered membrane sandwich has a rectangular shape where d is the width (cm), h is the membrane length (cm), and $S = dh$ is the membrane surface area. Let D_1, σ_1, l_1, D_2, σ_2, l_2 and D_3, σ_3, l_3 be diffusion coefficients, solubility coefficients of gases, and layer thicknesses for the inlet membrane, the liquid layer, and the outlet membrane, respectively. The partial pressure of the feed gas is p_{10}, and that of the permeant is p_{H0}. The concentration of dissolved gas in the liquid supplied to the SMV inlet is C(0). The gas concentrations in the input membrane, in the liquid, and in the output membrane of SMV (module A) are C_1, C_2, and C_3, respectively. P is the permeability.

When the gas diffusion through the sandwich is in steady-state conditions for local fluxes, it is valid that

$$|i_2| = |i_1| + |i_3|$$

We suppose that $|i_1| > |i_3|$. Taking into account Fick's first law, we have

$$vl\frac{dC_2}{dy} = -D_1\frac{dC_1}{dx}\bigg|_{x=l_1} + D_3\frac{dC_3}{dx}\bigg|_{x=l_1+l_2} \tag{1}$$

We also stipulate that $D_2 \gg D_1$ and $D_2 \gg D_3$. In the steady-state the gas concentration profile along coordinate x in the polymeric membrane is known to be linear. Therefore, the derivatives in eq 2 may be replaced by concentration differences. Thus, the gas concentration in the liquid, $C_2(y)$, when $t\to\infty$ can be defined as

$$vl\frac{dC_2}{dy} = \frac{D_1\left(C_{10} - (\sigma_1/\sigma_2)C_2\right)}{l_1} + \frac{D_3\left(C_{30} - (\sigma_3/\sigma_2)C_2\right)}{l_3} \tag{3}$$

A solution of eq 3 under the boundary conditions $C_2(y=0) = C(0)$; $C_1(x=0) = C_{10} = \sigma_1 p_{10}$; $C_3(X=H) = C_{30} = \sigma_3 p_{H0}$ (where $H = l_1 + l_2 + l_3$ is the total sandwich thickness) is as follows:

$$C_2 = (1/A_2) [A_1 + (A_2 C(0) - A_1 \exp(-A_2 y/A)]\qquad (4)$$

where

$$A = \sigma_1 \sigma_2 v l_1 l_2 l_3 \qquad A_1 = \sigma_2 (P_1 l_3 C_{10} + P_3\, l_1 C_{30});$$
$$A_2 = \sigma_1(P_1 l_3 + P_3 l_1);\ P = D\sigma$$

The local gas flux through the sandwich, taking into account the concentration profile linearity along coordinate *x,* is

$$i_3(y)\big|_{x=H} = D_3 \left(C_3\big|_{x=l_1+l_2} - C_{30}\big|_{x=H}\right)/l_3 \qquad (5)$$

Since $C_3\big|_{x=l_1+l_2} = (\sigma_3/\sigma_2)C_2$, the local flux is

$$i_3(H,y) = \frac{D_3 \sigma_3}{A_2 \sigma_2 l_3}\left[A_1 + (A_2 C(0) - A_1)\exp\left(-\frac{A_2 y}{A}\right)\right] - \frac{D_3 C_{30}}{l_3} \qquad (6)$$

The complete permeant transfer rate through the sandwich is

$$J_3 = d\int_0^h i(y)dy$$

hence

$$J_3 = \frac{P_3 d}{\sigma_2 l_3 A_2}\left\{A_1 h + \left(\frac{A_2 C(0) - A_1}{A_2}\right)A\left[1 - \exp\left(-\frac{A_2 h}{A}\right)\right]\right\} - \frac{SD_3 C_{30}}{l_3} \qquad (7)$$

The complete feed gas transfer rate into the sandwich is

$$J_1 = \frac{SD_1 C_{10}}{l_1} - \frac{P_1 d}{l_1 \sigma_2 A_2}\left\{A_1 h + \left(\frac{A_2 C(0) - A_1}{A_2}\right)A\left[1 - \exp\left(-\frac{A_2 h}{A}\right)\right]\right\} \qquad \textbf{(8)}$$

Then the gas transfer rate carried away from module (A) by the flowing liquid is

$$J = J_1 - J_3 = \frac{Svl_2}{h}\left[\frac{A_1}{A_2} - C(0)\right]\left[1 - \exp\left(-\frac{A_2 h}{A}\right)\right]$$

In order to simplify the mathematical analysis of the SMV operation, we consider the case of two similar membranes and a two-component (G_1 and G_2) gas mixture.

1. **The SMV Flowing Mode without a Desorber (Figure la).** In this case a fresh ($C^A(0) = 0$) liquid is supplied to the SMV inlet and the liquid upon leaving the permeator is not used. Under conventional boundary conditions of the permeability method for the gas A, $p_{10}{}^A = p_0{}^A$, $p_{H0}{}^A = 0$, i.e., $C_{10}{}^A = C_0{}^A$, $C_0{}^A = 0$, we have for one gas transfer rate ($P_1{}^A = P_3{}^A = P$, $l_1 = l_3 = l$, $\sigma_1{}^A = \sigma_3{}^A = \sigma$, $\sigma_2{}^A \neq \sigma$)

$$J_3 = A_0\left[1 - \frac{1}{B_1}(1 - \exp(-B_1))\right] \qquad (9)$$

where

$$A_0 = \frac{SPp_0}{2l} = \frac{B_0 p_0}{2};\ B_1 = \frac{2SP}{\sigma^* l\sigma_2} = \frac{2B_0}{\sigma^*\sigma_2};\ B_0 = \frac{SP}{l}$$

$v^* = vl_2 d$ is the liquid volume velocity (cm^3/s). At $v\to\infty$, $J_3 \to 0$; at $v \to 0$, $J_3 \to A_0$.

Thus the gas flux through SMV can be varied from the value $J_3 = (Sp_0/2l)$ to zero; i.e., the membrane valve can be completely closed.

In the flowing mode of the SMV operation a complete steady-state ideal selectivity α for gases A and 6 is

$$\alpha = \frac{P^A}{P^B}\frac{1 - 1/B_1^A\left[1 - \exp(-B_1^A)\right]}{1 - 1/B_1^B\left[1 - \exp(-B_1^A)\right]} \qquad (10)$$

$$\lim_{v\to 0}\alpha = \frac{P^A}{P^B} \text{ and } \lim_{v\to\infty}\alpha = \frac{\sigma_2^B}{\sigma_2^A}\frac{3-B_1^A}{3-B_1^B} \cong \frac{\sigma_2^B}{\sigma_2^A}$$

With increased rate of liquid pumping, the selectivity will be changed from $\alpha = P^A/P^B$ to the value σ_2^B/σ_2^A. Thus, if the value of v is small, the selectivity factor is solely determined by the gas permeation properties of the applied polymeric membranes, whereas, at high v values α is determined by the ratio of gas solubility coefficients in the liquid. By varying the liquid flux, one can change the composition of the gas mixture separated by the SMV. Thus the selectivity and productivity of the SMV can be balanced for particular purposes.

2. The Flowing Mode of the Permeator Operating with a Desorber (Figure lb).

The membrane parameters of desorber are D_{id}, σ_{1d}, and l_{1d}; h_d and d_d are the desorber length and width, l_{2d} is the liquid layer thickness. The outlet gas concentration after membrane is C_{10d}. The gas concentration in the liquid of desorber is as follows:

$$C_{2d} = \frac{A_{1d}}{A_{2d}} + \left[C(0) - \frac{A_{1d}}{A_{2d}}\right]\exp\left(-\frac{A_2 h_d}{A}\right) \tag{11}$$

where

$$C(0)_d = \frac{A_1}{A_2} + \left[C(0) - \frac{A_1}{A_2}\right]\exp\left(-\frac{A_2 h}{A}\right)$$

If the modules (A) and (B) consist of the same membranes and one flowing liquid, the gas transfer rate from the desorber is

$$J_{des} = \frac{v^* C_0 \sigma_2}{2\sigma}\left[1 - \exp\left(-\frac{2PS}{v^*\sigma_2 l}\right)\right]^2 \tag{12}$$

$$\lim_{v\to 0} J_{des} = 0 ; \ \lim_{v\to\infty} J_{des} = 0$$

The selectivity factor is

$$\alpha_{des} = J^A_{des}/ J^B_{des} \tag{13}$$

If $\sigma_2^A = \sigma_2^B$ (absorption liquid being nonspecific), the consequences of $\lim_{v\to 0}\alpha_{des} = \sigma^B/\sigma^A$ and $\lim_{v\to\infty}\alpha_{des} = D^A/D^B$ mean that, in both the flowing desorber and in the permeator, the gas separation will take place, even in the case when the membrane is not selective ($P^A = P^B$, but $D^A \neq D^B$) and whose efficiency depends on the absorbent motion speed v^*.

3. The Circulation Mode of the Permeator Operating with a Desorber (Figure lc).

In the circulation SMV a liquid from module (B) is returned to module (A) by a pump operating in a circle. The liquid passed through module (B) is degassed to some extent. In this version the SMV allows separation of a mixture of three gases.

A system of equations for steady-state gas diffusion in modules (Figure lc) in the circulation mode is as follows:

$$vl_2\frac{dC_2}{dy} = \frac{D_1\left(C_{10} - \frac{\sigma_1}{\sigma_2}C_2\right)}{l_1} + \frac{D_3\left(C_{30} - \frac{\sigma_3}{\sigma_2}C_2\right)}{l_3} \tag{14}$$

$$vl_{2d}\frac{dC_{2d}}{dy} = \frac{D_{1d}\left(C_{10d} - \frac{\sigma_{1d}}{\sigma_{2d}}C_{2d}\right)}{l_{1d}} + \frac{D_{3d}\left(C_{30d} - \frac{\sigma_{3d}}{\sigma_{2d}}C_{2d}\right)}{l_{3d}} \tag{15}$$

The desorber parameters are the same as above. The permeator length is h, and the desorber length is h_d. For the circulation mode with one-membrane desorber the system (eqs 14 and 15) is simplified to

$$\frac{dC_2}{dy} = \frac{D}{vll_2}\left(C_0 - \frac{2\sigma}{\sigma_2}C_2\right), \qquad \frac{dC_{2d}}{dy} = \frac{D\sigma}{vll_2\sigma_2}C_{2d} \tag{16}$$

The solution of these equations is as follows:

$$C_2 = K_1 \exp(-2\Omega y) + C_0\sigma_2/2\sigma_1 \qquad 0 \le y \le h$$
$$C_2 = K_2 \exp(-\Omega y) \qquad 0 \le y \le h + h_d \tag{17}$$

where $\Omega = D\sigma/vll_2\sigma_2$. Constants K_1 and K_2 can be obtained from boundary conditions $C_2(0) = C_{2d}(h+h_d)$ and $C_2(h) = C_{2d}(h)$. The distribution of gas concentration in module (A) is the following:

$$C_2 = \frac{C_0\sigma_2}{2\sigma}\left[1 - \frac{(1-\exp(-\Omega h_d)\exp(-2\Omega y))}{1-\exp(-\Omega(2h+h_d))}\right] \tag{18}$$

Gas distribution in module (B) is as follows:

$$C_{2d} = \frac{C_0\sigma_2}{2\sigma}\left[\frac{1-\exp(-\Omega h)}{1-\exp(-\Omega(2h+h_d))}\right]\exp(-\Omega(y-h)) \tag{19}$$

The gas transfer rate from the permeator (module A) will be

$$J_3 = \frac{dDC_0\sigma_2}{2\sigma l}\left[h - \frac{(1-\exp(-\Omega h_d))(1-\exp(-2\Omega h))}{2\Omega(1-\exp(-\Omega(2h+h_d)))}\right] \tag{20}$$

The gas transfer rate from the desorber (module B) will be

$$J_{des} = \frac{dDC_0\sigma_2}{2\sigma l\Omega}\frac{[1-\exp(-2\Omega h)][\exp(-\Omega h)-\exp(-2\Omega(h+h_d))]}{[1-\exp(-\Omega(2h+h_d))]} \tag{21}$$

Here we are going to deal with the simplest case when $h = h_d$ and $\sigma^A_2 = \sigma^B_2$; then

$$J_3 = A_0\left[1 - \frac{1}{B}\frac{(1-\exp(-B_1))(1-\exp(-0.5B_1))}{1-\exp(-1.5B_1)}\right] \tag{22}$$

where $B_1 = \Omega h$.

The consequences of $\lim_{v\to 0} J_3 = A_0$ and $\lim_{v\to\infty} J_3 = (2/3)A_0$ mean that (see eq. 9), in the circulation mode with a one-membrane desorber, the gas flux through the permeator can never be completely closed in distinction from the flowing mode.

Table I.   Gas Permeability Parameters of PVTMS[a].

$P_{CO2,} = 2\cdot10^{-8}$	$P_{CH4} = 1.8\cdot10^{-9}$	$P_{H2} = 2\cdot10^{-8}$
$\sigma_{CO2,} = 40\cdot10^{-3}$	$\sigma_{CH4} = 10\cdot10^{-3}$	$\sigma_{H2} = 1.1\cdot10^{-3}$
$D_{CO2,} = 5\cdot10^{-7}$	$D_{CH4} = 1.8\cdot10^{-7}$	$D_{H2} = 180\cdot10^{-7}$

[a] σ [cm^3/(cm^3 cmHg)]; D [cm^s/s]; $P = [\sigma D]$ (Teplyakov, 1990)

The selectivity factor α for the permeator in this case for a nonspecific liquid ($\sigma^A_2 = \sigma^B_2$) is as follows:

$$\alpha_{perm} = J^A/J^B$$

The consequences of $\lim_{v\to 0} \alpha = \frac{D^A\sigma^B}{D^B\sigma^A}$ and $\lim_{v\to\infty} \alpha = \frac{D^B\sigma^A}{D^A\sigma^B}$ mean that the selectivity of the circulation

permeator with a desorber is the same at the both hig and low fluxes of liquid.

In this case the gas transfer rate from desorber will b

$$J_{des} = 0.5v^*C_0\left(\frac{\sigma_2}{\sigma}\right)^2 \frac{1-\exp(-B_1)-\exp(-2B_1)+\exp(-3B_1)}{1-\exp(-3B_1)} \quad (24)$$

The consequences of $\lim_{v\to 0} J_{des} = 0$ and $\lim_{v\to\infty} J_{des} = 0$ mean that there are possibilities to control the compositions and fluxes of permeable gas mixture through gas-membrane-liquid systems by optimization of liquid flow rates. The selectivity parameter for the desorber

$$\alpha_{des}=J^A_{des}/J^B \quad (25)$$

The consequences of

$$\lim_{v\to 0} \alpha_{des} = \left(\frac{\sigma^B}{\sigma^A}\right)^2 \text{ and } \lim_{v\to\infty} \alpha_{des} = \frac{D^A\sigma^B}{D^B\sigma^A} = \lim_{\substack{v\to 0 \\ v\to\infty}} \alpha_{perm}$$

mean that the SMV operating in the circulation mode characterized by two factors of selectivity.

4. The Circulation Mode of the Permeator Ope; ating without a Desorber (Figure Id). If the liquid flux is returned to the permeator inlet again, then $C(0)= C(h)$ and $dC_2/dy = 0$, from eq 4. For C_2 we will have

$$C_2 = \frac{\sigma_2(P_1l_3C_{10}+P_3l_1C_{30})}{\sigma_1(P_1l_3+P_3l_1)}$$

i.e., C_2 depends neither on 1; nor on h and the membran valve does not operate. If $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$, $P_1l_3 = P_3l_1$, $C_{10} = C_0$, and $C_{30} = 0$; then $J_3 = C_0DS/2l$ Thus the circulation without a desorber is not of practical interest.

Results of Mathematical Simulation

To illustrate the operation of the membrane valve the flowing and circulation modes (Figure la, c), the dependences of normalized permeant transfer rates (J through the SMV and the selectivity factors (α) on t absorbent liquid pumping (v) have been computed.

For the case of a three-component (A, B, and C) separation under conditions where $P_A = P_B$, $P_C < P_A$, $P_C < P_B$; $\sigma_A < \sigma_C < \sigma_B$, $\sigma_B = 50\sigma_A$; and $D_A = 50D_B$ in a give polymer, we can consider the $CO_2/CH_4/H_2$ mixture. He A, B, and C are H_2, CO_2, and CH_4, respectively. The value correspond to those for poly(vinyltrimethylsilane) (PVTMS) membranes (Teplyakov, 1990) (see Table I).
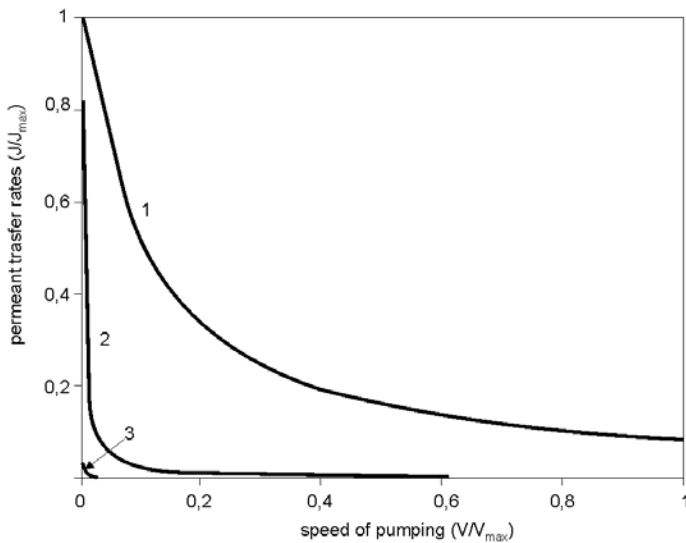

Figure 3. Dependences of permeant transfer rates on speed of pumping in module (A) of SMV in flowing mode. Hydrogen is the most permeable component. 1, H_2 (gas A); 2, CO_2 (gas B); 3, CH_4 (gas C).$J_{max} = 0.03$ cm^3/s, $v_{max} = 900$ cm/s. The thickness of liquid is 0.2 cm. The thickness of membrane is 0.0001 cm.

A typical dependence of the normalized permeate transfer rates (J_3) passing through the membrane valve on the liquid pumping rate is presented in Figure 3. Flux (J_3) of A, B, and C components decrease smoothly will increasing speed of liquid pumping. In this case H_2 (A component) diffuses through the membrane sandwich, CO_2 (B component) passes away by the liquid due to high solubility ($\sigma_B > \sigma_C < \sigma_A$). and CH_4 (C component) is the retentate. Thus by means of varying the liquid pumping it is possible to control permeate fluxes directly during gas separation.
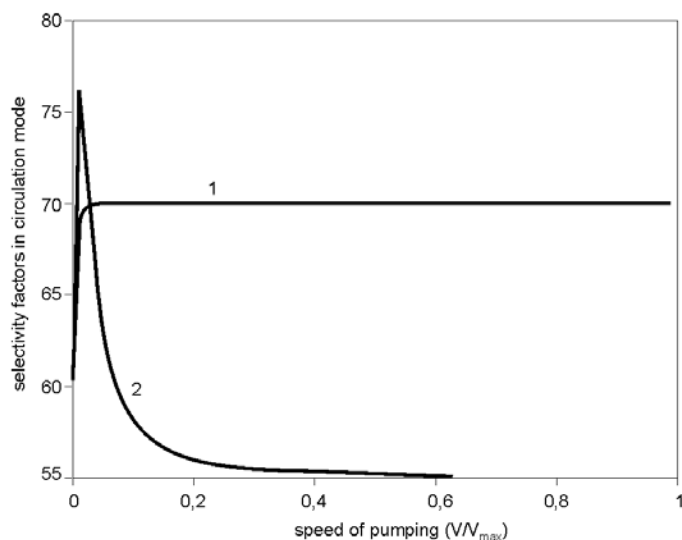

Figure 4. Dependences of selectivity factors on speed of pumping in module (A) of SMV in flowing mode. The high value of selectivity factor (H_2/CH_4) is due to the low permeability of methane in SMV. 1, Selectivity factor H_2/CH_4; 2, selectivity factor CO_2/CH_4; 3, selectivity factor H_2/CO_2. $v_{max} = 900$ cm/s. The thickness of liquid is 0.2 cm. The thickness of membrane is 0.0001 cm.

Figure 4 shows the dependences of selectivity factors for the SMV in the flowing mode upon the liquid pumping. The selectivity factor $\alpha(A/C)$ is considerably increased with pumping and achieves the steady-state level. There is a similar dependence for $\alpha(A/B)$. By contrast, the selectivity factor $\alpha(B/C)$ is decreased in this case ($\sigma_B > \sigma_C$).

Figure 5 presents the dependences of selectivity factors $\alpha(A/C)$ and $\alpha(B/C)$ on the liquid pumping for the circulation mode of SMV with a desorber. In this case there is a maximum of selectivity factors $\alpha(B/C)$. This is due to the fact that in the circulation mode of the SMV operation in the absorption liquid there is invariably some background concentration of dissolved gases which have not been desorbed in the desorption module.
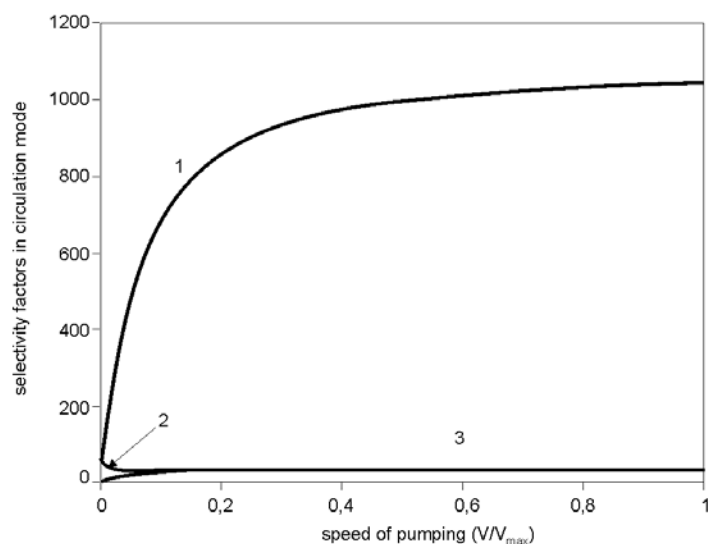

Figure 5. Dependences of selectivity factors on speed of pumping in module (A) of SMV in circulation mode with module (B). 1, Selectivity factor H_2/CH_4; 2, selectivity factor CO_2/CH_4. $v_{max} = 900$ cm/s. The thickness of liquid is 0.2 cm. The thickness of membrane is 0.0001 cm.

The SMV has been experimentally tested by separating the three-component gas mixture $CO_2/CH_4/H_2$ with the use of the membrane valve operating in different modes. Asymmetric membranes produced from PVTMS and aqueous monoethanolamine (MEA) solutions of different concentrations served as working elements.

TableII. Separation of $CO_2/CH_4/H_2$ Gas Mixture SMV

feed	liquid membrane	speed of pumping, cm^3/s	retentate	permeant	desorber gas
40% CO_2, 30% CH_4, 30% H_2	water	0.04	75% CH_4 20% CO_2, 5% H_2	2% CH_4, 7% CO_2, 91% H_2	24% CH_4, 75% CO_2, 1% H_2
40% CO_2, 30% CH_4, 30% H_2	25% water solution	0.04	94%CH4,1%CO2, 5% H_2	l%CH$_4$,0%CO$_2$, 99%H$_2$	

In order to separate $CO_2/CH_4/H_2$ mixture using SMV, we have developed an original construction of it. This construction allows alteration of the effective volume of chambers for liquid. The main element of this construction is the metallic frame with hermetically attached asymmetric membranes from PVTMS. In this study the length of the frames was 29 cm, and the width was 6 cm. The useful work surface of the two membranes in one module was 144 cm^2. A porous insertion is placed inside the frame between polymeric nonporous membranes. This insertion also prevents the fouling of membranes when the pressure of feed changes. There are a number of metallic capillaries in the frame to feed liquid evenly between the membranes. The thickness of liquid is 0.1 cm. The metallic frame with membranes is fixed by special clamps between two gas chambers, with inlet and outlets for feed, permeant, and retentate. The total module volume is 21 cm. The desorber module of the SMV is analogous to the permeation module. The feed gas mixture consisting of 40% CO_2, 30% CH_4, and 30% H_2 is fed to the module with a rate of 0.1 - 0.7 cm^3/s. The three gas outlets are controlled by a gas chromatograph with a thermal conductivity detector. The gas carriers were He and Ar. The values of liquid pumping rates were from 0.0013 to 0.4 cm^3/s under normal conditions. The results of the experimental tests are shown in Table II.

As seen from Table II, the application of SMV can provide the ternary gas mixture separation.

Thus the combination of nonporous gas separation membranes with liquid carriers of a different nature can be prospective for separation of multicomponent mixtures.

Nomenclature

SMV = selective membrane valve
(A)= permeation module of SMV
(B)= desorption module of SMV
A, B, C = components of gas mixture (A = H_2, B = CO_2, C =CH_4)
D = diffusion coefficient
i = local flux
J = complete permeant transfer rate
l_1 and l_3 = thicknesses of the membranes
l_2 = thicknesses of the liquid layer
p_{10} = partial pressure of the feed gas
p_{H0} = partial pressure of the permeant
P - permeability
S = membrane surface area
x = transverse direction to SMV
y = direction along SMV
v = linear velocity of pumping (cm/s)
v^* = volume velocity of pumping (cm^3/s)
α = selectivity factor
σ_1 and σ_3 = solubility coefficients of gases in membranes
σ_2 = solubility coefficients of gases in liquid

Literature Cited

Beckman, I. N. Mass-transfer control in membrane. In *International Symposium on membranes for gas and vapour separation,* NPO "Polymerisintez", Zuzdal; 1989; p 24.

Beckman, I. N.; Shelekhin, A. B.; Teplyakov, V. V. Separation of gas mixtures in unsteady-state conditions. *J. Membr. Sci.* **1991,** 55, 283-297.

Higuchi, Akon; Nakagawa, Tsutomu. Permselectivities through artificial membranes at a non-steady state. *J. Appl. Polym. Sci.* 1989, *37,* 2181-1290.

Klass, D. L.; Landahl, C. D. U.S. Patent 3, 797, 200, 1974.

Paul, D. R. Membrane Separation of Gases Using Steady Cyclic Operation. *Ind. Eng. Chem. Process Des. Dev.* 1971,*10* (3), 376.

Roman, I. C; Baker, R. W. U.S. Patent 4, 642, 010, 1986.

Scholander, P. F. Oxygen transport through hemoglobin solutions. *Science {Washington, D.C.)* 1960, *131, 665.*

Schultz, J. S.; Goddard, J. D.; Suchdeo, S. R. Facilitated transport via carrier-mediated diffusion in membranes. *AIChEJ.* 1974, 20, 417.

Sengupta, A.; Siikar, K. Multicomponent gas separation by an asymmetric penneator containing two different membranes. *J. Membr. Sci.* 1984, *21,* 73-109.

Sengupta, A.; Sirkar, K. K. Ternary gas mixture separation in two-membrane permeators. *AIChE J.* 1987, *33,* 529-539.

Sengupta, A.; Sirkar, K. K. Ternary gas separation using two different membranes. *J. Membr. Sci.* 1988, 39, 61-77.

Shelekhin, A. B.; Beckman, I. N.; Teplyakov, V. V.; Gladkov, V. S. SU Patent 1637850A1 (Russia), 1989.

Shelekhin, A. B.; Beckman, I. N. Ideal model for gas separation processes in membrane absorber. In *Proceeding! of the 1990 International Conference in Membrane Processes,* North American Membrane Society, Chicago; 1990; Vol. 2, pp 1419-1421.

Teplyakov, V. V.; Meares, P. Correlation aspects of the selective gas permeabilities of polymeric materials and membranes. Go» Sep. *Purif.* 1990, *4* (2), 66-75.

Teramoto, Maaaaki; Matsuyama, Hideto; Yamashiro, Takumi; Okamoto, Sueaki. Separation of ethylene from ethane by a flowing liquid membrane using silver nitrate as a carrier. *J. Membr. Sci.* 1989, *45,* 116-136.

Ward, W. J., III. U.S. Patent 4, 147, 754, 1979.