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Aqueous Membranes for the Separation of Gaseous Mixtures

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Abstract

Gas mixture separation characteristics of aqueous surfactant films were studied. Permeation constants of carbon dioxide, oxygen, nitrogen, helium, and propane through aqueous films of 2 wt % Ivory Liquid and of 2 wt % Duponol WN were determined. Binary gas mixtures of carbon dioxide–nitrogen and carbon dioxide–propane were enriched in one of the components using a thermally induced driving force.

INTRODUCTION

Membrane separation processes have been studied for years, but are just becoming of industrial importance (*1–3*). Present applications generally make use of a solid membrane through which the phase to be separated is preferentially passed. The work reported here involves the use of a liquid membrane, an aqueous surfactant film, to separate gas mixtures. Liquid membranes have both advantages and disadvantages for gas separation when compared with solid membranes. Liquid membranes can be made extremely selective, can be made extremely thin resulting in large gas fluxes across the membrane, can be reused many times, and can be very inexpensive. The major disadvantage is that liquid membranes cannot support an appreciable pressure drop, the common method of achieving gas enrichment in a solid membrane system.

Separation characteristics of 2 wt% aqueous solutions of Duponol WN (*4*) and of Ivory Liquid were investigated. Pure gases were placed on either side of the film in a side-arm buret. The permeation characteristics were obtained from observations of the film movement. Gas mixture separation by selective permeation through the liquid film was found to be possible using a sweep gas to maintain a concentration driving force. However, the problem of disposing of the sweep gas makes this method of enrichment impractical for most applications. Therefore, since no appreciable pressure drop could be maintained by the liquid films, a temperature gradient across the film was used to achieve the driving force for enrichment.

MEMBRANE SEPARATION CHARACTERISTICS

Figure 1 shows the setup and nomenclature for the moving film experiments. A typical plot of volume of Side A vs time is shown in Fig. 2. The following general diffusion relationship was used to describe the movement of Gas A through the film (*5–7*):

$$Q_A = \frac{A}{W} K_A P (c_{AA} - c_{AB}) \qquad (1)$$

where Q_A = flux of Gas A (g moles/sec)
A = area (sq cm)
P = pressure (Torrs)

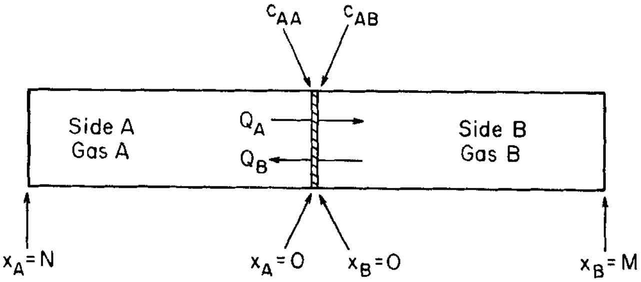

FIG. 1. Membrane separation nomenclature.

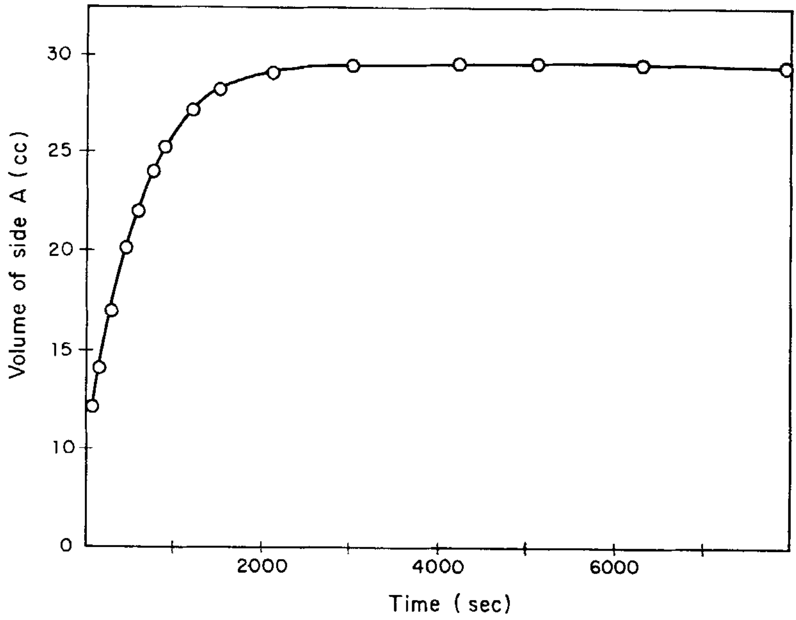

FIG. 2. Volume-time relationship for carbon dioxide-nitrogen with Ivory film.

w = film thickness (cm)
K_A = permeation constant (cm-g moles/sq cm-Torr-sec)
c_{AA} = concentration of Gas A on Side A (on gas side of gas-liquid interface)
c_{AB} = concentration of Gas A on Side B (on gas side of gas-liquid interface)

A similar relationship can be written for the passage of Gas B. Material balances of the form:

$$dV_A/dt = -Q_A - Q_B \tag{2}$$

where V is the volume of Side A (cc) and t is the time (sec) can be written over each side. Substituting the values of Q_A and Q_B into Eq. (2) yields:

$$\frac{dV_A}{dt} = \frac{AP}{w}(K_B - K_A)(c_{AA} - c_{AB}) \tag{3}$$

If $\alpha = K_A/K_B$, further reductions yield

$$\frac{V_A{}^f}{V_A{}^0} = \frac{\alpha + (1.0 - \alpha)c_{AA}{}^0}{\alpha + (1.0 - \alpha)c_{AA}{}^f} \tag{4}$$

where f indicates final values and 0 indicates initial values.

In the above system, if we assume $c_{AA}{}^f = c_{AB}{}^f$ (mole faction of Gas A at time infinity is equal on either side of the film) and we have $c_{AA}{}^0 = 1$, then

$$\alpha = \frac{V_A{}^0 - V_A{}^f c_{AA}{}^f}{V_A{}^f - V_A{}^f c_{AA}{}^f} \tag{5}$$

Two methods were used to obtain the values of K_A and K_B. The first used Eq. (3), assuming that during the inital few seconds of each run $c_{AA} - c_{AB} \cong 1.0$. The initial slope of the plot of film position vs time gave a value for $K_A - K_B$, and this value and the value of α yielded values for K_A and K_B. A more rigorous method (*8*) involved solving the above differential equations to yield an equation in terms of volume of Side A and time, incorporating K_A and K_B. Using this equation, a computer search on values of K_A and K_B was used to obtain values which yielded a curve closely approximating the experimental curve of V_A vs time.

Tables 1 and 2 show the values obtained. The A components are grouped and are listed in order of decreasing permeability. In each of the groups

TABLE 1

Ivory Permeation Parameters

System A–B	Calculated using initial slope			Calculated using curve fitting		
	α	$K_A \times 10^9$	$K_B \times 10^9$	α	$K_A \times 10^9$	$K_B \times 10^9$
CO_2–N_2	45.6	8.13	0.178	94.2	10.3	0.109
CO_2–O_2	21.1	6.86	0.455	20.5	9.88	0.481
CO_2–He	12.1	13.9	1.14	12.1	9.24	0.763
CO_2–ethane	23.0	8.55	0.372	23.0	7.19	0.312
CO_2–propane	29.3	5.98	0.204	27.8	5.82	0.209
O_2–N_2	2.24	2.84	1.27	2.99	1.82	0.608
O_2–ethane	1.16	3.26	2.81	1.38	1.35	0.975
O_2–propane	1.49	1.38	0.929	1.72	0.940	0.545
He–O_2	1.34	3.41	2.54	1.76	1.55	0.880
He–N_2	3.22	5.79	1.80	6.20	3.86	0.623
He–ethane	1.22	4.35	3.56	1.65	2.03	1.23
He–propane	2.15	4.61	2.14	3.64	2.70	0.742
Ethane–N_2	2.19	2.71	1.24	2.39	1.66	0.690
Ethane–propane	1.41	1.84	1.30	1.48	1.13	0.763
Propane–N_2	1.47	1.67	1.13	1.65	1.09	0.663

TABLE 2

Duponol WN Permeation Parameters

System A–B	Calculated using initial slope			Calculated using curve fitting		
	α	$K_A \times 10^9$	$K_B \times 10^9$	α	$K_A \times 10^9$	$K_B \times 10^9$
CO_2–N_2	47.6	20.1	0.423	47.6	14.0	0.293
CO_2–O_2	19.4	12.5	0.641	19.4	10.1	0.521
CO_2–He	19.4	20.0	1.03	19.4	20.0	1.03
CO_2–ethane	24.1	9.58	0.396	31.3	7.28	0.233
CO_2-propane	37.6	12.3	0.326	37.6	8.50	0.226
O_2–N_2	2.22	2.51	1.13	2.34	2.61	1.12
O_2–ethane	1.12	1.20	1.07	1.25	0.465	0.372
O_2–propane	1.70	1.24	0.729	1.89	0.992	0.525
O_2–He	1.02	6.23	6.10	1.02	2.99	2.93
He–N_2	2.29	6.43	2.80	3.44	3.34	0.972
He–ethane	1.15	3.44	2.99	1.15	1.19	1.04
He–propane	1.70	3.95	2.32	2.36	1.90	0.803
Ethane–N_2	2.12	2.20	1.04	2.22	1.91	0.861
Ethane–propane	1.50	2.02	1.35	1.64	1.24	0.755
Propane–N_2	1.48	1.67	1.13	1.65	1.09	0.663

the run with nitrogen has the largest α value, the propane run has the second largest, etc. The rates of mass passage through the film are in decreasing order: carbon dioxide, oxygen and helium, ethane, propane, and finally nitrogen. Oxygen and helium rates were similar, with the helium rate slightly greater in the Ivory film and oxygen slightly greater in the Duponol film. However, overall the surfactant used did not appear to have a great effect on permeation rates.

A model of the form

$$K = DS \tag{6}$$

where D is gas the diffusivity in the film and S is the soludility of gas in the film was found to yield good predictions of permeability constants. Since water amounted to 98 wt% of the film, and the diffusivity and the solubility values were available for the gases used in this study in water, these values were used to test the model. The results are tabulated in Table 3. The diffusivities for propane and ethane in water were estimated using the method reported by Wilke and Chang (*14*). References are listed for the other values.

The permeability values obtained for the gases using the model are close to the experimental values obtained. The value for propane appears

TABLE 3

Values for Model: $K = DS$

Gas	Diffusivity, $D \times 10^5$		Solubility, $S \times 10^5$		Permeability, $K \times 10^9$
CO_2	1.96	(9)	61.0	(12)	12.0
He	9.02	(10)	0.800	(12)	0.722
O_2	2.50	(9)	2.28	(12)	0.571
Ethane	1.61	(11)	3.31	(13)	0.533
Propane	1.32	(11)	5.22	(13)	0.691
N_2	1.90	(9)	1.16	(12)	0.220

to be out of order. However, due to the uncertainty in the predicted values of diffusivity, this cannot be positively stated. The true model might have to include a combination of the diffusivity and the solubility values of the surfactant and of the water. The values of S and D were unavailable for the surfactants used, so this could not be verified.

GAS MIXTURE ENRICHMENT

Enrichment of one component of a gas mixture can be achieved using liquid membranes by maintaining a concentration difference across the membrane. The desired component can be preferentially permeated into

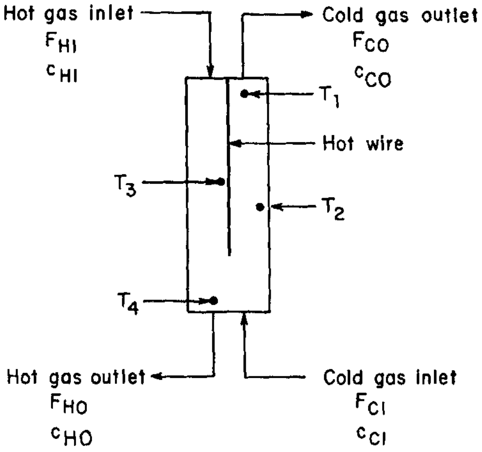

FIG. 3. Enrichment system with nomenclature.

or out of a stream of sweep gas. However, since the problem of recovery from the sweep gas generally presents a problem, a scheme of enrichment without the use of a sweep gas would be more desirable. It was found that a mixture of two gases could be enriched in one gas using a thermal gradient across the liquid membrane. Figure 3 shows the basic setup used.

The inlet gas, inside a single-layer foam (2 wt% Ivory Liquid), flowed down the hot wire. As the foam was heated by the hot wire, a stream of cold gas flowed countercurrent to the foam. The equilibrium operating temperatures were approximately 50°C below the cold gas outlet (T1), 48°C at the wall midway down the cell (T2), 60°C in the foam midway down the wire (T3), and 48°C above the bottom outlet (T4). The flow of the cold gas was eight to nine times greater than the flow of the hot gas in the foam. The above values varied somewhat from run to run and within each run due to poor control inherent in the design of the apparatus. Gas concentrations were determined by gas chromatography.

The purpose of the study was to demonstrate that thermal gas enrichment was possible; and consequently, after this was demonstrated, no attempt was made to optimize the design of the equipment used to achieve high values of enrichment.

Experimental values are shown in Table 4. Statistical tests (*15*) showed significant differences between the hot gas concentration and the concentrations of the other two streams. The cold gas concentrations do not show large variations from the feed gas concentrations since large quantities of cold gas were used compared with small quantities of hot gas.

In the carbon dioxide–propane system, the carbon dioxide was enriched in the hot gas stream; whereas, in the carbon dioxide–nitrogen system, the nitrogen was enriched in the hot gas stream.

TABLE 4

Mole Fraction CO_2 in Mixture

	Feed gas	Hot gas	Cold gas
CO_2–propane system			
1. Mean concentration at equilibrium	0.319	0.330	0.318
Standard deviation	0.0018	0.0029	0.0016
2. Mean concentration at equilibrium	0.374	0.383	0.377
Standard deviation	0.0011	0.0022	0.0019
CO_2–N_2 system			
1. Mean concentration at equilibrium	0.364	0.321	0.362
Standard deviation	0.0035	0.0133	0.0041

The actual mechanism by which the enrichment process takes place is not understood, but it is hypothesized that it is an unsteady state phenomenon which possibly results from a combination of several factors. The important variables seem to be the raising of the temperature of the gas inside the bubble and the temperature gradient through the liquid membrane. As the temperature of the inside gas is continuously raised, its density is continuously lowered. A temperature gradient existing through the film will cause the solubilities of the gases in the liquid film to change. Also, the permeability constants of the gases in the membrane are temperature-dependent. A concentration difference through the film can result in producing diffusive flow, and, if the diffusion coefficients of the two gases are not equal, an enrichment can occur. Changing permeability constants through the film due to temperature gradients can also contribute to enrichment by causing depletion or buildup of material at some point in the film.

The combination of the above factors could be extremely complex and favor enrichment of either gas, making predictions difficult until the true mechanisms are understood. It should be pointed out, however, that if a sweep gas is used to achieve a concentration driving force rather than the temperature difference, prediction is simplified since the values caldulated from the buret membrane separation runs should apply.

Liquid membranes possess excellent potential for gas mixture separations. If future work were to produce higher enrichment values, many potential applications could be realized.

SYMBOLS

A	area (sq cm)
c	concentration (mole fraction)
D	diffusivity (sq cm/sec)
F	gas flow rate (cc/sec)
K	permeation constant (cm-g moles/sq cm-Torr-sec)
P	pressure (Torrs)
Q	flux (g moles/sec)
S	solubility (mole solute/mole solvent)
t	time (sec)
T	temperature (°C)
V	volume (cc)
w	film thickness (cm)
x	distance (cm)

α separation factor

Subscripts and Superscripts

A = Gas A
AA = Gas A on Side A
AB = Gas A on Side B
B = Gas B
CI = cold inlet
CO = cold outlet
f = final
HI = hot inlet
HO = hot outlet
0 = initial
T = total

REFERNCES

1. N. Li, *Chem. Eng.*, *77* (24), 52 (1970).
2. J. R. Morgan, "Interstitial Liquid Flow in Stable Foams," Ph.D. Thesis, Univ. Iowa, 1969.
3. H. M. Schoen, *New Chemical Engineering Separation Techniques*, Wiley (Interscience), New York, 1962, pp. 1–98.
4. E. I. du Pont de Nemours and Co. "Industrial Chemicals," Unpublished Information Bulletin.
5. R. B. Bird, W. E. Steward, and E. N. Lightfoot, *Transport Phenomenon*, Wiley, New York, 1960, pp. 495–685.
6. J. Crank, *The Mathematics of Diffusion*, Oxford Univ. Press, New York, 1970, pp. 1–326.
7. J. Crank and G. S. Park (eds.), *Diffusion in Polymers*, Academic, New York, 1968, pp. 41–72.
8. J. O. Osburn, "A Problem in One-Dimensional Diffusion," Unpublished, 1971.
9. J. H. Perry (ed.), *Chemical Engineers Handbook*, 4th ed., 1963.
10. R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1966, pp. 553–559.
11. C. R. Wilke and P. Chang *Amer. Inst. Chem. Eng. J.*, *1* (2), 264–270 (1955).
12. R. C. Weast (ed.), *Handbook of Chemistrv and Physics*, 47th ed., 1966.
13. *International Critical Tables*, Vol. 5, McGraw-Hill, New York, 1929.
14. C. R. Wilke, *Chem. Eng. Progr.*, *45* (3), 218–224 (1949).
15. N. L. Johnson and F. C. Leone, *Statistics and Experimental Design*, Wiley, New York, 1964, pp. 213–248.

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