

A Note on the Effect of Water Vapor on the Permeability of Gases Across Ethyl Cellulose Membranes

The presence of water vapor has little effect on the permeability of gases in hydrophobic membranes such as polyethylene, but large increases occur at high relative humidities in very hydrophilic membranes such as cellulose and poly(vinyl alcohol).¹⁻³ Ethyl cellulose is a glassy polymer with an affinity for water intermediate to these extremes. Water vapor was reported to reduce the permeability of CO₂ in this and similar membranes in experiments with uniformly wet membranes.⁴ However, a small increase in the permeability of CO₂, about 7%, was observed for a permeation experiment in which only the high-pressure face of a plasticized membrane was wet.⁵

This paper reports the effect of water vapor on the permeabilities P of N₂, O₂, and CO₂ in ethyl cellulose (Ethocel) under two experimental conditions—permeation in a membrane with a water concentration gradient and with a constant water concentration.

EXPERIMENTAL

In type I permeation experiments, a gas–water vapor mixture was placed in the high-pressure compartment of a permeation cell. The water vapor transported through the membrane to the low-pressure compartment was trapped by freezing in three U-tube traps, and the remaining penetrant gas was pumped into a fixed volume by a mercury diffusion pump and its pressure measured with a McLeod gauge.² The water vapor was admitted to the high-pressure compartment at least 2 hr before the gas–water vapor mixture to establish the water gradient in the membranes. The temperature reported is that of the bath surrounding the cell. However, a temperature gradient across the membrane is necessarily associated with a dynamic water concentration gradient. As a check on the experimental procedure, P was determined for dry and wet CO₂ using a poly(vinyl alcohol) membrane. The presence of water vapor produced the expected large increase in P for CO₂.

In type II permeation experiments, the same pressure of water vapor was maintained on both sides of the membrane by using saturated salt solutions, and the system was equilibrated in the water vapor for at least 4 hr before introducing the gas–water vapor mixture on the high-pressure side. The pressure increase in a small low-pressure chamber was followed with a mercury manometer.¹ The high-pressure portion of the apparatus was much larger, including a 2-liter ballast compartment. In addition, a centrifugal gas-circulating pump was included in the high-pressure compartment, and most measurements were made with a circulating mixture although no effect on P was detected.

The permeation cell holding the membrane could be mounted in both apparatuses. The cell was made from a glass-pipe joint, with a perforated aluminum plate support for the membrane. Teflon gaskets were used and the joint sealed with beeswax and Apiezon Q. Using the same membrane and dry gases only, P agreed within 10% when measured by the two procedures. All measurements were made at 30°C, and P is reported as [cm³ (S.T.P.) / cm min cm Hg].

P was determined in both experiments by the equation

$$P = \frac{VT_s L}{TA p_s p_1} \frac{dp}{dt} \quad (1)$$

where p and V are the pressure and volume of the low-pressure compartment; L and A are the thickness and area of the membrane, respectively; p_s and T_s are the standard pressure and temperature, respectively; p_1 is the pressure in the high-pressure compartment, and t is the time. In type II permeation experiments, where V is small, this simplified equation still gave values of P within 3% of a more exact equation.

The unplasticized Ethocel, provided by the Dow Chemical Company research laboratories, had an ethoxy content of (48.7 ± 0.7)%, corresponding to about 2.5 ethoxy groups per glucose unit. The average density at 30°C was 1.124 g/cm³. The thickness of the membrane as supplied was 1.35 ×

TABLE I
Permeability of Gases in Ethocel at 30°C

Gas	Type I experiments			Type II experiments		
	$P \times 10^8$ ^a	Relative H ₂ O pressure, $p/p \cdot$	P/P_{dry}	$P \times 10^8$ ^a	Relative H ₂ O pressure $p/p \cdot$	P/P_{dry}
He	120	0.00	1.0			
	110	0.50	0.9			
	100	0.57	0.8		(not measured)	
O ₂	43	0.00	1.0	8.0	0.00	1.00
	41	0.60	0.95	2.5	0.99	0.31
	39	0.00	1.0	8.6	0.00	1.00
	39	0.47	1.0	4.7	0.87	0.51
N ₂	4.4	0.00	1.0	2.9	0.00	1.00
	4.2	0.88	0.95	1.8	0.75	0.62
CO ₂				3.4	0.00	1.00
				2.4	0.87	0.71
	82	0.00	1.0	60	0.00	1.00
	74	0.47	0.9	42	0.43	0.70
	61	0.88	0.75	37	0.49	0.62
				38	0.74	0.63
				37	0.75	0.62
			32	0.99	0.53	

^a In units of [cm³ (S.T.P.)/cm min cm Hg].

10⁻² cm. Thinner membranes, used in a few experiments, were prepared by casting from an acetone solution.

RESULTS AND DISCUSSION

Table I provides permeability data for dry and wet gases across Ethocel membranes at 30°C, with P measured for the wet gases under the two experimental conditions. In addition to the experiments with O₂, N₂, and CO₂, type I experiments were also conducted with He.

The value of P was constant to $\pm 3\%$ for a series of experiments using a dry gas and for a series using a wet gas. However, P measured for dry-gas experiments following a series of wet-gas experiments was greater than that measured prior to the wet-gas experiments. The effect was as large as 30% in type II experiments, although much less for type I. For example, in a sequence of type II experiments using CO₂ as the permeate, the permeability ($P \times 10^7$) was: (1) dry, 4.8; (2) wet, 4.0; (3) wet, 2.5; (4) dry, 6.1; (5) dry, 6.0; (6) dry, 5.9; and (7) dry, 6.1. This change in P introduced by the sorption-desorption of water vapor could be the result of structural changes in the bulk of the membrane or the development of surface defects. Since the presence of water reduces P for the gas, this drift in barrier properties could mean that the effect of water has been underestimated. In each of the experiments reported in Table I, it is the permeability in the dry-gas experiments run prior to the wet-gas experiment that is reported.

In the dry-gas experiments, there was no dependence of P on pressure in the range tested (5–69 cm Hg). As observed for many polymers,⁷ P measured for the dry gases decreased in the order He > CO₂ > O₂ > N₂.

Data in Table I indicate that the presence of water vapor generally decreases the permeability of gases in ethyl cellulose at 30°C. In type I experiments the decrease was small or negligible, except for CO₂. Larger decreases occurred in type II experiments, especially for O₂. Ito⁴ reported $P = 3.5 \times 10^{-7}$ for dry CO₂ and 2.9×10^{-7} at a relative humidity of 87% under type II experimental conditions at 15°C, a decrease of about one half that observed in this work.

The effect of water vapor on P is expected to be smaller under type I than under type II conditions. In type I experiments, the low-pressure region of the membrane contains little water because the diffusion coefficient D for water is a decreasing function of concentration.⁸ The water structure in the two experiments may also differ.⁹

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References

1. F. L. Pilar, *J. Polym. Sci.*, **45**, 205 (1960).
2. J. A. Mayer, C. E. Rogers, V. Stannett, and M. Szwarc, *Tappi*, **23**, 28 (1962).
3. J. A. Barrie, in *Diffusion in Polymers*, J. Crank and G. S. Park, Ed., Academic Press, London, 1968, p. 286.
4. Y. Ito, *Kobunshi Kagaku*, **18**, 158 (1961).
5. V. L. Simril and A. Hersberger, *Mod. Plast.*, **27**(11), 95 (1950).
6. J. A. Barrie, H. G. Spencer, and A. Quig, *J. Chem. Soc., Faraday Trans. I*, **71**, 2459 (1975).
7. M. Salame, *ACS Polym. Prepr.*, **8**(1), 137 (1967).
8. R. M. Barrer and J. A. Barrie, *J. Polym. Sci.*, **28**, 377 (1958).
9. H. Yasuda and V. Stannett, *J. Polym. Sci.*, **57**, 907 (1962).

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