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Facilitated Transport of Oxygen in Copolymer Membranes of Styrene and 4-Vinylpyridine Containing Cobalt Schiff Base Carrier : Effect of Membrane Thickness and Carrier Concentration

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Abstract : The validity of the simple mathematical model for facilitated transport in a solid state membrane developed previously has been examined against the carrier concentration and membrane thickness. Membranes are prepared with copolymer of styrene and 4-vinylpyridine as a matrix and Co(salen) as a carrier. 4-Vinylpyridine is incorporated to provide the coordination site for Co(salen) carrier. Oxygen permeability through the facilitated transport membrane is linearly increased with the square of its thickness, as predicted by the mathematical model. However, the oxygen permeability does not increase linearly with the carrier concentration. This seems to be due to the deactivation of the carrier by dimerization at high carrier concentrations as well as the reduced chain mobility by coordination of bulky Co(salen) carrier.

Introduction

Facilitated transport membrane is very attractive because of its possibility for simultaneous

increase in both permeability and selectivity. There have been many papers concerning the facilitated transport in solid state membrane.^{1,3} Nevertheless, there have been only a few mathematical models explaining the facilitation action of carriers in solid state.^{4,7}

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Nishide *et al.*² explained their experimental results showing facilitated transport with the dual sorption theory, which was introduced to explain sorption isotherm of glassy polymers. A more rigorous analysis was presented by introducing a concept of the effective diffusion coefficients between fixed site carriers by Noble.⁴ This is valid only when a large excess of carrier is present and therefore its prediction deviates gradually from the experimental data as the solute pressure increases. Cussler *et al.*⁵ also developed a mathematical model by assuming that no uncomplexed solute can exist in membrane, and the reaction between a carrier and solute occurs only at a surface of the membrane and is fast. Consequently, solute diffusion is only allowed over a limited distance due to the limited mobility of the chained carriers, which in turn leads to a percolation threshold. However, the existence of a percolation threshold is unlikely for many systems because facilitated transport has been experimentally observed with the low concentration of carriers, as low as 0.6 wt%.²

Kang *et al.*^{6,7} developed a new simple mathematical model for facilitated transport membrane with fixed site carrier. The local concentration in a facilitated transport membrane with fixed site carrier was assumed to be instantaneously fluctuated because of the continuous reversible reaction between solute and carrier. The fluctuated concentration resulted in a higher free energy,⁸ higher driving force for diffusion, and higher flux for facilitation.⁶ From an analogy between electron transfer in a parallel resistor-capacitor circuit and facilitated mass transport in a fixed site carrier membrane, a new simple mathematical model was developed⁶:

$$\frac{\bar{P}_f}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right) \frac{2\pi k_2 L^2 C_B^0}{\bar{P}} \frac{\ln(1 + Kp_0)}{P_0} \quad (1)$$

where \bar{P}_f and \bar{P} are the permeabilities [mol cm/cm² sec cmHg] of facilitated transport membrane and of pure matrix, respectively. p_0 and p_d are applied pressure and pressure fluctuation [cmHg], respectively. k_2 is a reverse reaction constant [1/sec] between solute and carrier, and K is its equilibrium reaction constant [1/cmHg]. L is membrane thickness [cm]. C_B^0 is the initial carrier con-

centration loaded [mol/cm³]. In this treatment, it was further assumed that a single capacitor represents the total carrier in the membrane and therefore a solute can not interdiffuse between matrix and carrier, representing only two diffusional pathways. This assumption was, however, relaxed in the serial combination of the parallel resistor-capacitor to account for four diffusional pathways.⁷

In this paper, poly(styrene-co-vinylpyridine) membranes containing Co(salen) were prepared with varying the thickness and carrier concentration. Their transport properties were measured and examined against the new mathematical model [equation (1)] developed by Kang *et al.*⁶

Experimental

Synthesis of Co(salen). Co(salen), N,N-bis(salicylidene)ethylene diimine cobalt (II), was synthesized by the method of Bailes and Calvin.^{9,10} Ethylene diamine (4.1 g, 0.068 mol) dissolved in ethanol (100 mL) and salicylaldehyde (11.6 g, 0.094 mol) dissolved in ethanol (20 mL) were mixed at room temperature with stirring. Yellowish crystal was precipitated immediately. The crystals were washed with ethanol two times. 60 mL of oxygen free aqueous solution of cobalt acetate tetrahydrate (11.5 g, 0.046 mol) was introduced to ethanol solution through needle to avoid contact with oxygen. Co(salen) hydrate was formed with dark red crystals, which was subsequently washed with ethanol in a nitrogen atmosphere and was dried *in vacuo*.

Copolymerization of Styrene and 4-Vinylpyridine. A mixture of styrene (104 g, 1.0 mol), 4-vinylpyridine (3.2 g, 0.03 mol) and AIBN (10 mg, 7.0 × 10⁻⁵ mol) was dissolved in toluene (100 mL) and allowed to react for 3 days at 50°C. The reaction mixture was precipitated in methanol two times and dried *in vacuo*. Dissolved oxygen of the copolymer solution in chloroform was removed by purging N₂ for 30 min.

Preparation of Co(salen) Bound Membrane. Co(salen) hydrate was heated up to 180°C *in vacuo* to remove hydrated water. After cooling to room temperature, Co(salen) was dissolved in oxygen-free chloroform. The chloroform solution

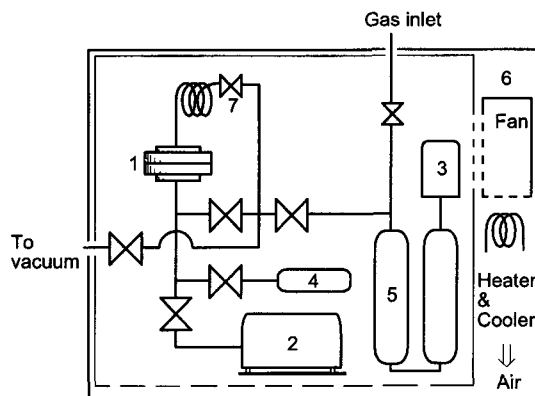


Figure 1. Schematic diagram of permeation apparatus. (1: permeation cell, 2: downstream pressure gauge, 3: upstream pressure gauge, 4: bomb for volume increase, 5: upstream volume, 6: thermostatic bath, 7: remote control valve).

of Co(salen) was transferred through double tipped needle to the freshly prepared oxygen-free copolymer solution in chloroform. The resulting solution was stirred for 10 min and become bright brown. Subsequently, the solution was cast onto a Teflon plate in a nitrogen atmosphere and dried *in vacuo* to form a transparent membrane with brown color.

Measurement of Ultraviolet Spectra. Reversible binding of oxygen to Co(salen) Schiff base was investigated by a spectral change in an UV spectroscopy (Shimadzu UV-240). To avoid oxygen contact with both the polymer solution and its membrane, the polymer solution of poly(styrene-co-4-vinylpyridine) in chloroform was cast onto an inner wall of an UV cell with a rubber septum cap and dried *in vacuo* to make a thin film. Its UV absorbance was monitored with various oxygen pressures.

Measurement of Permeability Coefficient. Permeabilities of a membrane at various upstream pressures were measured with a conventional constant volume, time-lag method. Figure 1 shows the schematic diagram of the permeation apparatus. The permeability was calculated from the slope of the time-lag curve at steady state.¹¹ Effective membrane area was 13.85 cm². Both oxygen (99.95% pure) and nitrogen (99.99% pure) were supplied by Korea Special Gas Inc.

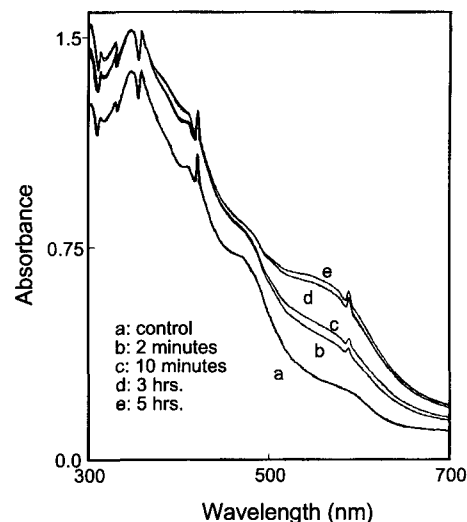


Figure 2. UV spectra of poly(styrene-co-4-vinylpyridine) membrane containing 0.56 wt% Co(salen) with oxygen expose time.

and were passed through water and oil absorbing tube (RGF 125-400, Labclear Inc.). An oxygen absorbing tube (Oxy-purge N, Alltech Associate Inc.) was also attached for nitrogen.

Results and Discussion

Reversible Oxygen Binding of Co(salen) Fixed Membrane. It has been well known that Co(salen) binds oxygen reversibly.^{1,3} The oxygen binding characteristics with Co(salen) was demonstrated here again. 4-Vinylpyridine is incorporated to provide the coordination site for Co(salen). Figure 2 shows UV spectra of a copolymer membrane containing 0.56 wt% Co(salen) with oxygen exposing time. When a constant oxygen pressure is applied to the UV cell, the peak intensity of 555 nm, a characteristic peak for 1:1 adduct of cobalt and oxygen, was increased from curve (a) to (e) with time. This verifies the binding of oxygen with Co(salen) carriers. When the membrane was exposed to oxygen, its color was also changed from transparent bright brown to deep dark brown with time.

Effect of Membrane Thickness and Carrier Concentration on Permeability. According to equation (1), the permeability of a

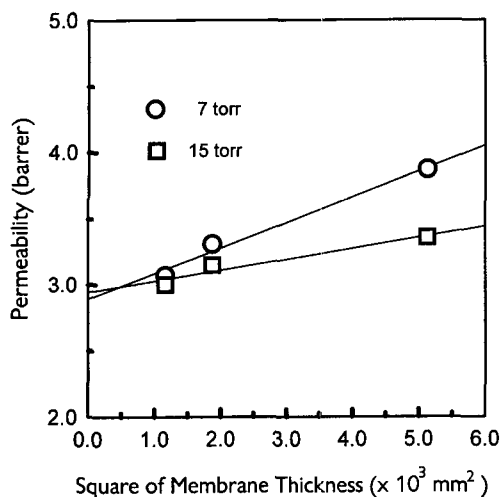


Figure 3. Plot of oxygen permeability as a function of the square of membrane thickness.

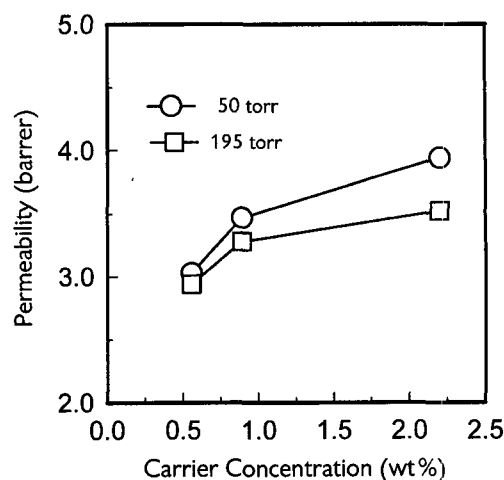


Figure 5. Plot of oxygen permeability as a function of the carrier concentration.

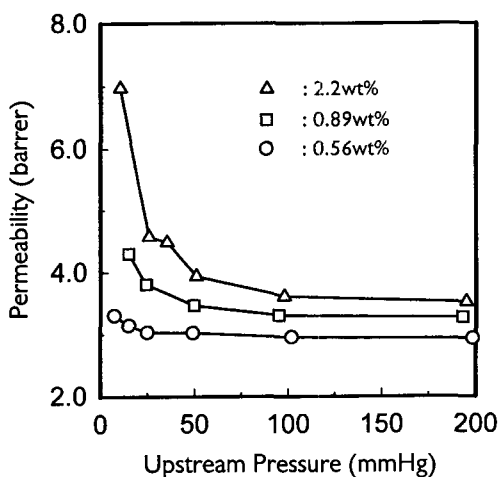


Figure 4. Effect of the carrier concentration on the oxygen permeability.

facilitated transport membrane increases with the pressure fluctuation, the carrier concentration, the reverse reaction constant and its equilibrium constant, and the membrane thickness. It decreases, however, with the applied pressure and the facilitation factor, $F = \bar{P}_f/P$, decreases with the matrix permeability. Here, the effects of the membrane thickness and the carrier concentration on oxygen permeability were measured experimentally and tested against equation (1).

In order to investigate the effect of the mem-

brane thickness on the permeation characteristics of facilitated transport membrane, the oxygen permeabilities through membranes were measured with varying thickness. Their oxygen permeabilities increased with their thickness, as expected. Equation (1) predicts that the permeability of a membrane linearly increases with the square of its thickness. In order to verify this, the permeability \bar{P}_f is plotted against the square of membrane thickness L^2 as shown in Figure 3. As can be seen, the permeability linearly increases with L^2 . This result verifies the validity of equation (1). The solid lines in Figure 3 are from the linear regression of the experimental data points. When the membrane thickness is extrapolated to zero, two solid lines approach to the close value of 2.95 barrer, which represents the permeability of the matrix without carrier according to equation (1). This value is slightly lower than the measured oxygen permeability value of 3.27 barrer for the pure matrix of poly(styrene-co-4-vinylpyridine). The lowered permeability appears to be arisen from the reduced chain mobility owing to the coordination of bulky side group of Cobalt Schiff base to the copolymer backbone.

Figure 4 shows the effect of upstream pressure on the permeability with varying carrier concentration. As expected, the permeability increases as the upstream pressure decreases and as the carrier concentration increases. According to equa-

tion (1), \bar{P}_f is linearly proportional to the carrier concentration loaded C_B^0 . Figure 5 is a plot of \bar{P}_f vs. C_B^0 . As can be seen, the permeability initially increases with the carrier concentration and levels off at high carrier concentrations. The leveling-off appears to be due to both the deactivation of carrier and the reduced chain mobility at high carrier concentrations. It has been known that the Co(salen) carrier dimerize and readily lose its reaction activity to oxygen at high carrier concentrations.¹² Therefore, the carrier will be deactivated, and its facilitation effect will be vanished. As described previously, the facilitation effect of carrier will, also, be offset by the decreased oxygen diffusivity due to the reduced chain mobility when the bulky carrier like Co(salen) is coordinated into the polymer backbone.

Conclusion

Facilitated transport membranes with varying thickness and carrier concentration were prepared and their permeation properties were measured. The results were examined against the new mathematical model for the facilitated transport in solid state. The linear relationship was found between the permeability and the square of membrane thickness. However, the oxygen permeability does not increase linearly with the carrier

concentration. This seems to be due to the deactivation of the carrier by dimerization at high carrier concentrations as well as the reduced chain mobility by coordination of bulky Co(salen) carrier.

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