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Oxygen Transport Behavior through the Membrane Containing a Fixed Carrier and Adhered to a Second Polymer

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We have recently reported[1,2] on facilitated transport of molecular oxygen in membranes containing a cobalt porphyrin complex or a cobalt Schiff-base complex as a fixed carrier of oxygen. Oxygen sorption and desorption to and from such complexes in the membranes were very rapid and reversible and exhibited the form of a Langmuir isotherm. Oxygen permeability was enhanced by a decrease in upstream oxygen pressure ($p_2(O_2)$), an observation which was explained by a dual-mode transport theory.[1,3] The permselectivity (P_{O_2}/P_{N_2}) became greater than 10 under a lower $p_2(O_2)$, but the ratio remained at ca. 5 under a practical upstream oxygen pressure, e.g., an increase above $p_2(O_2)$ of 50 mmHg.[1] Here we describe our efforts to overcome this problem. We have prepared membranes in which a poly(butylmethacrylate) membrane containing a cobalt porphyrin complex as a fixed carrier was adhered to a second membrane prepared from poly(hydroxyethyl acrylate-*co*-hydroxyethyl methacrylate), which has a smaller oxygen solubility coefficient, and also to a membrane prepared from poly(dimethylsiloxane), which has a larger one. We report the effect of the second membrane adhered to the upstream side of the membrane containing the complex on the facilitated oxygen transport.

Experimental Section

Materials. The poly(butyl methacrylate) (PBMA) membrane with a thickness of 60 μm containing 2.5 wt % [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt(II)–1-methylimidazole (CoPIm) was prepared as in the previous papers.[1] A poly(hydroxyethyl acrylate-*co*-hydroxyethyl methacrylate) (PHAM) membrane with a thickness of 60 μm was prepared by casting from a methanol solution of the polymer, which had a hydroxyethyl acrylate content of 40 mol % and a molecular weight of 30 000. A poly(dimethylsiloxane) (PDMS) membrane with a thickness of 60 μm was prepared using a room-temperature vulcanizing silicone rubber (KE-103, Shinetsu Silicone Inc.). The PBMA–CoP membrane was physically adhered to the PHAM or the PDMS membrane. Adhesion of the membranes without gaps was confirmed by scanning electron microscopy.

Permeation Measurements. Oxygen and nitrogen permeation coefficients (P_{O_2}, P_{N_2}) were separately measured with a low-vacuum permeation apparatus in a thermostated chamber (Rika Seiki Inc. gas permeation apparatus K-315 N-03), as previously described.[1] For the PHAM and PDMS membranes themselves, the diffusion coefficient (D) was calculated from the time lag (θ) of the permeation curve, and the solubility coefficient (k_D) was calculated from the measured permeability coefficient and the measured diffusion coefficient (D), based on Fick's and Henry's laws ($P = K_D D$, $D = L^2/6\theta$, where L is the thickness of the membrane). The thickness of the single membrane used to measure the time lag is 60 μm for PHAM (θ = 710 s) and 200 μm for PDMS (θ = 2.2 s). The adhered membranes were placed in the apparatus in such a way that the PBMA membrane containing the CoP complex was on the downstream side.

Results and Discussion

The membrane containing the CoP complex sorbs oxygen by a dual mode:[1] the sorption to the polymer domain according to Henry's law and Langmuir sorption to the complex, as shown in Figure 1.[4] Although the sorbed oxygen concentration based on Henry's law is larger than the sorbed oxygen concentration based on the Langmuir isotherm under a higher oxygen pressure, the oxygen sorbed by the Langmuir mode becomes larger than that of the Henry's law mode with decreasing oxygen pressure. The oxygen permeability coefficient according to the Henry's law mode is constant at any upstream oxygen pressure. Thus, the contribution of the Langmuir mode to the oxygen permeation is expected to be much greater under lower $p_2(O_2)$, and P_{O_2} for the PBMA membrane containing the CoP complex actually increased with decreasing $p_2(O_2)$ by the additive Langmuir mode.[1] For the PBMA–CoP membrane adhered to a second membrane having a low oxygen solubility coefficient—the PHAM/PBMA–CoP membrane in this study—it is expected that the oxygen concentration on the upstream side of the PBMA–CoPIm membrane will be much reduced and that the contribution of the Langmuir mode will be still greater than that of the Henry's law mode even under relatively high $p_2(O_2)$.

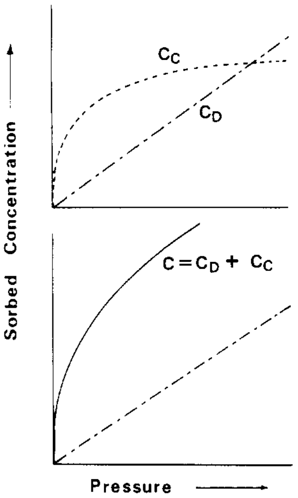

Figure 1. Dual-mode sorption in a fixed carrier membrane: C, total concentration of sorbed oxygen; C_D, concentration of sorbed oxygen according to Henry's law; C_C, concentration of sorbed oxygen according to Langmuir isotherm.

This p_2 dependence of P is also easily understood from the following equations. The oxygen permeability coefficient is equal to the sum of the first term representing the Henry's law mode and the second term for the Langmuir mode (eq 1).[1,3] Here, D_D and D_C are the diffusion

$$P = k_D D_D + D_C C'_C K/(1 + Kp_2) = k_D D_D[1 + FC'_C K/k_D(1 + Kp_2)] \quad (1)$$

coefficients for Henry-type and Langmuir-type diffusions, F is the ratio of D_C/D_D, C'_C is the saturated amount of oxygen reversibly bound to the binding site or fixed carrier, and K is the oxygen binding and dissociation equilibrium constant. Equation 1 is a function of p_2, P increases with a decrease in p_2, and the p_2 dependence of P is also enhanced when the oxygen solubility coefficient according to the Henry's law k_D becomes smaller.

Figure 2 shows the effect of $p_2(O_2)$ on P_{O_2} in the PBMA membrane containing the CoP complex and the PBMA–CoP membrane adhered to the PHAM membrane with small k_D (2.6×10^{-4} cm^3(STP)/(cm^3 cmHg)) at 25 °C and to the PDMS membrane with large k_D (2.1×10^{-3}). As predicted above, the p_2 dependence of P_{O_2} is greatest for the PHAM/PBMA–CoPIm membrane. The degree of p_2 dependence of P is presented as a ratio of p_{O_2} (50 mmHg)/P_{O_2} (760 mmHg) and is shown in Figure 3. P_{O_2} (50 mmHg)/P_{O_2}(760 mmHg) increases to 1.6 at 25 °C for the PHAM/PBMA–CoP membrane, while it is 1.2 and 1.0 for the PBMA–CoP membrane and the PDMS/PBMA–

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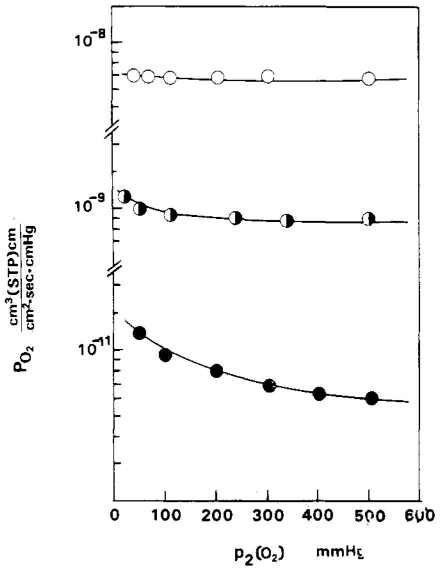

Figure 2. Effect of $p_2(O_2)$ on P_{O_2} at 25 °C: [CoP] = 2.5 wt % (in (○) the PDMS/PBMA–CoP membrane, (◑) the PBMA–CoP membrane, (●) the PHAM/PBMA–CoP membrane).

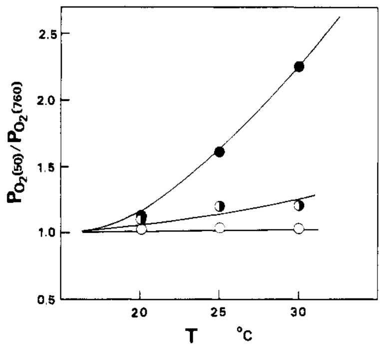

Figure 3. Effect of temperature on the p_2 dependence of P_{O_2}: [CoP] = 2.5 wt % (in (○) the PDMS/PBMA–CoP membrane, (◑) the PBMA–CoP membrane, (●) the PHAM/PBMA–CoP membrane).

CoP membrane, respectively. The p_2 dependence of P_{O_2} is enhanced at higher temperature, except for the PDMS/PBMA–CoP membrane, as can be seen in Figure 3. This is explained as follows. The oxygen binding/dissociation rate to and from the fixed carrier increases with temperature, and the Langmuir mode contributes strongly to the transport at higher temperature. The effect of temperature is more clearly observed for the PHAM/PBMA–CoP membrane because of its small oxygen solubility on the upstream side.

The oxygen permselectivity (P_{O_2}/P_{N_2}) in the membranes is given in Table I with the estimated mean values for the membranes adhered to the second polymers, which were calculated with the equation

$$L/P = l_1/P_1 + l_2/P_2 \qquad (2)$$

Here, L and P are the thickness and the permeability coefficient of a composite membrane; l_1 and l_2 and P_1 and P_2 are the thickness and the permeability coefficient of individual membranes.[5] The permselectivity for the PBMA–CoP membrane is a little larger than those for the PBMA membrane and blank PBMA–Co*P membrane at the upstream oxygen pressure of 50 mmHg: the last membrane contained the corresponding inert cobalt(III) porphyrin complex which does not interact with or bind oxygen. At the same upstream oxygen pressure of 50 mmHg, the selectivity is increased from ca. 5 for the PBMA–CoP membrane to 12 for the PHAM/PBMA–CoP membrane. The positive effect of adhering the second membrane to the upstream side is not observed for the PDMS/PBMA–CoP membrane, because in this system the second membrane has a large oxygen solubility coefficient and the Henry's law mode is not suppressed. This is also supported by the fact that the selectivity values for the blank PDMS/PBMA–Co*P and PHAM/PBMA–Co*P membranes are not increased or rather decreased by adhering the second membranes and are consistent with the mean selectivity values estimated with eq 2. The permselectivity for the composite PHAM/PBMA–CoP membrane is much greater than the simply estimated mean value of 2.8. These results suggest the possibility of a high oxygen selectivity for a construction in which the membrane containing the fixed oxygen carrier is adhered to an appropriate second membrane.

Table I
Oxygen Permselectivity[a]

membrane	P_{O_2}/P_{N_2}	$(P_{O_2}/P_{N_2})^b$
PDMS	2.0	
PHAM	2.8	
PBMA	3.4	
PBMA–CoP[c]	4.7	
PBMA–Co*P[d]	3.4	
PDMS/PBMA–CoP	3.4	3.5
PDMS/PBMA–Co*P[d]	3.4	3.4
PHAM/PBMA–CoP	12	2.8
PHAM/PBMA–Co*P[d]	2.8	2.8

[a] Upstream gas pressure: 50 mmHg at 25 °C. [b] Mean P_{O_2}/P_{N_2} estimated with eq 2. [c] [CoP] = 2.5 wt %. [d] Blank membranes. The PBMA–Co*P membrane contained the inert cobalt(III) complex (2.5 wt %), which does not interact with oxygen.

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