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Effect of Polymer Matrices on Oxygen-Binding of a Cobalt Porphyrin Complex

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Synopsis. Oxygen-binding of the (1-methylimidazole)-[$\alpha,\alpha',\alpha'',\alpha'''$-5,10,15,20-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt(II) complex fixed in polymer membranes, poly(dimethylsiloxane), poly(butyl methacrylate), and poly(methyl methacrylate), was studied spectroscopically. The apparent oxygen-binding affinity increased with oxygen solubility in the polymer matrix, which was corrected with the solubility coefficient of oxygen in the polymer.

A polymer membrane containing a carrier which interacts specifically and reversibly with oxygen is of great interest as a facilitated transport membrane of oxygen. The authors have recently reported[1)] that oxygen transport through a polymeric membrane was augmented by the addition of a (1-methylimidazole)-[$\alpha,\alpha',\alpha'',\alpha'''$-5,10,15,20-tetrakis(*o*-pivalamidophenyl)-porphinato]cobalt(II) (CoPIm) complex or a (*N,N'*-disalicylideneethylenediamine)cobalt(II) complex, which form oxygen adducts rapidly and reversibly, even in the solid state. One important point in a discussion of the facilitated transport mechanism is to quantitatively elucidate the oxygen-binding property of the carrier, i.e. the cobalt complex, fixed in a membrane.

In this work, the effect of polymer matrices on the oxygen-binding equilibrium of a CoPIm complex was studied spectroscopically by embedding the complex in three polymer membranes with greatly different T_g: poly(dimethylsiloxane) (PDMS), poly(butyl methacrylate) (PBMA), and poly(methyl methacrylate) (PMMA). This situation is discussed in connection with the oxygen solubility in these polymers.

Experimental

Preparation of the Membranes. Toluene solutions of the CoPIm complex and PBMA (Mw=320000) or PMMA (Mw=540000) were mixed, carefully cast on a Teflon plate under an atmosphere free of oxygen, then dried in vacuo to yield a transparent membrane with a thickness of about 60 μm containing 2.5 wt% CoPIm. A PDMS membrane with a thickness of 200 μm was prepared by using a room-temperature vulcanizing silicone rubber (KE-103, Shinetsu Silicone Inc.). The membrane became swollen in a toluene solution containing a large amount of CoPIm; the solvent was carefully evaporated under an atmosphere free of oxygen. The content of the CoPIm, thus prepared, PDMS membrane was also adjusted to 2.5 wt%.

Spectroscopic Measurements. Reversible oxygen-binding to the CoPIm complex fixed in the membranes was observed through the spectral change in the visible absorption using a highly sensitive spectrophotometer Shimazu UV-2000 with a kinetic data processor according to a previously reported method.[1)] The spectrophotometer was equipped with a cell having a gas inlet and outlet tube. A membrane sample was attached to the cell wall. A gaseous mixture of oxygen and nitrogen was introduced into the cell through a gas inlet and outlet tube with a standing pressure such that the total pressure in the cell became 1 atm.

Determination of the Solubility Coefficient. The solubility coefficient (k_D) of oxygen in the rubbery PDMS and PBMA membranes and the apparent solubility coefficient of the glassy PMMA membrane were calculated from the results of the following permeation experiment. The oxygen permeation coefficient (P_{O_2}) was measured with a low-vacuum permeation apparatus in a chamber with stable thermostating (Rika Seiki Inc. gas permeation apparatus K-315 N-03). The diffusion coefficient (D) was calculated from time-lag (θ) of the permeation curve ($D=L^2/6\theta$, L; thickness of the membrane), and the division of P_{O_2} by D yields k_D ($P=K_D D$).

Results and Discussion

Oxygen-Binding Equilibrium The visible absorption spectrum of the deoxy CoPIm complex (λ_{max}=528 nm) fixed in the transparent membranes was changed to a spectrum with λ_{max}=545 nm, assigned to the oxy CoPIm complex (O_2/Co=1/1 adduct, Eq 1) immediately after the exposure to oxygen. The oxy-deoxy spectral change was rapid and reversible with isosbestic points at 480, 538, and 667 nm. These visible absorption spectra agreed with those for the corresponding complex in a toluene solution.[2)]

$$\text{CoPIm} + \text{O}_2 \overset{K}{\rightleftarrows} \text{CoPIm-O}_2 \qquad (1)$$

Oxygen-binding isotherms of the CoPIm complex fixed in the membranes are shown in Fig. 1; these were drawn by analyzing the spectral changes in response to the exposed oxygen pressure with Drago's equation.[3)] The apparent oxygen-binding equilibrium constant (K_{app}) of the CoPIm in the membranes was determined from Fig. 1 and is given in Table 1. The K_{app} value for the CoPIm in the PDMS membrane is larger than those for the CoPIm in the methacrylate polymers. It is considered that a larger amount of oxygen dissolves in the PDMS matrix with a larger k_D (Table 2, mentioned later) and brings about the larger K_{app}.

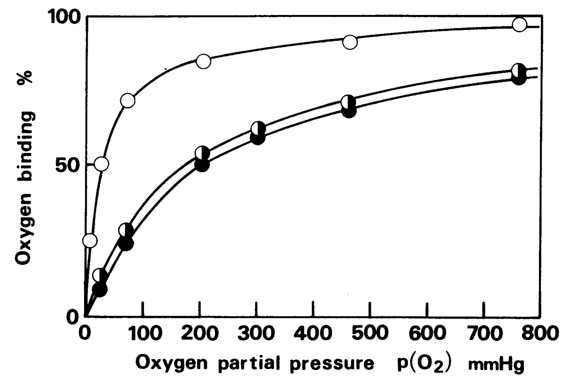

Fig. 1. Oxygen-binding equilibrium curves for the CoPIm membranes at 25 °C. (○; PDMS, ◑; PBMA, ●; PMMA) [CoPIm]=2.5 wt%.

Table 1. The Oxygen-Binding Equilibrium Constants at 25 °C and the Thermodynamic Parameters

Membrane	T_g	K_{app} 10^2	K $cm^3\,10^{-2}$	$\Delta H^{a)}_{app}$	$\Delta H^{b)}$	$\Delta S^{a)}_{app}$	$\Delta S^{b)}$
	°C	cmHg	$cm^3(STP)$	kcal mol^{-1}	kcal mol^{-1}	e.u.	e.u.
PDMS	−120	$37._7$	1.0_4	$-16._0$	$-13._1$	$-54._9$	$-34._9$
PBMA	20	5.6_2	0.51_3	$-14._3$	$-13._1$	$-53._6$	$-35._8$
PMMA	105	5.1_7	—	$-12._9$	—	$-49._3$	—

a) Data for van't Hoff plots (ln K_{app} in $cmHg^{-1}$). b) (ln K in $cm^3/cm^3(STP)$).

Table 2. The Oxygen Solubility Parameters of the Membranes without a Complex

Membrane	$k^{a)}$ $cm^3(STP)$ / $cm^3\,cmHg$	$k_D^{b)}$ $cm^3(STP)$ / $cm^3\,cmHg$	ΔH_d kcal mol^{-1}
PDMS	3.8×10^{-5}	3.8×10^{-3}	−2.8
PBMA	1.3×10^{-4}	9.6×10^{-4}	−1.2
PMMA	7.9×10^{-5}	5.9×10^{-4}	−1.2

a) The preexponential factor of Eq. 5. b) At 25 °C.

The apparent thermodynamic parameters for the oxygen-binding were estimated from the temperature dependence of K_{app} (in atm^{-1} in Fig. 2) and are also given in Table 1. The apparent enthalpy change (ΔH_{app}) becomes more negative with a decrease in Tg of the polymer matrix. These apparent thermodynamic parameters for the oxygen-binding equilibrium are corrected with those for oxygen dissolution in the polymer matrix, as follows;

$$K = [CoPIm\text{-}O_2]/[CoPIm][O_2] \qquad (2)$$

and

$$[O_2] = k_D p(O_2), \qquad (3)$$

where $[O_2]$ is the oxygen concentration around the CoPIm complex and $p(O_2)$ is atmospheric oxygen pressure to which the membrane is exposed. When $[CoPIm\text{-}O_2]/[CoPIm]$ is 1, K can be written as

$$K = K_{app}/k_D. \qquad (4)$$

Accordingly, the thermodynamic parameters from van't Hoff plots of K_{app} ($=k_D K$) are just affected by the k_D values and its heat of dissolution (ΔH_d) as shown in Eq. 7.

$$k_D = k e^{-\Delta H_d/RT} \qquad (5)$$

$$\ln K = -\Delta H_{app}/RT + \Delta S_{app}/R \qquad (6)$$

$$\Delta H = \Delta H_{app} - \Delta H_d,\ \Delta S/R = \Delta S_{app}/R - \ln k \qquad (7)$$

Here, ΔH and ΔS is the thermodynamic parameters in which the effect of the polymer matrix is reduced. ΔH and ΔS are calculated with Eq. 7 by using ΔH_{app}, ΔH_d, and k in Tables 1 and 2 and is shown in Table 2. Both the values of ΔH and ΔS in the PDMS membrane are equal to the ones in the PBMA membrane. Although the apparent equilibrium and thermodynamic parameters of the oxygen-binding reaction of the CoPIm complex fixed in polymer membranes are found to be fairly affected by the oxygen solubility in the polymer matrices, the parameters corresponding to the oxygen-binding reaction to the CoPIm complex are not essentially dependent on the species of the polymer matrix.

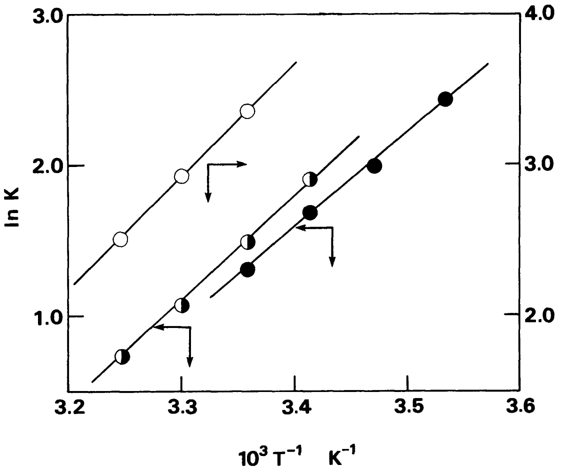

Fig. 2. Van't Hoff plots of the oxygen-binding equilibrium constants for the CoPIm membranes. (○; PDMS, ◑; PBMA, ●; PMMA) [CoPIm]=2.5 wt%.

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