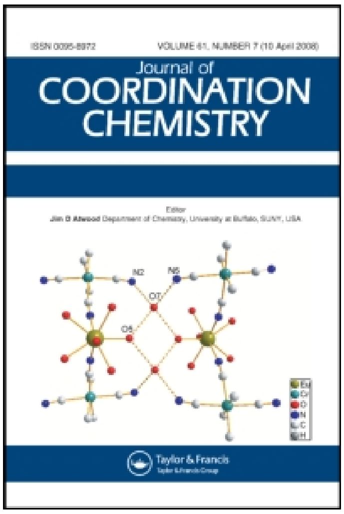

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FACILITATED OXYGEN-TRANSPORT IN POLYMER LIGAND-COORDINATED PORPHINATO COBALT MEMBRANE

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Abstract Facilitated oxygen-transport is discussed in terms of a dual-mode transport model in the membrane of poly(octylmethacrylate-co-4-vinylpyridine) or poly(octylmethacrylate-co-1-vinylimidazole) complexed with [α,α′,α″ ,α‴ -meso-tetrakis(o-pivalamidophenyl)porphinato]cobalt(II).

Keywords: Oxygen transport, dual-mode, membrane

INTRODUCTION

It has been noted that a polymer membrane containing metal complexes interacts specifically and reversibly with gaseous molecules which is suitable for the efficient gas-separation.[1,2] Recently this approach has been successfully applied to an oxygen-separating liquid membrane:[2] The liquid membrane containing [N,N'-bis(3-methoxysalicylidene)tetramethylethylenediamine]cobalt(II)/4-dimethylaminopyridine complex exhibited a high oxygen permselectivity. However, it is difficult to employ the wet membrane as an oxygen enriching membrane from air. Hence a dry polymer membrane in which such metal complexes are fixed has been recently studied.[3] We have reported the oxygen permselectivity through a dry polymer membrane prepared by dispersing in poly(butylmethacryrate)[α,α′,α″,α‴-meso-tetrakis(o-pivalamidophenyl)porphinato]cobalt(II)(CoP)/1-methylimidazole(Im) complex, whose sixth coordination site is vacant even in the solid state to bind molecular oxygen rapidly and reversibly.[4] The oxygen permselectivity was discussed by a dual-mode transport model.

The present paper describes the selective and the dual-mode transport of oxygen in the membranes of CoP coordinated to polymeric ligands. The polymer membranes were prepared by homogeneously complexing CoP to poly(octylmethacrylaye-co-4-vinylpyridine)(POMPy) or poly(octylmethacrylate-co-1-vinylimidazole)-(POMIm). Oxygen-binding capability of the polymer-coordinated CoP in the membrane state was characterized by means of spectroscopic method. Oxygen permeation behavior was measured in connection with the upstream oxygen pressure and was discussed in terms of the combination of the dual-mode transport model and the spectroscopic parameters.

EXPERIMENTAL

Materials: [$\alpha,\alpha',\alpha'',\alpha'''$-meso-tetrakis(o-pivalamidophenyl)porphinato]cobalt(II)(CoP) was synthesized by literature method.[5] Poly(octylmethacrylate-co-4-vinylpyridine)(POMPy) and poly(octylmethacrylate-co-1-vinylimidazole)(POMIm) were prepared by the radical copolymerization of octylmethacrylate and 4-vinylpyridine and 1-vinylimidazole with azobisisobutyronitrile. Vinylpyridine and vinylimidazole residue content and molecular weight of the copolymers were determined to be 5.0 mol%, 1.5×10^5 for POMPy and 3.7 mol%, 1.0×10^5 for POMIm, by elemental analysis and gel-permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as the standard) respectively. The chloroform solution of the copolymer and CoP was carefully cast on a Teflon plate under an air atmosphere, then dried in vacuo, to yield a transparent and flexible membrane with thickness of ca. 60 μm. **Spectroscopic Measurement:** Reversible oxygen-binding to the CoP complex in the membrane was observed with spectral changes in the visible absorption, using a high-sensitive Shimazu UV-2000 spectrophotometer. **Permeation measurement:** Oxygen permeation coefficient for various upstream gas pressures was measured with a low-vacuum permeation apparatus (Rika Seiki Inc. Type K-315 N-03) at a constant temperature. The pressure on the upstream side was maintained essentially constant. The pressures on the upstream and the downstream side were detected by using Baratron's absolute pressure gauge (MKS Instruments Inc.). The membrane was set in the apparatus and kept in vacuo over half a day before the measurement to exclude gas leakage. Nitrogen permeation coefficient was measured by the same procedure as for oxygen.

RESULTS AND DISCUSSION

Preparation of the polymer-coordinated CoP membrane. We previously prepared[4] the membrane by dispersing the CoP complexed with a low molecular nitrogeneous ligand such as 1-methylimidazole in a polymer. But this preparation procedure was often accompanied with an irreversible oxidation of CoP to Co(III)P and was to be carried out under an atmosphere absolutely free of oxygen. The membranes of the CoP-POMPy and -POMIm complexes are obtained by casting the chloroform solution of their complexes even under an air atmosphere, which is a great merit in the preparation procedure. The CoP coordinated an axial ligand of a low molecular weight, even so-called "picket fence cobalt-porphyrin",[5] often exhibits the oxidation due to the dimerization resulting in six-coordination complex at the higher concentration. However, the usage of the polymer ligand may depress the dimerization, as steric hindrance of the picket fence prevents polymer axial base from ligation to the fence side of CoP.

Oxygen-binding to the CoP complex in the membrane. The spectrum of the deoxy CoP-POMPy or CoP-POMIm complex of the reddish colored and transparent membrane (λ_{max} = 528 nm) was changed to the spectrum with λ_{max} = 545 nm assigned to the oxy CoP complex (O_2/Co = 1/1 adduct) immediately after the exposure to oxygen. The oxy-deoxy spectral change was reversible in response to a partial pressure of oxygen with isosbestic points at 480, 538, and 667 nm. These visible absorption spectra agreed with those for the corresponding CoP complex in poly(butylmethacrylate).[4] The oxygen-binding equilibrium constant (K) of the polymer-coordinated CoP complex in the solid membrane was determined from the oxygen-binding and -dissociation equilibrium measurement using Drago's equation[6] and listed in Table I. The oxygen-binding affinity of CoP-POMIm is found to be larger than that of CoP-POMPy because of the higher basicity of the imidazole axial ligand.

Facilitated oxygen-transport in the polymer-coordinated CoP membrane. Figure 1 shows the effect of upstream gas pressure (p_2) on the permeability coefficients (P_{O_2} and P_{N_2}) in CoP-POMPy membrane containing 1.8 wt% of the CoP. P_{O_2} increases with the decrease in $p_2(O_2)$, which is in accordance with eq 1 (presented 2 pages later). Although the dependence of P on p_2 has been often reported for glassy polymers,[7] glass transition temperatures were ca. -10 and -15°C for the CoP-POMPy and the CoP-POMIm membranes, respectively, and the membranes were in a rubbery state at the

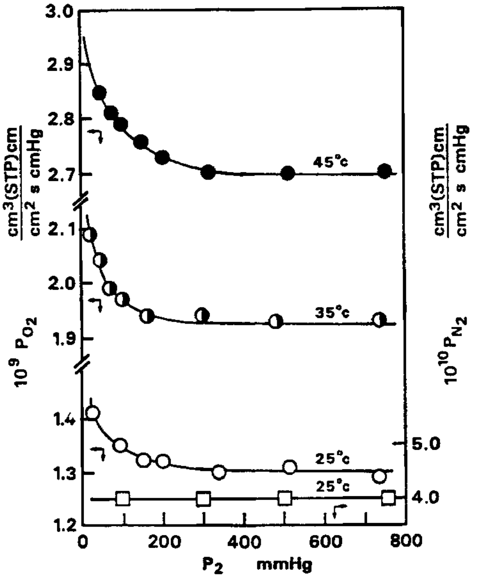

FIGURE 1 Effect of upstream gas pressure on permeation coefficient for the CoP-POMPy membrane. [CoP]= 1.8 wt%

temperatures employed for the permeability measurements. In fact P_{N_2} was independent of $p_2(N_2)$ because the fixed complex does not interact with nitrogen. From the results, the oxygen transport through the CoP-POMAPy membrane is found to be substantially enhanced in comparison with the membrane containing no complexes.

Time course of the permeation of gaseous molecules through membranes often shows an induction period (time lag) followed by a permeation with a constant slope (steady state). For the CoP-POMPy membrane the time lag for the oxygen permeation is expected to be enhanced because the fixed CoP complex interacts with oxygen and reduces its diffusiveness in the membrane. Figure 2 shows that the time lag (θ) also depended on $p_2(O_2)$ in the same manner as the permeation coefficient. This behavior is in agreement with eq 2 (presented on the next page) and indicates that oxygen clearly interacts with the CoP complex in the membrane. This is further supported by the results that θ for nitrogen permeation in the membrane containing the complex are independent of the upstream

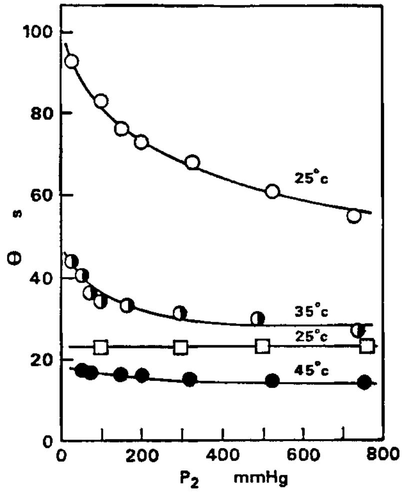

FIGURE 2 Effect of upstream gas pressure on time lag for the CoP-POMPy membrane. [CoP]= 1.8 wt% (circle; O_2, square; N_2)

oxygen pressures. In Figure 2 one also notices that θ_{O_2} and the $p_2(O_2)$-dependency of θ_{O_2} decrease with temperature. θ_{O_2} and the $p_2(O_2)$-dependency of θ_{O_2} are based on oxygen-binding to the fixed CoP complex and enhanced at lower temperature because the oxygen-binding equilibrium constant of the CoP complex increases with decreasing temperature.

A dual-mode transport model[4,7] is applicable to oxygen transport in the polymer-coordinated CoP membrane, as mentioned below. Eq 1 shows the oxygen permeability in the fixed complex membrane which is governed by both the Henry and the Langmuir mode. That is, the oxygen permeation coefficient is equal to the sum of a first term representing the Henry mode and a second term for the Langmuir mode.

$$P = k_D D_D + D_C C'_C K / (1 + K p_2) \qquad (1)$$

Here, P is a permeability coefficient, k_D is a solubility coefficient for Henry's law, D_D and D_C are diffusion coefficients for Henry-type and Langmuir-type diffusion, C'_C is a saturated amount of oxygen reversibly bound to the binding site or fixed carrier, K is a oxygen-binding and -dissociation equilibrium constant, and p_2 is an upstream gas pressure. Eq 1 is a function of p_2 and P increases with decreasing p_2.

The time lag for the polymer-coordinated CoP membrane is to be also governed by both the Henry and Langmuir modes (eq 2).

$$\frac{6\theta[1+FR/(1+y)]^3}{[f_0(y)+FRf_1(y)+(FR)^2f_2(y)]l^2}(Y) = \frac{R}{D_D} + \frac{1+FRf_3(y)+(FR)^2f_4(y)}{f_0(y)+FRf_1(y)+(FR)^2f_2(y)}(X)\frac{1}{D_D} \qquad (2)$$

Here, θ is the permeation time lag, F is defined as D_C/D_D, R is defined as KC'_C/k_D, l is a thickness of membrane, and y is equal

Table I.

Dual-Mode Transport Parameters for the CoP-POMPy and CoP-POMIm Membrane

Polymer	T ^{o}C	D_D $\frac{cm^2}{s}$	D_C $\frac{cm^2}{s}$	$F(D_C/D_D)$	k_D $\frac{cm^3(STP)}{cm^3 cmHg}$	C_C' $\frac{cm^3(STP)}{cm^3}$	K $\frac{1}{cmHg}$
POMPy	25	$1.3x10^{-6}$	$2.4x10^{-8}$	0.02	$9.9x10^{-4}$	0.3	$2.4x10^{-2}$
	35	$2.6x10^{-6}$	$4.7x10^{-8}$	0.02	$7.2x10^{-4}$	0.3	$1.1x10^{-2}$
	45	$4.9x10^{-6}$	$9.8x10^{-8}$	0.02	$5.3x10^{-4}$	0.3	$5.5x10^{-3}$
POMIm	25	$1.2x10^{-6}$	$1.1x10^{-8}$	0.01	$1.1x10^{-3}$	0.3	$1.3x10^{-1}$
	35	$4.6x10^{-6}$	$2.5x10^{-8}$	0.01	$4.4x10^{-4}$	0.3	$5.9x10^{-2}$
	45	$8.6x10^{-6}$	$7.7x10^{-8}$	0.01	$3.3x10^{-4}$	0.3	$3.0x10^{-2}$

to Kp_2. θ also depends on p_2. The combination of eq 2 and 1 gives R/D_D and $1/D_D$, and the permeation parameters, D_C,k_D and C'_C, can be estimated. The function of $y, f_0(y) \sim f_4(4)$ are given in the previous papers.[4,7]

The oxygen permeability coefficients and time lags were analyzed according to this dual-mode transport model as described in the previous papers[4] and the parameters calculated were given in Table I. The C'_C values in both membranes are calculated to be independent of temperature and a constant, which supports the validity of the analysis using the dual-mode transport model for the oxygen transport in the polymer-coordinated CoP membrane. The ratio of D_C and D_D, that is, F value indicating the mobility of the adsorbed or coordinated oxygen molecule to the CoP complex in the CoP-POMPy membrane is larger than that of the CoP-POMIm membrane. This may be for the reason that the oxygen-dissociation kinetic rate of the polymer-coordinated CoP is larger in the CoP complex coordinated the pyridine axial base with the smaller oxygen-binding affinity. Facilitated oxygen-transport is found to be strongly affected by character of the axial ligand coordinated to the CoP complex.

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