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CORRELATION OF MAGNETIC SUSCEPTIBILITY OF POLYMER-HEMIN COMPLEX TO THE STRUCTURE OF POLYMERIC LIGAND

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The electronic configuration of the polymer-hemin complex was at equilibrium between the high spin state and the low spin state and varied with the sort of the coordinating group and its neighbouring group of the polymer ligand bonded to the axial site of hemin.

The present authors have extensively studied the oxygenation reaction in the solid state and in a solution containing heme bonded to a synthetic polymer, that is, a polymer-heme complex.[1~3] In particular, the environmental effects on oxygenation due to the polymer conformation have been discussed in order that a resultant oxygen complex is stabilized by the complex formation between heme and a synthetic polymer. In this paper, the electronic configuration of hemin-iron bonded to a polymer ligand was studied by the measurement of magnetic susceptibility which gives an important information concerning the behavior of oxygen uptake. That is, chlorohemin (chloroprotoporphyrinato iron (III)) was bonded to some polymeric ligands and the magnetic susceptibility of the resultant polymer-hemin complex was studied in order to discuss the correlation of the magnetic susceptibility to the structure of the axial ligand.

On the basis of the measurement of temperature dependence of magnetic susceptibility, the spin state of a ferric ion of met-hemoglobin is believed to be at thermal equilibrium between the high spin state and the low spin state.[4~7] Such a phenomenon is generally observed for a chelate compound having a strong bidentate or quadridentate chelate ligand such as porphyrin, monothio-β-diketone and so on,[8~10] and these metal complexes, which are called "cross-over complex", are very interesting in the research of magnetochemistry. We are also interested in the spin equilibrium of a polymer-hemin complex and have specially studied how the electronic and magnetic properties of a metal ion changes by including into a synthetic polymer domain.

Metal complexes used for the measurement of magnetic susceptibility are monomeric and polymeric pyridine hemichromes. A monomeric pyridine hemichrome was prepared according to the following method: 65 mg of chlorohemin was dissolved in 14 ml of pyridine at room temperature and the solvent was evaporated under reduced pressure and the crystals obtained were dried up in vacuo at room temperature. A polymeric analogue was prepared as follows: A dimethylformamide solution (50 ml) dissolving 70 mg of chlorohemin was slowly mixed at room temperature with 50 ml of a methanol solution dissolving 130 mg of poly-4-vinylpyridine (PVP : $\overline{Mn}$ = 5150) and then the mixed solution was evaporated under reduced pressure, so that a blackish brown powder was formed. Another type of polymeric pyridine hemichrome, which is included into a polyion complex consisting of partially-quaternized poly-4-vinylpyridine (QPVP : quaternization by benzyl chloride, 30%) and sodium polystyrenesulfonate (NaSS : sulfonation 77%, $\overline{Mn}$ = 58700), was prepared as follows: Chlorohemin (65 mg) and QPVP (69 mg) were dissolved together in 40 ml of 0.02M sodium carbonate buffer solution (pH = 11), and 10 ml of 0.02M sodium carbonate buffer solution dissolving 110 mg of NaSS was slowly mixed with the above solution, so that a blackish brown precipitate was immediately formed and then filtered and dried up. Other types of polymeric hemichromes were also prepared according to a similar method as mentioned above. The results of the elemental analysis for chlorohemin and polyvinylpyridine used here are as follows: for a black needle crystal of chlorohemin, anal.: C 62.43%, H 4.80%, N 8.62%, Fe 8.49%; calcd. as $C_{34}H_{32}N_4O_4FeCl$: C 62.63%, H 4.96%, N 8.59%, Fe 8.56%, and for PVP, anal.: C 78.9%, H 7.38%, N 13.1%; calcd. as C_7H_7N: C 79.9%, H 6.71%, N 13.3%. The purity of chlorohemin determined from the molar extinction coefficient of the Soret band (404 nm) was 99.3%. Partially-quaternized polyvinylpyridine used was purified by a reprecipitation method with a methanol-ethyl ether system, and sodium polystyrenesulfonate was similarly purified with an ethylacetate-ethyl ether system. Other reagents were purified according to a conventional method. Polymer-hemin complexes were prepared from these pure materials and the products were used for analysis after complete drying without further purification. Measurements of magnetic susceptibility of the above-prepared solid samples were made with Faraday method.

The coordination structure of the above-prepared hemichromes is five-coordinate in both cases of the monomeric and polymeric ones. That is, the molar ratio of a pyridine nitrogen to hemin-iron at the axial site is nearly 1.0 at 25°C, and the visible absorption spectra also indicate the characteristics of a five-coordinate pyridine hemichrome. The fine analysis of the complex formation has already reported in the preceding papers[1,11] and so the details are omitted here.

When the molar magnetic susceptibilities(χ_M) of these polymeric metalloporphyrins were measured at room temperature, all of the observed values were intermediate between the calculated χ_M of the high spin state and that of the low spin state. This result indicates the following two possibilities: (1) A sample used for the measurement is only a mixture of the high spin complex and the low spin complex. (2) Two species of the high spin complex and the low spin complex are at equilibrium. Then, the temperature dependence of magnetic susceptibility was studied in order to confirm which of these conclusions is valid.

The eqilibrium constant of the spin exchange can be calculated according to the following equations.[4,5]

$$\chi_M = a\cdot\chi_L + (1 - a)\cdot\chi_H \qquad (1)$$

where χ_M is the observed magnetic susceptibility, χ_L the calculated value of the low spin complex, χ_H the calculated value of the high spin complex, a is the mole fraction of the low spin complex, and 1-a that of the high spin complex.

$$K = a / 1\text{-}a = (3\gamma)^{-1} \cdot e^{\varepsilon/kT} \qquad (2)$$

where K is the spin equilibrium constant, ε the difference in energy between two spin states, is an entropic parameter called the state ratio. k is a Boltzmann's constant, and T an absolute temperature. The parameters ε and γ are correlated to the enthalpic change and the entropic change by equation (3) and (4), respectively.

$$\Delta H^\circ = - N\varepsilon \qquad (3)$$

$$\Delta S^\circ = - R \ln 3\gamma \qquad (4)$$

where N is an Avogadro number and R is a gas constant.

Figure 1 shows a plot of the logarithmic equilibrium constant (logK) against inverse temperature (1/T), which was calculated by applying equations (1) and (2) to the result of the temperature dependence of the magnetic susceptibility. The linear relationship of logK vs 1/T plot suggests that the high spin complex and the low spin complex are at thermal equilibrium. The parameters (ε and γ) were calculated from the slope and the intercept of the straight line and converted into ΔH° and ΔS° by equations (3) and (4), respectively. The results are summarized in Table 1.

The following conclusions are deduced from the results shown in Table 1. The enthalpic parameter of ε appreciably varies with the sort of the axial ligand of hemin-iron, as explained below. (1) When the ε values of chloro-hemin(Cl-hemin), pyridine hemin(Py-hemin), and poly-L-lysine-hemin(PLL-hemin) are compared with each other, it is found that the larger the basicity of the axial ligand becomes, the ε value becomes the larger. (2) When the ε value of PVP-hemin, QPVP-hemin and QPVP-NaSS-hemin are compared with each other, it is suggested that the ε value are affected by the neighbouring substituent of the coordination site of hemin-iron on the polymer matrix, although the coordination structure is mono-pyridine in all cases. (3) Such a result cannot be obtained, if hemin is situated in a polymer domain without a tight bonding. This is confirmed by the fact that the magnetic susceptibility of such a sample as occluding a Cl-hemin or Py-hemin into a non-coordinating polystyrene matrix, which was prepared by kneading a Cl-hemin of a Py-hemin and polystyrene powder in a paste, was nearly equal to the magnetic susceptibility of the untreated sample.

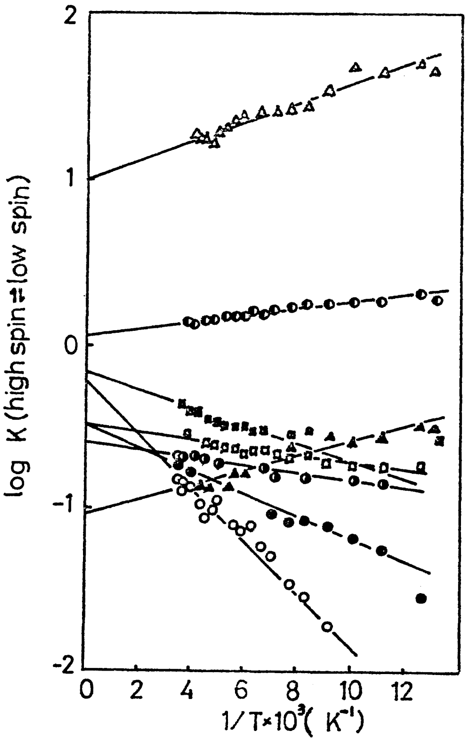

Fig.1 Relationship between the Spin Equilibrium Constant and Inverse Temperature

Cl-hemin(◑), Py-hemin(●), PVP-hemin(○), QPVP-hemin(◐), QPVP-NaSS-hemin(▲), PLL-hemin(△), Cl-hemin included in PSt.(□), Py-hemin included in PSt.(■)

Table 1 Various Parameters of Spin Equilibrium of Hemin Complexes

Ligand	Ground state	ε (cm^{-1})	γ	ΔH^0 ($cal.mol^{-1}$)	ΔS^0 (e.u.)
Cl	High	-33	1.31	+95	-2.73
Py	High	-111	0.98	+318	-2.16
PVP	High	-225	0.55	+649	-0.99
QPVP	Low	+32	0.30	-92	+0.23
QPVP-NaSS	Low	+138	3.92	-398	-4.93
PLL*	Low	+93	$3.35 \cdot 10^{-2}$	-268	+4.60
Cl(PSt.)**	High	-33	0.98	+95	-2.16
Py(PSt.)**	High	-86	0.36	-246	-0.71

* PLL: Hexa-coordinate structure
** (PSt.): included in polystyrene

The ground state of a ferric complex with $3d^5$ electronic configuration varies from $^6A_{1g}$ to $^2T_{2g}$ with the strength of the ligand field and the spin equilibrium between the sextet and doublet states has been confirmed for several metal complexes.[9,10,12,13] On the other hand, about a ferrous complex with $3d^6$ electronic configuration there are some cross-over complexes which have a ligand of phenanthroline, dipyridyl or others.[14,15] We have also measured the magnetic susceptibility of a ferro-protoporphyrin bonded to the polyion-complex ligand(QPVP-NaSS) from liquid nitrogen temperature. As Figure 2 shows, the relationship between χ_g and 1/T was linear, and this result suggests the non-existence of the spin equilibrium. It is considered from the χ_g value that the QPVP-NaSS-heme complex is at high spin state. We are studying in detail about this result.

The result that the magnetic susceptibility of the polymeric hemichrome is influenced by the primary structure of the polymer chain indicates the possibility that the electronic property of a central hemin-iron can be changed by arranging the sequence of a polymer ligand or the chemical environmental property of an aggregated polymer domain. This is very significant for studying the oxygenation of a polymer-heme complex. The present authors have already reported[16] that by polarographic studies, the redox potential of a central ferric ion of hemichrome was found to be sensitive to the environmental property of the polymer domain surrounding the hemichromes. It can be qualitatively understood from the above-mentioned polarographic and magnetic studies that the electric and magnetic properties of a metal complex are affected by the chemical environment of a polymer domain including the metal complex. The chemical environment of a polymer domain will be quantitatively represented by using various analytical methods, so that the more clear discussions on the environmental effect may be developed in a following paper.

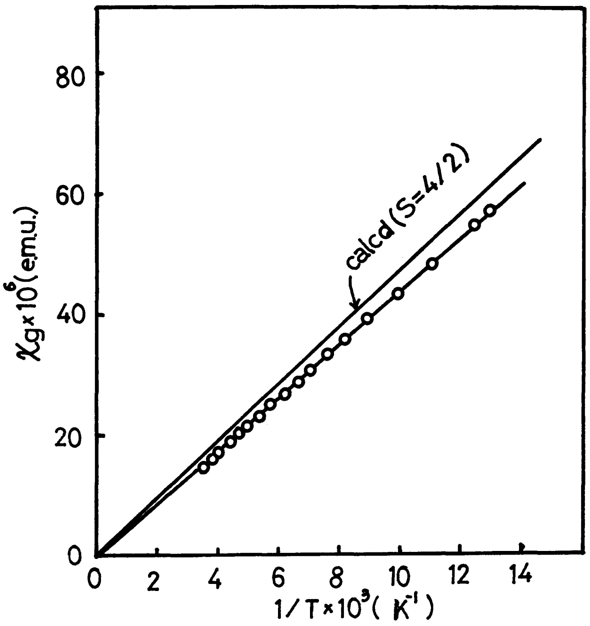

Fig.2 Relationship between the Magnetic Susceptibility and Inverse Temperature of QPVP-NaSS-heme

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