Thermochromism of Metal Exchange Reaction between Zinc(II) and Mercury(II) Porphyrins

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

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Thermochromism was observed for an aqueous solution containing zinc(II) and mercury(II) cations and N-/?-nitrobenzyl-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin anion (NO2 Bz(Htpps)4−) in the temperature range 10 to 70 °C. The equilibrium constants and the thermodynamic parameters of Zn(NO2 Bztpps)3− and Hg(NO2 Bzttps)3− have been determined spectrophotometrically to elucidate the thermochromism at 10, 15, 20, 25 and 30 °C in 0.1 mol dm−3 NaNO3. The protonation and metalation constants of NO2 Bz(Htpps)4− are defined as K2 = [H2P][H+]−1[HP]−1, K3 = [H3P][H+]−1[H2P]−1 and KMP = [MP][H+]2[M2+]−1 [HP]−1, where HP and MP denote the free base form of the prophyrin and the metalloporphyrins of zinc(II) and mercury(II), respectively. Charges of the prophyrin and metalloporphyrins are omitted for simplicity. The following values were found: logK2 = 7.75 ± 0.02 (25 °C), ΔH°/kJ mol−1 = −21.2 ± 0.5 and ΔS°/J mol−1 K−1 = 77 ± 1, logK3 = 2.55 ± 0.02 (25 °C), ΔH°/kJ mol−1 = −25 ± 0.8 and ΔS°/J mol−1 K−1 = −35 ± 3 and log KZnP = 0.63 ± 0.03 (25 °C), ΔH°/kJ mol−1 = 116 ± 3, logKHgP = 6.22 ± 0.03 (25 °C), ΔH°/kJ mol−1 = 4.5 ± 0.7 and ΔS°/J mol−1 K−1 = 34 ± 2. The distribution curve calculated from the thermodynamic parameters sufficiently agrees with the observed metal exchange reaction between the metalloporphyrins.

Introduction

Relatively inflexible non-N-substituted porphyrins make it difficult to exchange the metals of the metalloporphyrins, but a rapid metal exchange reaction is expected for N-substituted porphyrins because of their deformed structures [1]. There are a few quantitative data available for the metal exchange reactions of N-substituted metalloporphyrins [2,3]. Lavallee et al. have observed the acid demetalation of a series of metal complexes of N-methyl-tetrakis(1-methylpyridinium-4-yl)porphyrin in aqueous solutions, and have found that the complexes of mercury(II), cadmium(II), iron(II) and manganese(II) are readily demetalated at about physiological pH, and that the complexes of zinc(II), cobalt(II), nickel(II) and copper(II) are stable even at pH 5 for several hours [1]. However, we found a rapid metal exchange reaction for the zinc(II) complex of N-p-nitrobenzyl-5,10,15,20-

tetakis(4-sulfonatophenyl)porphyrin, NO2 Bz(Htpps)4−, (HP) with mercury(II) at room temperature:

\[ \text{ZnP} + \text{Hg}^{2+} \rightleftharpoons \text{HgP} + \text{Zn}^{2+} \]  

(1)

were HP denotes the free base form of NO2 Bz(Htpps)4−, and ZnP and HgP are the zinc(II) and mercury(II) porphyrins with HP, respectively. Charges of the free base porphyrin and the metalloporphyrins are omitted for simplicity. Interestingly, the metal in the mercury(II) porphyrin formed was rapidly substituted by zinc(II) again at high temperature. The metal exchange reaction was driven by temperature and thermochromism was observed.

The present paper describes the metal exchange reactions between ZnP and Hg2+ or HgP and Zn2+ in the range 10–70 °C and the determination of the thermodynamic parameters of the protonation and metalation of HP with Zn2+ and Hg2+. The spectral change with temperature is discussed as a function of the change in the distribution of the chemical species at different temperatures.

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Experimental

Reagents

N-p-Nitrobenzyl-5,10,15,20-tetakis(4-sulfonato-phenyl)porphyrin was synthesized by the method of Lavallee et al. [4] and purified with Sephadex LH-20 resin. The purity was checked by $^1$H NMR and absorption spectra. The yield was 10%. Sodium nitrate used for adjusting the ionic strength was purified by recrystallization of analytical grade sodium nitrate. Other zinc(II) and mercury(II) nitrates were of analytical grade and were used without further purification. The concentrations of metal ions (Zn$^{2+}$ and Hg$^{2+}$) in the stock solutions were determined by titration with N,N'-1,2-ethanediylbis[N-(carboxymethyl)glycine]-H$_2$edta). The buffer solutions were prepared by addition of nitric acid or sodium hydroxide to solutions of sodium acetate for pH 4 to 6, MES-[2-N-morpholinoethanesulfonic acid] for pH 6 to 7, EPPS [3-{4-(2-hydroxyethyl)-1-piperazinyl}propanesulfonic acid] for pH 7 to 8.5, and sodium borate for pH 8.5 to 10 (Wako Pure Chemical Industries, Osaka, Japan). All solutions were prepared in water that had been distilled, deionized and redistilled from alkaline permanganate solutions.

Apparatus

Absorption spectra were recorded on a Shimazu UV-2100 spectrophotometer. The temperature was controlled by a Neslab RTE-100 thermostat and the temperature of the sample solutions in a cuvette was directly measured by a needle-type thermistor. The pH values were determined by a Radiometer Ion 85 Ion Analyzer with a combined electrode (GK2401C). A 1.000×10$^{-2}$ mol dm$^{-3}$ nitric acid solution containing 0.09 mol dm$^{-3}$ sodium nitrate was employed as the standard hydrogen ion concentration ($-\log[H^+] = 2.000$). From the pH-meter readings in various hydrogen ion concentrations, the pH-meter and electrode system were calibrated in terms of $-\log[H^+]$ at an ionic strength of 0.1 mol dm$^{-3}$ (HNO$_3$–NaNO$_3$).
Results

Effect of temperature on the metal exchange reaction between ZnP and HgP

The solution containing the N-substituted porphyrin (1.99×10⁻⁶ mol dm⁻³), Zn²⁺ (0.996×10⁻⁴ mol dm⁻³), and Hg²⁺ (0.974×10⁻⁵ mol dm⁻³) was controlled in a range 10 to 70 °C, and the absorption spectrum was measured at pH 5.03 and I = 0.1 (NaNO₃). The absorption maxima were observed at 450 and 436 nm in acidic and alkaline solutions, respectively. The relationship between the apparent molar absorptivities (ε) of NO₂Bz(Htpps)⁺⁻ at 450 and 436 nm and -log([H⁺]/mol dm⁻³) is shown in Fig. 3. The change in ε is attributable to the following equilibria

\[ \text{HP} + \text{H}^+ \rightleftharpoons \text{H}_2\text{P} \]  \hspace{1cm} (2)
\[ \text{H}_2\text{P} + \text{H}^+ \rightleftharpoons \text{H}_3\text{P} \]  \hspace{1cm} (3)

The protonation constants of NO₂Bz(Htpps)⁺⁻ were determined at various pHs (1 to 9.5), different temperatures (10, 15, 20, 25, 30 °C) and I = 0.1 (NaNO₃). Absorption maxima were observed at 450 and 436 nm in acidic and alkaline solutions, respectively. The relationship between the apparent molar absorptivities (ε) of NO₂Bz(Htpps)⁺⁻ at 450 and 436 nm and -log([H⁺]/mol dm⁻³) is shown in Fig. 3. The change in ε is attributable to the following equilibria

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Protonation constants of NO₂Bz(Htpps)⁺⁻

The protonation constants of the N-substituted porphyrin were determined at various pHs (1 to 9.5), different temperatures (10, 15, 20, 25, 30 °C) and I = 0.1 (NaNO₃). The absorption maxima were observed at 450 and 436 nm in acidic and alkaline solutions, respectively. The relationship between the apparent molar absorptivities (ε) of NO₂Bz(Htpps)⁺⁻ at 450 and 436 nm and -log([H⁺]/mol dm⁻³) is shown in Fig. 3. The change in ε is attributable to the following equilibria

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Fig. 3. Typical apparent molar absorptivities (ε) at different pHs and temperature 10 (□), 20 (●) and 30 (○) °C for the determination of the protonation constants of NO₂Bz(Htpps)⁺⁻ at [NO₂Bz(Htpps)⁺⁻]₀ = 1.99×10⁻⁶ mol dm⁻³ and I = 0.1 (NaNO₃). The solid lines are calculated using the determined log $K_2$ and log $K_3$ values.
where the charges of the protonated porphyrins are omitted. The protonation constants of eqs (2) and (3) are defined as $K_2 = [H_2P][HP]^{-1}[H^+]^{-1}$ and $K_3 = [H_2P][H_2P]^{-1}[H^+]^{-1}$. The apparent molar absorptivity is given by eq. (4)

$$
\bar{\varepsilon} = \frac{\varepsilon_1 + \varepsilon_2[H^+]K_2 + \varepsilon_3[H^+]^2K_2K_3}{1 + [H^+]K_2 + [H^+]^2K_2K_3}
$$

where $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$ are the molar absorptivities of HP, H$_2$P and H$_3$P, respectively. The apparent molar absorptivity is plotted against $-\log[H^+]$ in Fig. 3. The values of log $K_2$ and log $K_3$ were determined to be 7.75 ± 0.02 and 2.55 ± 0.02 at 25 °C, respectively. The enthalpies and entropies of eqs (2) and (3) were $\Delta H^0/[kJ\cdot mol^{-1}] = -21.2 ± 0.5$; $\Delta S^0/J\cdot mol^{-1} = 77 ± 1$ for log $K_2$ and $\Delta H^0/[kJ\cdot mol^{-1}] = -25.0 ± 0.8$; $\Delta S^0/J\cdot mol^{-1} = -35 ± 3$ for log $K_3$.

**Formation constants of Zn(NO$_2$Bzttps)$^{3-}$**

As shown in Fig. 2a, the Zn(NO$_2$Bzttps)$^{3-}$ forms at higher temperature. The formation constant was determined at various concentrations of Zn$^{2+}$ (2.0×10$^{-5}$ to 5.0×10$^{-3}$ mol dm$^{-3}$) and at pH 5 and $I = 0.10$ (NaNO$_3$). The formation constant of Zn(NO$_2$Bzttps)$^{3-}$ is defined as $K_{ZnP} = [ZnP][H^+]^{-1}[Zn^{2+}]^{-1}[HP]^{-1}$. Since NO$_2$Bz(Https)$^{4-}$ exists in a monoprotonated form, H$_2$P, at pH 5, the equilibrium between Zn$^{2+}$ and H$_2$P and the apparent molar absorptivity, $\bar{\varepsilon}$, are given as follows

$$
Zn^{2+} + H_2P \rightleftharpoons ZnP + 2H^+
$$

(5)

and

$$
\bar{\varepsilon} = \frac{\varepsilon_2[H_2P]^2 + \varepsilon_{ZnP}[ZnP]}{[H_2P]^2 + [ZnP]}
$$

(6)

$$
\bar{\varepsilon} = \frac{\varepsilon_2 + \varepsilon_{ZnP}K_2^{-1}K_{ZnP}[ZnP]^2[H^+]^{-2}}{1 + K_2^{-1}K_{ZnP}[ZnP]^2[H^+]^{-2}}
$$

(7)

where $\varepsilon_{ZnP}$ is molar absorptivity. The absorbance of 434 nm was measured at various concentrations of zinc(II), and the left-hand side of eq. (7) is plotted against the concentration of zinc(II) in Fig. 4. The value of $K_{ZnP}$ was determined by a non-linear least squares minimization program and was found to be 0.63 ± 0.03 and $\Delta H^0/[kJ\cdot mol^{-1}] = 31.0 ± 0.8$; $\Delta S^0/[J\cdot mol^{-1} \cdot K^{-1}] = 116 ± 3$. The positive enthalpy value of ZnP suggests the increase of the formation of ZnP at higher temperature.

**Discussion**

The log $K_2$ values for N-substituted porphyrins are generally larger than for non-N-substituted porphyrins. The values are 7.76 for NO$_2$Bz(Https)$^{4-}$, 8.82 for N-methyl-tetrakis(4-sulfonatophenyl)porphyrin(Me(Https)$^{4-}$) [5] 9.93 for N-phenyl-tetrakis(4-sulfonatophenyl)porphyrin (Ph(Https)$^{4-}$) [6] and 4.99 for tetrakis(4-sulfonatophenyl)porphyrin (H$_2$ttps$^{4+}$) [8]. N-substituted porphyrins are relatively deformed and the pyrrole nitrogen atoms deviate more than 40° from the mean porphyrin plane [1]. Thus the lone pair of electrons of the pyrrole nitrogen is easily protonated. This leads to the relatively large log $K_2$ values for N-substituted porphyrins. Comparison of
the log $K_2$ value of NO$_2$Bz(Htpps)$^{4-}$ with those of Me(Htpps)$^{4+}$ and Ph(Htpps)$^{4-}$ indicates the decrease of the basicity of NO$_2$Bz(Htpps)$^{4-}$ because of the electron withdrawing property of the NO$_2$ group in NO$_2$Bz(Htpps)$^{4-}$. The small value for NO$_2$Bz(Htpps)$^{4-}$ mainly result from the small enthalpy change for log $K_2$ compared to other N-substituted porphyrins: $\Delta H^\circ/k$ mol$^{-1} = -21.2$ for NO$_2$Bz(Htpps)$^{4-}$, $-55.1$ for Me(Htpps)$^{4+}$, and $-55$ for Ph(Htpps)$^{4+}$ [5, 6].

Since the N-substituted porphyrins are highly distorted, zinc(II) in the N-substituted porphyrins is square pyramidal with a ligand molecule occupying the apical position with a long bond to the substituted nitrogen atom. Zinc(II) is not incorporated well into the porphyrin plane [8]. The formation constant of ZnP is smaller by a factor of 6 than that HgP, and the enthalpy of ZnP has a large positive value compared to HgP (see Table I). The formation constant of ZnP increases with increasing temperature. On the other hand, the enthalpy of HgP has a small value. The data indicate that ZnP forms at higher temperature, whereas HgP forms at lower temperature. In the case of macrocyclic amines, like cyclam, the zinc(II) complexes have large negative enthalpy values [9]. The large positive enthalpy value of ZnP could be attributed to the deformed structure of the metalloporphyrin and the electron withdrawing property of the NO$_2$ group. The large entropy value also suggests the ruffled and deformed structure of ZnP and HgP.

The large positive enthalpy value of ZnP compared to HgP can be explained qualitatively by the temperature dependent change in absorbance. We have determined the distribution curve of the chemical species of ZnP and HgP as a function of temperature to confirm quantitatively the thermochromism. The calculation has taken into account the temperature dependence of the protonation constants of HP, the formation constants of ZnP and HgP, and the hydrolysis constant of mercury(II) at various temperatures in the range 10 to 70 °C. The enthalpy and entropy values of the hydrolysis of mercury(II) are 42.2 kJ mol$^{-1}$ and 19 J mol$^{-1}$ K$^{-1}$ at $I = 3.0$, respectively, for the reaction of Hg$^{2+} + 2$H$_2$O $\rightleftharpoons$ Hg(OH)$_2$ + 2H$^+$. The formation of Hg(OH)$^+$ is negligible at pH 5. The pH values were also measured at the various temperatures. Fig. 5 shows the calculated distribution curve of HgP and ZnP at pH 5.0 and [Hg$^{2+}$]$_0$ = $1.0 \times 10^{-4}$ mol dm$^{-3}$ and [Zn$^{2+}$]$_0$ = $1.0 \times 10^{-5}$ mol dm$^{-3}$. The main chemical species are HgP at lower temperature and ZnP at higher temperature, and a small quantity (less than 10%) of the monoprotonated form of the free base porphyrin (HP) exists at lower temperature. The distribution curves is explained well by the thermochromism of the metal exchange reaction between ZnP and HgP in the range 10 to 70 °C.

The present paper, for the first time, shows a rapid metal exchange reaction of zinc(II) porphyrin with mercury(II) and a thermochromism resulting form the equilibrium shift between zinc(II)
and mercury(II) metalloporphyrins by the temperature change. The thermodynamic parameters of the chemical species involved in the reaction can sufficiently explain the temperature dependent change in absorbance. A metal separation study of zinc(II) and mercury(II) using the temperature dependence of the metal exchange reaction is also in progress in our laboratory, and the analytical application will be reported elsewhere.

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