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Partition Coefficient of 21*H*,23*H*-Porphine and Its Metal(II) Complexes between Heptane and Nonaqueous Polar Solvents

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Synopsis. The partition coefficients of 21*H*,23*H*-porphine (H_2por) and its copper(II) (Cu(por)) and zinc(II) (Zn(por)) complexes were determined in nonaqueous two-phase systems. A linear free-energy relationship was observed between the partition coefficients of H_2por and Cu(por). The partition coefficient of Zn(por) was suppressed by coordination bonding with the polar solvent molecules.

Porphyrin and its related compounds are important substances in biochemistry and geochemistry. Porphyrin and metal-porphyrin compounds occur extensively in nature as well-known chlorophylls, hemoglobins, and petroporphyrins, which usually contain magnesium, iron, vanadium, and nickel as central metals. In relation to chemical separation and natural migration of these porphyrin compounds, a systematic study on the solution behavior of porphyrins, and their metal complexes is desirable. However, little is known about the solubility and the liquid–liquid partition of these porphyrin compounds. The liquid–liquid partition coefficient is an important equilibrium constant which governs the behavior of organic substances and metal complexes in both solvent extraction and liquid chromatography.

In previous work[1)] we prepared a mother compound of porphyrins, 21*H*,23*H*-porphine, and investigated the liquid–liquid partition behavior between various nonpolar organic solvents and an acidic aqueous solution. In the present work we determine the liquid–liquid partition coefficients of 21*H*,23*H*-porphine (H_2por) and its copper(II) (Cu(por)) and zinc(II) (Zn(por)) complexes in a nonaqueous partition system, i.e., heptane as a nonpolar solvent and acetonitrile (AN), nitromethane (NM), dimethyl sulfoxide (DMSO), and methanol (MeOH) as polar solvents. The solvent effect and role of the central metals in the partition coefficient is discussed.

Experimental

Materials. 21*H*,23*H*-Porphine was synthesized and purified in the same manner as that described previously.[1)] Porphinatocopper(II) was synthesized by refluxing 0.014 mmol of purified 21*H*,23*H*-porphine and 0.042 mmol of bis(acetylacetonato)copper(II) in chloroform (200 cm^3) for 270 min. The chloroform solution obtained was passed through an alumina column (Merck, 200—400 mesh). The porphinatocopper(II) was eluted with chloroform and recrystallized from chloroform–methanol.

Porphinatozinc(II) was synthesized by mixing 0.014 mmol of purified 21*H*,23*H*-porphine in chloroform (50 cm^3) with 0.10 mmol of anhydrous zinc(II) acetate in methanol (20 cm^3) and heating for 45 min at 60 °C. The porphinatozinc(II) was purified in a similar manner as that for the copper(II) complex.

Table 1. Wavelength(nm) Used for the Absorbance Measurement of Porphine and Its Copper(II) and Zinc(II) Complex

Solvent	H_2por		Cu(por)	Zn(por)	
	$\lambda_{\max}^{a)}$	$\lambda_{\max}^{b)}$	$\lambda_{\max}^{a)}$	$\lambda_{\max}^{a)}$	$\lambda_{\max}^{b)}$
Heptane	391.5		389.5		
AN	389.5	486.3	387.8	396.9	529.6
NM	391.3	487.3	389.4	396.2	526.2
DMSO	393.9	488.4	392.1	404.0	533.6
MeOH	388.8	486.4	388.2	397.4	530.3

a) Soret band. b) Q band.

The purity of the metal complexes synthesized was ascertained by high-performance liquid chromatography (column, LiChrosorb RP-18, 250 mm×4 mm (i.d.); mobile phase, acetonitrile: acetone=70:30; detection wavelength, 388 nm for the copper(II) complex and 397 nm for the zinc(II) complex). Each metal complex gave a single peak on the chromatogram.

Heptane and polar organic solvents such as acetonitrile, nitromethane, dimethyl sulfoxide, and methanol were purified by fractional distillation after appropriate chemical treatment and dehydration.[2)]

Procedure. Heptane and a polar organic solvent were presaturated with each other before use. A certain volume of the solution of porphine, or its metal(II) complex, was shaken with the other phase for 5—60 min and centrifuged. The partition coefficient, *P*, which is defined as the ratio of the concentration in the heptane phase to that in the polar phase, was determined from the absorbance of the initially prepared phase and the equilibrated phase.

The wavelengths used for the absorbance measurements in different solvents are shown in Table 1.

The quartz cuvette and such glasswares as extraction vials, volumetric flasks, and pipettes were treated with dimethyldichlorosilane prior to use in order to prevent the adsorption of porphine and its metal(II) complexes onto the wall. All of the experiments were carried out in a thermostated room at 25 °C.

Results and Discussion

Partition equilibrium was completely attained within 5 min. A constant partition coefficient was obtained within the experimental error when the porphine concentration was altered in the concentration range 10^{-6} to 10^{-5} M (1 M=1 mol dm^{-3}). This demonstrates that a single species of porphine is present in both the heptane and polar phases under the experimental conditions. Measurements of the partition coefficient of porphinatocopper(II) and porphinatozinc(II) were also performed in a similar manner as that for porphine. The mean values and the standard deviations of the obtained partition coefficients are summarized in Table 2.

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Table 2. Partition Coefficients[a] of Porphine and Its Copper(II) and Zinc(II) Complex between Heptane and a Polar Solvent at 25 °C

Polar solvent	H_2por	Cu(por)	Zn(por)
AN	$(1.01\pm0.04)\times10^{-1}$	$(2.65\pm0.08)\times10^{-1}$	$(2.23\pm0.02)\times10^{-2}$
NM	$(5.54\pm0.20)\times10^{-2}$	$(1.38\pm0.03)\times10^{-1}$	$(4.74\pm0.12)\times10^{-2}$
DMSO	$(3.06\pm0.42)\times10^{-3}$	$(6.46\pm0.12)\times10^{-3}$	$(5.17\pm0.31)\times10^{-5}$
MeOH	$(2.65\pm0.20)\times10^{-1}$	$(7.04\pm0.12)\times10^{-1}$	$(9.11\pm0.23)\times10^{-2}$

a) Mean value±standard deviation.

The Gibbs free energy for the partition of a solute (denoted by the subscript 2) from a polar solvent to heptane is represented by the difference in the Gibbs free energy ($\Delta\overline{G}_s$) for the dissolution of the solute in both phases,

$$-RT\ln P_2=\Delta\overline{G}_{s,n}-\Delta\overline{G}_{s,p}, \tag{1}$$

where subscripts p and n denote the polar and nonpolar solvent, respectively. The dissolution process can be divided into two steps: the formation of a cavity to accommodate the solute molecule in the solvent, followed by an interaction of the surrounding solvent molecules with the solute introduced into the cavity. Equation (1) can be rewritten as

$$\begin{aligned} RT\ln P_2 &= (\overline{G}_{c,p}-\overline{G}_{c,n})+(\overline{G}_{i,p}-\overline{G}_{i,n}) \\ &= \Delta\overline{G}_c+\Delta\overline{G}_i, \end{aligned} \tag{2}$$

where $\Delta\overline{G}_c$ and $\Delta\overline{G}_i$ denote the cavity-formation energy and interaction energy, respectively. The solute–solvent interaction of porphine is probably dominated by the van der Waals interaction, since a specific solute–solvent interaction is not notable for porphine with not only nonpolar solvents (such as heptane, carbon tetrachloride, and benzene), but somewhat polar hydrogen bonding solvents (such as chloroform and 1-octanol), as we pointed out previously.[1)]

By applying Eq. 2 to the partition of both porphine and its metal complex, the following relation is obtained:

$$\begin{aligned} RT\ln P_M-RT\ln P_H &= (\Delta\overline{G}_{c,M}-\Delta\overline{G}_{c,H}) \\ &\quad +(\Delta\overline{G}_{i,M}-\Delta\overline{G}_{i,H}), \end{aligned} \tag{3}$$

where subscripts H and M denote porphine and its metal complex, respectively. It would be reasonable that the molecular diameter of porphine is approximately equal to that of porphinatometal(II) and, hence, the cavity formation energy ($\Delta\overline{G}_c$) for those compounds can be considered to be equal to each other. Therefore, the following equation is given:

$$\log P_M=\log P_H+\frac{(\Delta\overline{G}_{i,M}-\Delta\overline{G}_{i,H})}{2.303\,RT}. \tag{4}$$

Plots of $\log P_M$ against $\log P_H$ for porphinatocopper(II) and porphinatozinc(II) are shown in Fig. 1. Almost

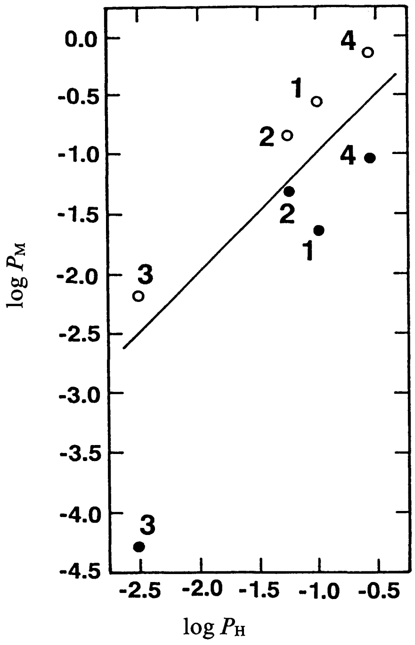

Fig. 1. Relationship between the partition coefficient of the copper(II) and zinc(II) complex and that of porphine.
○, Cu(por); ●, Zn(por).
1, heptane/acetonitrile; 2, heptane/nitromethane; 3, heptane/dimethyl sulfoxide; 4, heptane/methanol.

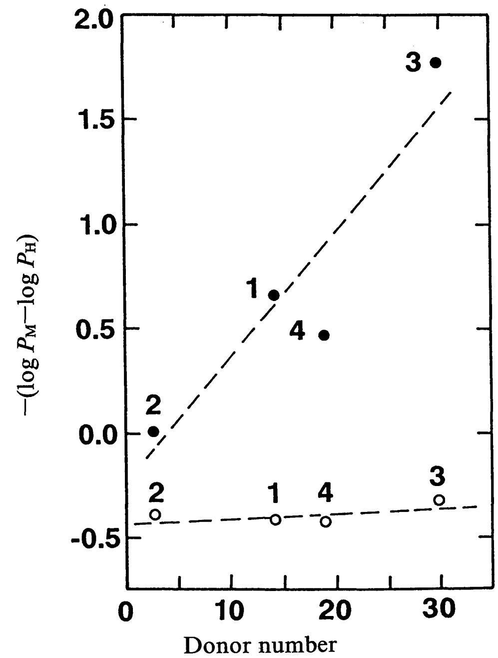

Fig. 2. Correlation between $-(\log P_M-\log P_H)$ and donor number of the solvents.
○, Cu(por); ●, Zn(por).
The numbers correspond to those in Fig. 1.

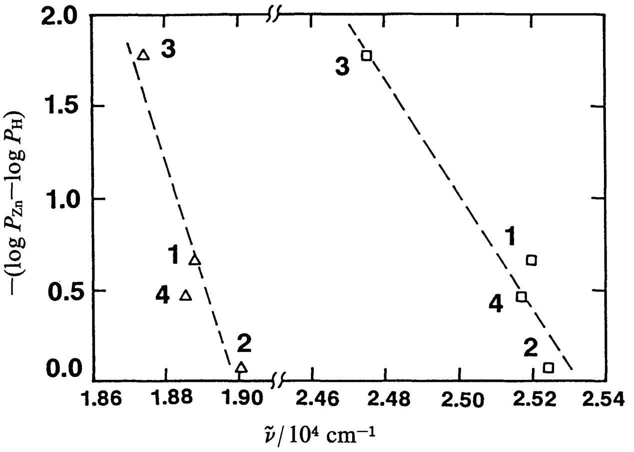

Fig. 3. Correlation between $-(\log P_{\mathrm{Zn}}-\log P_{\mathrm{H}})$ and the wavenumber at the absorption peak of Zn(por) in each polar solvent.
□, Soret band; △, Q band.
The numbers correspond to those in Fig. 1.

linear plots were observed for the copper(II) complex; they fall almost along a straight line with a slope of unity passing through the origin. The observed linear free-energy relationship (LFER) indicates that the value of the interaction term, $\Delta\overline{G}_{\mathrm{i,M}}-\Delta\overline{G}_{\mathrm{i,H}}$, in Eq. 4 should be small and nearly constant. This result means that the solute-solvent interaction for the copper(II) complex is quite similar to that for the ligand, itself. Accordingly, the central copper(II) ion in the complex can be concluded to have no specific interaction with the polar solvents used.

On the other hand, the plot of the zinc(II) complex is located in a region lower than the solid line, except for the nitromethane system. Additionally, the degree of deviation from the solid line is very different for each polar solvent; LFER is not observed. This means that the interaction term, $\Delta\overline{G}_{\mathrm{i,M}}-\Delta\overline{G}_{\mathrm{i,H}}$, in Eq. 4 has negative values and is fairly different with the polar solvents used.

Figure 2 shows the correlation between $-(\log P_{\mathrm{M}}-\log P_{\mathrm{H}})$ and the donor number of the polar solvents, which is a measure of the coordination efficiency of solvent molecules. The value of $-(\log P_{\mathrm{M}}-\log P_{\mathrm{H}})$, corresponding to the interaction term in Eq. 4, for the zinc(II) complex increases with an increase in the donor number; that for the copper(II) complex, however, is nearly constant. This result suggests that the partition coefficient of the zinc(II) complex is strongly influenced by specific interactions, such as the coordination bond with the polar solvents.

In studies of the solvent effect on the absorption spectrum of tetraphenylporphinatozinc(II),[3-6] the red shift of the absorption peak at the Soret and Q bands has been reported and ascribed to the axial coordination of solvent molecules to the central metal in the zinc(II) complex. Figure 3 shows plots of $-(\log P_{\mathrm{Zn}}-\log P_{\mathrm{H}})$ against the wavenumber $\tilde{\nu}$ at the absorption peak of porphinatozinc(II) (Table 1). A good correlation is observed; the absorption peak is shifted to the lower energy region as the interaction term for the zinc(II) complex becomes larger. Therefore, the specific interaction of porphinatozinc(II) with the polar organic solvents should be attributed to the axial coordination of the solvent molecules to the central metal in the zinc(II) complex.

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