Specific Adsorption of Metal Complexes of Tetraphenylporphyrin at Dodecane-Water Interface

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Interfacial adsorption of the metal complexes of tetraphenylporphyrin (TPP) was found out in the dodecane-water system by a high-speed stirring method. Among metalloporphyrins of five metals examined, ZnTPP and VOTPP showed appreciable adsorptivity at dodecane-water interface and adsorption constants were determined by applying Langmuir isotherm. The interfacial adsorptivity of complexes decreased in the order, ZnTPP > VOTPP > CoTPP, NiTPP, CuTPP.

The investigation of the adsorption behavior of metalloporphyrins at the liquid-liquid interface is thought to be very important to understand the role of interface in liquid-liquid separation as well as to understand catalytic activities of porphyrin derivatives in liquid-membrane systems. Interfacial adsorptivity of a solute is usually measured by means of an interfacial tension lowering. This method, however, can not be applied for the solute which is sparingly soluble and can not offer any information about chemical species which may be adsorbed at an interface. On the contrary, a high-speed stirring method can be applied for a dilute solution provided that the concentration of the solute is measurable by spectrophotometry. Furthermore, the chemical species responsible for the adsorption can also be determined.[1] The metal complexes of tetraphenylporphyrin (TPP) are especially well suited for spectrophotometric studies, because they have large molar absorptivity at Soret band. Since the metalloporphyrins derived from TPP are highly hydrophobic, the dissolution into aqueous phase could be neglected. In this work, the adsorption behavior of several metal complexes of TPP as a model compound of biological porphyrin derivatives from a bulk dodecane phase to dodecane-water interface was evaluated by employing the high-speed stirring method.

The complexes of cobalt(II), nickel(II), copper(II) and zinc(II) were prepared from 5,10,15,20-tetraphenylporphyrin (Dojindo Laboratories) and the corresponding metal acetate by the method available in literature.[2] 5,10,15,20-Tetraphenylporphyrinato vanadyl(IV) (VOTPP) was obtained from Wako Chemicals. Dodecane, nacalai tesque G.R., was purified by distillation after being washed with a mixture of fuming sulfuric acid and sulfuric acid and used as an organic solvent. The aqueous phase was a distilled and deionized water purified by the use of Milli-Q SP.TOC.(Millipore).

The interfacial adsorption of metalloporphyrins in the dispersed liquid-liquid system was observed by using the high-speed stirring apparatus. 5.0×10^{-2} dm^3 of dodecane phase containing a metalloporphyrin and the same volume of aqueous phase were put into the stirring cell thermostated at 298±1 K. The extent of dispersion of the liquid-liquid system was controlled by changing the rotation rate of the stirrer made up of polychlorotrifluoroethylene resin (PCTFE), with a motor speed controller, from 200 rpm to 5000 rpm. The high-speed stirring (5000 rpm) produced an emulsion state, while in the low-speed stirring (200 rpm) the emulsion was promptly separated to the clear phase. The absorption spectrum of an organic phase, that was continuously separated from the dispersed liquid-liquid system by means of a Teflon® phase separator and circulated through a flow cell, was measured by photodiode array UV/VIS detector (Simadzu, SPD-M6A). Thus, we could determine the amount of interfacial complex by evaluating the difference between the absorbances of the bulk organic phase under a high-speed stirring (5000 rpm) and a low-speed stirring (200 rpm) at the absorption maximum wavelength.

The adsorption isotherms could be measured from the high-speed stirring experiments that were conducted with various concentrations of metalloporphyrins. In the present system, Langmuir isotherm was given by[3]

$$[\mathrm{MP}]_i = \frac{aK'[\mathrm{MP}]_o}{a + K'[\mathrm{MP}]_o} \qquad (1)$$

where $[\mathrm{MP}]_i$ and $[\mathrm{MP}]_o$ denote the concentrations of matalloporphyrin adsorbed at the liquid-liquid interface (mol dm^{-2}) and in the bulk organic phase (mol dm^{-3}), respectively. a is the saturated interfacial concentration (mol dm^{-2}) and K' is the interfacial adsorption constant (dm) defined under the condition of $a \gg [\mathrm{MP}]_i$,

$$K' = \frac{[\mathrm{MP}]_i}{[\mathrm{MP}]_o} \qquad (2)$$

The difference between the absorbances of the bulk organic phase under high-speed stirring and low-speed stirring, ΔA and the absorbance of the bulk organic phase under stirring, A_o can be described as follows

$$\Delta A = \varepsilon l\,[\mathrm{MP}]_i\,S_i/V_o \qquad (3)$$

$$A_o = \varepsilon l\,[\mathrm{MP}]_o \qquad (4)$$

where ε, l, S_i and V_o are the molar absorptivity in dodecane, the optical path length, the total interfacial area and the organic phase volume, respectively. The total interfacial area, S_i, in the dodecane-water system was evaluated from individual high-speed stirring experiments and interfacial tension measurements for 2-hydroxy-5-nonyl-benzophenone oxime (LIX65N). The interfacial adsorptivity of β-hydroxyl oximes in the other solvent systems have been investigated by Watarai *et al.*[3] The adsorption isotherm of LIX65N at 298±1 K was measured by the same apparatus used for the experiment of metalloporphyrins. The interfacial tension measurements were carried out in the dodecane-water system by employing a drop volume method at 298±0.1 K. In both measurements, the aqueous phase was perchloric acid solution of 1.0×10^{-3} mol dm^{-3} and the ionic strength was maintained at 0.10 by sodium perchlorate. The analysis of interfacial tension with Gibbs adsorption isotherm gave a as 2.0×10^{-8} mol dm^{-2}. From the values of $\varepsilon = 3.91\times10^3$ dm^3 mol^{-1} cm^{-1} at 320.8 nm of LIX65N in dodecane, S_i and K' were determined as 1.9×10^2 dm^2 and

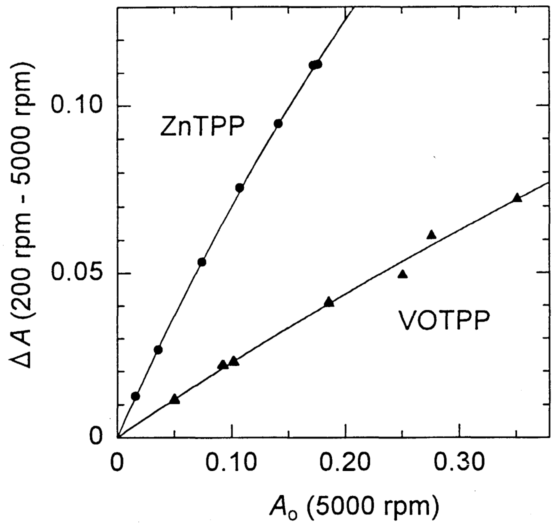

Figure 1. The adsorption isotherms at 298 K of metal complexes of TPP. The closed circle and triangle denote ZnTPP and VOTPP, respectively.

1.5×10^{-4} dm, respectively.

In the high-speed stirring experiments in the dodecane-water system, ZnTPP and VOTPP showed appreciable adsorption to the interface and the other divalent metal complexes were not adsorbed. CoTPP was apparently adsorbed at the interface in the dodecane-water system, but the concentration in the bulk dodecane phase decreased gradually through the stirring experiment. We thought that the cause of the decrease of the bulk concentration was the oxidation of cobalt(II) to cobalt(III) at dodecane-water interface. In the presence of ascorbic acid of 0.10 mol dm^{-3} as a reductant, CoTPP was not adsorbed. Hence, it was suggested that the adsorption behavior of CoTPP results from the adsorption of the cationic cobalt(III) complex. The adsorption of a neutral complex such as ZnTPP at the liquid-liquid interface has been scarcely reported.

In this work, the adsorption isotherms for metalloporphyrins of zinc(II) and vanadyl(IV) were determined as shown in Figure 1. The measurements were made on the solutions ranging in concentration from 5.7×10^{-8} to 5.8×10^{-7} mol dm^{-3} for ZnTPP and from 6.7×10^{-7} to 4.6×10^{-6} mol dm^{-3} for VOTPP, respectively. Interfacial adsorption parameters obtained from the analysis of adsorption isotherms by Eqs.1-4 are summarized in Table 1. The value of K' for zinc(II) complex in the dodecane-water system is larger than vanadyl(IV) complex and LIX65N that has a relatively large value among oxime derivatives.[3] The adsorption constants for cobalt(II), nickel(II) and copper(II) complexes were estimated to be less than 10^{-6} dm from the detection limit of $\Delta A = 0.0005$. Therefore, the adsorptivity of TPP metal complexes decreased in the order, ZnTPP > VOTPP > CoTPP, NiTPP, CuTPP. The values of a were calculated as 3.3×10^{-10} mol dm^{-2} for ZnTPP and 1.5×10^{-9} mol dm^{-2} for VOTPP. They are much lower than the reported values in other reagent systems,[3] in which a typical value of a is the order of 10^{-8} mol dm^{-2}. The values determined in the present system may contain some uncertainty, because of the low solubility of TPP complexes in dodecane.

The observed interfacial adsorption behavior of metal complexes agreed with the retention behavior observed in a reversed-phase HPLC[4] and TLC.[5] The chromatographic studies suggest that the hydrophilic property decreases in the order ZnTPP > VOTPP > NiTPP > CuTPP, namely zinc(II) and vanadyl(IV) complexes are more hydrophilic as compared with nickel(II) or copper(II). The hydrophile-lipophile balance (HLB) is important to consider the interfacial adsorption mechanism, since it is thought that the adsorption of metal complexes results from the coordination of water molecule to the metal ion. Thus the more hydrophilic complex is more liable to be adsorbed at the interface. The large value of adsorption constant of ZnTPP can explain chromatographic results.

We can consider that the adsorptivity of VOTPP is due to the strong polar site (i.e. vanadyl oxygen), and in ZnTPP the geometry. Zinc ion has a small ionic radius, 73 pm, and the M-N bond length between zinc ion and nitrogen atoms of the pyrrole ring in the solid crystal state is reported as 203.6 pm by X-ray analysis.[6] The M-N bond length of ZnTPP is the longest among the divalent metal complexes investigated in this work, and the long bond length will prefer to make the axially coordinated complex like a ZnTPP(H_2O) stable. The structure of five-coordinated monoaquo complex, ZnTPP(H_2O) has been confirmed in the solid state, in which the zinc(II) ion is displaced by 20 pm from the plane of the pyrrole ring toward the coordinated water molecule.[7] Thus, it can be expected that the zinc(II) complex is adsorbed as the form of ZnTPP(H_2O).

Recently, the partial molar volumes of the divalent metal complexes of TPP in benzene were reported, which decreased in the order, NiTPP > CuTPP > ZnTPP.[8] It suggested that zinc(II) complex has the strongest interaction with the solvent molecule, and the result also supported the highest adsorptivity of zinc(II) complex observed in the present study.

Table 1. The interfacial adsorption constants at 298 K in the dodecane-water system

complex	λ_{max}/nm[a]	ε/dm^3 mol^{-1} cm^{-1} [b]	K' /dm [c]
CoTPP	408.2	2.04×10^{5}	$< 10^{-6}$
NiTPP	413.0	3.13×10^{5}	$< 10^{-6}$
CuTPP	413.8	6.50×10^{5}	$< 10^{-6}$
ZnTPP	416.6	4.98×10^{5}	2.1×10^{-4}
VOTPP	421.0	9.12×10^{4}	6.1×10^{-5}
LIX65N	320.8	3.91×10^{3}	1.5×10^{-4}

[a] The absorption maximum wavelength in dodecane. [b] The molar absorptivity at λ_{max} in dodecane. [c] The limit value of K' is evaluated from the detection limit of $\Delta A = 0.0005$.

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