Axial Hydration and Adsorption of Chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III) at the Toluene/Water Interface, Studied by External Reflection Spectrophotometry

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Interfacial adsorption of chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III), [Mn(tpp)Cl], at the interface of toluene/aqueous sodium hydrogensulfate was studied by means of an UV/vis external reflection (ER) spectroscopy and interfacial tension measurements. The s-polarized ER spectrum showed higher sensitivity than the p-polarized one at the incident angle of 70.8°. A linear correlation sililar to Beer's law was obtained between the s-polarized ER absorbance and the interfacial concentration determined from the interfacial tension. The molar ER coefficient at the maximum wavelength of 478 nm was determined as -8.41×10^5 ($\mathrm{mol^{-1}\,dm^2}$). The effect of chloride ion concentration on the ER spectra suggested that the interfacial species at toluene/0.1 mol $\mathrm{dm^{-3}}$ sodium hydrogensulfate solution (pH 1.7) was $\mathrm{Mn(tpp)(H_2O)^+{}_i}$. The interfacial adsorption could be analyzed according to the Langmuir isotherm; the equilibrium constant for the adsorption reaction of $\mathrm{Mn(tpp)Cl_o + H_2O \rightleftarrows Mn(tpp)(H_2O)^+{}_i + Cl^-}$ was determined as 59.6. Furthermore, it was suggested that chloride ions were preferentially distributing at the diffuse layer under low chloride ion concentrations.

Recently, the liquid/liquid interface has become an attractive subject in relation to the electron transfer in immiscible two-phase systems, solvent extraction kinetics of metal ions and the molecular recognition in biological membranes.[1,2] Previously, the interfacial adsorption of porphyrin and metalloporphyrin in solvent extraction systems has been investigated by means of a high-speed stirring method,[3] a centrifugal liquid membrane method[4] and a two-phase stopped-flow method.[5] In addition, for the in situ measurement of adsorbed species, some reflection spectroscopic methods have been developed. Total internal reflection (TIR) spectroscopy and total internal reflection fluorescence (TIRF) spectroscopy succeeded in obtaining the interfacial adsorption of a rhodamineB derivative and porphyrins at the liquid/liquid interfaces.[6–8] Relaxation kinetic measurements of tetra-(*N*-methylpyridyl)porphine at the toluene/water interface using TIR were also reported.[9]

Recently, Ogawa et al. demonstrated that UV/vis external reflection (ER) spectroscopy was useful for the measurement of the adsorption of protonated tetraphenylporphine at the toluene/sulfuric acid interface with a sensitivity comparable that of the TIR method.[10,11] ER spectroscopy is expected to be useful in such systems containing light absorbing solutes in the organic phase. However, the relationship between the UV/vis reflection absorbance and the interfacial concentration of the solute has not been established yet. Polarized FT-IR external reflection spectroscopy has already been reported as an excellent method to measure the orientation of the molecules in Langmuir–Blodgett films on solid substrates.[12,13] As for UV/vis ER spectrometry, the polarization technique has not been fully developed for the study of interfacial adsorption at the liquid/liquid interface.

In this paper, we report an external reflection spectroscopic study of the adsorption of manganese(III) complex of tetraphenylporphyrin ($\mathrm{H_2tpp}$) at the toluene/water interface. The manganese(III) complex of $\mathrm{H_2tpp}$ has been studied in regard to its electrochemical reaction[14,15] and catalytic behavior in epoxidation.[16] However, the adsorption behavior of this complex at the liquid/liquid interfaces is still unexplored.

The theoretical method used in the analysis of FT-IR external reflection spectra[22] cannot be applied straightforwardly to the quantitative analysis of UV/vis ER spectra of this study, because of the lack of information on the thickness and complex refractive index of the adsorbed layer. Alternatively, we have examined the relationship between the ER absorbance and the interfacial concentration determined by the interfacial tension measurement. Furthermore, the polarization ER measurements were carried out to find out the optimum conditions for the measurement with higher sensitivity. The interfacial adsorption mechanism of Mn(tpp)Cl from the toluene phase to the interface was investigated by changing the chloride ion concentration.

Experimental

Materials. Chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III) [Mn(tpp)Cl] and chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) [Fe(tpp)Cl] were obtained from Aldrich and used without purification. Toluene (GR) was purchased from nacalai tesque and purified by distillation after the treatment with concentrated sulfuric acid. The other reagents used in this work were all G.R. grade of nacalai tesque or Wako Chemicals. Aqueous solutions were prepared by using distilled and deionized water by a Milli-Q system (Millipore).

Interfacial Tension Measurements. The interfacial tension of the toluene/aqueous solution system was measured by means of a drop volume method employing a water-jacketed vessel containing toluene phase and a flat-ended glass capillary immersed in the organic phase. The capillary was connected to a micrometer syringe on a syringe pump (HARVARD 11) which could press out an aqueous phase from the capillary end into the toluene phase. The measurements were carried out at 298 ± 0.5 K. The aqueous phase contained 0.1 mol dm^{-3} sodium hydrogensulfate (pH 1.7). The concentration of Mn(tpp)Cl in toluene was changed in the range from 3.4×10^{-7} mol dm^{-3} to 1.0×10^{-5} mol dm^{-3}.

External Reflection Spectroscopy. A Jasco V-550 UV/vis spectrophotometer was used for the measurements. The optical arrangement for ER spectroscopy, which is similar to that originally reported by Ogawa et al., is schematically illustrated in Fig. 1. Both the sample cell and the reference cell in the cell compartment of the spectrometer had the same optical configuration. On both of the light-passing sides of the 20 mm glass cell, a pair of right-angle prisms was attached at the appropriate position so that the incident beam could strike the center of the interface with the incident angle of 70.8°. The upper inside surface of the cell was treated with dichlorodimethylsilane in toluene to make a flat toluene/aqueous solution interface in the cell. The incident beam was reflected in part at the interface and the reflected beam was introduced into the detector through another rectangular prism. In the measurements of polarized spectra, the source beam was polarized with a visible-wavelength sheet polarizer. As the first step for the ER spectral measurements, the reference ER spectra for the tolu-

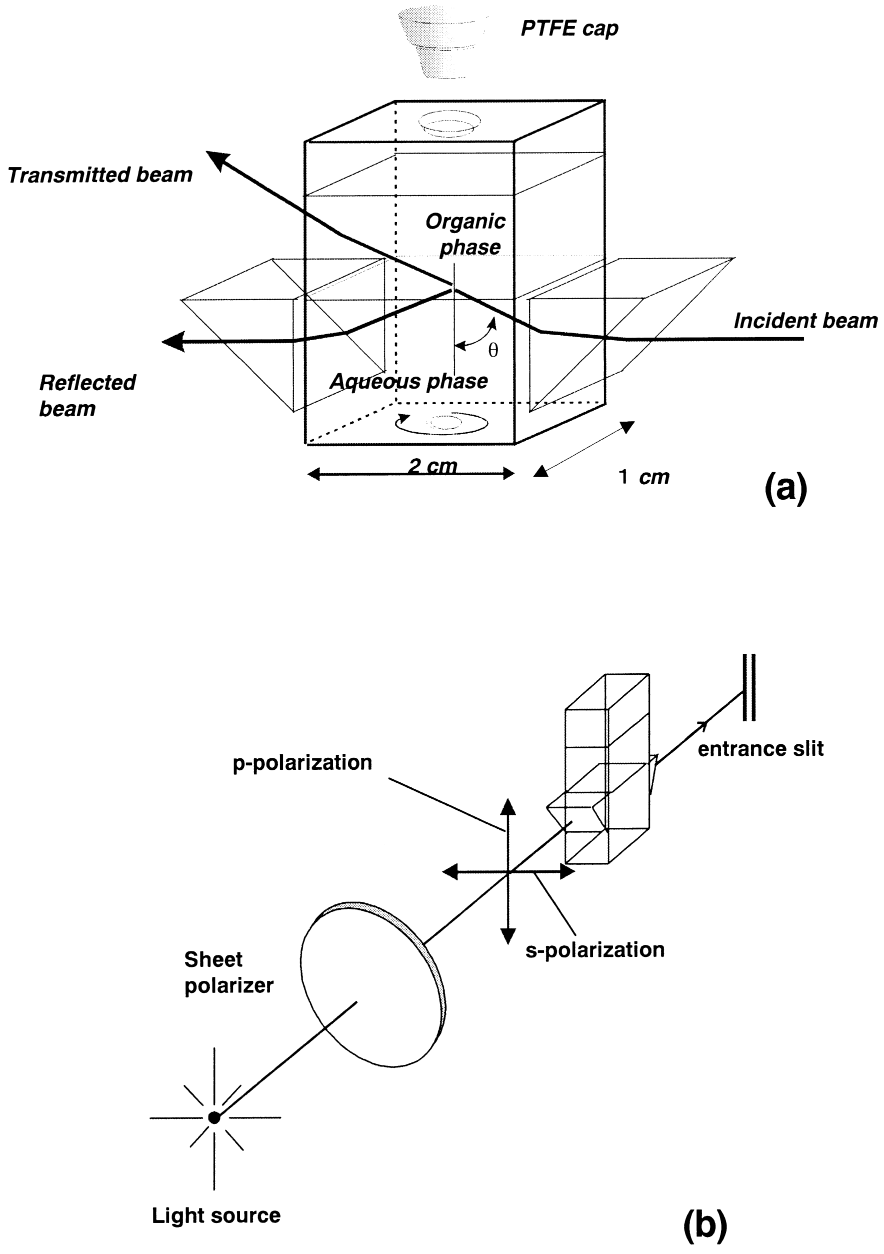

Fig. 1. Schematic drawing of the optical cell of ER spectroscopy (a) and the experimental configuration of the polarized ER measurement (b), which are similar to those reported by Ogawa et al.[10]

ene/0.1 mol dm^{-3} aqueous sodium hydrogensulfate was measured in the absence of the complex. Then, 5 to 50 μL portion of Mn(tpp)Cl solution was added stepwise to the organic phase and the ER spectra were measured after each equilibration. ER absorbance, A_{ER}, was defined as log (R_0/R), where R_0 and R are the reflectivities in the absence and presence of Mn(tpp)Cl, respectively. A thermostated cell holder kept the temperature of the sample solution in the cell at 298 ± 0.5 K.

Results and Discussion

External Reflection Spectra. The s-polarized (solid line) and p-polarized (broken line) ER spectra of Mn(tpp)Cl at toluene/water interface are shown in Fig. 2 along with a normal transmission absorption spectrum in toluene. As for the p-polarized spectrum, a weak positive and a weak negative maxima were obtained around the Soret band[23], while the s-polarized spectrum had a negative and strong absorption band. That is, for s-polarized beam, the reflected light intensity was increased at the wavelengths corresponding to the absorption maxima in the transmission absorption spectra.[17] So the shape of s-polarization spectrum was the inverted shape of the transmission spectrum in toluene. The negative absorption maxima at 387 nm and 478 nm in the ER spectra were assigned to the ligand (tpp) to metal charge transfer (LMCT) band and to the Soret band, respectively, and those at 573 nm and 605 nm to the two Q-bands.[18,19] On the other hand, chloro(tetraphenylporphyrinato)iron(III) (Fe(tpp)Cl) did not show any ER spectra at the toluene/water interface. This indicated that the chemical potential of Fe(tpp)Cl in toluene is more stable than that at the interface, or that the chloride ions coordinated to Fe(III) are not dissociated at the interface.

s-Polarized ER absorbance increased with the increase of the Mn(tpp)Cl concentration in toluene, as shown in Fig. 3a. ER spectra were clearly measured even at the low concentration of 1.0×10^{-7} mol dm^{-3} Mn(tpp)Cl. Since the negative absorption maxima did not shift with the increase of the complex concentration, intermolecular interactions among the adsorbed

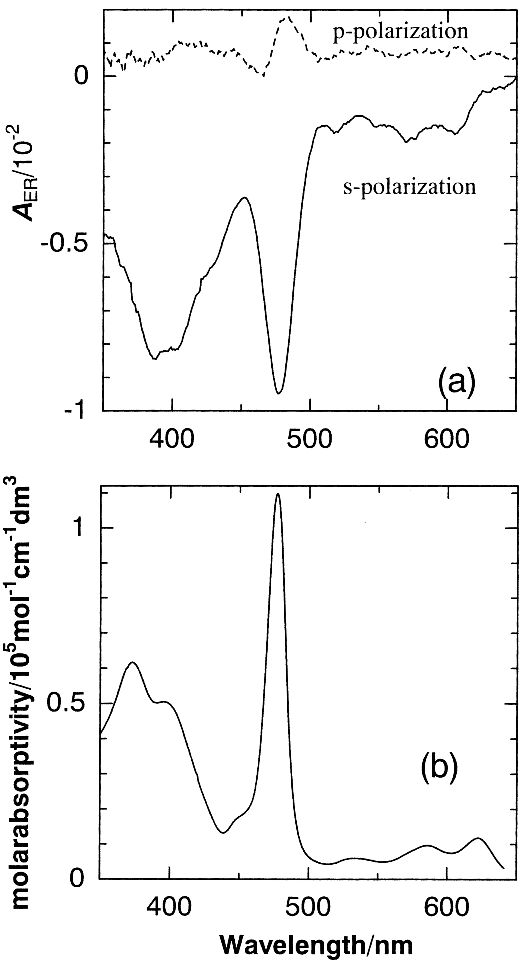

Fig. 2. (a) s-Polarized (solid line) and p-polarized (broken line) ER spectra of Mn(tpp)complex at the toluene/water interface, where the aqueous phase was 0.1 mol dm^{-3} sodium bisulfate (pH 1.7), and the toluene phase contained initially 3.1×10^{-6} mol dm^{-3} Mn(tpp)Cl. (b) A transmission absorption spectrum of Mn(tpp)Cl in toluene.

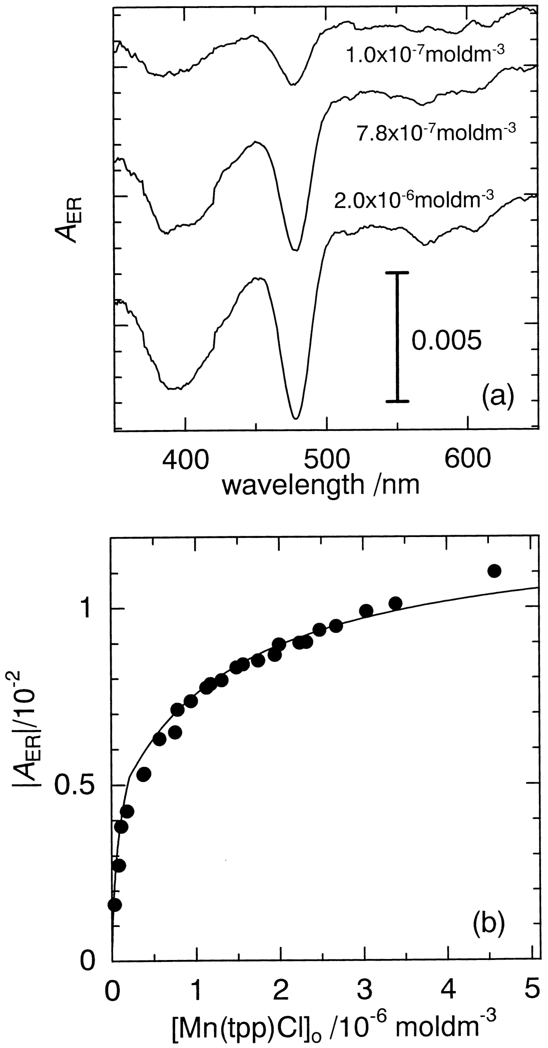

Fig. 3. (a) s-Polarized ER spectra in the three different concentration of Mn(tpp)Cl in the toluene phase. The aqueous phase was 0.1 mol dm^{-3} sodium bisulfate, (pH 1.7). (b) The adsorption isotherm measured by means of s-polarized ER spectrometry in the toluene/water system.

species could be neglected. The absolute value of s-polarized ER absorbance at the Soret band was plotted against the concentration of Mn(tpp)Cl in the toluene phase, as shown in Fig. 3b. This Figure showed a saturation curve like an adsorption isotherm.

Linear Relationship between ER Absorbance and the Interfacial Concentration. To examine the relationship between the ER absorbance and the interfacial concentration, the interfacial tension, γ (mN m^{-1}), of the toluene/sodium hydrogensulfate solution was measured as a function of the concentration of Mn(tpp)Cl as shown in Fig. 4. Gibb's Eq. 1 was used for the determination of interfacial excess, Γ (mol dm^{-2}), from the observed interfacial tensions and a fitting curve was drawn with the non-linear least squares method:

$$\Gamma = \frac{1}{2.303RT}\frac{d\gamma}{d\log[\mathrm{Mn(tpp)Cl}]_\mathrm{o}} \tag{1}$$

where R, T, and $[\mathrm{Mn(tpp)Cl}]_\mathrm{o}$ are the gas constant (8.31 N m^{-1} mol^{-1} K^{-1}), the absolute temperature (298 K) and the concentration of Mn(tpp)Cl in toluene (mol dm^{-3}), respectively.

s-Polarized ER absorbance in Fig. 3b was replotted in Fig. 5 against the interfacial concentration, $[\mathrm{Mn(tpp)}]_\mathrm{i}$, which was equal to Γ under the diluted concentration of Mn(tpp)Cl. The fitted straight line in Fig. 5 definitely indicated that a linear correlation like a form of Beer's law held between the ER absorbance, A_ER, and the interfacial concentration. Thus, we could conclude the following relationship:

$$A_\mathrm{ER} = \log\left(R_0/R\right) = f[\mathrm{Mn(tpp)}]_\mathrm{i}. \tag{2}$$

The value of the ER coefficient, f (mol^{-1} dm^2), was determined as -8.41×10^5 (mol^{-1} dm^2), which had an analogous meaning with the molar absorptivity in a normal Lambert–Beer equation. The present system might be the first case that the linear relationship was experimentally proved in the UV/vis ER spectrometry. Equation 2 provides the most important relationship in the determination of the interfacial concentration by ER spectrophotometry.

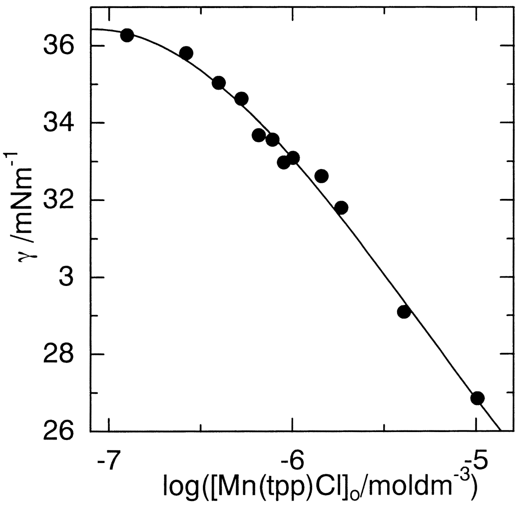

Fig. 4. The plots of interfacial tension, γ, vs logarithmic concentration of Mn(tpp)Cl in toluene at 298 K. The solid line was obtained from the non-liner least-square curve fitting for the second order polynomial equation.

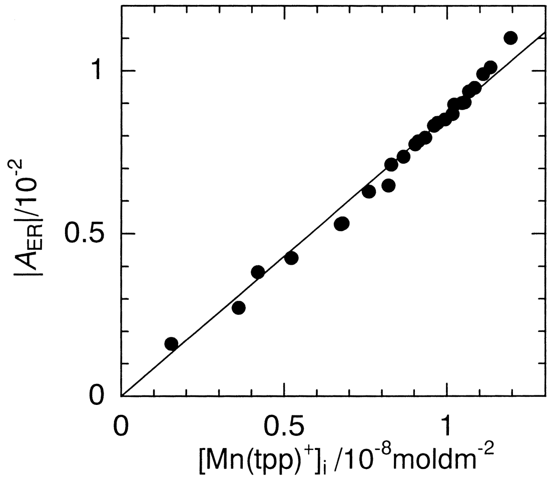

Fig. 5. Linear correlation between s-polarized ER absorbance at the Soret band (478 nm) vs the interfacial concentration calculated from Gibb's equation.

Adsorption Mechanism of Mn(tpp)Cl. We examined the effect of anions on the s-polarized ER spectra of Mn(tpp)$^+$ complex at the toluene/water interface. The ER absorbance at the Soret band was decreased with the increase of the concentration of chloride ion in the aqueous phase, as shown in Fig. 6. This result suggested that the axial ligand of chloride ion was dissociated, as Mn(tpp)Cl adsorbed at the interface. Thus, the following adsorption mechanism was postulated:

$$\mathrm{Mn(tpp)Cl_o} + \mathrm{S} \rightleftarrows \mathrm{Mn(tpp)^+}_\mathrm{i} + \mathrm{Cl^-} \tag{3}$$

where S (mol dm^{-2}) means the hypothetical interfacial concentration of the vacant adsorption site. Considering that the saturated interfacial concentration, a (mol dm^{-2}), is equal to the sum of S and $[\mathrm{Mn(tpp)}]_\mathrm{i}$, one may derive the next equation:

$$\frac{1}{[\mathrm{Mn(tpp)}^+]_\mathrm{i}} = \frac{[\mathrm{Cl}^-]}{aK[\mathrm{Mn(tpp)Cl}]_\mathrm{o}} + \frac{1}{a}, \tag{4}$$

where K is the equilibrium constant of the Eq. 3. The effect of chloride ion concentration on the adsorption of Mn(tpp)$^+$ was analyzed according to Eq. 4. The interfacial concentration of Mn(tpp)$^+$ was determined from the s-polarized ER absorbance. The straight line shown in Fig. 7 confirmed that the adsorption of Mn(tpp) could be represented by the Langmuir type equation of Eq. 4. The values of a and K were obtained as 1.46×10^{-8} mol dm^{-2} and 59.6 ± 5.9, respectively. The area per molecule was calculated as 1.14 nm^2 from the saturated interfacial concentration. This value was smaller than the area of 1.9 nm^2 estimated by MM2, suggesting that the porphyrin ring is somewhat tilted at the interface. For the determination of the averaged tilt angle of the porphyrin, further ER measurements with various incident angles are required.

When 0.1 mol dm^{-3} $\mathrm{HNO_3}$ or $\mathrm{HClO_4}$ solution was used as the aqueous phase (pH = 1.0), ER spectra could not be observed at all, indicating no adsorption of the complex in these anion systems. Furthermore, the transmission spectra of toluene phase measured after treatment with 0.1 mol dm^{-3} $\mathrm{HNO_3}$

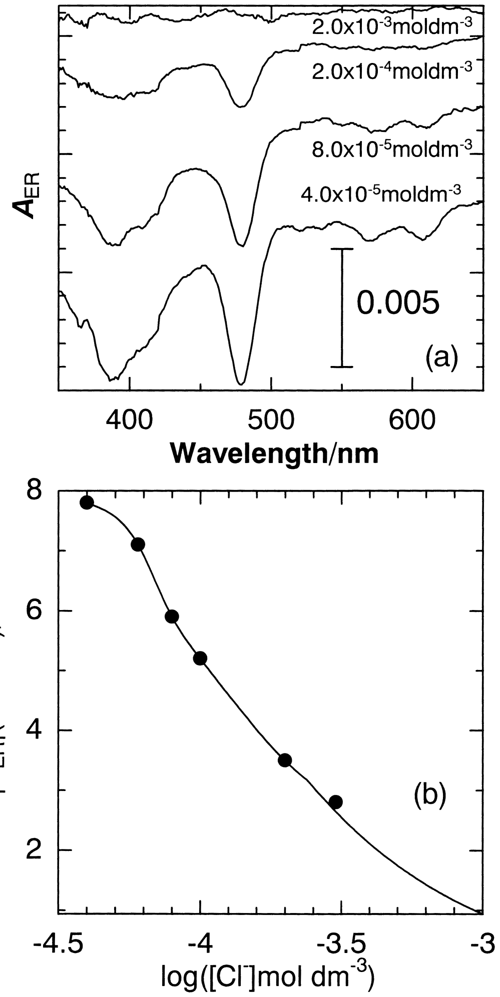

Fig. 6. Chloride ion concentration dependence of s-polarization ER spectra (a) and the ER absorbance change at the Soret band (478 nm) (b). The aqueous phase was 0.1 mol dm^{-3} sodium bisulfate, pH 1.7, and the toluene phase contained initially 1.4×10^{-6} mol dm^{-3} Mn(tpp)Cl.

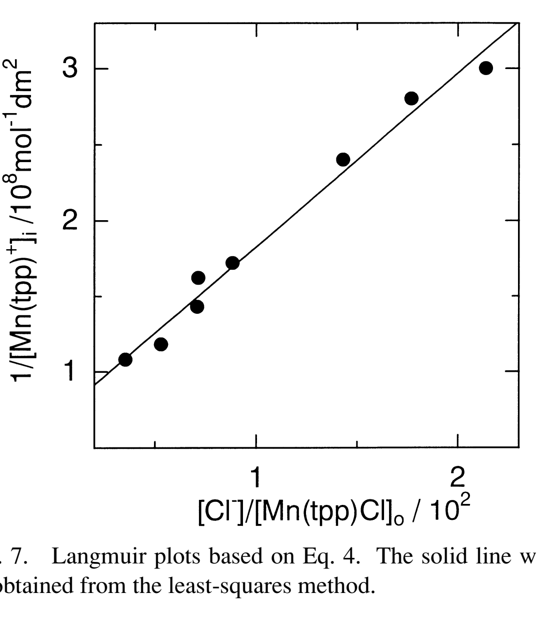

Fig. 7. Langmuir plots based on Eq. 4. The solid line was obtained from the least-squares method.

or $HClO_4$ solution could be assigned to those of $Mn(tpp)(NO_3)$[19,24] or $Mn(tpp)(ClO_4)$,[24] respectively. On the other hand, ER spectra could be measured at the interface of toluene/0.1 mol dm^{-3} H_2SO_4 ($pH \ll 1.0$) as almost the same as those at the toluene/0.1 mol dm^{-3} $NaHSO_4$ interface. From these results, we concluded that the highly hydrated anions of SO_4^{2-} and HSO_4^- did not coordinate to the axial position of $Mn(tpp)^+$ and the less hydrated anions of Cl^-, NO_3^- and ClO_4^- could be extracted into toluene phase with $Mn(tpp)^+$ by the axial coordination or ion pairing.

The maximum wavelengths of LMCT bands in the ER spectra were slightly red-shifted in comparison with those in the transmission spectra in toluene (Fig. 2b). This is not due to the interaction between Mn(tpp) complexes at the interface, because the red shift of LMCT band was observed at a sufficiently low concentration (Fig. 3). The shift in the LMCT bands of $Mn^{III}(tpp)$ complex have been correlated to the hardness of an axial anion.[19,20] According to the reports,[19,20] the wavelengths of the LMCT bands of $Mn^{III}(tpp)$ tends to become shorter with increasing of the hardness of the axial anion. For example, in the case of halogen anions, the maximum wavelength became shorter in the order of I^-, Br^-, Cl^- and F^-. In the present system, the only ligand which could coordinate to $Mn(tpp)^+$ and which was softer than chloride ion was molecular water. Furthermore, the ER spectra were different from the transmission spectra of sulfate or hydrogensulfate coordinated complex.[25] Hence, the interfacial species was thought to be the hydrated complex, $Mn(tpp)(H_2O)^+$. Therefore, the adsorption reaction of Eq. 3 can be written as

$$Mn(tpp)Cl_o + H_2O + S \rightleftarrows Mn(tpp)(H_2O)^+{}_i + Cl^-. \quad (5)$$

Chloride Ion Concentration at the Interfacial Region. We analyzed the effect of axial hydration of Eq. 5 in the systems with no addition of sodium chloride. When the concentration of $Mn(tpp)Cl_o$ was changed in the system, the amount of chloride ion in the aqueous phase can be assumed to be equal to the interfacial amount of $Mn(tpp)(H_2O)^+$. That is, the chloride ion concentration is expressed by the following equation, provided that the chloride ion is dissolved homogeneously in the aqueous phase,

$$[Cl^-] = S_i[Mn(tpp)(H_2O)^+] \big/ V_a \quad (6)$$

where S_i and V_a means the interfacial area (0.02 dm^{-2}, the cross section area of the optical cell) and the volume of the aqueous phase (0.003 dm^{-3}), respectively. On the other hand, the chloride ion concentration in the interfacial region is expressed by the Langmuir type equation of Eq. 4, which was obtained from the effect of chloride ion concentration on the adsorption of $Mn(tpp)(H_2O)^+$,

$$[Cl^-] = \frac{K[Mn(tpp)Cl]_o(a - [Mn(tpp)(H_2O)^+])}{[Mn(tpp)(H_2O)^+]}. \quad (7)$$

The chloride ion concentrations calculated with Eqs. 6 and 7 were plotted as a function of the interfacial concentration of $Mn(tpp)(H_2O)^+$, as shown in Fig. 8. This figure shows that $[Cl^-]$ calculated with Eq. 7 is larger than the one calculated with Eq. 6. This means that $[Cl^-]$ at the vicinity of interface is

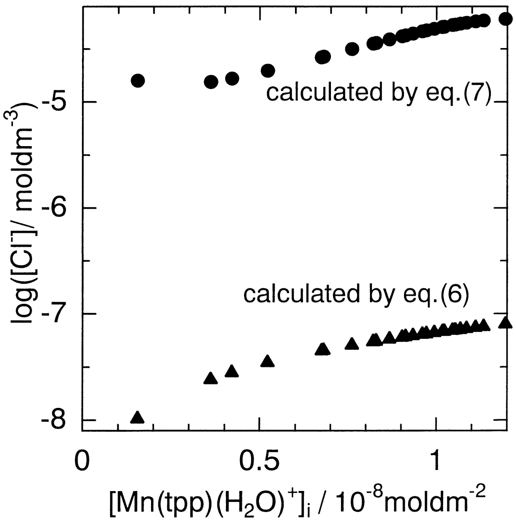

Fig. 8. Calculated logarithmic [Cl^-] plotted as a function of interfacial concentration of Mn(tpp)complex.

10^3 times larger than the bulk phase concentration calculated by Eq. 6. Interfacial adsorption of the cationic Mn(tpp) complex produces a positively charged interface, and the concentrated layer of chloride anion might be formed at the vicinity of interface in the aqueous phase side as predicted by Gouy, Chapman and Stern.[21] Because the charge density of Cl^- ion is lower than that of HSO_4^- ion, Cl^- might be concentrated at the interfacial layer. The solid line shown in Fig. 3b was drawn by using the [Cl^-] calculated by Eq. 7.

Conclusion

The interfacial hydration and adsorption of Mn(tpp)Cl at the toluene/sodium hydrogensulfate solution (pH 1.7) interface was elucidated by in situ UV/vis external reflection spectroscopy. From the effect of chloride ion concentration on the adsorptivity and the ER spectra suggested that the interfacial species was Mn(tpp)$(H_2O)^+$. By employing the interfacial tension measurement, We confirmed for the first time that the ER absorbance at the liquid/liquid interface could be linearly correlated to the interfacial concentration of the complex. The linear correlation similar to Beer's law established in the present study will be applied for the future studies of various interfacial reactions that are interested in solvent extraction, organic synthesis or enzyme reactions.

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