Bull. Chem. Soc. Jpn., ***69***, *341—347 (1996)*

Interfacial Adsorption and Ion-Association Extraction of Protonated Tetraphenylporphyrin and Octaethylporphyrin

Yoshito Chida and Hitoshi Watarai*,†

Department of Chemistry, Faculty of Education, Akita University, Akita 010

†Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received June 30, 1995)

Protonation of tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP) in toluene/acid systems was investigated by a high-speed stirring method. In toluene/sulfuric acid system, the adsorption of the diprotonated TPP and the monoprotonated OEP at the liquid–liquid interface was found, while in other acid systems including hydrochloric acid, perchloric acid, and trichloroacetic acid, the ion-association extraction of H_2TPP^{2+} and $HOEP^+$ was observed as well, depending on the nature of the counter anions and the concentration of the acids. An inverted correlation was suggested between the adsorption constants of the protonated porphyrins and the extraction constants of the acids with the porphyrins.

Liquid–liquid distribution of chelating ligands has fundamental importance as a primary step in the solvent extraction of metal ions. The distribution equilibria of the ligands are essentially governed by their solubilities into each solvent composing the two-phase systems. A series of our recent studies, however, discovered the significant role of the liquid–liquid interface in the distribution equilibria of the ligands, especially under highly agitated conditions. For example, in the distributions of dithizones,1) β-diketones,2) 1,10-phenanthrolines,3) and 2-hydroxy oximes,4) significant interfacial adsorption of the ligands was observed, depending on pH. These phenomena were ascribed to the preferential interfacial adsorption of their dissociated or protonated forms, though the neutral forms of 2-hydroxy oximes showed significant but less interfacial activity than the dissociated forms. Furthermore, it was shown that the adsorbed ligands at the interface could react with metal ions such as Ni(II),5) Zn(II),6) and Cu(II)7) in the aqueous phase with rate constants about one order larger than those in the bulk aqueous phase, and the interfacial reaction to form a 1 : 1 complex was the rate-controlling step of the extraction rates. Now, it is desirable to accumulate data on the interfacial adsorptivity of various kinds of ligands and to discover the factors governing the interrelationships among the extractability, the adsorptivity, and the molecular structure.

Porphyrins are currently recognized as outstanding highly sensitive colorimetric reagents because of the molar absorptivity as high as $10^5\ \mathrm{M^{-1}\,cm^{-1}}$. Some colorimetric applications of porphyrins in liquid-chromatography,8) capillary electrophoresis,9) and optodes10) have been reported recently, but direct applications for the extraction-colorimetry have rarely been attempted.

In this paper, we will describe the interfacial protonation of tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP), both being representative porphyrins, in toluene/acid systems and the subsequent ion-association extraction of the protonated forms with anions. The interfacial adsorptivity and extractability of the protonated porphyrins will display a new function of the porphyrins as sensitive ion-association "adsorption" and extraction reagents for the measurement of aqueous phase acidity.

Experimental

Chemicals. Tetraphenylporphyrin (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, TPP) and octaethylporphyrin (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine, OEP), both analytical reagent grade, were purchased from Dojindo Laboratories and Tokyo Chemical Industry Co., Ltd., respectively, and used without further purification. Toluene, Wako Pure Chemical Industries, Ltd., G.R., was fractionally distilled after treating with concentrated sulfuric acid. Stock solution of sulfuric acid, hydrochloric acid, and perchloric acid, all Wako Pure Chemical Industries, Ltd., G.R., were titrated with aqueous sodium hydroxide standardized by oxalic acid solution. Trichloroacetic acid (TCA), Nacalai Tesque Inc., G.R., was used without further purification. Water used was purified by a Millipore Milli-QII system after distillation by Yamato Autostill WAG25.

Protonation Equilibria. The protonation equilibria of TPP in toluene/acid systems were studied by a batch technique. Ten mL of 2.0×10^{-6} M ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$) TPP in toluene was stirred with the same volume of acid solution in a Teflon® vial for 24 h in a thermostated room at 25±1.5 °C. After the equilibration, the vial was set in the cell holder of a spectrophotometer (HP-8452A) and the organic phase spectrum was measured without transferring the organic phase into a glass cell to avoid the unfavorable adsorption of TPP to the glass wall. The effective optical pathlength of the Teflon® vial was 1.41 cm and Beer's law was confirmed up to about 3.0 in the organic phase absorbance. The extractability of the protonated OEP was examined using a high-speed stirring apparatus.

High-Speed Stirring Experiments. The interfacial adsorptivity of the protonated TPP and OEP and the extractability of the protonated forms in toluene/acid systems were examined by the high-speed stirring method reported previously.[5] The procedure was briefly that 45 ml of toluene was introduced in a 200-ml three-necked round flask with two baffles, the solvent was circulated through a flow cell, 5 ml of TPP in toluene and 50 ml of acid were added after the base line absorbance became stable, and then the two phases were stirred at the rate of 200 rpm (low-speed stirring) or 4700 rpm (high-speed stirring). The organic phase was continuously separated by a Teflon® phase separator and circulated by a Flumax-J® pump at the rate of 2.0 ml min^{-1} through a flow cell in a Shimadzu SPD-M6A photodiode array detector. The spectra of the organic phase from 380 to 670 nm were recorded in a PC-9801 computer at the acquisition interval of 2 s.

Interfacial Tension Measurements. The interfacial tension between toluene and aqueous phase was measured by a drop-volume method at 25±0.1 °C. The volume of an aqueous drop was measured by a Gilmont micrometer syringe with a minimum reading value of 0.2 μl. From the mean volume for one aqueous drop, the interfacial tension was calculated by using the Harkins–Brown correction factor.[11]

Results

Ion-Association Extraction. In toluene/acid systems, the extraction behavior of TPP and OEP was studied varying the concentration of the acids. In the toluene/sulfuric acid system, the protonated form of the porphyrins was formed neither in the organic nor aqueous phase under the concentration range $[H_2SO_4] = 0.18$—2.87 M. In the systems including HCl, $HClO_4$, and TCA, the formation of the protonated forms of TPP in the toluene phase was observed from the appearance of new Soret bands at 448 nm ($\varepsilon = 3.90\times10^5$ $M^{-1}\,cm^{-1}$), 440 nm ($\varepsilon = 4.47\times10^5$ $M^{-1}\,cm^{-1}$), and 442 nm ($\varepsilon = 4.39\times10^5$ $M^{-1}\,cm^{-1}$), respectively. In Fig. 1, the protonation ratios of TPP were plotted against the acid concentration (on an activity scale) of HCl, $HClO_4$, and TCA. The protonated OEP was also extracted significantly in $HClO_4$ and TCA systems, with absorption maxima at 412 and 410 nm, respectively. Figure 2 shows the protonation ratio of OEP as a function of the acid activity of $HClO_4$ and TCA.

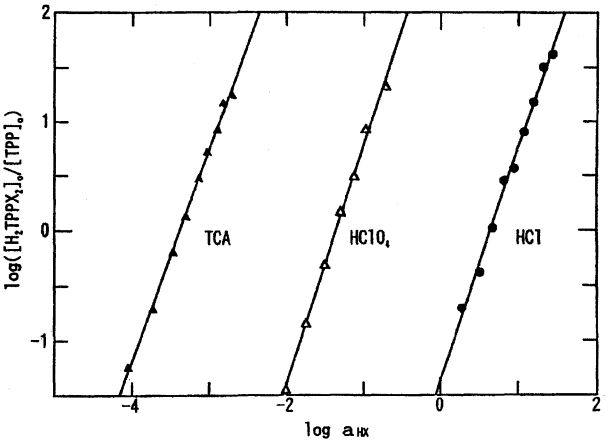

Fig. 1. Linear plots for the protonation equilibria of TPP in toluene/acid systems: $[TPP] = 2.0\times10^{-6}$ M, [HCl] = 0.574—4.02 M, $[HClO_4] = 0.200$—0.800 M, [TCA] = 0.010—0.052 M.

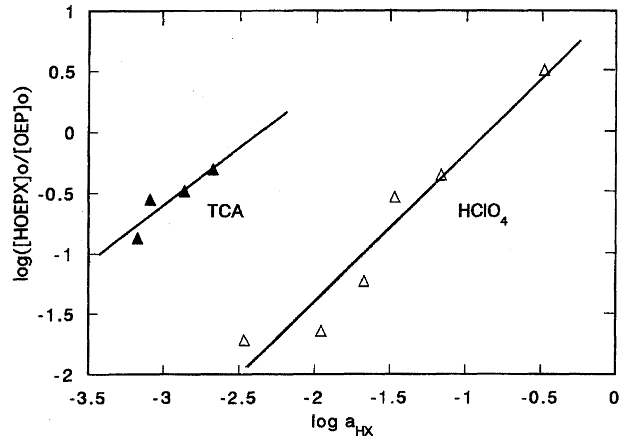

Fig. 2. Linear plots for the protonation equilibria of OEP in toluene/acid systems: $[OEP] = 2.0\times10^{-6}$ M, $[HClO_4] =$ 0.103—1.03 M, [TCA] = 0.031—0.055 M.

In the HCl system, the extraction of the protonated OEP was suggested, but it was difficult to measure its concentration because of the lesser extractability than $HClO_4$ system. The activities of the acids were calculated from the reported mean activity coefficients,[12] except for TCA solution in which the Debye–Hückel equation was used for the calculation of the activity coefficients.[13]

Stirring Effect on the Distribution of TPP and OEP. High-speed stirring of TPP or OEP in toluene with aqueous acid solution lowered the organic phase absorbance of the porphyrins, depending on the nature of the acids and its concentration, as shown in Fig. 3 for TPP. The most drastic stirring effect was observed in the sulfuric acid systems, in which no ion-association extraction was observed. In Fig. 4, typical examples of the stirring effect under different H_2SO_4 concentrations are shown. The absorbance of TPP was decreased under high-speed stirring and restored when this was lowered to 200 rpm. The decrement in the absorbance caused by the stirring was increased by the acid concentration as shown in Figs. 5 and 6 for TPP and OEP, respectively. The largest stirring effect was found in sulfuric acid and the smallest in TCA systems. These phenomena strongly suggest the interfacial adsorption of the protonated species. The total decrement of the organic phase concentrations of the neutral and protonated porphyrins was thought to be proportional to the interfacial amount.

Interfacial Tension Lowering. Interfacial tension in the systems of TPP in toluene/H_2SO_4, HCl or $HClO_4$ was lowered with the increase in the TPP concentration (0—6.0×10^{-3} M). The experimental results were analyzed according to the Gibbs equation and the saturated interfacial concentrations were calculated as follows; 1.41×10^{-10} $mol\,cm^{-2}$, 0.844×10^{-10} $mol\,cm^{-2}$ and 0.540×10^{-10} $mol\,cm^{-2}$ for toluene/H_2SO_4 (1.99 M), HCl (2.00 M), and $HClO_4$ (0.800 M) systems, respectively. In the H_2SO_4 and HCl systems, some aggregation of the protonated TPP was noticed in the higher TPP concentration and this may be part of the reason of the higher interfacial concentration in these systems.

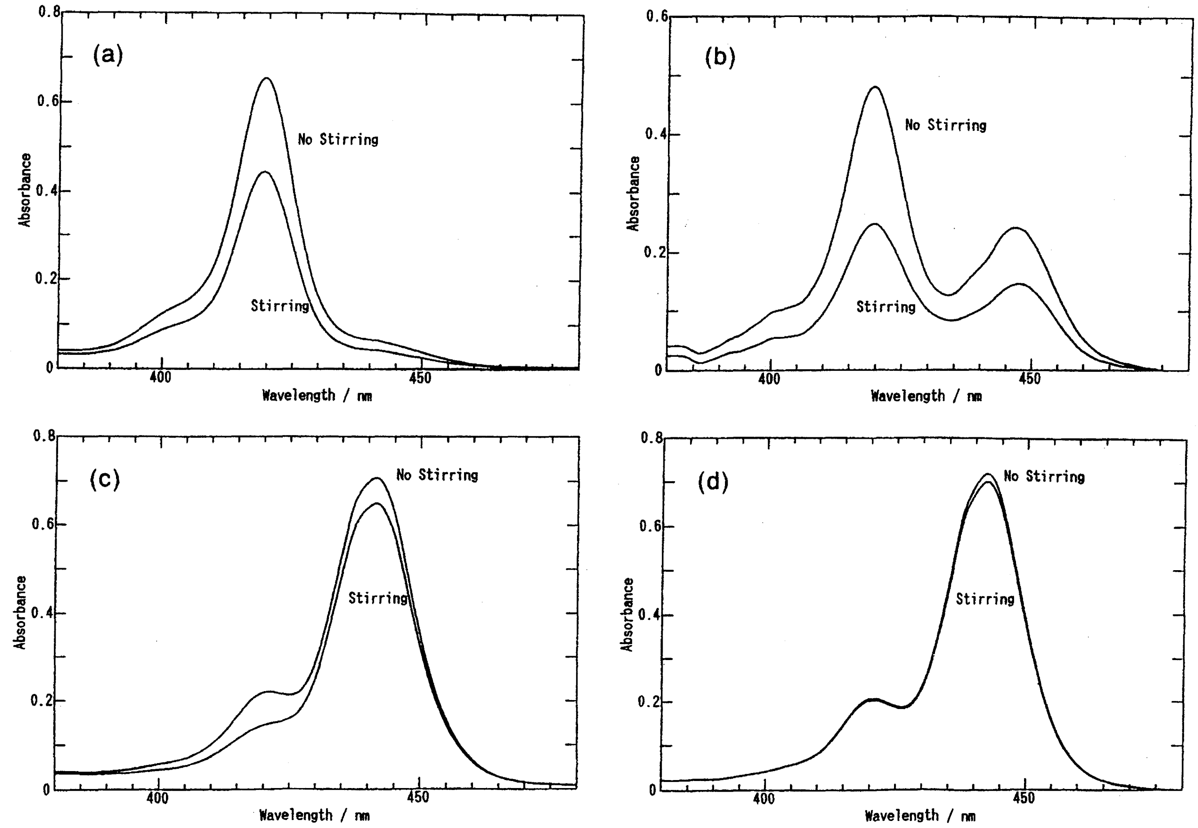

Fig. 3. Stirring effect on the organic phase spectra of TPP in toluene/acid systems: (a) $[H_2SO_4]=2.55$ M, (b) $[HCl]=1.83$ M, (c) $[HClO_4]=0.618$ M, (d) $[TCA]=0.0425$ M; $[TPP]=2.0\times10^{-6}$ M.

Discussion

Ion-Association Extraction of the Protonated Porphyrins. The distribution experiments showed the ion-pair formation of the protonated porphyrins in toluene phase. The extraction of acid, HX, with porphyrin, L, is represented by,

$$L_o + nHX = H_nLX_{n,o} \quad (1)$$

where the subscript o refers to an organic phase. The acid HX is entirely dissociated in solution. The extraction constant is defined as

$$K_{ex} = \frac{[H_nLX_n]_o}{[L]_o a_{HX}{}^n} \quad (2)$$

where the concentration of the acid was represented by activity, a_{HX}, because the concentration was varied in a wide range, so that the ionic strength was also changed. The activity, a_{HX}, is defined as the second power of the mean activity of HX, $a_\pm^2$, which takes into account the dissociation of HX in solution. Equation 2 is expressed by,

$$\log \frac{[H_nLX_n]_o}{[L]_o} = n\log a_{HX} + \log K_{ex}. \quad (3)$$

The experimental values of $[H_nLX_n]_o/[L]_o$ were plotted against $\log a_{HX}$ in Figs. 1 and 2 for TPP and OEP, respectively. The slopes of the fitted lines were close to 2 for TPP and to 1 for OEP, suggesting that the diprotonated forms were extracted in TPP systems and the monoprotonated forms in OEP systems. The extraction of $HOEP^+$ into toluene phase was indicated by the spectral change at the Q band: The absorbance at 532 nm decreased and the one at 552 nm increased with the increase of HCl concentration.[14] These results proved the next extraction reactions,

$$TPP_o + 2HX = H_2TPPX_{2,o} \quad (4)$$

and

$$OEP_o + HX = HOEPX_o. \quad (5)$$

The lack of extraction of $HTPP^+$ must be due to its instability and the higher stability of H_2TPP^{2+}, which results from the conjugation of the *meso*-phenyl groups with the π system of the porphine ring in the diprotonated form.[15] From the intercepts in Figs. 1 and 2, the values for $\log K_{ex}$ were obtained as shown in Table 1. The decreasing order in the magnitude of $\log K_{ex}$, $TCA > HClO_4 > HCl > H_2SO_4$, corresponded to the expected increasing order in the hydration energies of the counter anions.[16] This order seems to obey the Hofmeister series widely observed in extractability of anions.[17] The highest extractability of trichloroacetate ion with the diprotonated TPP will probably be applied to the extraction-spectrometry of traces of halogenated carboxylate anions.

Interfacial Adsorption of the Protonated Porphyrins. The results of the stirring effect and interfacial tension measurements demonstrated the interfacial adsorption of the protonated porphyrins under the higher acid concentrations. Therefore, the extraction reaction, Eq. 1, must be divided into

Table 1. Ion-Association Extraction and Adsorption of the Diprotonated TPP and the Monoprotonated OEP in Toluene/Acid Systems at 25 °C

Porphyrin	Acid	$[H^+]_{1/2}$[a]	$\log K_{ex}$	$\log K'A_i$	$\log K'_D A_i$
TPP	H_2SO_4	—	<-3	0.81 ± 0.11	>4
	HCl	1.71	-1.37 ± 0.07	-1.54 ± 0.06	-0.17 ± 0.09
	$HClO_4$	0.380	2.96 ± 0.07	0.79 ± 0.23	-2.17 ± 0.24
	TCA[b]	0.218	6.54 ± 0.12	3.45 ± 0.21	-3.09 ± 0.24
OEP	H_2SO_4	—	<-3	-0.61 ± 0.10	>2
	HCl	—	—	-1.88 ± 0.02	—
	$HClO_4$	0.685	1.04 ± 0.27	-0.54 ± 0.04	-1.58 ± 0.27
	TCA	0.0740	2.23 ± 0.92	1.04 ± 0.28	-1.19 ± 0.96

a) Acid concentration at half protonation (M). b) Trichloroacetic acid.

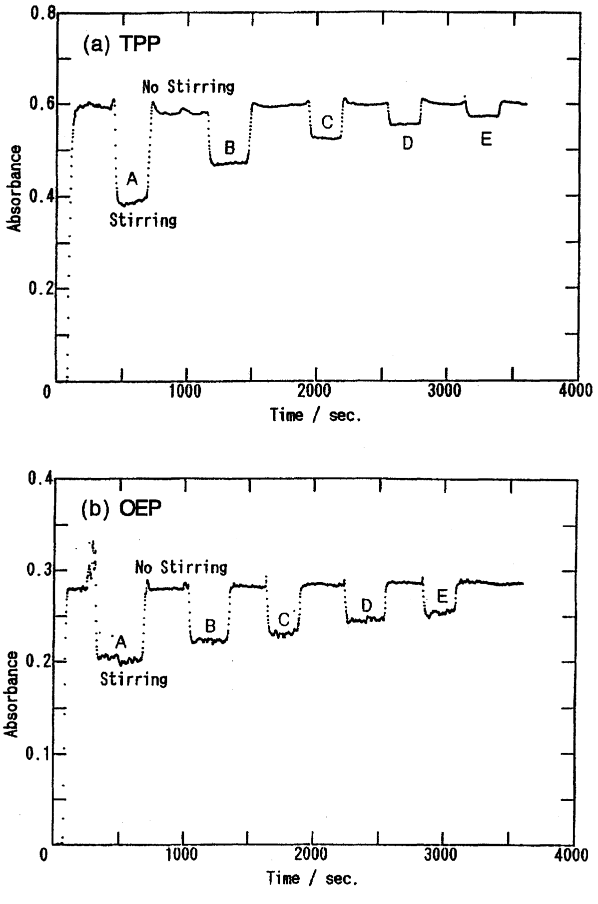

Fig. 4. Stirring effect on the toluene phase absorbance in H_2SO_4 systems: (a) $[H_2SO_4]$ = A, 2.55 M; B, 2.29 M; C, 2.06 M; D, 1.86 M; E, 1.67 M, [TPP] = 2.0×10^{-6} M at 420 nm (b) $[H_2SO_4]$ = A, 1.30 M; B, 1.17 M; C, 1.05 M; D, 0.946 M; E, 0.851 M, [OEP] = 2.0×10^{-6} M at 402 nm.

two processes; the interfacial protonation and the interfacial adsorption of the protonated form, which are respectively represented by,

$$L_o + nHX = H_nLX_{n,i} \tag{6}$$

and

$$H_nLX_{n,o} = H_nLX_{n,i} \tag{7}$$

where the subscript i refers to the interface and the formation constant of $H_nLX_{n,i}$ is defined by $K' = [H_nLX_n]_i/[L]_o a_{HX}{}^n$, and the adsorption constant of H_nLX_n by $K'_D = [H_nLX_n]_i/[H_nLX_n]_o$. The mass balance equation is,

$$[L]_T V_o = [L]_o V_o + [H_nLX_n]_o V_o + [H_nLX_n]_i A_i \tag{8}$$

where A_i is the total interfacial area under the high speed-stirring of 50 ml of organic phase with 50 ml of aqueous phase, which was calculated previously as 2×10^4 cm^2.[18] From the above equations, the next equation is derived,

$$\log \frac{[L]_T - [L]_o - [H_nLX_n]_o}{[L]_o} = \log \frac{K'A_i}{V_o} + n \log a_{HX}. \tag{9}$$

Among the equilibrium constants of K_{ex}, K', and K'_D, the next relation holds,

$$K_{ex} = K'/K'_D \tag{10}$$

Figure 7 (a) and (b) show the plots of the experimentally observed stirring effect according to Eq. 9 for TPP and OEP, respectively. In both porphyrins, the plots showed fairly good linearity. The slopes of the linear plots were close to 2 in TPP and to 1 in OEP, which proved the adsorption of the diprotonated TPP and the monoprotonated OEP, respectively. It is important that even in the sulfuric acid systems in which no extraction of the protonated forms was observed, the interfacial adsorption of the protonated forms could definitely be measured. This means that from the interfacial adsorption of the protonated form of a basic compound like TPP, the acid concentration in the aqueous phase could be measured indirectly with no need of bulk phase extraction of the protonated species. The adsorption of the monoprotonated form of OEP was confirmed by the linear correlation between the interfacial concentration and the organic phase concentration (Figure not shown). The values of $K'A_i$ obtained from Fig. 7 were listed in Table 1 together with $K'_D A_i$ calculated by using Eq. 10 and K_{ex} values. The decreasing order of $\log K'_D A_i$ with the acids, $H_2SO_4 > HCl > HClO_4 > TCA$, was in inverse order to that in the extractability, $\log K_{ex}$. The dependence of the adsorptivity on the counter anions was essentially the same as that in tris(4,7-diphenyl-1,10-phenanthroline)iron(II) complex.[19]

Comparison between TPP and OEP Systems. The spectral shifts caused by the protonation were 20 and 8 nm in TPP and OEP systems, respectively. The larger shift in the protonated form of TPP was attributed to the favorable π electron conjugation between the phenyl rings and the porphine ring. In the neutral TPP, the phenyl rings are in

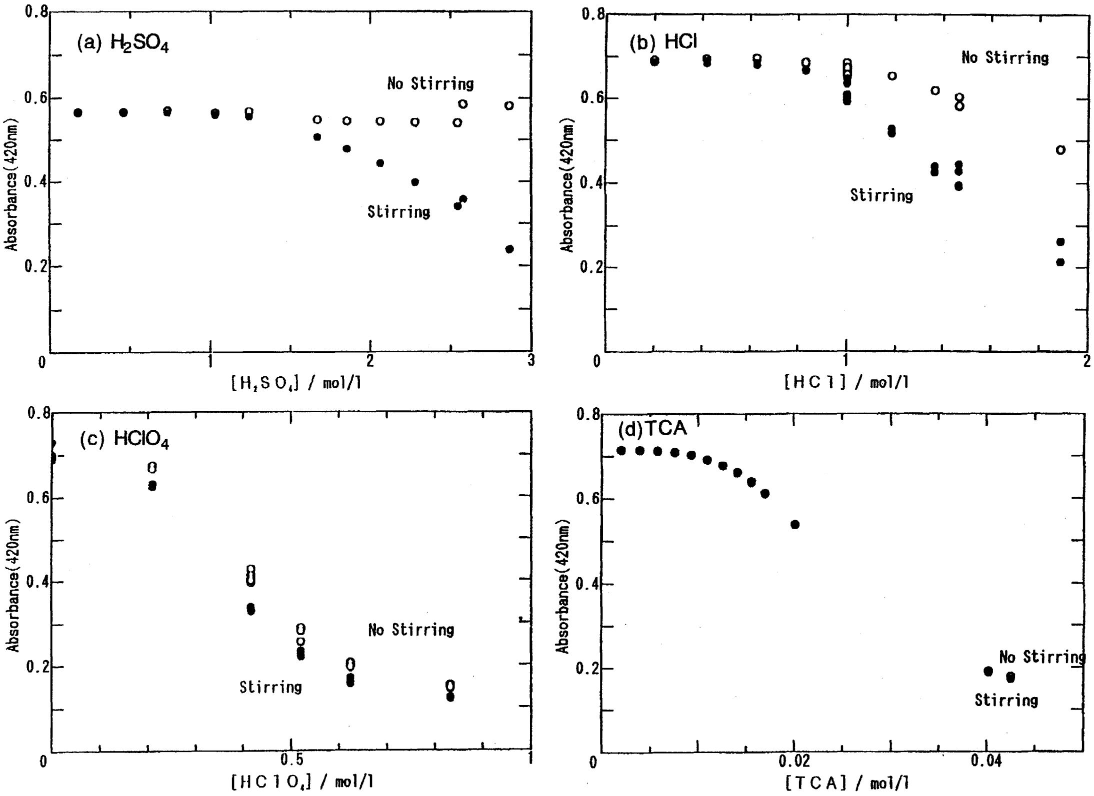

Fig. 5. Acid concentration dependence of the stirring effect in the TPP in toluene/aqueous acid systems: (a) [H_2SO_4]=1.12—2.87 M, (b) [HCl]=0.200—1.89 M, (c) [$HClO_4$]=0.208—1.21 M, (d) [TCA]=0.002—0.0425 M, [TPP]=2.0×10^{-6} M.

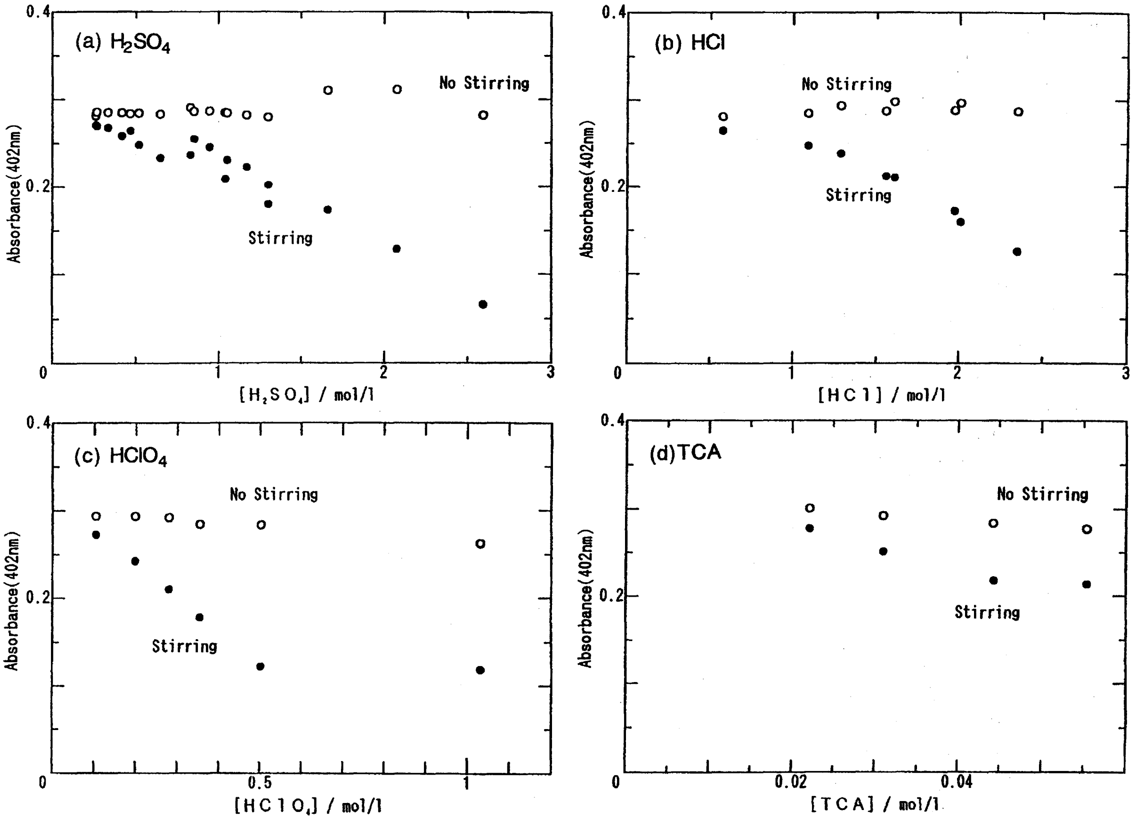

Fig. 6. Acid concentration dependence of the stirring effect in the OEP in toluene/aqueous acid systems: (a) [H_2SO_4]=0.258—2.59 M, (b) [HCl]=0.574—2.69 M, (c) [$HClO_4$]=0.103—1.03 M, (d) [TCA]=0.022—0.055 M, [OEP]=2.0×10^{-6} M.

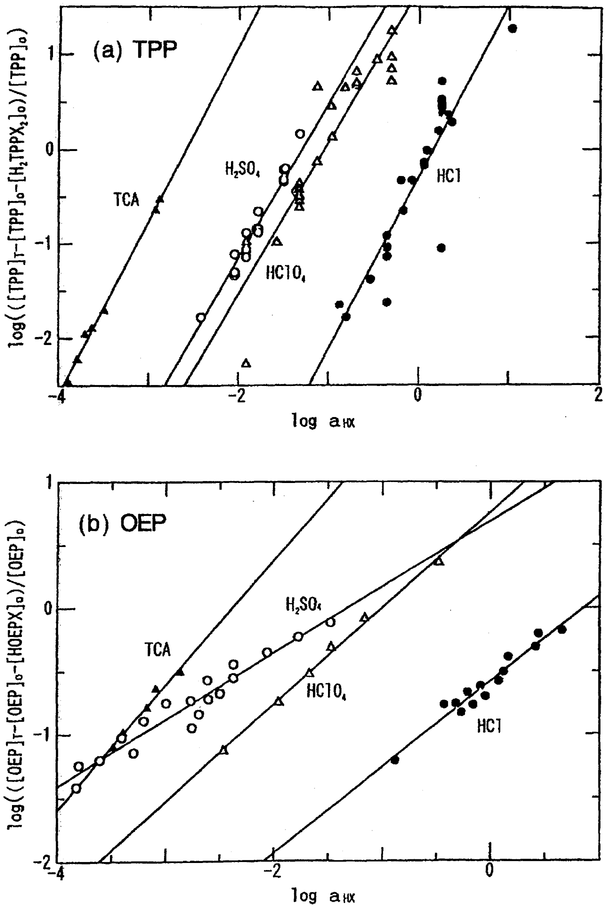

Fig. 7. Linear plots of the interfacial adsorptivity against acid concentration: (a) [TPP] = 2.0×10^{-6} M, [H_2SO_4]=1.24—2.87 M, [HCl]=0.200—3.00 M, [$HClO_4$]= 0.204—1.04 M, [TCA] = 0.013—0.043 M and (b) [OEP]=2.0×10^{-6} M, [H_2SO_4]=0.258—2.59 M, [HCl]= 0.574—2.35 M, [$HClO_4$] = 0.103—1.03 M, [TCA] = 0.022—0.055 M.

perpendicular to the porphine ring plane, while in H_2TPP^{2+}, the porphine ring is thought to be distorted because of the electrostatic repulsion between the two proton charges and the van der Waals repulsion among the four protons in the ring. As a result, the phenyl rings in H_2TPP^{2+} can get some freedom to rotate and to conjugate with the parent ring π-electrons. In OEP which has no phenyl group, there is no π–π interaction like TPP.

The dominant protonated species in TPP was the diprotonated form. It has been suggested that the protonation constant of the monoprotonated TPP is about 10^{10} times larger than that of the free TPP.[20,21] Thus, the amount of $HTPP^+$ is practically negligible. The stability of the diprotonated form may be further enhanced by the hydrogen bonding between the protons and the counter anions. OEP showed only a monoprotonated form under these conditions, but in a mixture of sulfuric acid and acetic acid, the formation of the diprotonated OEP was reported.[22]

The distribution constants K_D, which are an excellent measure of hydrophobicity of neutral compounds, have not been measured for TPP and OEP, and the difference in $\log K_D$ between TPP and OEP can be estimated by using the substituent π values.[23] This suggested that the K_D value of TPP is about two orders higher than that of OEP. The $\log K'_D A_i$ values measured experimentally reflected the difference in the K_D values between TPP and OEP as shown in Table 1. This shows clearly that the adsorption process from the organic phase to the interface is governed by the hydrophobic moiety, which must reside in the organic phase side at the interface, as well as by the anions which contact water at the interface. In the case of tris(1,10-phenanthroline)iron(II) complexes also, the adsorption constants of the ion-pair with perchlorate from chloroform to the interface were decreased when the $\log K_D$ values of 1,10-phenanthrolines with hydrophobic substituents were increased.[23]

Further studies on the interfacial reaction of porphyrin compounds are now in progress to discover the mechanism of the ion-association extraction using porphyrin compounds and the environmental effects at the liquid–liquid interface, and finally to invent a new colorimetric adsorption-detection method using the interfacial reaction.

This work was supported by a Grant-in-Aid for Scientific Research No. 07404042 from the Ministry of Education, Science and Culture.

References

1) H. Watarai and H. Freiser, *J. Am. Chem. Soc.*, **105**, 191 (1983).

2) H. Watarai, K. Kamada, and S. Yokoyama, *Solvent Extr. Ion Exch.*, **7**, 37 (1989).

3) H. Watarai, *J. Phys. Chem.*, **89**, 384 (1985).

4) H. Watarai and K. Sasabuchi, *Solvent Extr. Ion Exch.*, **3**, 881 (1985).

5) H. Watarai and K. Satoh, *Langmuir*, **10**, 3913 (1994).

6) H. Watarai and H. Freiser, *J. Am. Chem. Soc.*, **105**, 189 (1983).

7) H. Watarai and M. Endoh, *Anal. Sci.*, **7**, 137 (1991).

8) S. Igarashi, A. Obara, H. Adachi, and T. Yotsuyanagi, *Bunseki Kagaku*, **35**, 829 (1986).

9) T. Saitoh, H. Hoshino, and T. Yotsuyanagi, *Anal. Sci.*, **7**, 495 (1991).

10) T. L. Blair, J. R. Allen, S. Daunert, and L. G. Bachas, *Anal. Chem.*, **65**, 2155 (1993).

11) J. L. Lando and H. T. Oakley, *J. Colloid Interface Sci.*, **25**, 526 (1967).

12) D. Dobos, "Electrochemical Data," Elsevier, Amsterdam (1975), p. 184.

13) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

14) R. Grigg, R. J. Hamilton, M. L. Jozefowicz, C. H. Rochester, R. J. Terrell, and H. Wickwar, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 407.

15) M. Moet-Ner and A. D. Adler, *J. Am. Chem. Soc.*, **97**, 5107 (1975).

16) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

17) F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.*, **24**, 247 (1888); S. Motomizu, *Bunseki Kagaku*, **38**, 147 (1989); K. Goto, S. Taguchi, H. Miyano, and K. Haruyama, *Bunseki Kagaku*, **32**, 678 (1983); T. Yotsuyanagi, *Bunseki Kagaku*, **34**, 583 (1985).

18) H. Watarai, M. Takahashi, and K. Shibata, *Bull. Chem. Soc. Jpn.*, **59**, 3469 (1986).

19) H. Watarai and Y. Shibuya, *Bull. Chem. Soc. Jpn.*, **62**, 3446 (1989).

20) F. Hibbert and K. P. P. Hunte, *J. Chem. Soc., Chem. Commun.*, **1975**, 728.

21) F. Hibbert and K. P. P. Hunte, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1624.

22) R. Grigg, R. J. Hamilton, M. L. Jozefowicz, C. H. Rochester, R. J. Terrell, and H. Wickwar, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 407.

23) H. Watarai, K. Sasaki, and N. Sasaki, *Bull. Chem. Soc. Jpn.*, **63**, 2797 (1990).