

## Anion-Selective Electrodes Based on Porphyrin Complexes of Tetravalent Metal Ions

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The performance of tetravalent metal complexes with tetraphenylporphine ( $H_2tpp$ ) as ionophores for ion-selective electrodes was studied. In the case of  $[MO(tpp)]$  (M: Ti, V), protonation to the oxo group is responsible for pH response, and anionic response following a Hofmeister series is ascribed to their coextraction as counter anions. In the case of  $[M(tpp)Cl_2]$  (M: Zr, Hf), replacement of chloride with anions including  $OH^-$  is responsible for pH and anionic responses, and Lewis acid-base interactions produce preferential response to  $F^-$ ,  $NO_2^-$ , and acetate. The  $[Zr(tpp)Cl_2]$ -based electrode was successfully used for potentiometry of acetic acid in rice vinegar.

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Supramolecular chemistry of anions has been studied intensively in the last decade and has created a lot of artificial anionophores.<sup>1,2</sup> Some of them have been applied to potentiometric sensing of anions.<sup>3</sup> Lewis acid-base interactions may compensate the difficulty in transferring strongly hydrated anions into a membrane phase and thereby produce novel selectivities. In a previous work, we examined the anionic response of a zirconium(IV) complex with *N*-dodecyliminodiacetate and found a unique selectivity, but the potential slope was not satisfactory enough; e.g., -43 mV/decade for salicylate  $> 10^{-5}$  mol dm<sup>-3</sup>.<sup>4</sup>

Since the pioneering work by Simon, porphyrins have mainly been used to introduce Lewis acidic metal-centers in the membrane phase, because of the stability and lipophilicity of the resulting complexes. The performance of trivalent metal  $[Mn(III), Fe(III), Co(III), Ga(III), In(III), Tl(III), Tb(III)]$  complexes as ionophores has extensively been studied, while that of higher oxidation states has not, except  $Sn(IV)$  and  $Mo(V)$  complexes with tetraphenylporphine( $H_2tpp$ );  $[Sn(tpp)Cl_2]$  and  $[MoO(tpp)X]$  ( $X^-$ : an auxiliary monodentate anion, such as  $OEt^-$ ,  $SCN^-$ ).<sup>5-7</sup>

Among other tetravalent metal ions, titanium(IV) and vanadium(IV) form the  $[MO(tpp)]$ -type complexes, while zirconium(IV) and hafnium(IV) form the  $[M(tpp)X_2]$ -type complexes (Fig. 1). Since two auxiliary anions on  $[M(tpp)X_2]$  adopt a *cis*-configuration in contrast to a *trans*-configuration of two chlorides on  $[Sn(tpp)Cl_2]$ ,<sup>8-10</sup> a different selectivity is expected. In this work, we have made a systematic investigation on the pH and anionic responses of these four porphyrin complexes,  $[MO(tpp)]$  (M: Ti and V) and  $[M(tpp)X_2]$  (M: Zr and Hf).

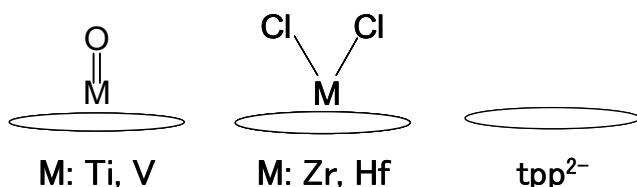


Fig. 1 Tetravalent metal complexes with tetraphenylporphine used as ionophore

### Experimental

#### Reagents

The ionophores of  $[TiO(tpp)]$ ,  $[Zr(tpp)Cl_2]$ , and  $[Hf(tpp)Cl_2]$  were prepared and purified as described previously.<sup>11-13</sup> Their purities were confirmed by TLC and visible absorption spectrometry. The other ionophore,  $[VO(tpp)]$ , and added salts, tridodecylmethylammonium chloride (TDMACl) and sodium tetraphenylborate ( $NaTPB$ ), were used as received. 2-Nitrophenyl octyl ether (*o*-NPOE) was prepared by modifying the method in literature. Polyvinyl chloride (PVC) was purified by pouring the tetrahydrofuran solution into methanol.

#### EMF measurement

The polymeric membrane consisted of 1 % ionophore, 66 % *o*-NPOE, and 33 % PVC by weight; no salt was added except otherwise stated. The electromotive force of the cell,  $Ag/AgCl | KCl(satd) || test\ solution | membrane | internal\ solution | Ag/AgCl$ , was measured with a potentiometer (IOL-50, Denki Kagaku Keiki Co., Tokyo, Japan) at  $25 \pm 0.1$  °C. The selectivity coefficients against interfering anion of  $X^-$ ,  $k_{AcO,X}$ , were determined by the separate solution method at a fixed concentration of  $10^{-1}$  mol dm<sup>-3</sup>. With regard to anions involved in acid-base equilibria, apparent coefficients against the total concentration,  $k'_{AcO,X}$ , were also calculated from the practical point of view.

### Results

#### pH response

The potential response of four ionophores to pH is shown in Fig. 2. Since the ionic strength was not adjusted, the concentration of counter cations increased with an increase in pH in alkaline media, while that of counter anions increased with a decrease in pH in acidic media. In alkaline media,  $[MO(tpp)]$ -type ionophores showed appreciable cationic response (in the order of  $K^+ > Na^+ > Li^+$ ), which was lost by the addition of TDMACl in the membrane. In contrast,  $[M(tpp)Cl_2]$ -type ionophores maintained the linearity up to pH 13.

In acidic media, both  $[MO(tpp)]$ - and  $[M(tpp)Cl_2]$ -type ionophores showed anionic response. The potential of

[MO(tpp)]-based electrode decreased in the order of media:  $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{HClO}_4$ . This coincides with the order of difficulty in dehydration of constituting anions.<sup>15</sup> The addition of NaTPB effectively diminished the anionic response. In contrast, the potential of [M(tpp)Cl<sub>2</sub>]-based electrode decreased in the order of media:  $\text{HCl} > \text{H}_3\text{PO}_4 \sim \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$ . Lower potentials for  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  media than HCl medium were remarkable. The addition of NaTPB up to 50 mol% did not retard the anionic response.

Linear response to pH was observed between these two extremes for all the ionophores. Table 1 enumerates the pH ranges and potential slopes for linear response, together with those for other porphyrin complexes reported elsewhere.<sup>5,6,14</sup> Porphyrin complexes of hydrolyzable metal ions generally show pH response.

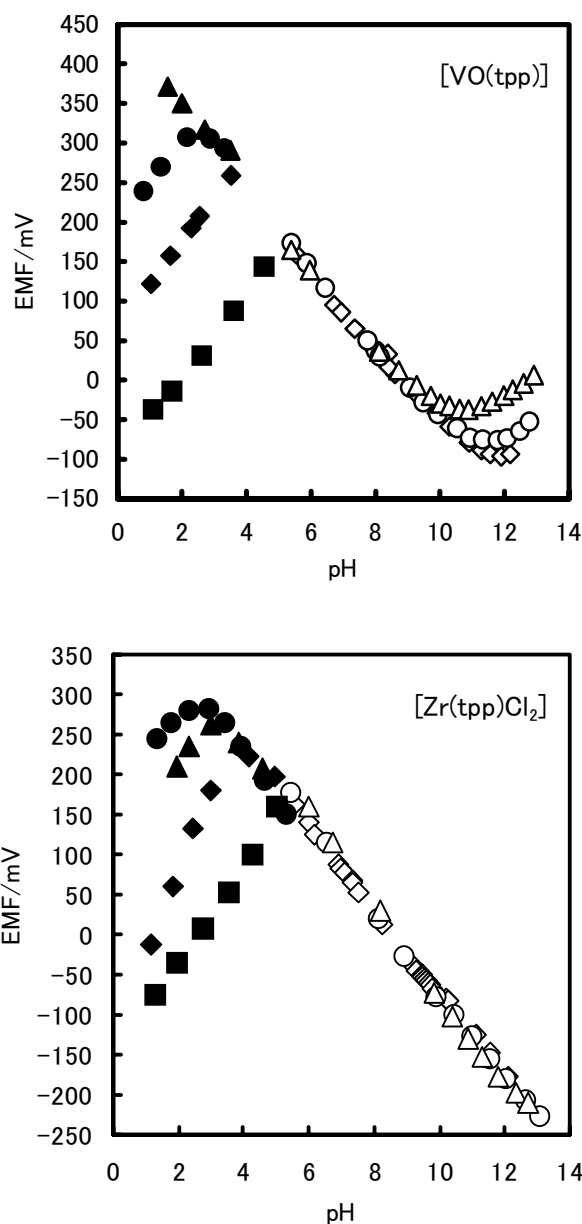


Fig. 2 Effects of pH, acid, and alkali on the potential response of [VO(tpp)]- and [Zr(tpp)Cl<sub>2</sub>]-based ISEs. Acid: ▲,  $\text{H}_3\text{PO}_4$ ; ●, HCl; ◆,  $\text{HNO}_3$ ; ■,  $\text{HClO}_4$ ; alkali: △, KOH; ○, NaOH; ◇, LiOH.

Table 1 pH response of porphyrin complex-based ISEs

ionophore	linear range	slope(mV/decade)	ref.
TiO(tpp) <sup>a)</sup>	pH 2-11	44	this work
VO(tpp) <sup>a)</sup>	pH 4-11	48	this work
Zr(tpp)Cl <sub>2</sub> <sup>b)</sup>	pH 3.5-13	53	this work
Hf(tpp)Cl <sub>2</sub> <sup>b)</sup>	pH 7-12	52	this work
Mn(tpp)Cl	pH 3.5-10	49	14
Sn(tpp)Cl <sub>2</sub>	pH 2.5-10	38	5
MoO(tpp)(OEt)	pH 2-12.5	56	6

a) using  $\text{H}_3\text{PO}_4$  in acidic and LiOH in alkaline media

b) using HCl in acidic medium

#### Anionic response

The selectivity of [VO(tpp)]- and [TiO(tpp)]- based ISEs towards further anions,  $\text{ClO}_4^- > \text{salicylate} > \text{SCN}^- > \text{I}^- > \text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{H}_2\text{PO}_4^-$ , was quite common and showed no remarkable anionic response. The addition of 62 mol% NaTPB diminished all the anionic response, but the response to salicylate remained in a concentration range  $> 10^{-3} \text{ mol dm}^{-3}$ . Even strongly chelating ligands like salicylate may not effectively replace the oxo ligand tightly bound to the central metal ion.

The potential response curves of [Zr(tpp)Cl<sub>2</sub>]-based electrode to typical anions at pH 4.8 are shown in Fig. 3. The ionophore of [Hf(tpp)Cl<sub>2</sub>] showed practically the same performance as [Zr(tpp)Cl<sub>2</sub>]. Near-Nernstian responses were obtained for  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{I}^-$ , and  $\text{NO}_3^-$ . Double-Nernstian responses were observed for acetate and  $\text{NO}_2^-$  and a rather sigmoidal response for  $\text{F}^-$ . Thus, the ISE is more selective to these three ions at higher concentrations. Hereafter, the performance of [Zr(tpp)Cl<sub>2</sub>] as an ionophore for acetate was evaluated. The apparent anion selectivity coefficients of various common anions relative to acetate are shown in Table 2. The Zr(IV) center acts as a Lewis acid to create a new selectivity, which is definitely different from that of a classical anion-exchanger, TDMACl.

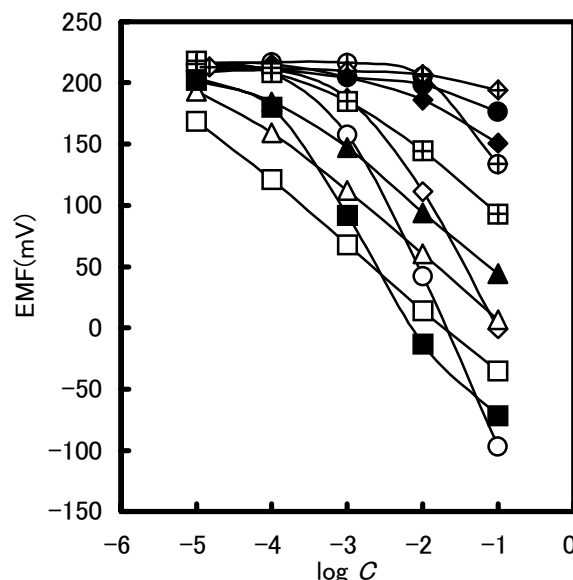


Fig. 3 Anionic response of [Zr(tpp)Cl<sub>2</sub>]-based ISE. pH 4.8; anions: ○, acetate; ◇,  $\text{NO}_2^-$ ; ⊕,  $\text{SO}_4^{2-}$ ; ■,  $\text{F}^-$ ; □,  $\text{ClO}_4^-$ ; △,  $\text{SCN}^-$ ; ▲,  $\text{I}^-$ ; ⊞,  $\text{NO}_3^-$ ; ◆,  $\text{Br}^-$ ; ●,  $\text{H}_2\text{PO}_4^-$ ; ⊕,  $\text{Cl}^-$ .

Table 2 Selectivity Coefficients of  $[\text{Zr}(\text{tpp})\text{Cl}_2]$ - and TDMACl-based ISEs

anion	$[\text{Zr}(\text{tpp})\text{Cl}_2]$		TDMACl	
	$\log k_{\text{AcO},X}$	$\log k'_{\text{AcO},X}$	$\log k_{\text{AcO},X}$	$\log k'_{\text{AcO},X}$
acetate	0.0	0.0	0.0	0.0
$\text{F}^-$	-0.4	-0.2	-0.3	0.0
$\text{ClO}_4^-$	-0.7	-0.4	4.5	4.7
$\text{NO}_2^-$	-1.0	-0.7	0.5	0.7
$\text{SCN}^-$	-1.0	-0.7	3.3	3.6
$\text{I}^-$	-1.3	-1.0	2.0	2.3
$\text{NO}_3^-$	-1.6	-1.4	1.7	1.9
salicylate	-1.9	-1.6	2.9	3.1
$\text{SO}_4^{2-}$	-1.9	-1.7	-0.2	0.0
$\text{Br}^-$	-2.1	-1.8	0.8	1.0
$\text{H}_2\text{PO}_4^-$	-2.2	-2.0	-0.3	0.0
$\text{Cl}^-$	-2.4	-2.1	-0.1	0.1

The effects of pH on the response to the fixed total concentrations ( $C_{\text{AcO}}$ ) of acetate are shown in Fig. 4. At  $C_{\text{AcO}} = 10^{-3} \text{ mol dm}^{-3}$ , the potential was constant in  $\text{pH} > \text{p}K_{\text{a}}$ . At  $C_{\text{AcO}} = 10^{-2} \text{ mol dm}^{-3}$ , on the other hand, there found a convex in  $\text{pH} > \text{p}K_{\text{a}}$ , the reason for which is not clear. From the practical point of view, pH 4.8 is recommended for acetate determination. Under such conditions, the acetate content in some rice vinegar was determined to be  $(0.65 \pm 0.03) \text{ mol dm}^{-3}$ , which agreed well with the results by acid-base titration.

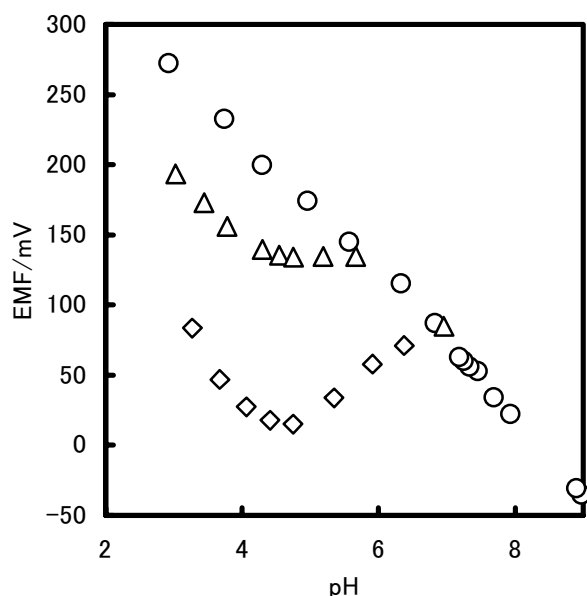


Fig. 4 Effects of pH on the potential response of  $[\text{Zr}(\text{tpp})\text{Cl}_2]$ -based ISE to acetate.  $C_{\text{AcO}}/\text{mol dm}^{-3}$ :  $\diamond$ ,  $10^{-2}$ ;  $\triangle$ ,  $10^{-3}$ ;  $\circ$ , none.

## Discussion

### Response mechanism

Chloroform solutions of ionophores ( $3 \times 10^{-6} \text{ mol dm}^{-3}$ ) were shaken with a sodium hydroxide solution ( $1 \text{ mol dm}^{-3}$ ). The absorption maxima shifted from 417, 538, and 570 to 414, 545, and 582 nm, respectively (Fig. 5). Phase transfer of  $\text{Cl}^-$  from an organic to an aqueous phase was also confirmed. Thus,  $\text{Cl}^-$  was replaced by  $\text{OH}^-$ . In contrast, no spectral change was observed for  $[\text{MO}(\text{tpp})]$ -type ionophores.

Lipophilic amines half neutralized are well known as ionophores for pH-sensitive electrodes.<sup>16</sup> The linear response range is usually limited to pH-width of 7 or less, due to cationic response in alkaline media and anionic response in acidic media. The pH response behaviors of  $[\text{MO}(\text{tpp})]$ -type ionophores were just the same as those of lipophilic amine-type ionophores. Since the  $[\text{MO}(\text{tpp})]$ -type ionophores do not react with a base, protonation to the oxo group is responsible for the pH-response. Once protonated, the ionophores become cationic, and anions may be coextracted. As no interaction between a metal center and an anion is expected, the selectivity follows a Hofmeister series. Anionic response is observed at higher pH for more lipophilic anions in Fig. 2, because the concentration of anions is proportional to that of hydrogen ions in these systems. The addition of NaTPB in the membrane suppresses the ion-pair extraction and extends the linearity of pH response in acidic media.

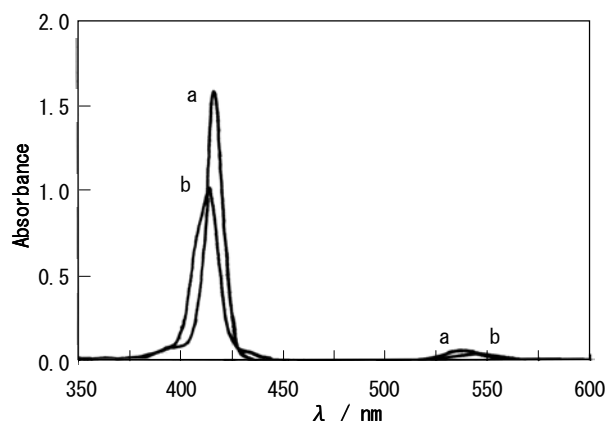


Fig. 5 Change in absorption spectra by two-phase reaction of  $[\text{Zr}(\text{tpp})\text{Cl}_2]$  with  $\text{OH}^-$ . Organic phase:  $4.1 \times 10^{-6} \text{ mol dm}^{-3}$  chloroform solution of  $[\text{Zr}(\text{tpp})\text{Cl}_2]$ ; aqueous phase:  $1 \text{ mol dm}^{-3}$  NaOH solution. a: before reaction; b: after reaction.

The pH response behaviors of  $[\text{Zr}(\text{tpp})\text{Cl}_2]$ -type ionophores were quite different from those of  $[\text{MO}(\text{tpp})]$ -type and lipophilic amine-type ionophores; the  $[\text{Zr}(\text{tpp})\text{Cl}_2]$ -type ionophores have no site to be protonated. Instead, chlorides on Zr(IV) are replaced by hydroxides and this may be responsible for the pH response. Such replacement reaction is expected for other anions;  $[\text{Zr}(\text{tpp})(\text{AcO})_2]$ , which may be responsible for the potential response to acetate, has structurally been characterized by X-ray crystallography.<sup>10</sup> The selectivities are governed by the affinities of anions to the metal center as well as the dehydration energies. No change in potential response by the addition of NaTPB indicates that the Lewis acid-base reaction plays a major role in determining the selectivity. The complex,  $[\text{Zr}(\text{tpp})\text{Cl}_2]$  is thus so called an associated charged carrier.

In summary, a PVC membrane electrode, containing  $[\text{Zr}(\text{tpp})\text{Cl}_2]$  as an anionophore, affords a unique selectivity, compared with the conventional ionophores. The effects of the central metal ions and the auxiliary ligands on the performance of this type of ion-selective electrodes are now under systematic investigation in this laboratory.

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