Potentiometric Response Mechanism of a Poly(acrylamide)-phthalocyaninato Tin(II) Film Coated Platinum Electrode in Acetonitrile and *N*,*N*-Dimethylacetamide

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A new sensor constructed by a platinum electrode coated with a non-plasticized poly(acrylamide) polymer (PAA) film coupled with phthalocyaninato tin(II) ([Sn(II)(pc)]) was developed. The potentiometric response behavior of this PAA-[Sn(II)(pc)] electrode for such anions as CN^-, F^-, Cl^-, and Br^- in dimethylacetamide and acetonitrile were investigated. The electrode showed a Nernstian response to CN^- and F^- and a quite poor response to Cl^- and Br^-. The mechanism of the peculiar selective response was studied by cyclic voltammetric and spectrophotometric methods. The voltammetric investigation suggested that the charge of the host compound in the sensor membrane had no effect on the potential response of the electrode. It was also found by a spectrophotometric investigation that the complexing of [Sn(II)(pc)] with CN^- and F^- lead to the selective response of the electrode. The motive force of the complexing was considered to be a ligand exchange of CN^- or F^- with molecules at the axial site of [Sn(II)(pc)] due to solvent effects to the interest anions.

Introduction

Both for a fundamental study and to develop ion selective electrodes, it is very important to elucidate how the ion-selective electrode membrane potential is established. Complexes of porphyrins and phthalocyanines have been used as hosts of sensors for various anions. However, they are almost for use in aqueous solution systems. Studies concerning the coordination chemistry of metalloporphyrins were compiled in a book edited by Smith,[1] and many studies about metallphthalocyanines in nonaqueous solutions were reported by Nyokong *et al.*[2] The so-called double-decker phthalocyanines were synthesized and characterized electrochemically.[3,4] Ion sensors, which consisted of a poly(acrylamide) polymer (PAA) membrane conjugated by polyethers as host compounds and responded to Li^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} ions in aprotic solvents have been reported.[5] The potentiometric response behavior of electrodes consisting of a non-plasticized PAA coupled to phthalocyaninates ([M(pc)]; M = Co, VO) was also studied and the selective Nernstian response of the electrodes to CN^- and F^- in acetonitrile (AN) and propylene carbonate (PC) was elucidated.[6] The roles of the center atom of phthalocyanine on the response behaviors of the electrode should be very important information for this type of electrode. In this work, a new sensor constructed by a platinum electrode coated with a non-plasticized PAA film coupled with phthalocyaninato tin(II) ([Sn(II)(pc)]) was developed. Here, firstly the potentiometric response behavior of the electrode in *N*,*N*-dimethylacetamide (DMA) and AN is reported. Next, a cyclic voltammetric (CV) study concerning the influence of the charge of the host compound in the sensor membrane on its

potentiometric response is presented, and finally a spectrophotometric (UV-vis) investigation on the special selectivity of the sensor is discussed.

Experimental

Reagents

Tetraethylammonium perchlorate (Et_4NClO_4), silver nitrate ($AgNO_3$), molecular sieves, and calcium hydride (CaH_2) were purchased from Nacalai Tesque, Inc. (No. 330-16, 310-19, 233-11, and 068-34, respectively). Phthalocyanine (pc), (phthalocyaninato)tin(II), phosphorus(V) oxide (P_2O_5), *N*,*N*-dimethylacetamide and acetonitrile were all purchased from Wako Pure Chemical, Ltd. (No. 160-18021, 041-21671, 042-02546, and 014-00386, respectively). DMA was purified by fractional distillation (under 20 mmHg) two times after removing water with molecular sieves, first with the existence of barium oxide (BaO, from Kanto Chemical Co. Inc.) and second with calcium hydride. AN was purified by the same method as that for DMA, except for the first time with the existence of P_2O_5 and the second with CaH_2 under atmospheric pressure. Tetraethylammonium cyanide (Et_4NCN), tetrabutylammonium fluoride (Bu_4NF), and pc were purchased from Fluka Co., Ltd., and were used without further purification.

Synthesis of the PAA-[Sn(II)(pc)]

(Phthalocyaninato)tin(II) was converted to amino-(phthalocyaninato)tin(II) by similar method as that used in Ref. 6. A part of the amino groups of the derivative were then conjugated to the carboxyl group of the carboxyl-modified PAA in *N*,*N*-dimethylformamide (DMF) to obtain the final PAA-[Sn(II)(pc)]. A schematic scheme of the synthesis is shown in Scheme 1. PAA-(pc) was also synthesized by a similar method

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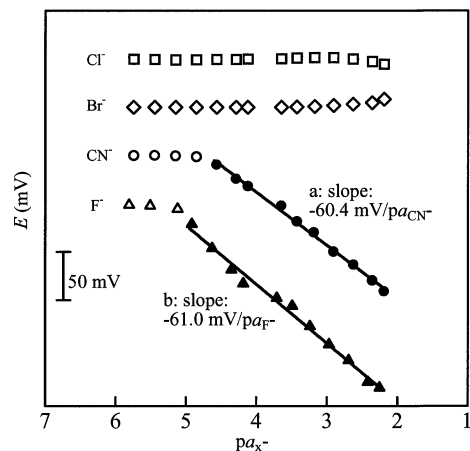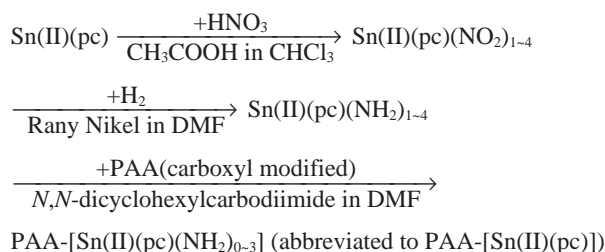E-mail: toshion@gipac.shinshu-u.ac.jp

Fig. 1 Calibration curves for the ions in *N,N*-dimethylacetamide at a platinum electrode coated with poly(acrylamide) conjugated to (phthalocyaninato)tin(II), PAA-[Sn(II)(pc)].

Fig. 2 Cyclic voltammograms of [Sn(II)(pc)] at a Pt electrode in a DMA solution containing 10 mM Et$_4$NClO$_4$. Concentration of [Sn(II)(pc)]: (A) 0 mM, (B) saturated. Scan rate, 200 mV/s.

as that described above.

$$Sn(II)(pc) \xrightarrow[CH_3COOH \text{ in } CHCl_3]{+HNO_3} Sn(II)(pc)(NO_2)_{1\sim4}$$

$$\xrightarrow[Rany \text{ Nikel in DMF}]{+H_2} Sn(II)(pc)(NH_2)_{1\sim4}$$

$$\xrightarrow[N,N\text{-dicyclohexylcarbodiimide in DMF}]{+PAA(carboxyl \text{ modified})}$$

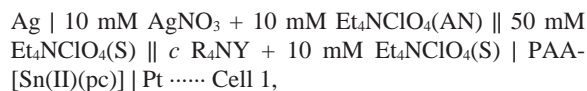PAA-[Sn(II)(pc)(NH$_2$)$_{0\sim3}$] (abbreviated to PAA-[Sn(II)(pc)])

Scheme 1
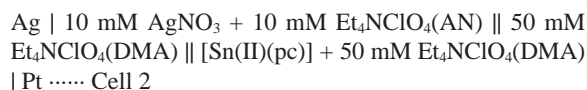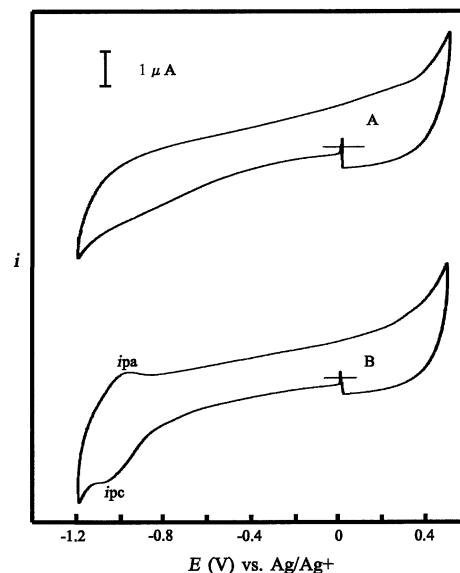
Indicator electrode and electrochemical measurement

A small amount of PAA-[Sn(II)(pc)] was dissolved in 20 μL of water and spread on the end of a platinum rod with a diameter of 2 mm housed in a Teflon body. After storing in silica-gel desiccator for more than 4 h, a thin membrane (thinner than 0.2 mm) was formed on the end of the electrode. The electrode was then conditioned in a DMA or AN solution containing 10 mM of Et$_4$NClO$_4$ for several hours.

The potentiometric response behavior of the PAA-[Sn(II)(pc)] electrode to various anions was investigated by Cell 1.

Ag | 10 mM AgNO$_3$ + 10 mM Et$_4$NClO$_4$(AN) ‖ 50 mM Et$_4$NClO$_4$(S) ‖ c R$_4$NY + 10 mM Et$_4$NClO$_4$(S) | PAA-[Sn(II)(pc)] | Pt ······ Cell 1,

where S = DMA and AN, and Y$^-$ = CN$^-$, F$^-$, Cl$^-$ and Br$^-$. R$_4$N$^+$ = Et$_4$N$^+$ and Bu$_4$N$^+$, c means concentration (M). All compartments of Cell 1 were prepared freshly every time. Steady state potentials were read to 0.1 mV.

Cyclic voltammograms of [Sn(II)(pc)] in DMA at a platinum electrode were obtained by a cyclic voltammetric (CV) measurement with Cell 2.

Ag | 10 mM AgNO$_3$ + 10 mM Et$_4$NClO$_4$(AN) ‖ 50 mM Et$_4$NClO$_4$(DMA) ‖ [Sn(II)(pc)] + 50 mM Et$_4$NClO$_4$(DMA) | Pt ······ Cell 2

The measurement was carried out at 25°C under an aerobic

condition with a potentiostat/galvanostat (HA150 Hokuto Denko) and an arbitrary function generator (HB105 Hokuto Denko), and recorded with an x-y recorder. The auxiliary electrode was a platinum wire.

Measurement of UV-vis spectra

The UV-vis spectra of [Sn(II)(pc)], and pc with Et$_4$NCN, Bu$_4$NF, and Et$_4$NCl in DMA were carried out by a UV-visible recording spectrophotometer (UV 260, Shimadzu, Japan). At first, a solution of DMA saturated with [Sn(II)(pc)] or pc was prepared. The solubility of [Sn(II)(pc)] or pc in DMA was lower than 0.01 mM. A series of various concentrations of Et$_4$NCN, Bu$_4$NF, or Et$_4$NCl in the above solution were then prepared.

Results and Discussion

Potentiometric results

The potentiometric response behavior of a PAA-[Sn(II)(pc)] electrode for CN$^-$, F$^-$, Cl$^-$, and Br$^-$ in DMA was investigated. Typical response results are shown in Fig. 1. It can be seen from the figure that the electrode showed a Nernstian response to CN$^-$ and F$^-$ and a quite poor response to Cl$^-$ and Br$^-$. It was also found that the PAA-(pc) electrode showed a thermodynamic response to F$^-$ in AN with a linear concentration range of 10^{-2} to 10^{-4} M.

Cyclic voltammetric results

A CV measurement of [Sn(II)(pc)] in DMA at a platinum electrode was carried out using Cell 2. The results are shown in Fig. 2. The cathodic peak, i_{pc}, was observed at about –1.05 V *vs*. Ag/Ag$^+$, and the anodic peak i_{pa}, was at about –0.95 V. The cathodic peak, which was just before the reduction peak of dissolved oxygen, was considered to be the reduction of [Sn(II)(pc)], while the anodic peak was considered to be the oxidation of [Sn(II)(pc)]. The result means that the PAA-[Sn(II)(pc)] electrode may be negatively charged after five min standing at an applied potential of –1.2 V, since [Sn(II)(pc)] in

Table 1 Potentiometric responses for CN⁻ and F⁻ in *N,N*-dimethylacetamide (DMA) and acetonitrile (AN) at a PAA-[Sn(II)(pc)] electrode

Electrode	Solvent	CN⁻	F⁻
PAA-[Sn(II)(pc)]⁻	DMA	−59.6	—
		(2.2 – 4.6)	
PAA-[Sn(II)(pc)]	DMA	−60.2	−60.9
		(4.6 – 2.2)	(4.9 – 2.3)
	AN	−60.6	−62.0
		(4.5 – 2.3)	(4.2 – 2.9)

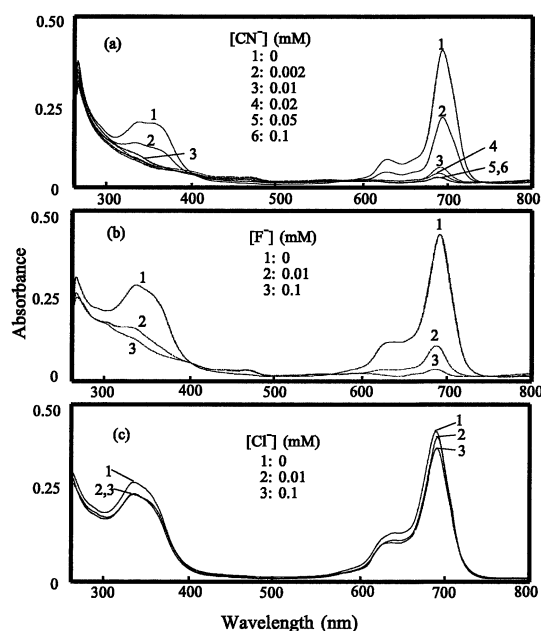At 25°C, slope in mV/log a_{x-}; ( ), linear range in pa_{x-}.

Fig. 3 UV-vis spectra of the interaction between (phthalocyaninato)tin(II) ([Sn(II)(pc)]) and (a) CN⁻; (b) F⁻; (c) Cl⁻ in *N,N*-dimethylacetamide (DMA). DMA was saturated with [Sn(II)(pc)]; the concentration of [Sn(II)(pc)] was lower than 0.01 mM.

the electrode membrane originally has no charge and it might become negatively charged at this potential.

The potentiometric response results for CN⁻ and F⁻ in DMA and AN at both charged and non-charged PAA-[Sn(II)(pc)] electrode are summarized in Table 1.

From the table it can be seen that the electrodes, before and after the voltage application, showed a similar response behavior to CN⁻ in DMA, *i.e.*, the slope was Nernstian. This means that the thermodynamic response of the PAA-[Sn(II)(pc)] electrode may not be affected by the charge of the host compound of the sensor membrane. The same experiments were carried out in the case of Cl⁻; also, the electrode did not show any difference before and after a potential application of −1.2 V. From the result we could conclude that the charge of the host compound in sensor membrane had no influence on the potentiometric response.

Spectrophotometric results

To consider why the electrode showed such a potentiometric response behavior as shown above, UV-vis spectrophotometric measurements were carried out. A series of different concentrations of CN⁻, F⁻, and Cl⁻ were prepared by a solution of DMA saturated with [Sn(II)(pc)] or pc. The UV-vis spectra of these solutions are shown in Figs. 3 and 4.

The spectrum of the original solution of DMA saturated with [Sn(II)(pc)] had a high peak at about 690 nm, then it decreased with increasing CN⁻ and F⁻, and finally almost disappeared. When the concentration of Cl⁻ in the [Sn(II)(pc)]-DMA solution was increased, however, the peak height changed slightly. The characteristics of the spectra of Br⁻ with [Sn(II)(pc)] in DMA was the same as that of Cl⁻. This means that [Sn(II)(pc)] interacted strongly with CN⁻ and F⁻, but did so weakly with Cl⁻ and Br⁻. To explain this, the complexing ability of CN⁻, F⁻, Cl⁻, and Br⁻ was considered first. According to the *ligand field theory* in coordination chemistry, the complexing ability of CN⁻, F⁻, Cl⁻, and Br⁻ is in the order of CN⁻ ≫ F⁻ ≫ Cl⁻ > Br⁻. Secondly, the solvent effect of solvent molecules on the interest ion was considered. It has to be considered especially when complexing occurs in various aprotic solvents.[7,8] From the acceptor number, defined by Gutmann,[9] of DMA being 13.6,[10] DMA molecules solvate weakly with anions. On the other hand, the standard molar Gibbs free energy of transfer values of F⁻, Cl⁻, and Br⁻ from water to AN, ΔG_t^o (i, W ⟶ AN) (i means the ions and W means water), are 71, 42.1, 31.3 kJ mol⁻¹, respectively.[11] This means that F⁻ should be more active in AN than Cl⁻ and Br⁻. Although the standard molar Gibbs free energy of transfer of F⁻ from water to DMA has not been known, when we consider that the accepter number of DMA is smaller than that of AN(18.9),[10] the difference in the activities between F⁻ and Cl⁻ or Br⁻ in DMA will be larger than in AN.

That is, F⁻ might be much more active in DMA than Cl⁻ and Br⁻.

From the above, it can be concluded that CN⁻ and F⁻, having a high complexing ability and a high activity in an aprotic solvent, will react with [Sn(II)(pc)] by a ligand exchange reaction at the axial site. The original ligand, *e.g.*, H₂O or DMA molecule, should have been changed to CN⁻ or F⁻ when CN⁻ or F⁻ was added to the [Sn(II)(pc)] saturated DMA solution. However, such a reaction did not occur between [Sn(II)(pc)] and Cl⁻, even in DMA. The potential might be established at the interface of the polymer membrane and nonaqueous solution due to complexation of the host compound [Sn(II)(pc)], which is conjugated to the PAA membrane, with CN⁻ and F⁻ in the dipolar aprotic solvent.

Although these results seem to be similar phenomena to the case of PAA-[Co(pc)] with CN⁻ and F⁻ [6], a big difference was observed in the spectra that there was a clear absorbance for the original DMA solution saturated with [Sn(II)(pc)] and no absorbance for AN solution saturated with [Sn(II)(pc)]. In addition, the center metal of the phthalocyanine and the solvent were changed from Co and AN to Sn and DMA. We then obtained a very important result that the center atom change does not show any substantial influence on the response behavior of the electrode, this result should play a very important role on any further understanding of the response mechanism of the electrode.

Besides, another relative electrode, a PAA-[(pc)] electrode, showed a similar property as the PAA-[Sn(II)(pc)] electrode showed above. In order to clarify the special potentiometric response behavior of the electrode, UV-vis spectrometric measurements concerning the interaction of pc and the ions in DMA were also carried out. The results are shown in Fig. 4.

A solution of DMA saturated with pc had symmetrical small peaks at about 690 and 655 nm. A new peak at about 665 nm increased as the concentration of CN⁻ and F⁻ became higher and the absorbance at about 325, 390 and 600 nm also increased.
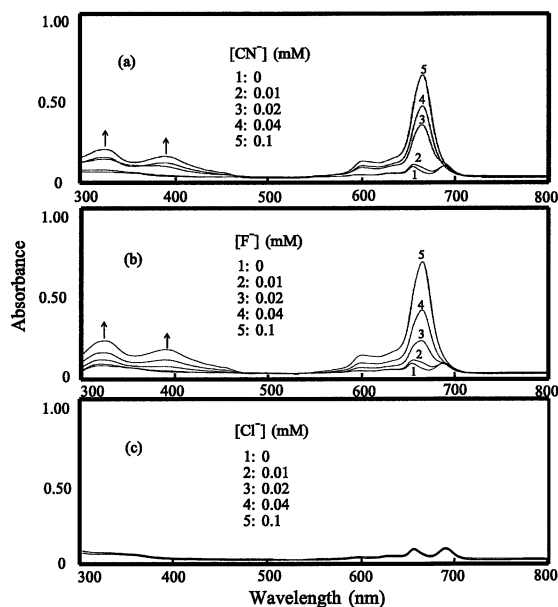
Fig. 4   UV-vis spectra of the interaction between phthalocyanine (pc) and CN⁻ (a), pc and F⁻ (b), pc and Cl⁻ (c) in *N,N*-dimethylacetamide (DMA).   DMA was saturated with pc; the concentration of pc was lower than 0.01 mM.

However, no change occurred when the concentration of Cl⁻ was increased. This means free pc in DMA interacts strongly with CN⁻ and F⁻, but does so very weakly with Cl⁻. This result is quite similar to the case of CN⁻, F⁻, and Cl⁻ with pc in AN, as had been reported.[6]   In this case, however, a symmetrical absorbance was observed in the original DMA solution containing pc only, and the complexing was definitely clarified by the dependence of the absorbance on the concentration change of CN⁻ or F⁻ in DMA. It seems to be reasonable that CN⁻ and F⁻ in DMA might enter into the hole of pc by hydrogen-bonding interactions when we consider the interaction between the ion and the expanded porphyrin reported by Tabata *et al*.[12]   A theory concerning the response of ion-selective electrodes was discussed by Pungor,[13] that the selective electrode potential was established by some chemical reactions. In this experiment it can be found that a complex formation reactions play an important role to establish thermodynamic response in both the PAA-[Sn(II)(pc)] and the PAA-(pc) electrodes.

Conclusions

A selective Nernstian response at the PAA-[Sn(pc)] electrode

for CN⁻ and F⁻ in DMA and AN was confirmed.   A thermodynamic response at PAA-(pc) electrodes for F⁻ in AN was also observed.   There has not been observed any substantial difference in the potentiometric response behavior when changing center atom of the phthalocyanine.   The charge difference of the host compound in the sensor membrane has no effect on the thermodynamic response of the electrode.   The peculiar selective response of the electrode in the paper was determined by the complexing ability of [Sn(II)(pc)] and pc with the ions, and the motive force of the reaction was due to the complexing ability, the ion basicity, and the solvent effect.

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