Potentiometric Response Properties of Sensor Membranes Based on Cobalt Phthalocyanine Conjugate-Polymer in Nonaqueous Solutions

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Some experiments are carried out in order to clarify the reason why the electrode prepared by coating a platinum disk with a non-plasticized membrane of polyacrylaminde polymer (PAA) coupled to cobalt phthalocyanine (CoPc) shows such a Nernstian response and a special selectivity for fluoride and cyanide ions in acetonitrile (AN). Special interactions between the ions and CoPc are observed spectrophotometrically. A complexing ability of the CoPc with only fluoride and cyanide ions works to respond in a Nernstian way for the ions at the electrode. Since the electrode shows quite poor response to chloride and bromide ions it can be understood that an ion exchange reaction of the ions in the solution at CoPc does not function to the response of the electrode. Furthermore, the PAA matrix of the membrane is found to produce the electrochemical masking effect on chloride and bromide ions. The PAA–CoPc electrode is confirmed as available for use of determining the solubility product constant of sodium fluoride in AN.

No F^- and CN^- selective-electrode is available for a thermodynamic study in aprotic solvents except for the electrode described in this paper and that constructed with LaF_3 single crystal membrane. Investigations of reactivity of metal phthalocyanine with anions[1] and of applications to anionic sensors of cobalt phthalocyanine (CoPc) complex for use in aqueous solutions[2—5] have been carried out. We expect to utilize the CoPc for making sensors for use in nonaqueous solutions. Preliminary results of the response for several ions at platinum electrode coated with a non-platicized polymer membrane of a polyacrylamide (PAA) coupled to CoPc had been reported.[6,7] The voltammetric behaviors of several anions in acetonitrile (AN) at the PAA–CoPc electrode were studied.[8] It will be interesting to learn why the PAA–CoPc electrode shows such a special potentiometric response to Cl^-, although Cl^- has originally been contained in the PAA membrane as the counter anion of CoPc.[6,7] In this paper we report firstly the potentiometric response behavior at the PAA–CoPc electrode for some anions in AN and propylene carbonate (PC). The responses for several anions in AN both at a PAA coated platinum electrode and at a naked platinum electrode are also studied. Secondly the spectrophotometric investigation to elucidate response characteristics of the electrode is described. Finally the thermodynamic application of the electrode to determine the solubility product constant of sodium fluoride in AN is reported.

Experimental

Indicator Electrode. Tetraaminophthalocyanine cobalt of Wako was conjugated at the carboxyl group of the carboxy-modified PAA (average M.W. 200000) from Aldrich by the same method as described in Refs. 9 and 10. The membrane made of PAA is hygroscopic and unstable against water attack, however, it is quite stable in aprotic solvents. The indicator electrode was constructed in the same way as that reported before,[6,9] i.e., small amounts of powder of the conjugated polymer were dissolved with 2 μL of water on the platinum disk electrode and dried up in a silica gel descicator. It was conditioned more than seven hours in AN-solution containing 0.5 mM analyte ion and 10 mM indifferent electrolyte shown in Cell 1 to be described later. When the PAA electrode was used as an indicator electrode it was conditioned in 10 mM in different electrolyte-AN solution. Here M denotes $\mathrm{mol\,dm^{-3}}$.

Reagents. Tetrabutylammonium fluoride ($Bu_4NF{\cdot}3H_2O$), tetraethylammonium cyanide (Et_4NCN), tetrabutylammonium nitrite (Bu_4NNO_2), and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) were products of Fluka. Tetraethylammonium perchlorate (Et_4NClO_4) and tetraethylammonium chloride (Et_4NCl) were purchased from Nacalai. Other chemicals and solvents were the same as those in the previous reports.[6,8]

Apparatus. Measurements of UV spectra were carried out with the UV visible recording spectrophotometer, UV-260, of Shimadzu. A ten mm crystal cell made of quartz was used. Other pieces of apparatus were the same as those in the previous reports.[6,8]

Measurement of Potentiometric Response. The following Cell 1 was used for the measurement of potentiometric responses for the various anions except for the case in which the analyte ion was PF_6^-. When the analyte ion was PF_6^-, tetraethylammonium perchlorate was used as the indifferent and salt bridge electrolytes.

$$\begin{array}{l}\mathrm{Ag/10\ mM\ AgNO_3{+}10\ mM\ Bu_4NPF_6(D)//}\\ \quad \mathrm{50\ mM\ Bu_4NPF_6(D)//}\\ \qquad c\mathrm{X^-{+}10\ mM\ Bu_4NPF_6(D)/PAA\text{–}CoPc/Pt}\cdots\ \text{Cell 1}\end{array}$$

where D denotes AN or PC and c means the concentration of the analyte ion, X^-, in $\mathrm{mol\,dm^{-3}}$. When D was PC, $AgClO_4$ was used instead of $AgNO_3$ because of its solubility and dissociation. The solutions in Cell 1 were prepared freshly every day and the emf change of Cell 1 was measured by standard addition method to investigate the response of the electrode, unless otherwise mentioned.

Results and Discussion

Potentiometric Response. The typical examples of time vs. potential curves for the response at the PAA and the PAA–CoPc electrodes to changes in F^- and CN^- concentration in AN and the calibration curves are shown in Fig. 1. The results of the potentiometric response for F^-, CN^-, I^-, and NO_2^- in AN and PC at the PAA and PAA–CoPc electrodes are summarized in Table 1, in which the slopes had the deviations of ±5 mV/pa_{x^-} and ±0.3 mV/pa_{x^-} on the experiments repeated five times, respectively. The PAA–CoPc electrode returned to a initial potential within five to fifteen minutes when the electrode was immersed again in AN and PC solution containing an initial F^-, CN^-, and NO_2^- concentration after a procedure of standard addition. Total potential changes at the PAA electrode for such other anions as Cl^-, Br^-, SCN^-, tetraphenylborate (BPh_4^-), and PF_6^- were only a few millivolts to the concentration change between 1.5×10^{-5} and 8×10^{-3} M, being quite different from the case of F^-, CN^-, I^-, and NO_2^-. The dynamic response to NO_2^- at the PAA–CoPc electrode was very quick and the steady state potential could be obtained, but the slope of the response was sub-Nernstian as can be seen in the Table 1. The total potential changes at a naked platinum electrode for several anions in Cell 1 were measured and a fairly stable potential could be obtained at each concentration step. Total change in about fifteen milivolts was observed in the negative direction with the concentration range from 5×10^{-6} to 8×10^{-3} M of Cl^-, but the PAA electrode showed very poor potential response to Cl^-. The response behaviors to Br^- both at a naked platinum electrode and at the PAA electrode were almost the same as the case in Cl^-. It can be considered from the results that the PAA membrane worked as a kind of electrochemical masking substance for Cl^- and Br^-. It could not be explained at this stage, however, why the PAA–CoPc electrode showed a small potential change in a positive direction for increasing concentrations of tetraalkylammonium salts, e.g., Et_4NCl, Et_4NBr, Et_4NClO_4, etc.[6,7] The residual carboxylate groups on the PAA might act as an ion exchanger for tetraalkylammonium cations, e.g., Et_4N^+ and Bu_4N^+. The total potential change of about seventy millivolts at a naked platinum electrode to the NO_2^- concentration range from 5×10^{-6} to 8×10^{-3} M was observed, but the PAA electrode did not show such a result, as can be seen in Table 1. This means that the PAA membrane also worked as electrochemical masking material for the ion to some extent. A naked platinum electrode showed the total potential change of more than ninety millivolts for I^-, about eighty millivolts for CN^-, and about a hundred and twenty millivolts for F^- to the respective ion concentration range from 5×10^{-6} to 8×10^{-3} M. From the results and Table 1 it can be found that PAA worked as an electrochemical masking membrane for F^- and CN^- to some extent, but it did not work any more for I^-. The CoPc in the membrane did not show a clear effect for membrane potential on changing the

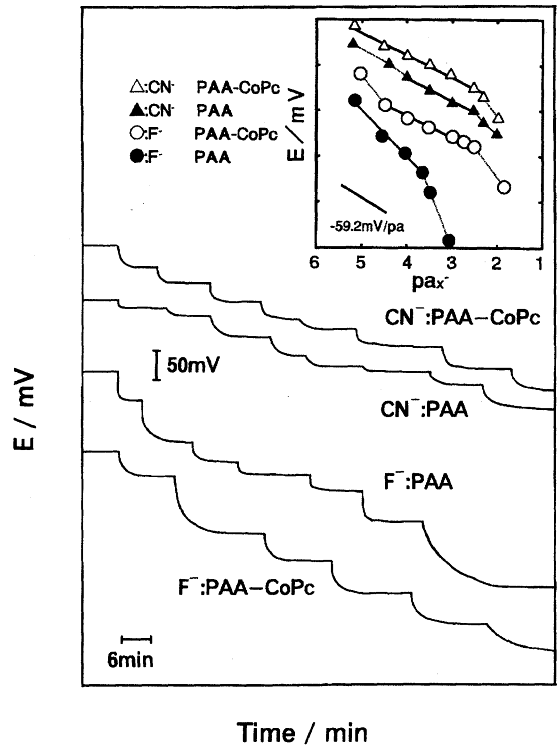

Fig. 1. Time vs. potential curves for the response of PAA–CoPc and PAA electrodes to change in fluoride and cyanide ion concentration in acetonitrile and calibration curves of the electrodes.

Table 1. The Response of the PAA and PAA–CoPc Electrodes for Some Anions in Acetonitrile (AN) and Propylene Carbonate (PC) at 25 °C

Ion	PAA Electrode		PAA–CoPc Electrode			
	AN		AN		PC	
	Slope (mV/log a_{x^-})	Linear range (pa_{x^-})	Slope (mV/log a_{x^-})	Linear range (pa_{x^-})	Slope (mV/log a_{x^-})	Linear range (pa_{x^-})
F^-	−80	3.5—5.8	−59.0[a)]	3.0—5.4	−58.7[a)]	3.2—5.3
CN^-	−55	2.7—5.7	−58.7[b)]	3.8—5.3	−59.0[b)]	2.8—4.2
I^-	−100	2.0—3.0	−104	2.2—5.3	−80	2.2—3.2
NO_2^-	−40	2.0—4.0	−35	1.9—4.0	−34	2.4—3.7

a) From Ref. 6. b) From Ref. 7.

concentration of I^- and $NO_2{}^-$, as can be seen in Table 1.

Spectrophotometric Measurement. UV and visible spectra were observed in AN to understand the response mechanism of the PAA–CoPc electrode. Some results are shown in Figs. 2, 3, 4, and 5. When F^- and CN^- was added to Pc–AN solution, the dark blue color changed into the greenish blue color for both cases. Here F^- and CN^- showed no absorbance at these wavelengths. From Figs. 2 and 3 we can expect a clear interaction of Pc with F^- and CN^-. As can be seen in Figs. 4 and 5, the peak at about 700 nm appeared in both cases between CoPc and F^- and between CoPc and CN^-. The peak was different from that obtained in the case of Pc (about 670 nm). The results suggest that the coordination of F^- and CN^- with CoPc as one of the ligands of the CoPc might occur. The reaction process of F^- in AN with Pc was not understood clearly at this stage. The report by Tabata et al.[11] might serve to explain the reaction. They used direct reaction of F^- with a kind of a synthesized

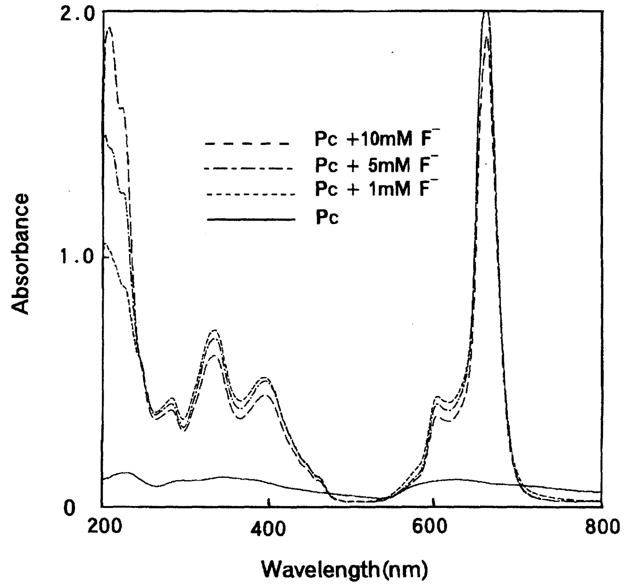

Fig. 2. UV and visible spectra of the interaction between phthalocyanine (Pc) and fluoride ion in acetonitrile. All of the solutions contained 2×10^{-5} M Pc. Reference was acetonitrile.

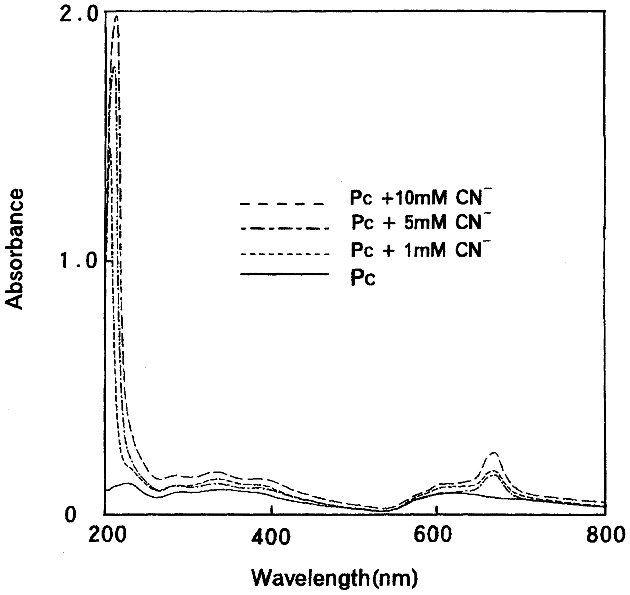

Fig. 3. UV and visible spectra of the interaction between phthalocyanine (Pc) and cyanide ion in acetonitrile. All of the solutions contained 2.0×10^{-5} M Pc. Reference was acetonitrile.

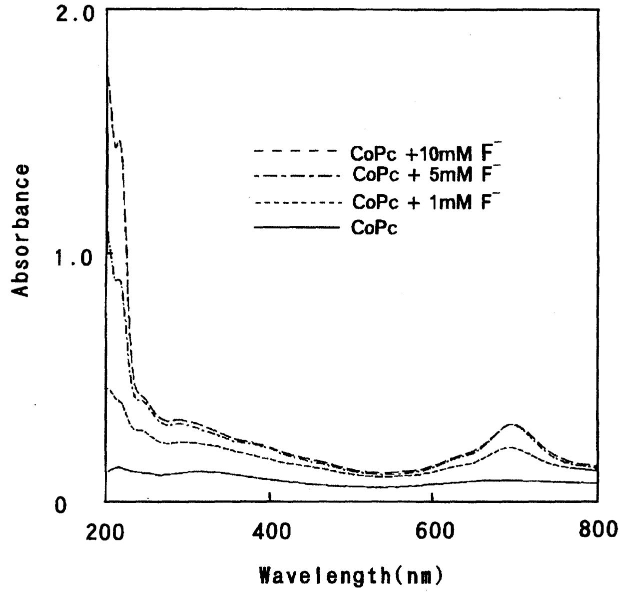

Fig. 4. UV and visible spectra of the interaction between cobalt phthalocyanine (CoPc) and fluoride ion in acetonitrile. All of the solutions contained 2.0×10^{-5} M CoPc. Reference was acetonitrile.

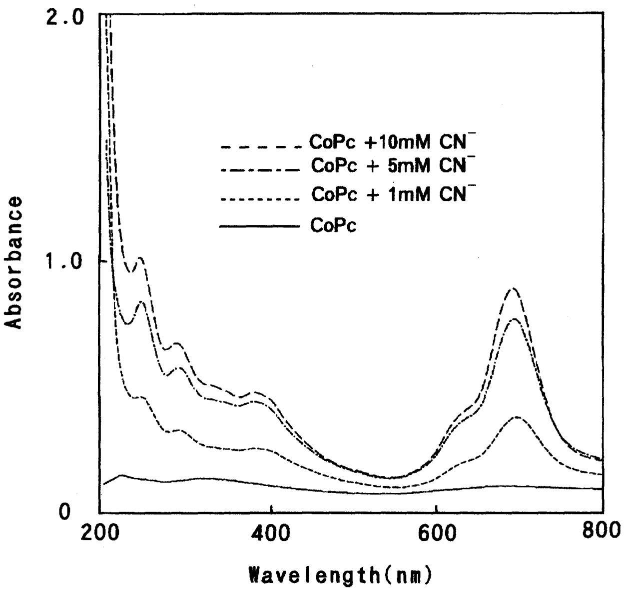

Fig. 5. UV and visible spectra of the interaction between cobalt phthalocyanine (CoPc) and cyanide ion in acetonitrile. All of the solutions contained 2.0×10^{-5} M CoPc. Reference was acetonitrile.

expanded porphyrin, on a determination of F^-. When NO_2^- was added to Pc–AN solution no peak appeared, but when it was added to CoPc–AN solution, a peak appeared at about 700 nm, although it was not so clear compared with those obtained in F^- and CN^-. In the cases of Cl^-, Br^-, and I^-, however, no change in spectra occurred either between the ions and Pc or between the ions and CoPc.

Establishment of Electrode Potential. The schematic diagram of the PAA–CoPc electrode is shown in Fig. 6. The CoPc conjugated with PAA at the close vicinity of the solution-membrane interface is considered to be in the AN solution since the CoPc is fond of the organic phase rather than the hydrophillic PAA membrane. It was described earlier that F^- and CN^- could coordinate with CoPc in AN while Cl^- and Br^- did not do so. It is apparent from Fig. 6 that the CoPc coordinates with F^- and CN^- to establish a membrane potential at the interface, resulting in the Nernstian response of the PAA–CoPc electrode. The consideration that the potential of the membrane electrode of this kind is mainly established at the membrane–solution interface had been reported in the previous paper,[12] in which the response for Ba^{2+} and Li^+ in AN at the PAA–B18C6, PAA–Cryp222, and PAA–POE4 electrodes had been discussed from the results obtained by cyclic voltammetric investigation. On the other hand the electrode showed a different response to Cl^- and Br^- which could not coordinate with CoPc in AN. The results were also explained by saying that the naked platinum electrode showed a potentiometric response to Cl^- and Br^- in AN but such responses were masked at the PAA electrode. We could conclude here that the ion exchange reaction does not work at the PAA–CoPc electrode to establish the membrane potential.

It is interesting that the PAA electrode showed super-Nernstian response to I^-, different from the case in Cl^- and Br^-. The I^- might transfer into PAA membrane from AN and PC solution and penetrate to reach the platinum surface, although the transfer of I^- seems to be suppressed some extent in PC as can be seen in Table 1, probably because of deterioration of an affinity of PC with PAA. Cl^- and Br^- seem not to be able to transfer into the PAA membrane under such electrostatic conditions as in the experiment. Sub-Nernstian response at the electrode to NO_2^- may result because of the insufficient complexing ability of the CoPc with NO_2^- in AN.

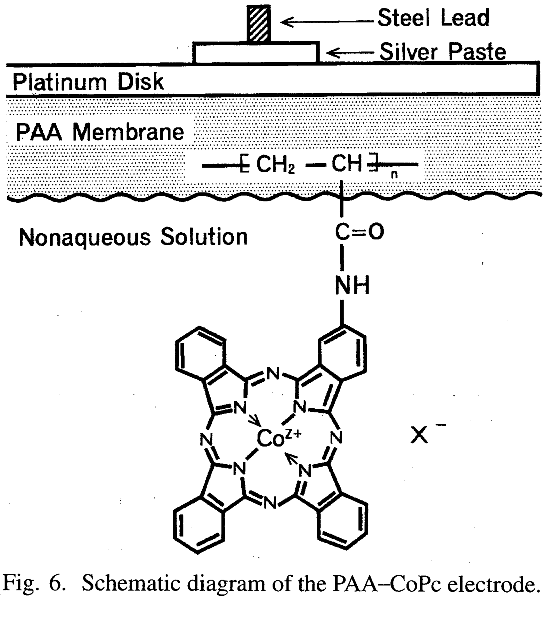

Fig. 6. Schematic diagram of the PAA–CoPc electrode.

Table 2. The Solubility Product Constant, pK_{sp}, of Sodium Fluoride in Acetonitrile at 25 °C

Initial Concentration of Bu_4NF	6×10^{-4} M	2×10^{-3} M	9×10^{-3} M
$(pK_{sp})_{AN}$	10.0	10.0 9.9[a]	10.1

a) See Ref. 6.

Solubility Product Constant. In order to confirm the applicability of the PAA–CoPc electrode for getting a solubility product constant, experiments were carried out under the different initial fluoride ion concentration. The values of the sodium fluoride in AN, $pK_{sp}(NaF)_{AN}$, obtained here are summarized in Table 2 along with that obtained before.[6] That the constants agreed well with each other means that the potential of the PAA–CoPc electrode is determined only by the change of the activity of F^- and not affected by that of other ions which coexist in the cell, such as Na^+, Et_4N^+, Bu_4N^+, ClO_4^-, and PF_6^-. It should be noted that the value was obtained under the condition of probable existence of NaF which was dissolved in AN.

Conclusion

The reason why such a Nernstian response and special selectivity generated at the PAA–CoPc electrode for F^- and CN^- in AN were examined. The main factor to respond in a Nernstian way is the complexing ability of CoPc with the ions in AN. The specific selectivity is established by two factors. The one is that the ion exchange reaction of the ions in AN at CoPc does not work for the response of the electrode and the other is that the PAA used as the matrix of the electrode creates an electrochemical masking effect to some ions. The PAA–CoPc electrode was confirmed as available for use for determining the solubility product constant of sodium fluoride in AN.

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