Selective response mechanism of a platinum disk electrode modified with polyacrylamide membrane conjugated with gallium (III) phthalocyaninate

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Abstract

A non-plasticized polyacrylamide polymer (PAA) coupled to (phthalocyaninato) gallium(III) ($[Ga(pc)]^+$) , PAA-([Ga(pc)], was synthesized firstly. The potentiometric response behavior of PAA-[Ga(pc)] modified platinum electrode was examined for some ions in such nonaqueous solvents as acetonitrile (AN), dimethylacetamide (DMA), and N-methylpyrrolidinone (NMP). The electrode showed a Nernstian or a near-Nernstian response to CN^- and F^- in AN, DMA, and NMP, but it showed a non-thermodynamic response to Cl^- and Br^- in all the above solvents. Besides spectrophotometric method, cyclic voltammetric investigation was performed to explain the reaction of $[Ga(pc)]^+$ with the ions in above solvents. The results revealed that such specially selective response phenomena were due to the complex formation reactions of the ions with $[Ga(pc)]^+$. The reactions were interpreted by the shift of the maximum absorption peak, the appearance of the new peaks on UV-vis spectra of $[Ga(pc)]^+$ with the existence of CN^- and F^- and the clear difference of the redox voltammogram of $[Ga(pc)]^+$ at platinum electrode between the adding of F^- and Br^- in DMA. The three solvents did not show obvious different influence on the complexing. The electrode could be applicable to obtain the solubility product of NaF in AN.

Keywords: nonaqueous solution; phthalocyanine complex; hydrophilic polymer membrane; fluoride; cyanide; potential response mechanism

1. Introduction

Potentiometric methods based on ion-selective electrodes have great advantages such as speed, ease of preparation, reasonable selectivity, low cost, and wide application. Potentiometric measurements can also reveals precise information of the chemical interactions occurred at polymer membrane-solution interface for polymer-modified electrode. In order to develop a highly specific ion-selective electrode, the interaction between the analyte ion and the membrane on electrode surface is a significant subject and it is a classical but essential problem to understand the selective response mechanism of ion-selective electrodes.

Metal phthalocyanines ($[M(pc)]$) and porphyrins have been used as a host compound of sensors for various anions, e.g., a porphyrin-gallium complex has been used to prepare an anion sensor for F^-, although those are almost for use in aqueous solution systems [1-3]. Some investigations concerning the characteristics of metallophthalocyanines in dipolar aprotic solvents have also been carried out by UV-vis spectrophotometric measurement [4-7]. Some anion sensing materials that were consisted of non-plasticized polyacrylamide polymer (PAA) coupled to phthalocyaninato complex ($[Co(pc)]$, $[VO(pc)]$ and $[Sn(pc)]$) have been developed for use in dipolar aprotic solutions[8-10]. All of these electrodes showed selective Nernstian response to CN^- and F^- in some aprotic solvent although the center metal of the host compound were different.

The aim of our study was to gain a better understanding of the response mechanism of this kind of electrode, the influences of the center metal of the host compound on the response of the electrode and the applicability of the electrode in different solvents, in the present work a new sensing material, non-plasticized PAA coupled to (phthalocyaninato) gallium(III) ($[Ga(pc)]^+$) was synthesized firstly. Next, the potentiometric response measurement of a platinum electrode modified with the membrane of this material (PAA-$[Ga(pc)]$) for such anions as CN^-, F^-, Cl^-, and Br^- in the aprotic solvents of AN, DMA and NMP were carried out. Thirdly, UV-vis spectrophotometric and cyclic voltammetric investigations about the interaction of $[Ga(pc)]^+$ with the

ions in AN, DMA, and NMP were performed to explain the selective response of the electrode. Fourthly, The selectivity coefficient of the electrode for F^- over CN^- in AN were also measured to explain the extent of the interaction of $[Ga(pc)]^+$ with F^- and CN^-. Finally, the PAA-[Ga(pc)] electrode was used to obtain the solubility product constant of NaF in AN.

2. Experimental

2.1 Reagents

[Ga(pc)]Cl was purchased from Aldrich (No. 40880-8) and conjugated to carboxy-modified PAA by the same method as that reported in a previous paper [8]. Tetraethylammonium perchlorate (Et_4NClO_4) was a polarographic grade product purchased from Nacalai Tesque (No. 330-16). It was dried at 65 ^{o}C for 3 hours under a high vacuum with P_2O_5. Tetrabutylammonium fluoride (Bu_4NF), bromide (Bu_4NBr) and Tetraethylammonium chloride (Et_4NCl), cyanide (Et_4NCN) were purchased from Fluka Co., Ltd., and were used without further purification.

2.2 Solvents

DMA was a reagent grade of Wako (No. 045-02916) and distilled two times by fractional distillation apparatus (packed column is the type of Shibata Scientific Technology Ltd) after treating with molecular sieves (4A 1/16). The first distillation was carried out in the presence of BaO, and second in the presence of CaH_2 under a reduced pressure (ca. 15 mmHg) and nitrogen gas. NMP was also a reagent grade of Wako (No. 136-07616) and fractionally distilled twice after treating with molecular sieves (4A 1/16) under reduced pressure (ca. 10

mmHg) and nitrogen gas.

2.3 Indicator electrode and potentiometric measurement.

The host compound, $[Ga(pc)]^+$, was converted to the amines via the respective nitro derivative. The modified host compound was then conjugated at the carboxyl group of carboxyl-modified polyacrylamide by reaction in DMF following the procedure of Bauminger and Wilchek to obtain the final polymer conjugate, PAA-[Ga(pc)]. A small amount of the conjugate polymer was dissolved in 20 μl water and spread on the end surface of a platinum rod with the diameter of 2 mm housed in the Teflon body. After the electrode stored in silica gel desiccators for about more than four hours, a thin (less than 0.02 mm) membrane was formed on the end of the electrode. Then, the electrode was conditioned for more than seven hours in the solution containing 10 mM indifferent electrolyte shown in Cell 1. The potentiometric response behavior of the PAA-[Ga(pc)] electrode to various anions was investigated by measuring Cell 1; the emfs were measured with a pH meter (Φ71, Beckman)and recorded by a recorder (LR4110E, Yokokawa Denki Co.). All compartments of Cell 1 were prepared freshly every time. Steady state potentials were read to 0.1 mV.

Ag｜10 mM AgNO$_3$+10 mM Et$_4$NClO$_4$(AN)‖50 mM Et$_4$N ClO$_4$ (AN)‖

c R$_4$NY+10 mM Et$_4$NClO$_4$ (D)｜PAA-[Ga(pc)]｜Pt ……Cell 1,

Where, D = AN, DMA, and NMP; $Y^- = CN^-$, F^-, Cl^-, and Br^-; R_4N^+ = tetraethylammonium ion (Et_4N^+) and tetrabutylammonium ion (Bu_4N^+), and c means concentration (mol dm^{-3}). R$_4$NY was added by microburet that was a type of Gilmont S-1200. The change of liquid-junction potentials of Cell 1 during emf measurements can be negligible in the experiment [11]

2.4 UV-vis spectra measurements

UV-vis spectra Measurements were carried out by the same method reported previously [8]. At first, [Ga(pc)]$^+$ saturated AN, DMA or NMP solutions (<0.01 mM) were prepared and for DMA and NMP, the solutions were diluted by a factor of five. Then, solutions with various concentrations of each anion in the above solution were made.

2.5 Cyclic voltammetric measurements

Cyclic voltammetric experiments were performed at room temperature using an arbitrary function generator (HB105 Hokuto Denko) and a potentiostat/galvanostat (HA150). The electrochemical cell was assembled with a three-electrode system: a Pt disk (diameter 2mm) working electrode, a Ag$^+$/Ag (Ag|10mM AgNO$_3$, 10mM Et$_4$NClO$_4$ in AN) reference electrode, and a Pt counter electrode. The scan rate was 100 mV/s over the relevant potential range.

3. Results and discussion

3.1 Potentiometric results

The potentiometric response behaviors of the PAA-[Ga(pc)] electrode to such anions as CN$^-$, F$^-$, Cl$^-$, and Br$^-$ in AN, DMA, and NMP was studied. A typical dynamic response curves for the addition of F$^-$ in AN at PAA-[Ga(pc)] electrode is shown in Fig.1 and the response results are summarized in Table 1.
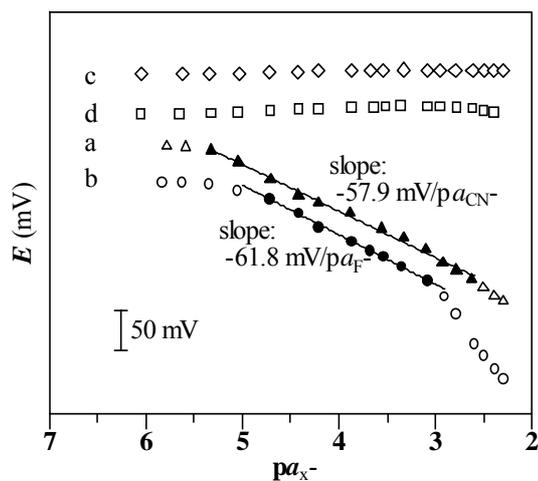
Fig. 1. Potentiometric calibration curves for the ions in acetonitrile at PAA-[Ga(pc)] electrode.

Table1   The response for various anions at the PAA-[Ga(pc)] electrode in
       acetonitrile, N,N-dimethylacetamide, and N-methl-2-pyrrolidinane

Slopes are in mV/loga_x- and figures in ( ) are the linear range in pa$_x$- at 25℃.

Ion	AN (14.1[a])	DMA (27.8[a])	NMP (27.3[a])
F$^-$	-58.6	-57	-59.7
	(3.0-5.0)	(3.0-5.9)	(3.3-4.7)
CN$^-$	-58.8	-55.1	-55.2
	(2.5-5.4)	(2.5-5.6)	(2.3-4.7)
Cl$^-$	+4.2	+3.8	+23.2
	(3.0-5.3)	(2.9-6.0)	(2.4-5.5)
Br$^-$	+2.2	+12.3	+8.8
	(3.0-5.4)	(4.5-5.9)	(2.3-4.2)

a: the donor number of the solvent

The slopes in the table have deviations of ± 0.3 mV/pa$_X$- for those ions showing a Nernstian or near-Nernstian response, and ± 4 mV/pa$_X$- for those showing a non-Nernstian response in the repeated four or five times experiments, respectively. The linear ranges of the slopes in the Nernstian equation are also shown under each slope. The lowest activities of these range was the lower detection limit of the electrode. The response can classified into two groups. The first group (Group A: CN$^-$ and F$^-$) showed a Nernstian or near-Nernstian

response in AN, DMA, and NMP. The second (Group B: Cl⁻ and Br⁻) showed a non-Nernstian response in all

solvents investigated, in that the slopes are positive in spite of anions. The time taken to reach steady tstate

potential was less than 5 minutes for the ions in Group A but longer for those in Group B.

3.2 Spectrophotometric results.

3.2.1 Spectra in AN

In order to understand the peculiar selective response mechanism of the PAA-[Ga(pc)] electrode to the anions

in aprotic solvents, spectrophotometric investigations were carried out. The AN solution of $Bu_4NF \cdot 3H_2O$ or

Et_4NCN were added stepwise to [Ga(pc)]Cl saturated AN solutions. Typical spectra are shown in Fig. 2.
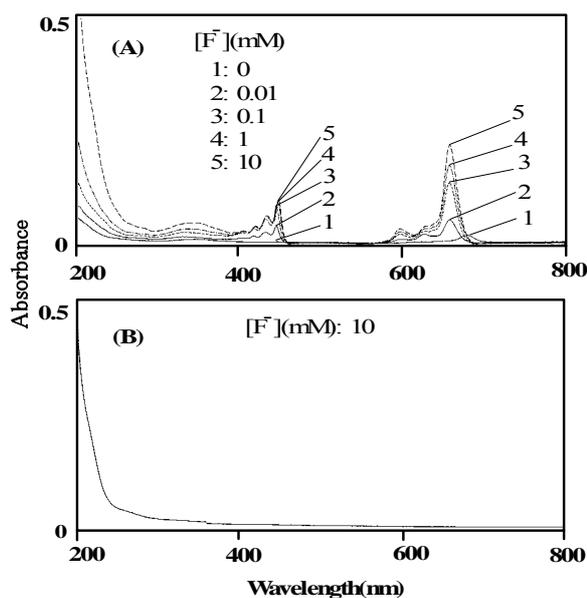
Fig. 2. UV-vis spectra of (A) (phthalocyaninato) Ga(III) ($[Ga(pc)]^+$) saturated acetonitrile

containing various concentration of F^- (the concentration of $[Ga(pc)]^+$ is lower than 0.01

mM); (B) Acetonitrile containing 10 mM of F^-. Reference was acetonitrile.

The original [Ga(pc)]Cl saturated AN solution had a small absorption peak at 678 nm. However, the peak

almost disappeared and new peaks at about 660 nm and 410-450 nm appeared and became higher according to

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the addition of F⁻. The adding compound itself did not exhibit any absorbance in AN. Almost the same behaviors were observed in the case of the adding of CN⁻. The phenomena were different from the UV-vis spectra of Co(pc) with F⁻ and CN⁻ in AN [8]. The original Co(pc) saturated AN solution showed no sharp absorption peak at the UV-vis spectra, however, after the addition of F⁻, a new adsorption peak appeared at longer wavelength but no new peak could be found at shorter wavelength region.

On the other hand, as shown in Fig.3, when Br⁻ was added to [Ga(pc)]Cl saturated AN solution the original absorption peak at 678 nm did not show any change even if the concentration of Br⁻ became higher. Furthermore, no new peak could be found at 410-450 nm although such peaks appeared in the case of CN⁻ and F⁻. Almost the same behaviors were observed both in the case of Br⁻ and Cl⁻. The results mean that [Ga(pc)]⁺ interact strongly with F⁻ and CN⁻ but only weakly with Cl⁻ and Br⁻.
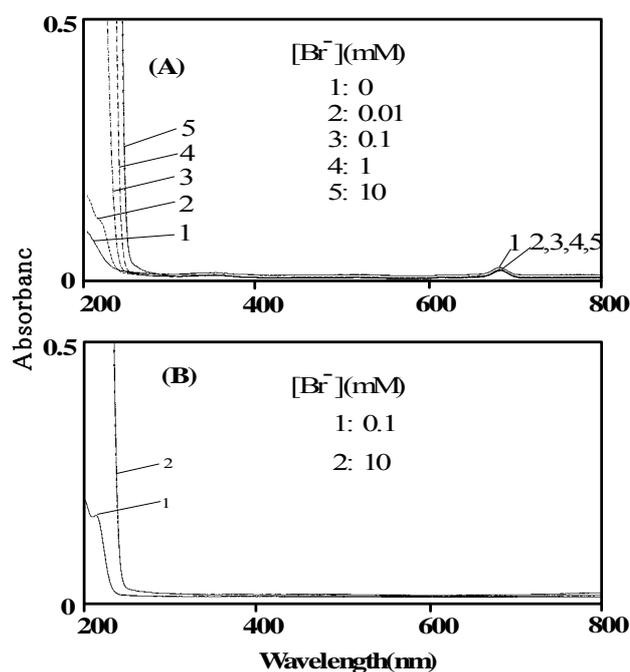
Fig. 3. UV-vis spectra of (A) (phthalocyaninato) Ga(III) ([Ga(III)(pc)]⁺) saturated acetonitrile containing various concentration of Br⁻ (the concentration of [Ga(pc)]⁺ is lower than 0.01 mM); (B) acetonitrile containing 0.1 and 10 mM of Br⁻ respectively. Reference was acetonitrile.

According to J. Wynne Kenneth's work [12], crystal and molecular structure of Ga(pc)Cl is that square-pyramidal coordination exists about Ga with Cl occupying the apex. The bond distances are as follows: Ga-Cl 2.217, Ga-N(1) 1.79, Ga-N(2) 1.981, Ga-N(3) 1.983, Ga-N(4) 1.9988 Å. On the other hand, the crystal and molecular structure of $[Ga(pc)F]_n$ is that Ga is octahedrally coordinated by 2F atoms and 4 N atoms of a virtually planar pc ring. The bond distances are as follows: Ga-F 1.936, Ga-N(1) 1.969, Ga-N(2) 1.970 Å. It should be noted that the bond distance of Ga-Cl is much larger than Ga-F and Ga-N. The bond energy should be in the order of $E_{Ga-N} \gg E_{Ga-Cl}$. From the UV-vis results shown above and the bond distance data, it can be deduced that when [Ga(pc)]Cl was dissolved in AN, it might be dissociated by the solvation of AN to form $[Ga(pc)]^+$, which showed an absorption peak at 678 nm on UV-vis spectra. When F^- was added to the solution, it should be considerable that a complexing reaction between $[Ga(pc)]^+$ and F^- would occur to form [Ga(pc)F] due to the larger bonding energy of Ga-F. According to the molecular orbital theory of coordination chemistry, the molecular orbital energy will be changed when the electron density of ligand become higher. It is apparent that the change would cause a change of the UV-vis spectra of the complexes. We can observe that the spectra of [Ga(pc)F] (2-5 in Fig.2 A) has an absorption peak at about 660 nm and three peaks at 410-450 nm, which is different from that of $[Ga(pc)]^+$ (1 in Fig.2 A). The three peaks at 410-450 nm should be all due to the complex of [Ga(pc)F] because [Ga(pc)]Cl or F^- itself in AN does not show any absorption in this region as can be seen in 1 of Fig.2 A and Fig.2 B. The complex formation reaction of F^- with $[Ga(pc)]^+$ may occur also because the acidity[13] of AN, whose acceptor number[14] is 18.9, is very weak, so F^- in AN is in a extraordinarily active. On the other hand, according to the theory of coordination chemistry the complexing ability of the ions is in the order of $CN^- \gg F^- \gg Cl^- > Br^-$, CN^- would complex with $[Ga(pc)]^+$ due to the high complexing ability of it. As a result, the equilibria both between F^- and [Ga(pc)F] and CN^- and [Ga(pc)(CN)] at the sensor membrane-solution interface were established.

In [Ga(pc)]Cl saturated AN solution, Cl$^-$ should be solvated with AN and exists as the counter ion of [Ga(pc)]$^+$ expecting by the fact that the relative permittivity of AN (35.9) [15] is not very low and the complexing ability of Cl$^-$ is very weak, although Cl$^-$ atom may be bonded with Ga in the crystal of [Ga(pc)]Cl crystal, suggests that in [Ga(pc)]Cl saturated AN solution, Cl$^-$ becomes solvated with AN and just acts as the counter ion to [Ga(pc)]$^+$. When Br$^-$ is added to the solution, it may also exist as a AN solvated ion for the same reason. Possibly, no coordination reaction occurs between [Ga(pc)]$^+$ and Br$^-$.

3.2.2 Spectra in DMA and NMP

We found here that the spectra of [Ga(pc)]Cl in DMA are quite different from that in AN. As can be seen in Fig.4, a quite strong absorption peak at 676 nm was originally appeared on the spectra of [Ga(pc)]Cl saturated
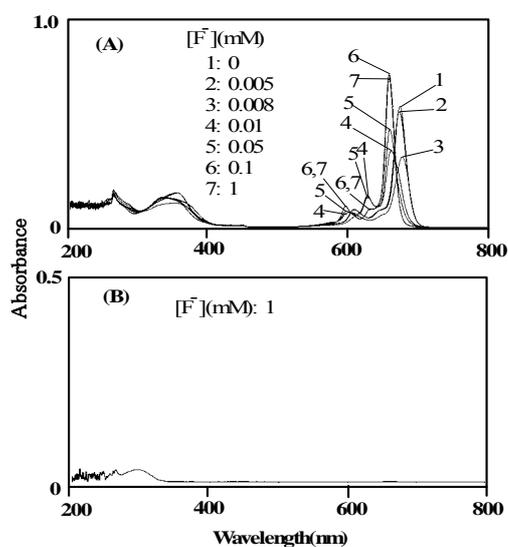
Fig. 4. UV-vis spectra of (A) (phthalocyaninato) Ga(III) ([Ga(pc)]$^+$) saturated N,N-dimethylacetamide (the concentration of [Ga(pc)]$^+$ is lower than 0.01 mM) diluted by a factor of five containing various concentration of F$^-$; (B) N,N-dimethylacetamide containing 1 mM of F$^-$. Reference was N,N-dimethylacetamide.

DMA solution, while just a small peak could be observed on the original UV-vis spectra of [Ga(pc)]Cl saturated

AN solution. It may be due to the more solubility of [Ga(pc)]Cl in DMA than in AN. The peak at 676 nm should

be due to [Ga(pc)]$^+$ from the same reason as mentioned for the case in AN,. Here, the peak shifts a few

nanometer to short wavelengths than in AN. It might be caused by the solvation strength difference between

DMA and AN. According to the addition of F$^-$, the peak decreased and a new peak at about 660 nm increased

gradually. A complex formation reaction of [Ga(pc)]$^+$ with F$^-$ in DMA would predominantly occur and the newly

appeared peak at about 660 nm should be attributed to the production of [Ga(pc)F$_2$]$^-$. In the case of CN$^-$, the

same behavior as that of F$^-$ in DMA was observed. As a result, like in AN, the complexing equilibria both

between F$^-$ and [Ga(pc)F] and CN$^-$ and [Ga(pc)CN] at the sensor membrane-solution interface were established,

respectively. Thus, the electrode potential could be established and the electrode could also show thermodynamic

response to CN$^-$ and F$^-$ in DMA.

When Br$^-$ was added to the [Ga(pc)]Cl saturated DMA solution, the UV-vis spectra of the solution just

showed a very little change as shown in Fig.5. Almost the same behavior could observed in the case of Cl$^-$ as

that of Br$^-$ in DMA. These also mean that the complex formation reaction of Br$^-$ and Cl$^-$ with [Ga(pc)]$^+$ did

not proceed appreciably. The behaviors of UV-vis spectra concerning all of the above ions in NMP were similar

to those in DMA.
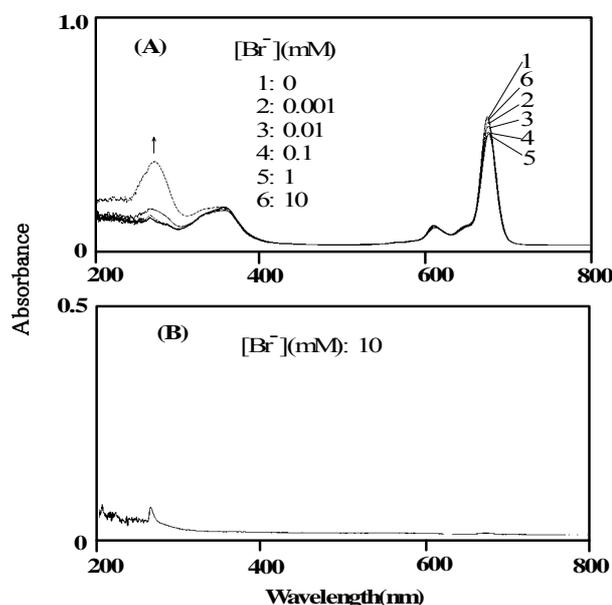
Fig. 5. UV-vis spectra of (A) (phthalocyaninato) Ga(III) ([Ga(pc)]$^+$) saturated

N,N-dimethylacetamide (the concentration of [Ga(pc)]$^+$ is lower than 0.01 mM) diluted by

a factor of five containing various concentration of Br$^-$; (B) N,N-dimethylacetamide

containing 10 mM of Br$^-$. Reference was N,N-dimethylacetamide.

The absorption maximum of [Ga(pc)]Cl saturated AN, DMA and DMF solution shifted more than 15 nm

when F$^-$and CN$^-$ were added while those were less than 3 nm at the case of   Cl$^-$and Br$^-$. It means that

[Ga(pc)]$^+$ interact strongly with F$^-$ and CN$^-$ but weakly with Cl$^-$ and Br$^-$ in all above solvents.

3.3 Cyclic voltammetric results

Cyclic voltammetric investigations for the interactions of [Ga(pc)]$^+$with F$^-$and Br$^-$ in DMA were carried

out. The results were shown in Fig.6: curve (a) was the CV of blank solution, i.e., 100 mM Et$_4$NClO$_4$ in
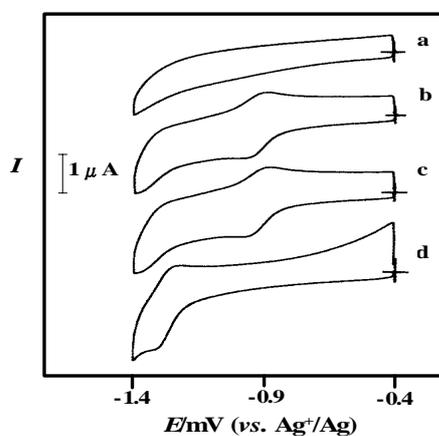
Fig. 6. Cyclic voltammograms recorded at platinum disk electrode in (a) 0.1 M Et$_4$NClO$_4$

DMA solutions; (b) [Ga(pc)]Cl saturated 0.1 M Et$_4$NClO$_4$ DMA; (c) [Ga(pc)]Cl

saturated 0.1 M Et$_4$NClO$_4$ DMA containing 1 mM Et$_4$NBr; (d) [Ga(pc)]Cl saturated

0.1 M Et$_4$NClO$_4$ DMA containing 1 mM Bu$_4$NF·3H$_2$O. Scan rate was 0.100V/s.

DMA; curve (b) was the CV of blank solution saturated with [Ga(pc)]Cl; curve (c) was the CV of blank solution

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saturated with [Ga(pc)]Cl containing 1 mM Et$_4$NBr; curve (d) was the CV of blank solution saturated with [Ga(pc)]Cl containing 1 mM Et$_4$NF·3H$_2$O. In this figure, the peak-to-peak separations indicate reversible electron transfer was taking place [16]. The half-wave potentials of this redox couple for [Ga(pc)]$^+$ in DMA was −920 mV (vs. Ag$^+$/Ag, which potential is 75 mV less than Fc$^+$/Fc). The redox peaks and half-wave potential had no change when Br$^-$ was added. However, it changed to −1.27 V as the adding of F$^-$. It means that F$^-$ coordinated strongly with the oxidized form than the reduced form.

The potentiometric, cyclic voltammetric, and spectrophotometric experimental results reveal that PAA-[Ga(pc)] electrode, similar to the PAA-[Co(pc)] and [Sn(pc)] electrode, showed Nernstian or near-Nernstian responses to F$^-$ and CN$^-$ obviously due to the reaction of the host compound in the sensor membrane with the ions, but showed a non-Nernstian response to the ions, Cl$^-$ and Br$^-$, that display a weak interaction with the host compound in all of the above solvents. There are not remarkable difference among the responses of PAA-[Ga(pc)], PAA-[Co(pc)], and PAA-[Sn(pc)] electrode to CN$^-$, F$^-$, Cl$^-$, and Br$^-$. The potentiometric response of the electrode is based on the coordination of the analyte ion as an axial ligand to the center metal of the host compound, [Ga(pc)]. This phase-boundary potential model was well discussed by E. Bakker et al [17].

3.4 Determination of the selectivity coefficient

The selectivity coefficient of PAA-[Ga(pc)] electrode for F$^-$ over CN$^-$, K_{F^-,CN^-}, and CN$^-$ over F$^-$, K_{CN^-,F^-}, in AN were measured by mixed solution method described by P. Buhlmann et al [18]. K_{F^-,CN^-} was obtained by preparing F$^-$ calibration curve in the presence of a fixed concentration of CN$^-$ (10^{-4} M) while K_{CN^-,F^-} was obtained by preparing CN$^-$ calibration curve in the presence of a fixed concentration of F$^-$ (10^{-4} M). The results showed that both K_{F^-,CN^-} and K_{CN^-,F^-} nearly equal to 1. This indicates that both F$^-$ and CN$^-$ have almost the

same ability to bind with the centre metal of $[Ga(pc)]^+$ at the axial position and the Standard Gibbs Energy of the reactions both between $[Ga(pc)]^+$ and F^- and $[Ga(pc)]^+$ and CN^- may be similar. This result can also be deduced from the UV spectra about the interaction of $[Ga(pc)]^+$ with F^- and CN^- in acetonitrile, i.e., when F^- and CN^- were added respectively to $[Ga(pc)]^+$ saturated AN solution, the peak at about 678 nm shifted similarly to the short wavelength.

3.5 Determination of the solubility product constant of sodium fluoride in AN ($K_{sp\,(NaF)}^{AN}$).

The single ion standard molar Gibbs free energy of transfer [19] is an important thermodynamic data to discuss the effects of solvent properties on chemical reactions. The solubility product of electrolyte is related to the single ion standard molar Gibbs free energy of transfer.

In order to confirm the thermodynamic applicability of the PAA-[Ga(pc)] electrode, an experiment was carried out for obtaining the solubility product of NaF in AN ($K_{sp\,(NaF)}^{AN}$). A 10 ml of 2 mM $Bu_4NF\cdot3H_2O$ in 10mM Bu_4NClO_4-AN solution was titrated with a 50 mM $NaClO_4$-AN solution at 25℃. The titration curve and dynamic response curve are shown in Fig.7. The $pK_{sp\,(NaF)}^{AN}$ obtained was 10 and it should be noted that the solubility product constant contains NaF dissolved in AN. The result agreed well with that obtained previously by the PAA-[Co(pc)] and the PAA-[VO(pc)] electrode[8, 9], suggesting the electrode developed in the work also should be able to use for the thermodynamic study in nonaqueous solutions.

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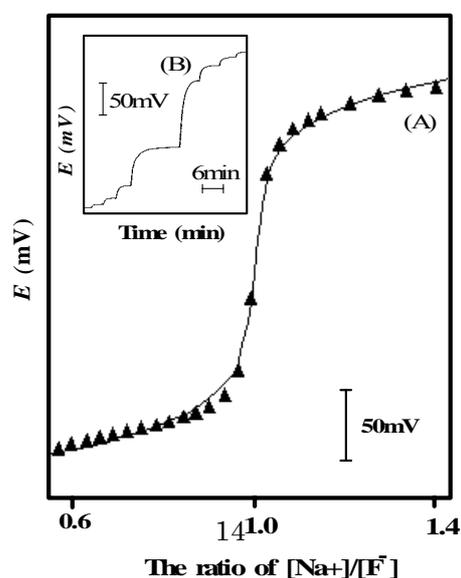
Fig. 7. (A) Titration curve of a 10 ml of 2 mM $Bu_4NF \cdot 3H_2O$ with 50 mM $NaClO_4$ in AN by PAA-[Ga(pc)] electrode. (▲) and (—) show the measured and calculated values, respectively. (B) Dynamic response curve near the end point of the titration of Bu_4NF with $NaClO_4$ in AN at PAA-[Ga(pc)] electrode. One step on the curve corresponds to one drop of the titrant.

4. Conclusions

The PAA-[Ga(pc)] electrode showed selective Nernstian or near-Nernstian responses to F^- and CN^- in AN, DMA, and NMP. The establishment of the membrane potential was successfully confirmed by UV-vis spectrophotometric and cyclic voltammetric measurement. The potentiometric response of the electrode was based on the coordination of the analyte ion as an axial ligand to the center metal of the host compound. F^- and CN^- have almost the same ability to bind with the center metal of $[Ga(pc)]^+$ at the axial position in all of solvents used in this study. The electrode developed here can be used to determine the solubility product of NaF in AN.

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