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Response Properties of a Platinum Electrode Coated with an Oxo(phthalocyaninato)vanadium(IV) Conjugate Polymer to Various Anions in Nonaqueous Solutions

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The potentiometric response behavior of an electrode consisting of a non-plasticized polyacrylamide polymer (PAA) coupled to oxo(phthalocyaninato)vanadium(IV) ([VO(pc)]) was examined for various anions in such nonaqueous solvents as acetonitrile (AN), propylene carbonate (PC), dimethylacetamide (DMA), and *N*-methylpyrrolidinone (NMP). The electrode shows a selective Nernstian or a near-Nernstian response to F^- and CN^- in AN, PC, DMA, and NMP. It shows a non-Nernstian response to I^-, $NO_2{}^-$, and $CF_3SO_3{}^-$, but a very poor response to Cl^-, Br^-, SCN^-, $BPh_4{}^-$, $PF_6{}^-$, and $ClO_4{}^-$. Complex formation reactions of [VO(pc)]s with F^- and CN^- are suggested based on the UV/vis spectra, and may occur due to ligand exchange reactions of F^- and CN^- with AN or water molecule(s) coordinated to [VO(pc)]s. The PAA–[VO(pc)] electrode has been confirmed as being available for use in determining the solubility product constant of sodium fluoride in AN.

Metal phthalocyanines ([M(pc)]) and porphyrins have been used as anion hosts of sensors for $ClO_4{}^-$, SCN^-, I^-, $NO_3{}^-$, Br^-, Cl^-, etc. Recently, an anion sensor for F^- prepared with a porphyrinatogallium(III) was reported, in which the selectivity pattern deviated significantly from the classical Hofmeister's series.[1)] Investigations of some types of the complex formation reactions of F^- with compounds have been reported, e.g., by bounding it within a cavity of a macrocyclic host[2)] and by chelation with two silyl groups,[3)] and a study concerning the potential establishment of ion-selective electrodes was reported.[4)] These sensors, however, have been developed for use in aqueous solution systems. Thermodynamic studies of the solubility of NaF and the Gibbs energies of transfer of F^- in nonaqueous solution systems[5)] have been reported. In the previous papers,[6,7)] the potentiometric response behavior of an electrode consisting of a non-plasticized polyacrylamide polymer (PAA) coupled to (phthalocyaninato)cobalt(II) ([Co(pc)]) and a Nernstian response at the electrode to F^- and CN^- in acetonitrile (AN) and propylene carbonate (PC) were reported; its response mechanism was deduced to the complex formation reaction of [Co(pc)] with ion. However, we could not certify the reason why the electrode showed such a very weak response to Cl^- and Br^-. In the present paper we firstly report on the potentiometric results of response properties for various anions in such nonaqueous solvents as AN, PC,dimethylacetamide (DMA), and *N*-methylpyrrolidinone (NMP) at an electrode consisting of a non-plasticized PAA coupled to oxo(phthalocyaninato)vanadium(IV) ([(VO(pc)]). Secondly, a UV/vis investigation is reported to explain the selective Nernstian response to F^- and CN^- and a special response to Cl^-, Br^-, I^-, trifluorometane sulfonate ($CF_3SO_3{}^-$), and tetraphenylborate ($BPh_4{}^-$), etc., in aprotic solvents. The mechanism of the complex formation reaction of F^- and CN^- in AN with [VO(pc)] is discussed. Finally, the application of the PAA–[VO(pc)] electrode to obtain the solubility product constant of NaF in AN is reported.

Experimental

Reagents. [VO(pc)] was purchased from Wako (No. 200-10631) and conjugated to caboxy-modified PAA by the same method as that reported in a previous paper.[6)] Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by synthesizing with tetrabutylammonium bromide and sodium tetraphenylborate, which were obtained from Fluka (No. 86857) and Kanto Chemicals (No. 37291-30), respectively. It was twice recrystallize from acetone. Other chemicals and solvents used in the study were prepared in the same way as that reported in previous papers[6,8)] if not otherwise mentioned.

Indicator Electrode and Potentiometric Measurement. The PAA–[VO(pc)] electrode was constructed in the same way as that reported in a previous paper[6)] and conditioned for more than seven hours in an AN-solution containing 0.5 mM analyte ion and 10 mM indifferent electrolyte shown in Cell 1. The thickness of the membrane on the platinum disk was less than 0.2 mm. The potentiometric response behavior to various anions at the PAA–[VO(pc)] electrode was investigated by measuring Cell 1; the emfs were measured with a pH meter equipped with a Hitachi-Horiba type F-8 AT and recorded by a Yokokawa Denki Co. type 3056. All compartments of Cell 1 were prepared freshly every time.

Ag|10 mM $AgNO_3$ + 10 mM Et_4NClO_4(AN)||50 mM Et_4NX(AN)||*c* M R_4NY + 10 mM R_4NX (D)|PAA–[VO(pc)]|Pt Cell 1, where D = AN, PC, DMA, and NMP, X^- = $ClO_4{}^-$ and $PF_6{}^-$, Y^- = F^-, CN^-, Cl^-, Br^-, I^-, $NO_2{}^-$, $CF_3SO_3{}^-$, SCN^-, $BPh_4{}^-$,

PF_6^-, and ClO_4^-, R_4N^+ = tetraethylammonium ion (Et_4N^+) and tetrabutylammonium ion (Bu_4N^+), M = mol dm^{-3}, and *c* means concentration. When ClO_4^- was examined, i.e., Y^- = ClO_4^-, PF_6^- was used as X^-. When D was PC the reference electrode and salt bridge were prepared with PC according to those used in the case of Ref. 9. The change of junction potentials of Cell 1 during emf measurements can be negligible in the experiment.[10)]

Measurement of UV/vis Spectra. Measurements of the UV-vis spectra were carried out by the same method reported previously.[6)] At first, a solution of 0.02 mM [VO(pc)]–AN solution was prepared; then, the solutions were made to 1, 5, and 10 mM both CN^-–AN and F^-–AN solution, respectively.

Results and Discussion

Potentiometric Results. The potentiometric response behavior at the PAA–[VO(pc)] electrode to various anions in AN, PC, DMA, and NMP was studied. The results are summarized in Table 1, in which the slopes 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 experiments repeated four or five times, respectively. The linear ranges of the slopes in the Nernstian equation are also shown under each slope. It can be found that the type response can be classified into three groups. The first group (Group A: F^- and CN^-) shows a Nernstian or near-Nernstian response in AN, PC, DMA, and NMP. The second (Group B: Cl^-, Br^-, SCN^-, BPh_4^-, PF_6^-, and ClO_4^-) shows a poor response in all solvents investigated, in which the slopes are positive in spite of anions. The third (Group C: I^-, NO_2^-, and $CF_3SO_3^-$) shows a non-Nernstian behavior, but sometimes responds in a super-Nernstian mannar, similar to the case at the PAA–[Co(pc)] electrode,[6)] as can be seen in Table 1. The response time of the electrode was 2—5 min for the ions of Group A and 5—15 min for the ions of B and C. A typical calibration curve obtained for CN^- in AN is shown in Fig. 1. The activities of the anions (a_{CN^-}) was calculated using the activity coefficient of (a_{CN^-}) obtained from the Debye–Hückel second approximation equation. We considered in a previous report[6)] that the smaller permeability of Cl^- and Br^- across a PAA membrane must result in the special response at the PAA–[Co(pc)] electrode. The difference in the permeability of the ion may occur by means of the extent of the solvation of AN molecules to each ion, i.e., the ion which has more solvated AN molecules has more difficulty to pass through the membrane. The numbers of the AN molecules solvated to each ion were reported to be 3.2, 1.7, and 0.7 for Cl^-, Br^-, and I^-, respectively.[11)] As a result, we can consider that the PAA membrane masked the response of the anions of Group B. Also, the poor response to the ions means that the ion exchange reaction does not work to establish the membrane potential at the solution–membrane interface of the electrode. A super-Nernstian response of I^- may occur upon reaching the ion to the platinum disk across a PAA membrane[6)] and/or on altering the oxidation state of the ion. Table 1 shows a

Table 1. The Response to Various Anions in Some Aprotic Solvents at PAA–[VO(pc)] Electrode. at 25 °C, in mV/log a_{x^-}, ( ): pa_{x^-}

Ion	PAA–[VO(pc)]				PAA–[Co(pc)]$^{a,b)}$		PAA$^{a)}$
	AN{19.3}	PC{18.3}	DMA{13.6}	NMP{13.3}	AN	PC	AN
F^-	−59.6	−57.5	−52.1	−51.2	−59.0	−58.7	−80
	(3.2—5.1)	(3.1—5.3)	(3.5—5.3)	(3.1—5.3)	(3.0—5.4)	(3.2—5.3)	(3.5—5.8)
CN^-	−59.7	−55.8	−60.4	−58.8	−58.7	−59.0	−55
	(3.2—4.6)	(3.2—5.0)	(2.3—4.7)	(3.2—4.6)	(3.8—5.3)	(2.8—4.2)	(2.7—5.7)
Cl^-	+14	+4	+7	+8	+14		Not respond
	(2.2—5.2)	(2.2—5.1)	(2.1—5.4)	(2.4—5.4)	(2.8—4.9)		
Br^-	+5	+5	+6	+7	+11	+2	Not respond
	(2.3—5.4)	(1.9—5.3)	(2.1—5.4)	(2.0—5.1)	(3.0—5.1)	(2.8—4.9)	
I^-	−98	−62	−38	−42	−104	−80	−100
	(2.2—3.2)	(2.2—3.0)	(2.0—3.0)	(2.2—3.9)	(2.2—5.3)	(2.2—3.2)	(2.0—3.0)
NO_2^-	−20				−35	−34	−40
	(2.3—4.2)				(1.9—4.0)	(2.4—3.7)	(2.0—4.0)
$CF_3SO_3^-$	−64	−76	−60	−27	−38		−47
	(2.3—3.3)	(2.2—3.2)	(2.3—3.0)	(2.3—3.3)	(2.2—3.2)		(2.0—3.2)
SCN^-	+14				+22		Not respond
	(2.3—3.6)				(2.1—4.9)		
BPh_4^-	+39				+7		Not respond
	(2.2—4.3)				(3.7—5.2)		
PF_6^-		+8	+3	+8	+20	+18	
		(2.0—4.9)	(2.3—5.4)	(2.1—5.4)	(2.2—4.7)	(2.9—4.6)	
ClO_4^-		+9			+18	+16	
		(3.7—5.2)			(2.6—5.1)	(3.3—5.1)	
BF_4^-					+0.4	+17	
					(2.8—4.9)	(2.9—5.1)	

The figures in { } show Acceptor Numbers and it is 54.8 for water. a, b): See Refs. 6 and 7.

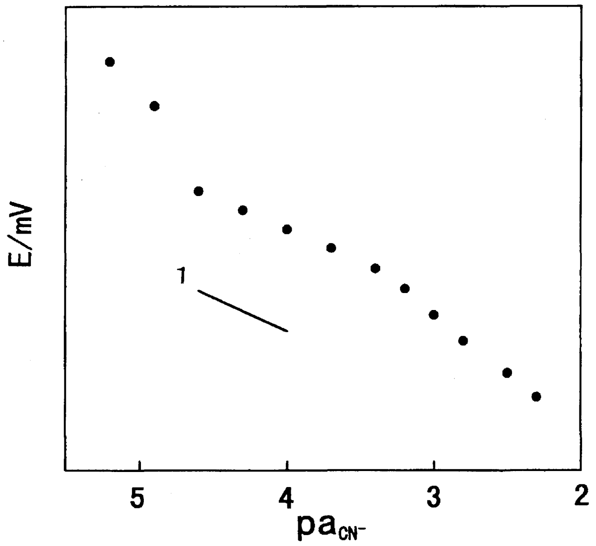

Fig. 1. The calibration curve for CN^- in acetonitrile at the PAA–[VO(pc)] electrode. Line 1 is the theoretical slope for the monovalent anion (−59.2 mV/log a_{x^-}) and ● indicates measured emf.

comparably high slope with a positive sign for BPh_4^- in AN at the PAA–[VO(pc)] electrode, although the response was very poor at such other electrodes as a PAA-coated platinum electrode and a PAA–[Co(pc)] electrode.[6)] An evident potential change for BPh_4^- in the positive direction in spite of an anion suggests that the special interaction of other than complexing may occur between [VO(pc)] in a PAA membrane and BPh_4^- in AN.

Spectrophotometric Results. In order to investigate the potentiometric response mechanism of the PAA–[VO(pc)] electrode, spectrophotometric investigations were carried out. The $Bu_4NF\cdot 3H_2O$ or Et_4NCN in AN was added to AN solutions which contained a constant concentration of [VO(pc)]. An example is shown in Fig. 2; also, the [VO(pc)]–AN solutions changed to have new absorption peaks at about 700, and became higher upon increasing the F^- concentration in AN from 1 to 10 mM. On the other hand, a very poor absorbance was exhibited at both the [VO(pc)]–AN and F^-–AN solutions. A similar situation almost occurred in the case of CN^-. From the results it can be considered that complex formation between [VO(pc)] and both F^- and CN^- in AN must occur. The complex formation of pc and [Co(pc)] with F^- and CN^- in AN was reported in a previous paper.[6)] Here, we assume a ligand exchange reaction, i.e., the replacement of F^- and CN^- with solvated AN or water molecule(s) at [VO(pc)] and [Co(pc)]. These unusual complexing phenomena, i.e., they have not been reported by any other person, except for in our paper,[6)] might occur under the conditions of a low concentration of water ($<$ 0.01%) being prepared as follows: AN was fractionally distilled twice after treating with molecular sieves (4A 1/16). The first distillation was carried out in the presence of P_2O_5, and second in the presence of CaH_2. The [M(pc)] (M = Co and VO) might conjugate to AN molecules as the ligand in place of H_2O molecules under the given conditions. Then, an exchange of AN molecules with F^- or CN^- would result due to the active F^- in AN and due to the complexing ability of CN^- with [M(pc)]. It should be noted that the acceptor number of the solvents used here are comparably small, as shown in Table 1, and thus the anions in such solvents seem to be in high activity. If water molecule(s) remain(s) as the ligand at [M(pc)] it would be drawn out into balk AN solution by F^-, which is very hygroscopic. As a result of such a ligand exchange reaction the equilibrium of F^- and CN^- at the sensor membrane–solution interface was established and a Nernstian or near-Nernstian responses of the ions in aprotic solvents at PAA–[M(pc)] electrodes must be established. When the ions were Cl^-, Br^-, I^-, or $CF_3SO_3^-$ instead of F^- and CN^-, no change appeared on the spectrum in spite of the fact that the concentration of ions in AN increased from 1 to 10 mM, although a spectrum change at about 200 nm occurred due to the ions, themselves. Concerning the super-Nernstian response to $CF_3SO_3^-$ at the PAA–[VO(pc)] electrode, we observed that an absorbance appeared at about 650 nm when the concentration of $CF_3SO_3^-$ was changed from 5×10^{-5} to 1×10^{-2} M in a 2×10^{-5} M pc–DMF solution. This suggests complex formation between the ion and pc in DMF; also, a precise investigation concerning the response of $CF_3SO_3^-$ at [M(pc)] electrodes must be accomplished. Although the PAA–[VO(pc)] electrode shows a well-defined response to F^- and CN^- in the solvents investigated, the linear ranges of the slopes become narrower compare with the case of the PAA–[Co(pc)] electrode, which may be caused by a weakness in the complexing ability of [VO(pc)] with F^- and CN^-. From these results we can conclude that an ion exchange reaction does not work for the response at the electrode to such ions of Group B, and we could consider

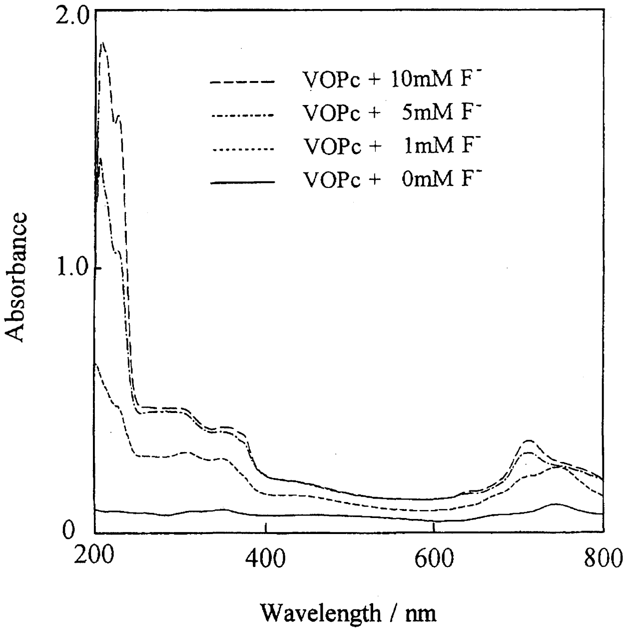

Fig. 2. UV-vis spectra obtained by the interaction between oxo(phthalocyaninato)vanadium(IV) and F^- in acetonitrile. All of the solutions contained 2.0×10^{-5} mol dm^{-3} [VO(pc)]. Reference was acetonitrile.

that [VO(pc)] might be in a non-charged state. VO might be divalent in positive sign, i.e., V should be in a tetravalent positive charge.

Determination of the Solubility Product Constant of Sodium Fluoride in AN ($K_{sp}(NaF)_{AN}$). In order to confirm the applicability of the PAA–[VO(pc)] electrode an experiment was carried out for obtaining the solubility product constant of NaF in AN ($pK_{sp}(NaF)_{AN}$). Ten ml of 1.9 mM $Bu_4NF \cdot 3H_2O$ in 10 mM Bu_4NPF_6–AN solution was titrated with a 50 mM $NaClO_4$–AN solution at 25 °C. The value was 10.0, which agreed well with that obtained previously$^{6)}$ by the PAA–[Co(pc)] electrode; we thus consider that the PAA–[VO(pc)] electrode can be used to determine the constant. It should be noted that the solubility product constant contains NaF dissolved in AN.

Conclusion

The PAA–[VO(pc)] electrode showed selective Nernstian or near-Nernstian responses to F^- and CN^- in AN, PC, DMA, and NMP. The response of the electrode was established due to the complex formation of [VO(pc)] with F^- and CN^- in such aprotic solvents. The complex formation reaction might occur by ligand exchange reactions between solvated AN or water molecule(s) and the ions. The ion exchange reaction did not work for the response at the electrode to such poor response anions as Cl^-, Br^-, and so forth in the solvents examined. The PAA–[VO(pc)] electrode can be used to determine the solubility product constant of NaF in AN.

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