COATED CARBON-ROD ANION ELECTRODES USING BIS(DIPHENYLPHOSPHINO)PROPANE-METAL COMPLEXES

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Abstract Several membrane-coated carbon rod anion-selective electrodes (CCRISE) were prepared by incorporating metal complex of bis(diphenylphosphino)propane (BDPPP) in a plasticized PVC film and their response characteristics were studied. Highly sensitive sensors were obtained with detection limit of 10^{-7} , 10^{-6} , $10^{-5.5}$ and $10^{-5.0}$ M for ClO_4^- ; SCN^- and I^- ; Br^- and NO_3^- ; Cl^- and benzoate (Bz^-) ions, respectively.

Key words: bis(diphenylphosphino)propane, Cu(II) or Ag(I) complex, membrane-coated carbon rod electrode, anion sensitive.

Certain transition metal-ligand complexes have shown selectivity to anion selective electrodes [1-5]. These include metal porphyrins and vitamin B₁₂ derivatives and other organic ligands which contain N, O, S as coordination atoms. These electrodes show a unique selectivity which differs from the well known Hofmeister series. The sensitivities of these electrodes based on the metal-ligand complex are improved by one or two decades more than those of the electrodes based on the ion-exchangers [6]. Transition metals such as Cu(II) and Ag(I) have been found to form stable complexes with BDPPP (Fig.1). In this work, we have investigated these metal complexes as anion sensing materials and developed various kinds of anion sensitive membrane-coated carbon rod electrodes.

EXPERIMENTAL

Reagents. Poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were obtained from Fluka AG (Buchs, Switzerland). o-Nitrophenyl octyl ether (o-NPOE) as a plasticizer was obtained from Dojindo laboratories (Kumamoto, Japan). BDPPP was purchased from Kanto Chemical (Tokyo, Japan) and was recrystallized twice with freshly distilled ethanol before use. All the inorganic salts used were of the highest purity available. Standard solutions of various anions were prepared with distilled-deionized water.

Electrode fabrication. The membrane coating solution was prepared by dissolving a batch of 10 mg of BDPPP, 200 mg of o-NPOE, and 100 mg of PVC in 3 ml of THF. Carbon rods with 2 mm diameter were obtained from Nippon Carbon Co. (Yokohama, Japan). A cleanly washed carbon rod was coated with a membrane by dipping it in the coating solution and drying it repeatedly five times. The membrane coated carbon rod was finally dried for 2 h and hosted into a PVC tube. Anion CCRISEs were prepared by immersing them in 10^{-3} M corresponding copper salts solutions to condition for 24 h, except for the Bz^- electrode which was immersed in a 10^{-3} M mixed solution of silver nitrate and sodium benzoate(1:1). All measurements were performed with the following cell assembly: carbon rod/ sensor membrane/

FIG.1 BDPPP

sample solution/ reference electrode. Orion microprocessor ionanalyzer (Model 901) was used for monitoring the potential. All the e.m.f.s were measured relative to a saturated calomel double junction electrode (IWAKI Glass, Japan).

RESULTS AND DISCUSSION

The trial electrodes were first tested in pure solutions of the appropriate sodium salts over a concentration range of 10^{-1} - 10^{-8} M. Equilibrium potentials were achieved quickly (<5 s) and the values were reproducible. All the electrode responses were Nernstian in a wide concentration range. The sensitivity of the electrode for ClO_4^- was $10^{-7.0}$ M; for SCN^- and I^- $10^{-6.2}$ M; for Br^- and NO_3^- , $10^{-5.5}$ M; for Cl^- and Bz^- , $10^{-5.0}$ M. These electrodes also respond similarly in Tris-buffer solutions at pH 7-8. The selectivity coefficients were determined by the separated solution method. The concentration of the interference ion was fixed at 10^{-1} M and buffered with tris(hydroxymethyl)aminomethane- H_2SO_4 mixed solution at pH 7.4. The logarithmus of the selectivity coefficients for various anion electrodes are shown in Table 1.

TABLE 1 Selectivity characteristics for various anion CCRISEs

ISE	linear range	slope	- Log $K_{i,j}^{\text{pot}}$							
	pA	mV/pA	ClO_4^-	SCN^-	I^-	Br^-	NO_3^-	Cl^-	Bz^-	OAc^-
ClO_4^-	1.0 - 7.0	-59.5	0.0	-0.59	-0.81	-2.23	-2.63	-2.78	-3.31	-4.33
SCN^-	1.0 - 6.0	-58.0	-0.85	0.0	-0.87	-2.24	-3.63	-3.43	-4.12	-4.18
I^-	2.0 - 6.0	-58.6	0.22	0.62	0.0	-1.75	-2.50	-2.95	-3.01	-3.82
Br^-	1.2 - 5.4	-57.6	2.26	2.01	1.47	0.0	-0.46	-1.22	-1.35	-2.25
NO_3^-	1.0 - 5.3	-58.6	2.64	1.92	1.50	-0.08	0.0	-1.14	-1.32	-2.10
Cl^-	1.0 - 5.0	-58.8	4.01	3.52	3.31	1.35	0.50	0.0	-0.30	-2.50
Bz^-	1.0 - 4.5	-60.0	3.75	2.99	2.48	0.92	0.52	-0.65	0.0	-1.34

Each electrode was highly interfered with by lipophilic anions, such as ClO_4^- , SCN^- and I^- while interference from hydrophilic ones like F^- and SO_4^{2-} was less. It is worth noting that electrodes for SCN^- and I^- showed a selectivity sequence which deviated from the Hofmeister series, and the interference against ClO_4^- was improved. This may be due to the high association ability of the SCN^- and I^- with Cu(II)-BDPPP complex that added the special selectivity to them. The anion CCRISEs show stable potential in the pH range of 4-10. In 10^{-3} M perchlorate ion solution, a fast response of 4 s with a reproducibility of 0.8 mV is obtained. The life time is 10 days.

The CCRISE for SCN^- was studied as an indicator electrode for potentiometric titration. The titration was carried out by using the reaction of SCN^- with Hg^{2+} to form sparingly insoluble precipitates. The titration curve of SCN^- with Hg^{2+} solution shows a sharp inflection break (100-150 mV) at the end point. A precision of 0.8% for the determination of SCN^- has been obtained.

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