ELECTROANALYTICAL BEHAVIOR OF COPPER(II) COMPLEXES WITH IMIDAZOLE AND ITS DERIVATIVES INCORPORATED IN NAFION FILMS ON GLASSY CARBON ELECTRODE SURFACES

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Abstract - Nafion films were coated on glassy carbon electrode surfaces and these chemically modified electrodes were used to characterize the incorporation of Cu(II) complexes with imidazole and its derivatives. These Cu(II) complexes could be concentrated inside Nafion films without the interference of another metal ions at pH 6.0. The calibration curve was linear in the range 10^{-7} - 10^{-6} M of Cu^{2+} containing 10^{-2} M imidazole.

Key words imidazole, copper(II) complexes, Nafion, ion-exchange voltammetry

The perfluoro sulfonic acid polymer, Nafion, which is conductive and very resistant to chemical attack, even by strong oxidants has found increasing use as a membrane material. Nafion is a cation exchanger, but its properties are significantly different from those of the conventional sulfonate resins. For example, Nafion has ostensibly no crosslinking and is soluble in ethanol but insoluble in water. Therefore, this material can be coated on the surface of electrode by evaporation of an ethanol solution. Nafion-coated electrodes promise well for future as sensitive and selective sensors for electroactive cations. It is well-known that cations can be concentrated into the Nafion films by electrostatic interaction with negatively charged sulfonate groups in the Nafion layer¹⁻⁴⁾, resulting in dramatically improved detection limits, relative to the naked electrode. Nafion-coated electrodes were used in a trace analytical technique which Martin et al. have called ion-exchange voltammetry⁵⁾. In ion-exchange voltammetry, the inherent thermodynamic driving force of the ion-exchange reaction is used to preconcentrate cations into Nafion films on the electrode surfaces. The concentrated cations into the films are then either oxidized or reduced. In this study, Nafion films were coated on glassy carbon electrode surfaces and these chemically modified electrodes were used to characterize the incorporation of copper(II) complexes with imidazole and its derivatives.

EXPERIMENTAL

Materials A Nafion solution (5 wt% solution, 1100 equivalent weights) was obtained from E. I. du Pont de Nemours & Co. and diluted in ethanol to give a solution of 0.5 W/V%. Imidazole and its derivatives obtained from Wako Pure Chemical Industries, Ltd. and Tokyo Kasei Kogyo Co., Ltd. were recrystallized from benzene or benzene-hexane mixed solvents except for 1-methylimidazole purified under reduced pressure. Stock aqueous solutions (10^{-2} M) of metal ions (Cu^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}) were prepared from the sulfates except for ferric chloride, and standardized by 10^{-2} M EDTA solution. All other chemicals were of analytical reagent grade and were used as received. The supporting electrolyte solution was 0.5 M NaBr adjusted to pH 6.0 with NaH_2PO_4 - Na_2HPO_4 buffer solution.

Apparatus and procedures Electrochemical measurements were carried out by

using a three-electrode cell. The working electrode was a 3 mm diameter glassy carbon electrode (Yanagimoto, GC-P2) and Nafion coatings were prepared by pipeting 10 μ l of the 0.5 W/V% solution onto the freshly cleaved electrode surfaces and allowing the solvent to evaporate (abbreviated hereafter as GC/NAF). A sodium chloride saturated calomel electrode (SSCE) as reference electrode and a spiral platinum as counter electrode were used. A Yanagimoto polarographic analyzer P-1100 was employed along with an X-Y recorder for cyclic voltammetry and differential pulse voltammetry. Prior to determine the amount of Cu^{2+} by the differential pulse voltammetry, the coated electrodes were soaked at constant time in solutions containing Cu^{2+} , imidazole and supporting electrolyte (0.5 M NaBr adjusted to pH 6.0 with phosphate buffer solution).

RESULTS AND DISCUSSION

The cyclic voltammograms of Cu(II) -imidazole complexes at GC and GC/NAF electrodes are shown in Fig. 1. The peak currents increased with scanning

Fig. 1 Cyclic voltammograms for 2×10^{-4} M Cu^{2+} containing 2×10^{-2} M imidazole in 0.1 M NaClO_4 at GC(A) and GC/NAF(B) electrodes ($v = 50 \text{ mV s}^{-1}$).

over the potential range +0.5 to -0.7V vs. SSCE by using a GC/NAF electrode. The results shown in Fig. 1 indicate that the Nafion films are incorporating Cu(II) -imidazole complexes from the solution via ion-exchange with the proton of the fixed sulfonic acid group. That is, Cu(II) -imidazole complexes can be concentrated in the Nafion films, resulting improved detection limits, relative to the naked electrode. Fig. 2 shows peak currents and peak potentials of the differential pulse voltammograms for GC/NAF electrode after equilibration with 2×10^{-6} M Cu^{2+} containing 10^{-2} M imidazole or

Fig. 2 Peak currents and peak potentials of the differential pulse voltammograms for 2×10^{-6} M Cu^{2+} containing 10^{-2} M imidazole or its derivative in 0.5 M NaBr at GC/NAF electrode.

its derivative. The values of peak potentials for the reduction of Cu(II) to Cu(I) complexes with imidazole or its derivative exhibit that the electroanalytical measurements of the system employed in this study can be carried out under an atmosphere of ordinary air. The values of peak currents shown in Fig. 2 indicate that 1-methylimidazole appears to be regarded as the best of the ligand. Cu(II) -1-methylimidazole complexes, however, requires longer equilibration times (see Fig. 3). It can be seen that at least 10 min are needed for imidazole as the ligand to equilibrate with the Nafion film. 1-Methylimidazole as the ligand, on the other hand, requires about 30 min to reach equilibrium with the Nafion film. It is suggested that the larger cations are exchanged slowly and require longer equilibration times. Imidazole is consequently practical in this study. Another metal(II)- and metal(III)-imidazole complexes (metal (II): Mn, Co, Ni, Zn, Cd, metal (III): Fe) were electroinactive in the potential range +1.0 to -1.0 V vs. SSCE at a GC/NAF electrode. However, the determination of Cu^{2+} could be affected by the presence of another metal ions as the mechanism of concentration is based on the ion-exchange equilibrium. The effect of pH on peak currents of the differential pulse voltammograms for 10^{-6} M Cu^{2+} containing 10^{-2} M imidazole in 0.5 M NaBr at a GC/NAF electrode. At higher pH (pH > 6.0) both Cu(II) - and Ni(II) -imidazole complexes were incorporated into the Nafion films, resulting in negative errors for the determination of Cu^{2+} . A linear calibration curve was obtained in the range 10^{-7} - 10^{-6} M of Cu^{2+} containing 10^{-2} M imidazole, with relative standard deviation of 1.2 % for 4 determinations of 5×10^{-7} M. The effect of some of the diverse ions on the determination of Cu^{2+} was studied. The results obtained are summarized in Table 1. Similar concentration of Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} did not influence the

Cu(II) response. Cu(II)-imidazole complexes incorporated into Nafion films on glassy carbon electrode surfaces dissociate into Cu^{2+} and imidazolium ions in 0.05 M H_2SO_4 within a few minutes.

Fig. 3 Effect of stirring time on peak currents of the differential pulse voltammograms for 2×10^{-6} M Cu^{2+} containing 10^{-2} M imidazole or 1-methylimidazole in 0.5 M NaBr at GC/NAF electrode.

Table 1 Effect of foreign ions on the determination of 10^{-6} M Cu^{2+} containing 10^{-2} M imidazole in 0.5 M NaBr adjusted to pH 6.0 at GC/NAF electrode

Tolerated ratio Ion added/ Cu^{2+}	Ion added
100	Mn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+}
50	Zn^{2+}
10	Fe^{3+}

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