Anodic Polarography of Pentacyanonitrosylferrate(III) Ion

Hitoshi MORI*, Masao SUGAWARA** and
Tomihito KAMBARA**

The anodic polarographic behavior of nitroprusside ion (NIP^{2-}), namely, pentacyanonitrosylferrate (III) ion, which forms slightly water-soluble compounds with mercurous ion as well as with mercuric ion, were investigated. In an acidified aqueous supporting electrolyte solution of sodium perchlorate, NIP^{2-} produces a two-step anodic wave. The first step is ascribed to the formation of a film $\text{Hg}_2[\text{Fe}(\text{CN})_5\text{NO}]$, which is adsorbed on the surface of mercury and inhibits the dissolution of mercury, resulting in the appearance of the second step.

1 Introduction

Sodium pentacyanonitrosylferrate(III), $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, known as sodium nitroprusside [Na_2NIP], has been employed as a sensitive reagent for detecting sulfide ion¹⁾. A slightly water-soluble compound HgNIP has been known, the solubility product²⁾ being $10^{-8.86}$. A mercurous compound has not been reported, but we found that mercury(I) also formed a precipitate with NIP^{2-} . It is then anticipated that NIP^{2-} produces anodic waves corresponding to the formation of the slightly soluble compound. In the present paper, properties of the anodic waves and the electrode process were investigated.

2 Experimental

Polarograms were recorded with a Yanagimoto polarograph, type PA-102. Unless otherwise noted, measurements were made with the mercury column height of $h=38.4$ cm, at which $m=1.87$ mg s^{-1} , $t=4.64$ s in the supporting electrolyte solution at 0.0 V vs. SCE. A Hitachi-Horiba glass electrode pH meter, type F-5, was used for pH measurements.

A stock solution of NIP^{2-} was prepared by dissolving sodium nitroprusside of the G.R. grade (Kanto Chemicals Co.) in water and stored in subdued light at a temperature below 6°C in order to protect NIP^{2-} from the decomposition.

The pH of solution was adjusted with acetate buffer solutions. At pH values below 2, a perchloric acid solution was used. Other reagents employed were of analytical reagent grade. Deionized water was used.

Polarograms were recorded at $(20 \pm 0.1)^\circ\text{C}$ after dissolved oxygen was removed by passing nitrogen gas.

3 Results and Discussion

3.1 Properties of the anodic wave

Figure 1 shows the DC and AC polarograms of NIP^{2-} . Two anodic steps and the corresponding two prominent peaks are observed in the DC and AC polarograms, respectively. The height of the first DC step increases with increasing concentration of NIP^{2-} up to 0.4 mM, as shown in Fig. 2. When the concentration of NIP^{2-} exceeds the critical value of 0.6 mM, the wave height remains constant, the second wave appearing at a more positive potential. The height of the second wave increases with increasing concentration of NIP^{2-} , but at the concentrations above 1.2 mM, the wave height becomes constant. The limiting current of the first and second waves shows a relative temperature coefficient of $0.46 \times 10^{-2} \text{ K}^{-1}$ and $5.68 \times 10^{-2} \text{ K}^{-1}$ at 20°C, respectively. The limiting current controlled by the formation of a monomolecular film of the adsorbate is known to be proportional to the mercury column height³⁾. Effect of the corrected height of mercury column on the limiting current of the first and the second

* Present address: Otsuka Chemicals Co. (Naruto)

** Department of Chemistry, Faculty of Science, Hokkaido University (Sapporo)

Fig. 1 DC and AC anodic polarograms of NIP^{2-} in the supporting electrolyte of 0.2 M NaClO_4 and 0.015 M HClO_4 , pH 1.8

(1), (1'): 0 mM; (2), (2'): 1.2 mM NIP^{2-}

Fig. 2 Variation of the wave heights of (1) 1st and (2) 2nd waves of NIP^{2-}

Other conditions are the same as in Fig. 1

waves is shown in Table 1. Both the limiting currents are approximately proportional to $h_{\text{corr.}}$, indicating that both are adsorption currents.

Drop time curves of NIP^{2-} show a uniform decrease in drop time over the wide potential

Table 1 Effect of mercury column height on the limiting current of the first (i_a^{I}) and second (i_a^{II}) waves of 1.2 mM NIP^{2-} in the supporting electrolyte of 0.2 M NaClO_4 and 0.015 M HClO_4 , pH 1.8

$h_{\text{corr.}}/\text{cm}$	$i_a^{\text{I}}/\mu\text{A}$	$i_a^{\text{II}}/\mu\text{A}$	$i_a^{\text{I}} h_{\text{corr.}}^{-1}/\mu\text{A cm}^{-1}$	$i_a^{\text{II}} h_{\text{corr.}}^{-1}/\mu\text{A cm}^{-1}$
29.4	0.453	1.46	0.0154	0.0497
33.4	0.514	1.72	0.0154	0.0514
38.5	0.570	1.94	0.0148	0.0505
43.4	0.648	2.16	0.0149	0.0498
48.3	0.751	2.36	0.0155	0.0488
53.4	0.808	2.54	0.0151	0.0476

region, accompanied by an additional decrease in drop time at the anodization potentials of the first and second steps, respectively, as shown in Fig. 3. The results indicate that both NIP^{2-}

Fig. 3 Drop time curves of (1) 0, (2) 0.6 and (3) 1.2 mM NIP^{2-}

The arrows indicate the half-wave potentials of the first and second steps, respectively. Other conditions are the same as in Fig. 1

and the anodization product are adsorbed on the surface of mercury.

In Fig. 4 the half-wave potentials and wave heights are plotted as a function of pH. The half-wave potential of the first step is constant in the pH range from 0.9 to 4.0, but at pH values below 0.9 and above 4.0, it shifts to more negative values. The half-wave potential of the second step is independent of pH between 0.7 and 1.8. At pH values above 1.8 the

Fig. 4 Effect of pH on the half-wave potential of (1) 1st and (2) 2nd steps and the wave height of (3) 1st and (4) 2nd steps of 1.2 mM NIP^{2-}

second step overlaps with the anodic dissolution of mercury.

3.2 Electrode reaction mechanism

The formation of an insoluble mercurous salt with NIP^{2-} has not been reported, but a quantitative test showed that a slightly water-soluble compound precipitated when NIP^{2-} was added to a solution of mercurous nitrate. Assuming the formation of either Hg_2NIP or HgNIP , one has $n=2$ in both cases, where n is the number of electrons. The electrode potential is given by

$$E = E_0 + \frac{RT}{2F} \ln K_{sp} - \frac{RT}{2F} \ln [\text{NIP}^{2-}] \quad (1)$$

where E_0 is the standard potential for the $\text{Hg}_2^{2+}/\text{Hg}$ or Hg^{2+}/Hg system and K_{sp} the solubility product of the corresponding mercury salt. A plot of the half-wave potential of the first step vs. $\log [\text{NIP}^{2-}]$ gives a straight line with a slope of -34 mV , as shown in Fig. 5. If the formation of HgNIP governs the electrode process of the first step, one finds that the anodic wave of 1.2 mM NIP^{2-} should start at $+0.43 \text{ V vs. SCE}$ ($E_0 = 0.854 \text{ V vs. NHE}^{(1)}$ and $K_{sp} = 10^{-8.86}$, according to reference⁽²⁾). However, as Fig. 1 shows, this is not the case. Hence, the electrode process of the first step in the pH range from 0.9 to 4.0, where the half-wave potential is independent of pH values, is given by

The appearance of the two adsorption waves

Fig. 5 Variation of the half-wave potential of 1st step with the logarithm of NIP^{2-} concentration

Other conditions are the same as in Fig. 1

can be explained by the deposition of the successive layers of Hg_2NIP , as observed in the case of anodization by tungstate⁽⁵⁾, oxalate⁽⁶⁾ and sulfide⁽⁷⁾. The mercurous compound is adsorbed on the surface of mercury and forms a film, which inhibits the further dissolution of mercury until the second step due to the formation of the second layer of Hg_2NIP is observed. The cross sectional area per unit molecule calculated from the mean adsorption current is $46 \text{ \AA}^2$ for the first step and $14 \text{ \AA}^2$ for the second step, respectively. The results suggest the different orientation of the adsorbate on the electrode surface.

The pH-dependence of the half-wave potential implies that at pH below 0.9 and above 4 hydrogen ion participates in the electrode process, however, further analysis was not carried out in the present work.

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