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Polarographic Behavior of Tris(2,2′-bipyridine)cobalt(II) and Tris(2,2′-bipyridine)cobalt(III) in Acetonitrile Solutions

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The electrode processes of tris(2,2′-bipyridine)cobalt(II) and tris(2,2′-bipyridine)cobalt(III) complexes at the dropping mercury electrode in acetonitrile solutions have been investigated by the measurement of direct current, alternating current and Kalousek polarograms. The cobalt(II) complex gave a one-step oxidation and a four-step reduction wave and the cobalt(III) complex, a five-step reduction wave, when tetraethylammonium perchlorate was used as supporting electrolyte. The solution containing the cobalt(II) and the cobalt(III) complexes gave a reversible composite wave. The limiting currents of the first two steps named from positive to negative potentials of the reduction wave of the cobalt(II) complex were diffusion-controlled, the first step being of a one-electron reduction process and the second step, of a two-electron reduction process. From the effect of free 2,2′-bipyridine and water on the reduction wave of the cobalt(II) complex and from the Kalousek polarograms, the electrode processes of the first two steps taking place in the presence of a large concentration of free 2,2′-bipyridine were estimated as,

$$[\mathrm{Co(bipy)_3}]^{2+} \underset{-e}{\overset{e}{\rightleftharpoons}} [\mathrm{Co(bipy)_3}]^{+} \underset{-2e}{\overset{2e}{\rightleftharpoons}} [\mathrm{Co(bipy)_3}]^{-}$$

The effect of a small concentration of acrylonitrile on the reduction wave of the cobalt(II) complex was studied.

As acetonitrile is an aprotic solvent and has less oxidizing power than water, the electrode process in acetonitrile is sometimes quite different in water. Tris(2,2′-bipyridine)iron(II) complex cation in acetonitrile solutions is reduced to univalent tris(2,2′-bipyridine)ferrate anion which cannot exist in aqueous solutions.[1,2] Such a low valent state is expected in bipyridine complexes of other metals.

In the present paper, the electrode processes of tris(2,2′-bipyridine)cobalt(II) and tris(2,2′-bipyridine)cobalt(III) complexes at the dropping mercury electrode (DME) are presented and the effect of acrylonitrile on the reduction wave of the cobalt(II) complex is discussed.

Experimental

Tris(2,2′-bipyridine)cobalt(II) perchlorate and tris(2,2′-bipyridine)cobalt(III) perchlorate were prepared according to Burstall and Nyholm[3] and identified by elementary analysis. Acetonitrile, tetraethylammonium perchlorate and sodium perchlorate were the same as described in a previous paper.[2] Acrylonitrile used was of a reagent grade. The dropping mercury electrode used had an m value of 0.63_1 mg/sec and a drop time t_d of 4.84 sec, when measured in an air-free acetonitrile solution containing 0.05 M of $(C_2H_5)_4NClO_4$ at 25°C and at -0.5 V *vs.* SCE at 50 cm of the height of mercury reservoir. An aqueous saturated calomel electrode (SCE) served as a reference electrode. The electrolysis cell and other apparatus are the same as previously described.[2]

Results

Tris(2,2′-bipyridine)cobalt(II) complex gave a one-step oxidation wave from cobalt(II) to cobalt(III) around $+0.2$ V *vs.* SCE, while tris(2,2′-bipyridine)cobalt(III) complex gave a reduction wave from cobalt(III) to cobalt(II) at almost the same potential. The plots of $\log \bar{i}/(\bar{i}_d-\bar{i})$ *vs.* E for the anodic and the cathodic wave gave straight lines. Half-wave potentials and the values of the slopes determined from the log-plot analysis were given in Table 1. The solution containing the same concentrations of the cobalt(II) and the cobalt(III) complexes showed a continuous oxidation-reduction wave and an equilibrium potential which was equal to the half-wave potentials of the oxidation wave of the cobalt(II) complex and the reduction wave of the cobalt(III) complex.

When tetraethylammonium perchlorate was used as supporting electrolyte, tris(2,2′-bipyridine)cobalt(II) complex gave a four-step reduction wave as reproduced in Fig. 1 (curve a). In the solutions

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TABLE 1. LOG-PLOT ANALYSIS FOR THE OXIDATION OF THE COBALT(II) AND THE REDUCTION OF THE COBALT(III) COMPLEXES (25°)*

Reaction	$E_{1/2}$, V vs. SCE	Slope, mV
Oxidation process	0.241	62
Reduction process	0.235	65

* Electrolytic solutions contain 0.5 mM complex and 0.05 M $(C_2H_5)_4NClO_4$.

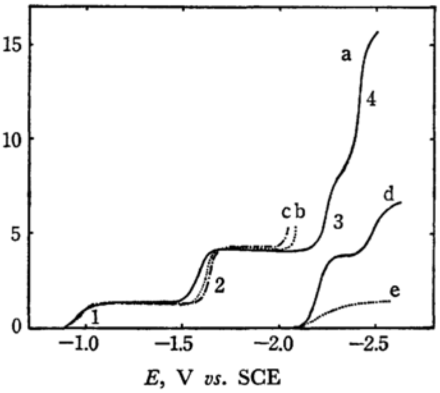

Fig. 1. D.c. polarograms of (a) 0.5 mM [Co(bipy)$_3$](ClO$_4$)$_2$, (b) (a) with 10.0 mM 2,2′-bipyridine, (c) (a) with 50.0 mM 2,2′-bipyridine, (d) 1.0 mM 2,2′-bipyridine and (e) 0.38 mM CH_2CHCN. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

containing sodium perchlorate as supporting electrolyte, the first two steps were observed, which were followed by the reduction of sodium ions. The cobalt(III) complex gave a five-step reduction wave, of which the second to the fifth steps were exactly the same as the first to the fourth steps of the cobalt(II) complex. In this paper, the polarographic behavior of the cobalt(II) complex is presented.

The limiting currents of the first (at −1.2 V) and the second step (at −1.8 V) named from positive to negative potentials were found to be proportional to the square root of the mercury pressure on the DME between 45 and 60 cm. The limiting currents were also proportional to the concentration of the complex. Upon the addition of free 2,2′-bipyridine to the solution containing 0.5 mM of the complex, the limiting currents of the first two steps were not affected, but those of the third and the fourth step were increased. The half-wave potential and the slope of the log-plot analysis (57 mV) of the first step were not affected, whereas the half-wave potential of the second step shifted to more negative potentials and the slope of the log-plot approached to the value of that of a reversible two-electron electrode process with increasing concentrations of free bipyridine (see Table 2). The half-wave potential of the third and the fourth step shifted to less negative potentials. Free 2,2′-bipyridine gave a two-step reduction wave at potentials corresponding nearly to the third and the fourth step of the polarogram of the complex as shown in Fig. 1.

TABLE 2. LOG-PLOT ANALYSIS FOR THE SECOND STEP OF THE REDUCTION OF THE COBALT(II) COMPLEX AT VARIOUS CONCENTRATIONS OF 2,2′-BIPYRIDINE*

Conc. of 2,2′-bipyridine, mM	$E_{1/2}$, V vs. SCE	Slope, mV
0	−1.580	57
10	−1.617	40
50	−1.632	35

* Electrolytic solutions contain 0.5 mM [Co(bipy)$_3$](ClO$_4$)$_2$, 0.05 M $(C_2H_5)_4NClO_4$ and various concentrations of 2,2′-bipyridine.

By the addition of a small concentration of water into the acetonitrile solution containing 0.5 mM of the complex and 0.05 M of $(C_2H_5)_4NClO_4$, the limiting currents of the first two steps of the reduction wave were scarcely affected, but the third and the fourth step shifted to less negative potentials and the limiting current of the third step increased (Fig. 2). By further addition of water, the third step shifted to less negative potentials and the second step became ill-defined. The polarogram of free 2,2′-bipyridine was also affected by the addition of water ; its reduction potential shifted to less negative potentials and its limiting current increased.

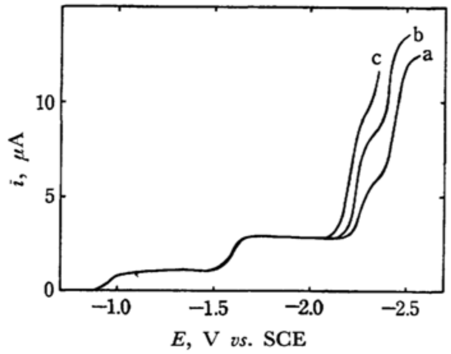

Fig. 2. D.c. polarograms of 0.5 mM [Co(bipy)$_3$](ClO$_4$)$_2$ (a) in the absence and in the presence of (b) 0.028 M and (c) 0.139 M of water. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

The reversibilities of the first two steps were confirmed by the measurement of Kalousek polarograms, which are shown in Fig. 3. A two-step oxidation wave was obtained, when the electrode potential was set up at −1.9 V (curves b and b′ in Fig. 3).

Acetonitrile often contains acrylonitrile as impurity, which gives a drawn-out cathodic wave at about −2.3 V as reproduced in Fig. 1 (curve e). Kalousek polarogram of acrylonitrile gave a one-step oxidation wave at about −0.6 V, when the electrode potential was set up at the potential of the limiting current of the reduction wave of acrylonitrile. When acrylonitrile was present in the solution, the reduction wave of cobalt(II)-bipyridine complex was affected and two new steps appeared, which were named 2 A and 2 B (curves b and c in Fig. 4). The 2 A step started from about −1.3 V followed by the second step, and its limiting current

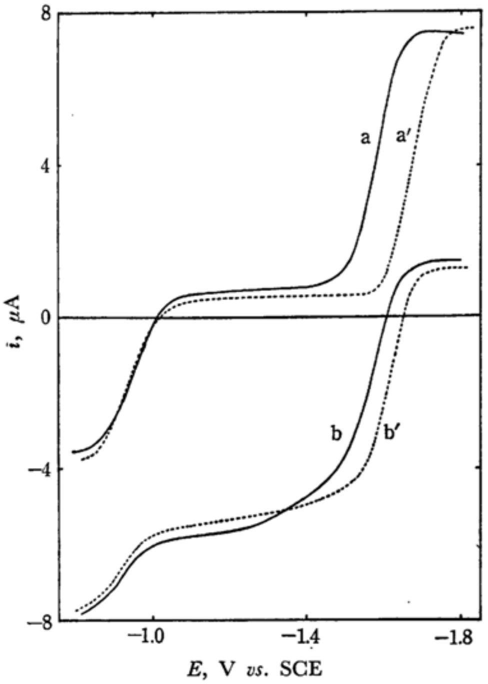

Fig. 3. Kalousek polarograms of 0.5 mM $[Co(bipy)_3](ClO_4)_2$ (a and b) in the absence and (a′ and b′) in the presence of 50 mM of 2,2′-bipyridine. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$. E_2 potentials are set up at −1.20 V for a and a′ and −1.90 V for b and b′.

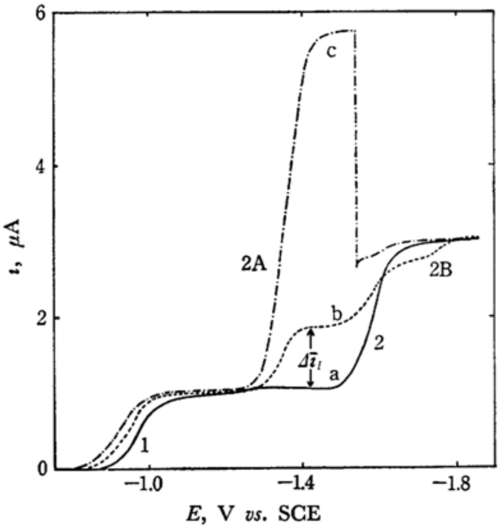

Fig. 4. D.c. polarograms of 0.5 mM $[Co(bipy)_3](ClO_4)_2$ (a) in the absence and in the presence of (b) 0.38 mM and (c) 1.9 mM of CH_2CHCN. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

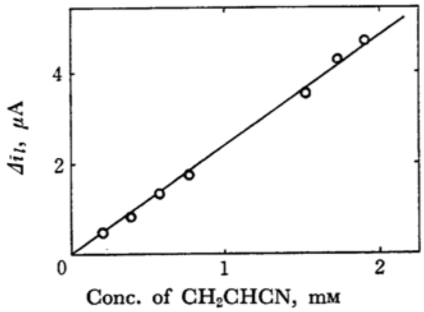

Fig. 5. Limiting current of the 2A step as a function of the concentration of acrylonitrile, obtained with the solutions containing 0.5 mM $[Co(bipy)_3](ClO_4)_2$, CH_2CHCN and 0.05 M $(C_2H_5)_4NClO_4$. For Δi_l, see curve b in Fig. 4.

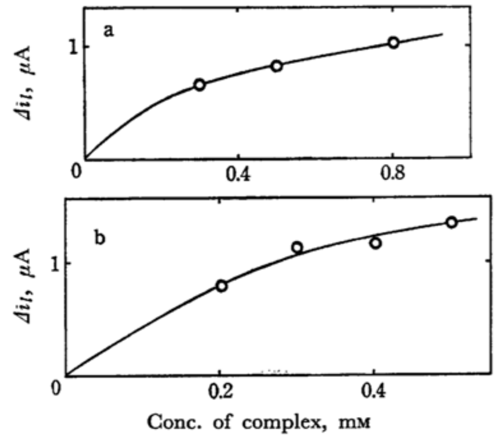

Fig. 6. Limiting current of the 2A step as a function of concentration of the complex, obtained with the solutions containing $[Co(bipy)_3](ClO_4)_2$, 0.05 M $(C_2H_5)_4NClO_4$ and (a) 0.38 mM CH_2CHCN and (b) 0.57 mM CH_2CHCN. For Δi_l, see curve b in Fig. 4.

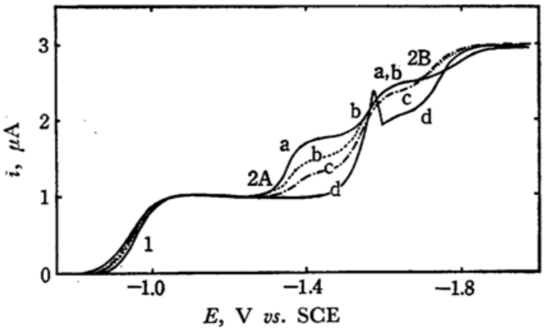

Fig. 7. D.c. polarograms of 0.5 mM $[Co(bipy)_3](ClO_4)_2$ in the presence of 0.38 mM CH_2CHCN and (a) 0, (b) 1.0 mM, (c) 2.0 mM and (d) 10.0 mM 2,2′-bipyridine. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

(the difference of the limiting currents at −1.45 V in the presence and the absence of acrylonitrile, $\Delta\bar{i}_l$) was proportional to the concentration of acrylonitrile at the constant concentration of the complex (see Fig. 5), and to the square root of the height of the mercury reservoir. Although the limiting current of the 2 A step was increased with increasing concentrations of the complex at the constant concentration of acrylonitrile, $\Delta\bar{i}_l$ was not proportional to the concentration of the complex, but approached to a definite value (Fig. 6). When the concentration of acrylonitrile was about five times larger than that of the complex, the 2 A step gave a peak current and its reproducibility was poor. By adding free 2,2′-bipyridine to the solution the 2 A step was depressed and the 2 B step became more noticeable, as seen in Fig. 7. In the solution containing 0.5 mM of the complex and 0.38 mM of acrylonitrile, the 2 A step almost disappeared by the addition of about 6 mM of free bipyridine.

A.c. polarograms of the cobalt(II) complex were recorded in the presence and in the absence of acrylonitrile and free bipyridine (Fig. 8). The solution containing only the complex showed four peakss which corresponded to the above-mentioned four steps of the d.c. polarogram. In Fig. 8, the first two peaks are reproduced. The other two peaks which appeared at more negative potentials are considered to be the reduction of the ligand coordinated to cobalt. By adding acrylonitrile two new peaks named 2 A and 2 B appeared. The addition of 10 mM of free bipyridine depressed the 2 A peak as shown in Fig. 8 (curve c). The solution containing only acrylonitrile showed a small peak of irreversible-type at about −2.2 V.

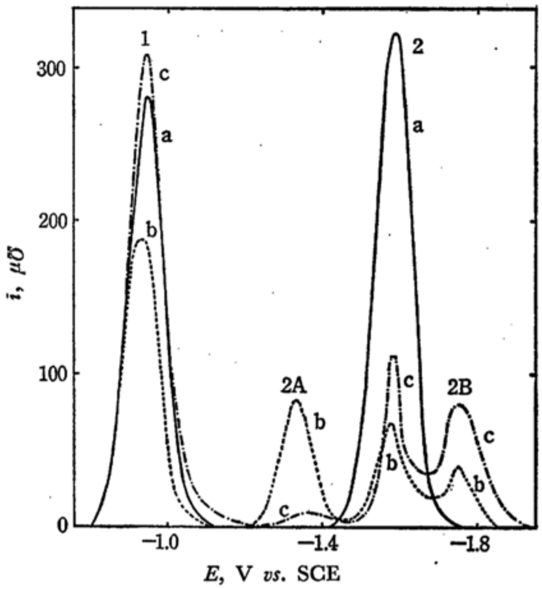

Fig. 8. A.c. polarograms of 0.5 mM [Co(bipy)$_3$]-(ClO$_4$)$_2$ (a) in the absence and in the presence of (b) 0.38 mM CH$_2$CHCN and (c) 0.38 mM CH$_2$CHCN and 10.0 mM 2,2′-bipyridine. Supporting electrolyte is 0.05 M (C$_2$H$_5$)$_4$NClO$_4$.

Discussion

The slopes of the log-plot and the half-wave potentials for the reduction of the cobalt(III) and the oxidation of the cobalt(II) complexes show that the electrode process of the coabalt(III) and the cobalt(II) system,

$$[\mathrm{Co(bipy)_3}]^{3+} + \mathrm{e} \rightleftharpoons [\mathrm{Co(bipy)_3}]^{2+}$$

is reversible at the DME. The continuous oxidation-reduction wave which was obtained with a solution containing the same concentrations of the cobalt(III) and the cobalt(II) complex confirmed the above conclusion.

The limiting currents of the first two steps of the reduction wave of the cobalt(II) complex are concluded to be diffusion-controlled from the linearities of the limiting currents on the square root of the mercury pressure and on the concentration of the complex. The diffusion current constant for the first step obtained by the Ilkovič equation is 2.17, which is nearly equal to the value of a one-electron reduction of tris(2,2′-bipyridine)iron(II) complex.[2] The ratio of the wave heights of the first two steps is 1 : 2 after corrected for the drop time. The fact that the wave heights of the first two steps of the complex are not influenced by the addition of free 2,2′-bipyridine and a small concentration of water but those of the last two steps are influenced shows that the electrode processes of the first two steps and the latter two steps are different in nature.

From the same considerations as in the case of the reduction of the iron(II) complex[2] in addition to the fact that the reduction potential of free 2,2′-bipyridine is equal to the potential of the third and the fourth step of the reduction wave of the complex (see Fig. 1), the first two steps are concluded to be due to the reduction of the cobalt(II) complex itself and the latter two steps, the reduction of free bipyridine liberated from the complex. The second step seems to be a two-electron reduction from the cobalt(I) complex to the cobalt(-I) complex and the electrode process is considered to consist of various paths, such as a reduction from [Co(bipy)$_3$]$^+$, and that from [Co(bipy)$_{3-n}$]$^+$, the reduction potentials of the latter being less negative than the former. As the concentration of free bipyridine is increased, the reaction path from [Co(bipy)$_3$]$^+$ will be predominant because the half-wave potential shifted to more negative potentials and the reciprocal slope of the log-plot became smaller and approached to the theoretical value of a two-electron reversible process (see Table 2).

Kalousek polarograms also suggested the formation of the cobalt(I) and the cobalt(-I) complex at the electrode surface at the potentials of the first and the second step, respectively. Thus, the reaction scheme may be written as,

$$\begin{tikzcd}
{[\mathrm{Co(bipy)_3}]^{2+}} & & \\
+ & & \\
\mathrm{e} \arrow[d, shift left] & & \text{(the first step)} \\
{[\mathrm{Co(bipy)_3}]^{+}} \arrow[u, shift left] \arrow[r, leftrightharpoons] & {[\mathrm{Co(bipy)}_{3-n}]^{+} + n\ \mathrm{bipy}} & \\
+ & + & \\
2\mathrm{e} \arrow[d, shift left] & 2\mathrm{e} \arrow[d, shift left] & \text{(the second step)} \\
{[\mathrm{Co(bipy)_3}]^{-}} \arrow[u, shift left] \arrow[r, leftrightharpoons] & {[\mathrm{Co(bipy)}_{3-n}]^{-} + n\ \mathrm{bipy}} \arrow[u, shift left] &
\end{tikzcd}$$

Vlček4) and Waind and Martin5) found the cobalt(I) state polarographically and were successful in preparing the compound. Herzog, Klausch and Lantos6) prepared the cobalt(0) complex, $[\mathrm{Co(bipy)_3}]$, from $\mathrm{CoCl_2}$ and $\mathrm{Li_2}$bipy in tetrahydrofuran. The bipyridine complex of cobalt(-I) has not been prepared yet according to the author's knowledge. The reason why the reduction process to the cobalt(0) complex is not observed at the DME is probably in the fact that the cabalt(0)-bipyridine complex is not sufficiently stable in acetonitrile and the cobalt(I) complex is reduced directly to the cobalt(-I) state.

The reduction mechanism of acrylonitrile at the DME in acetonitrile has not been discussed,7) although the reduction wave is often used for the analysis of residual acrylonitrile monomer in stylene-acrylonitrile copolymer.8) The electrode process of acrylonitrile is considered to be irreversible from the shape of the drawn-out wave (curve e in Fig. 1) and the small peak current of the a.c. polarogram. Kalousek polarogram also confirmed the irreversibility of the electrode process. Proton will not take part in the reduction process because the electrode reaction proceeds in acetonitrile of aprotic solvent. If proton took part in, the reduction product of acrylonitrile at the electrode surface would be propionitrile, $\mathrm{CH_3CH_2CN}$, as was found in aqueous solutions.9) This is not the case because propionitrile gives no oxidation wave at about -0.6 V10) where an oxidation wave is observed in a Kalousek polarogram. Since acrylonitrile polymer radical has been observed by e.s.r.11) the reduction product of acrylonitrile is likely to be an acrylonitrile radical, but not a propionitrile molecule. Stylene, $\mathrm{C_6H_5CH{=}CH_2}$, and crotonic acid, $\mathrm{CH_3CH{=}CHCOOH}$ also give a reduction wave at about -2.45V and -2.3V, respectively, and at the Kalousek circuit, an anodic wave at about -1.15 V and $+0.1$ V, respectively. Although acrylonitrile itself is reduced at such a negative potential as -2.3 V, the reduction wave of the cobalt(II) complex is affected at about -1.4 V (2 A wave) and -1.7 V (2 B wave) in the presence of a small concentration of acrylonitrile (curve b and c in Fig. 4). From the proportionalities of the limiting current of the 2 A step on the concentration of acrylonitrile at the constant concentration of the complex (Fig. 5) and on the square root of the height of the mercury reservoir, the 2 A step seems to be controlled by the diffusion of acrylonitrile. The temperature coefficient of the limiting current of the 2 A step was found to be 1.3%/deg at 25°. Even when the concentration of acrylonitrile is larger than that of the complex, the limiting current of the 2 A step is proportional to the concentration of acrylonitrile. However, the limiting current suddenly decreased at the potential of the first half of the second step and the limiting current at -1.9 V is constant irrespective of the concentration of acrylonitrile as far as the concentration of the complex is the same (curve c in Fig. 4). The dependency of $\Delta\bar{i}_l$ on the concentration of the complex at the constant concentration of acrylonitile is almost in agreement with the Langmuir isotherm. All these results suggest that the 2 A step is not due to a reduction of the complex but due to that of acrylonitrile in the presence of cobalt(I) species at the electrode. Since the 2 A step was suppressed by the addition of free 2,2′-bipyridine as shown in Fig. 7, the reduction of acrylonitrile seems to require the species of $[\mathrm{Co(bipy)}_{3-n}]^+$ at the electrode surface. The cobalt(I) complex formed at the electrode is considered to be substitution-labile, because the half-wave potential of the second step was shifted to more negative potentials with increasing concentrations of free bipyridine. Therefore, in the absence of free bipyridine, cobalt(I) species formed at the electrode surface at -1.1 to -1.5 V may be mainly $[\mathrm{Co(bipy)}_{3-n}]^+$. An acrylonitrile molecule to be reduced approaches to the electrode and may be coordinated to the central cobalt ion in $[\mathrm{Co(bipy)}_{3-n}]^+$ which is adsorbed on the surface of the electrode. The reduction of acrylonitrile will occur at this state. If free bipyridine is present in the solution, the coordination of acrylonitrile to the central cobalt(I) ion is hindered and consequently the limiting current of the 2 A step is decreased. In this electrode process, the cobalt(I) species acts as a role of bridge for the electron transfer from the electrode to acrylonitrile molecule. The complex formation between acrylonitrile and $[\mathrm{Co(bipy)}_{3-n}]^+$ does not occur in the bulk of the solution but at the electrode surface, because the limiting current of the 2 A step is proportional to the concentration of acrylonitrile but not to that of the complex. An acrylonitrile molecule seems to be coordinated at its double bond

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rather than at its CN group, because a solvent molecule (acetonitrile) has also a CN group and its concentration is about 5×10^4 times greater than that of acrylonitrile. In the case of iron(I) tetracarbonyl acrylonitrile ($Fe(CO)_4CH_2=CHCN$), both a double-bonded type and a σ-bonded type of bonding of acrylonitrile to the central iron are known.[12,13] The potential of the 2 A step is nearly the middle between the reduction potential of acrylonitrile and the oxidation potential of its reduction product obtained by the Kalousek circuit. The overpotential of acrylonitrile appears to be lessened by the coordination to cobalt(I) at the electrode surface. At the potentials of the 2nd step where cobalt(I) is reduced to cobalt($-$I) state, the 2 A step vanishes, and acrylonitrile cannot coordinate to the cobalt($-$I) and consequently the limiting current of the second step is constant at about -1.9 V irrespective of the concentration of acrylonitrile. A similar phenomenon as the 2 A step is observed in the case of crotonic acid but the situation seems to be more complicated. The 2B step appears to occur by the retardation of the electrode process of the acrylonitrile as the current-potential curve at the second step is seen to be cut off and the limiting current at about -1.9 V is always constant.

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