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Polarographic Behavior of Cobalt-1-Nitroso-2-naphthol Complex in Ammonium Citrate and Tartrate Solutions

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The reduction behavior of cobalt(II) in ammonium citrate and tartrate solutions containing 1-nitroso-2-naphthol was investigated by means of d.c., a.c., normal and differential pulse polarography (n. p. p. and d. p. p.). When cobalt(II) is added to the supporting electrolyte of citrate or tartrate in the presence of the nitrosonaphthol, the reduction potential of 1-nitroso-2-naphthol shifts to a more negative value, the well-defined a. c. and d. p. p. peaks appearing. The drop time-potential curve indicated that adsorption of nitrosonaphthol as well as its reduction product at the mercury surface occurs. The analytical potentiality of the use of nitrosonaphthol for the microdetermination of cobalt(II) is also described.

The enhancement of current intensity of metal ions is often observed in solutions containing complex-forming molecules adsorbable at the electrode surface.[1–7] The phenomenon has been used for increasing the sensitivity of determination of metal ions.[2–5,8,9]

The well-known specific reagent for cobalt, 1-nitroso-2-naphthol, is reduced at the mercury electrode in four-electron step to the amine.[10–13] We found that the nitrosonaphthol is adsorbed on the mercury surface in a wide potential region, and by adding cobalt(II), the reduction of nitrosonaphthol shifts to a more negative potential, giving well-defined a.c. and d.p.p. peaks. In the present work, the behavior of cobalt-1-nitroso-2-naphthol complex in ammonium tartrate and citrate solutions is investigated with various methods of polarization of the dropping mercury electrode.

Experimental

Apparatus. D.c. and a.c. polarograms were obtained with a Yanagimoto polarograph model P-8. The dropping mercury electrode used had the characteristics: $m=2.53$ mg s^{-1} in deionized water and $t=3.87$ s in 0.1 M (1 M=1 mol dm^{-3}) ammonium citrate solution of pH 9.1 at open circuit and $h=39$ cm. A saturated calomel electrode was used as the reference electrode. For the a.c. polarography, the reference electrode was connected to a platinum coil counter electrode via a pool condenser of 3300 μF. Normal and differential pulse polarograms were recorded with a Princeton Applied Research model 174A polarographic analyzer, equipped with a Rika Denki X-Y recorder, model RW-11. A PAR 174/70 drop timer was used. The dropping mercury electrode used had the characteristics: $m=3.99$ mg s^{-1} in deionized water and $t=2.41$ s in 0.2 M ammonium tartrate solution of pH 8.7 at open circuit, when $h=71$ cm. A platinum wire served as the counter electrode and SCE as the reference electrode.

Electrolysis solutions were deaerated by bubbling pure nitrogen gas which had been passed through the supporting elcetrolyte of the same pH value. During electrolysis, nitrogen gas was passed over the solution. All polarograms were recorded at 25±0.1 °C. A Hitachi-Horiba glass electrode pH meter, F-5, was used for the pH measurements.

Reagents. Commercially available 1-nitroso-2-naphthol (Wako Chemicals Co.) was purified according to the literature.[14] A 0.01 mol dm^{-3} stock solution of the nitrosonaphthol was prepared by dissolving the purified reagent by weight in 10 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution and diluting to 50 cm^3 with deionized water. A 1.0×10^{-2} mol dm^{-3} stock solution of cobalt(II) was prepared from chloride and standardized chelatometrically. Other reagents used were all of the G. R. grade. Deionized water was used.

The electrolysis solution was prepared as follows. To a known portion of cobalt(II) solution in a 50-cm^3 volumetric flask are added in sequence 10 cm^3 of 1 mol dm^{-3} ammonium citrate or tartrate solution and 0.1 cm^3 of 0.01 mol dm^{-3} nitrosonaphthol solution, in order to prevent the appearance of precipitate. After standing for 30 min, the pH of solution is adjusted by adding an appropriate amount of 5 mol dm^{-3} ammonia solution and the mixture is diluted to the volume with deionized water. According to the procedure, the citrate or tartrate concentration in the electrolysis solution is always kept at 0.2 mol dm^{-3}.

Results and Discussion

D.c. and a.c. Polarographic Behavior. The cobalt–1-nitroso-2-naphthol complex is sparingly soluble in aqueous solutions and the precipitate once formed does not dissolve in the aqueous solution, but when the amount of cobalt(II) is low, a red-orange solution appears instead of the precipitate. D.c. and a.c. polarograms of cobalt(II) in an ammonium citrate solution of pH 9.1 containing an excess amount of 1-nitroso-2-naphthol are shown in Figs. 1 and 2, respectively. The d.c. first wave corresponds to the reduction of 1-nitroso-

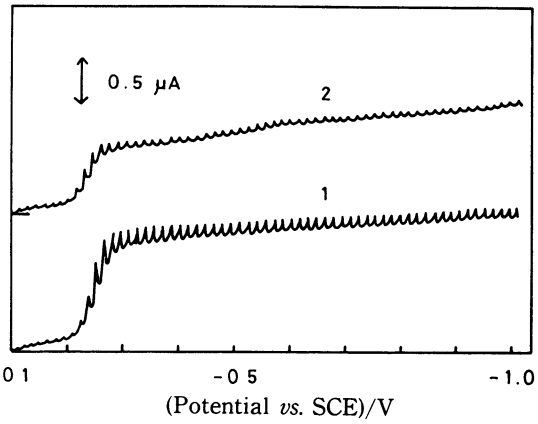

Fig. 1. D. c. polarograms of the cobalt–nitrosonaphthol system in 0.2 mol dm^{-3} diammonium hydrogencitrate-0.35 mol dm^{-3} ammonia buffer solution of pH 9.1.
(1) 60 μmol dm^{-3} R(NO)OH, (2) 1+10 μmol dm^{-3} cobalt(II).

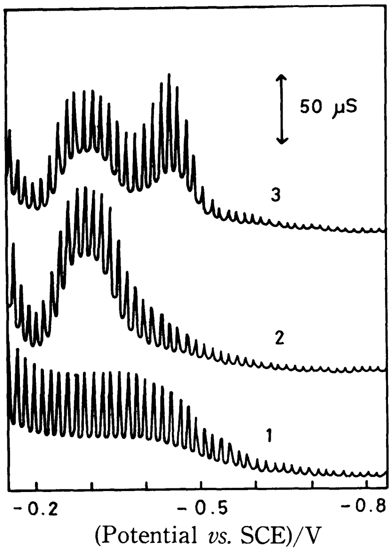

Fig. 2. A. c. polarograms of the cobalt–nitrosonaphthol system in the same supporting electrolyte as in Fig. 1. (1) Supporting electrolyte only, (2) 60 μmol dm^{-3} R(NO)OH, (3) 2+10 μmol dm^{-3} cobalt(II).

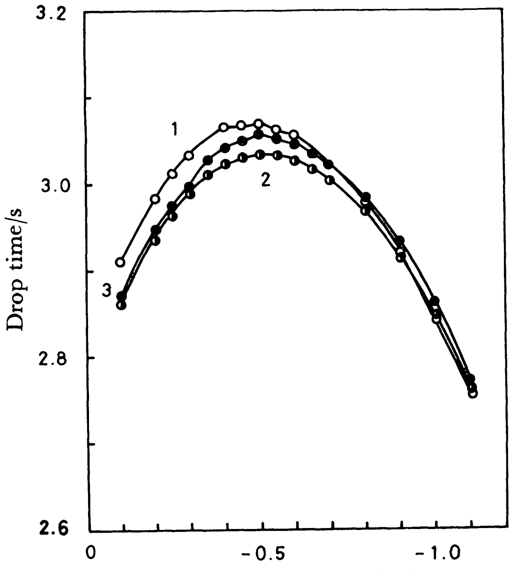

Fig. 3. Drop time *vs.* potential curves of the cobalt–nitrosonaphthol system in 0.2 mol dm^{-3} ammonium tartrate–0.05 mol dm^{-3} ammonia buffer solution of pH 8.7.
(1) Supporting electrolyte only, (2) 50 μmol dm^{-3} R(NO)OH, (3) 2+2 μmol dm^{-3} cobalt(II).

2-naphthol to the amine. When cobalt(II) is added to the solution, the first wave diminishes and an ill-defined second wave at about −0.52 V *vs.* SCE appears. The reduction of 1-nitroso-2-naphthol proceeds in a four-electron step involving four protons,[10,12] and is diffusion-controlled.[10,11] Tomes' method[15] applied to the first wave for evaluating the reversibility gave the difference of $E_{1/2}-E_{3/4}=25$ mV, which is fairly greater than 15 mV, expected from the reversible four-electron process. The d.c. second wave being ill-defined, the further analyses were impossible.

On the a.c. polarogram of cobalt ion, in the presence of an excess amount of 1-nitroso-2-naphthol, two well-developed peaks are observed. The first and second peaks correspond to the d.c. first and second steps, respectively, although the peak potential of the a.c. first peak is more negative by about 70 mV of the half-wave potential of the corresponding d.c. step. Compared with the a.c. polarogram of the supporting electrolyte alone, the depression of base current of the a.c. wave of nitrosonaphthol is observed. A plot of drop time *vs.* potential in the tartrate medium, as shown in Fig. 3, indicates that the nitrosonaphthol and its reduction product are adsorbed on the electrode surface. The similar results were obtained also in the citrate medium. The remarkably enhanced a.c. second peak, as compared with the d.c. second step, is ascribed to the adsorption of complex and its reduction product at the electrode surface, leading to the decrease in faradaic impedance.[1] In the citrate medium the peak height of the cobalt complex depends strongly on the solution pH, as shown in Fig. 4. The plot of peak potential *vs.* pH between 8.6 and 9.3 gave a straight line with a slope of −64 mV for the first and −76 mV for the second peak. The electrode process of nitrosonaphthol and its cobalt complex is seemingly not completely reversible in a.c. sense. The height of a.c. peak of the cobalt complex increases linearly with increasing concentration of cobalt(II) between 0.5 and 5 μmol dm^{-3}. At higher concentration of cobalt(II) above 5 μmol dm^{-3}, the linear relationship does not hold and the value of i_{AC}/C (μS mol^{-1} dm^{3}) increases with

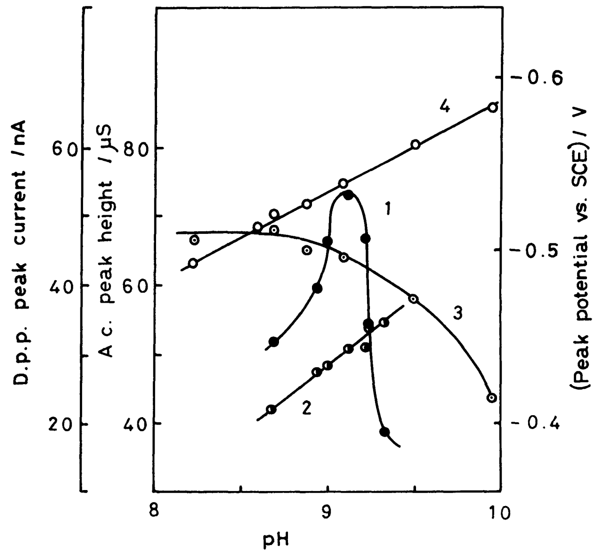

Fig. 4. Effect of pH on (1) a. c. peak height and (2) a. c. peak potential of the cobalt(II)–R(NO)OH complex in 0.2 mol dm^{-3} diammonium hydrogencitrate solution, (3) d. p. p. peak height and (4) d. p. p. peak potential of the cobalt–R(NO)OH complex in the 0.2 mol dm^{-3} ammonium tartrate solution.
(1) and (2): 10 μmol dm^{-3} cobalt(II)+184 μmol dm^{-3} R(NO)OH. (3) and (4): 0.5 μmol dm^{-3} cobalt(II)+10 μmol dm^{-3} R(NO)OH. D. p. p. condition: pulse amplitude $\Delta E=50$ mV; scan rate 5 mV s^{-1}; forced drop time $t_d=1$ s.

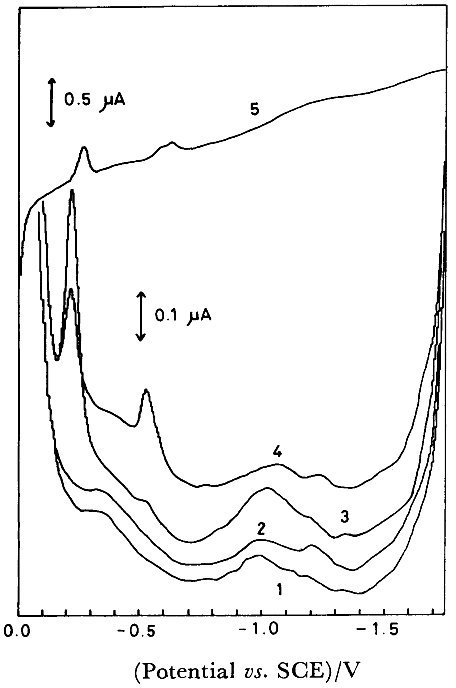

Fig. 5. D. p. and n. p. polarograms of the cobalt(II)–R(NO)OH system in the same supporting electrolyte as in Fig. 3. D. p. p. condition is the same as in Fig. 4. N. p. p. condition: scan rate 5 mV s^{-1}; initial potential $E_i=0.0$ V *vs.* SCE; $t_d=1$ s.
(1) Supporting electrolyte only, (2) 1+0.2 μmol dm^{-3} cobalt(II), (3) 1+1 μmol dm^{-3} R(NO)OH, (4) 2+1 μmol dm^{-3} R(NO)OH, (5) Normal pulse polarogram of solution (4).

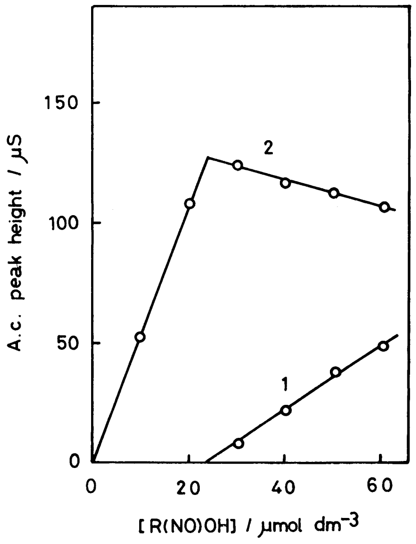

Fig. 6. Variation of a. c. peak height with R(NO)OH concentration in the same supporting electrolyte as in Fig. 1.
(1) First peak, (2) second peak, 9.8 μmol dm^{-3} cobalt(II).

increasing concentration *C* of cobalt(II).

Normal Pulse and Differential Pulse Polarographic Behavior. Normal and differential pulse polarograms of cobalt(II) in an ammonium tartrate solution containing an excess amount of nitrosonaphthol are shown in Fig. 5. On the normal pulse polarogram, a maximum, followed by a current suppression, is observed for the both waves at about −0.26 and −0.60 V. The phenomena are ascribed to Barker-Bolzan effect[1] indicating the rather strong adsorption of depolarizer at the electrode surface. On the differential pulse polarogram of the cobalt–nitrosonaphthol system three peaks are observed. The first peak at −0.21 V corresponds to the reduction of nitrosonaphthol and the second at −0.52 V to the reduction of nitrosonaphthol bound to cobalt(II). At a fairly negative potential (−1.20 V), an additional small peak appears, the potential of which coincides well with the potential of Co(II)/Co(Hg) system in the tartrate solution, as the polarograms 2 and 4 in Fig. 5 show. The height of the second peak was almost constant in the pH range from 8.2 to 8.9, and a plot of peak potential *vs.* pH gave a straight line having a slope of −52 mV, as shown in Fig. 4. The slope is in good accordance with the theoretical value of −59 mV for the reversible four-electron process involving four protons. The result indicates that the electrode reaction of cobalt complex is reversible in the d.p.p. sense. The peak height of cobalt complex increases with increasing concentration of cobalt(II) between 0.05 and 0.5 μmol dm^{-3}, but at the concentration of cobalt(II) above 0.6 μmol dm^{-3}, the increase in peak height becomes gradually saturated. The narrow concentration range, in which the calibration graph is linear, is one of the characteristic features indicating the adsorption of depolarizer. The calibration graph does not pass the origin, because a trace amount of cobalt(II) is present in the tartrate buffer solution as an impurity. The concentration of cobalt(II) impurity in the 0.2 mol dm^{-3} ammonium tartrate solution of pH 8.7 was found to be 0.11 μmol dm^{-3}.

The Composition of the Cobalt Complex and Electrode Reaction Mechanism. A plenty of data[10,11,16–20] on the composition of the cobalt–1-nitroso-2-naphthol complex indicate that the number of ligand bound to cobalt ion and the oxidation state of cobalt depend on the media employed. According to Kolthoff and Jacobsen,[11] bis(1-nitroso-2-naphtholato)cobalt(II) is formed in neutral and weakly alkaline solutions, and in an acidic solution, the cobalt(II) complex disproportionates rapidly, forming tris(1-nitroso-2-naphtholato)-cobalt(III). The similar disproportion process is suggested by Collahan *et al.*[18] based on the potentiometric titration in dioxane–water mixture. The formation of bis(1-nitroso-2-naphtholato)cobalt(II) in an ammonium citrate solution of pH 9.8 is also cited in the excellent monograph by Pyatnitskii.[20]

Dependence of a.c. peak height on various concentrations of 1-nitroso-2-naphthol in an ammonium citrate solution of pH 9.1 is shown in Fig. 6. The sharp increase in peak height of the cobalt complex is saturated at 2.3 of the molar ratio of nitrosonaphthol to cobalt(II). Further addition of the nitrosonaphthol decreases the peak height of the complex gradually, while the a.c. first peak of excess ligand appears. It seems that in the citrate solution bis(1-nitroso-2-naphtholato)cobalt(II) is predominantly formed according to

$$Co^{2+} + 2R(NO)OH \rightleftharpoons Co[R(NO)O]_2 + 2H^+, \quad (1)$$

where R(NO)OH indicates the 1-nitroso-2-naphthol. The reduction of R(NO)OH at the mercury electrode[11,12] is given by

$$R(NO)OH + 4H^+ + 4e \rightleftharpoons R(NH_2)OH + H_2O. \quad (2)$$

The nitrosonaphthol coordinated to cobalt(II) being stabilized, the reduction of the nitrosonaphthol in the complex shifts to a more negative potential. The overall electrode reaction is estimated to be

$$Co[R(NO)O]_2 + 8H^+ + 8e \rightleftharpoons$$
$$Co^{2+} + 2R(NH_2)O^- + 2H_2O. \quad (3)$$

In the ammonium tartrate solution of pH 8.7, the results of titration of 1 μmol dm^{-3} cobalt(II) with R(NO)OH gave the breaking point at around 2.6 of the molar ratio of the nitrosonaphthol to cobalt(II) for both the first and second waves. The results imply that a fraction of bis(1-nitroso-2-naphtholato)cobalt(II) in the tartrate solution differs slightly from that in the citrate medium. It should be noted that the decrease in a.c. and d.p.p. peak heights by adding excess amount of ligand is always observed and is due to the broadening of peaks. At 5 μmol dm^{-3} nitrosonaphthol, the half-width of d.p.p. peak of 1 μmol dm^{-3} cobalt(II) in the tartrate solution is 77 mV, however, it is 94 mV at 80 μmol dm^{-3} nitrosonaphthol. This is probably because the electrode reaction of the cobalt complex is hindered by the stronger adsorption of reduction product of nitrosonaphthol than the adsorption of the complex itself. The appearance of a small d.p.p. peak at −1.20 V in the tartrate solution, as described above, suggests that the cobalt(II) released by reduction is further reduced in the medium.

The adsorption of the cobalt complex at the mercury surface is not clear as judged from the drop time *vs.* potential plot, as shown in Fig. 3. However, the significantly enhanced response in a.c. polarography and also the narrow concentration range, for which the d.p.p. response is linear, imply that the cobalt complex is also adsorbed on the mercury surface.

TABLE 1. EFFECT OF FOREIGN METAL IONS ON THE d.p.p. DETERMINATION OF COBALT(II) IN 50 cm^3 OF 0.2 mol dm^{-3} AMMONIUM TARTRATE-0.05 mol dm^{-3} AMMONIA SOLUTION OF pH 8.7 CONTAINING 10 μmol dm^{-3} 1-NITROSO-2-NAPHTHOL

Metal	Metal added (μg)	Cobalt(II) found (μg)	Reovery %
Ni(II)	0.59	0.53	90
	2.94	0.49	83
Cd(II)	11.24	0.58	98
	22.48	0.31	53
Zn(II)	6.54	0.64	108
	13.08	0.66	112
	13.08	0.59	100 [a]
Fe(III)	5.58	0.62	105
	11.17	0.84	142
Cu(II)	0.64	0.93	158
	3.18	1.69	286

Cobalt(II) taken: 0.59 μg. a) Concentration of the nitrosonaphthol was increased by twice.

Analytical Potentiality. Although the remarkably enhanced a.c. response is obtained, the d.p.p. method is more sensitive, because of the inherent advantage to discriminate faradaic current from nonfaradaic one. In the alkaline solution of ammonium tartrate, cobalt at several ppb levels can be determined by differential pulse polarography. The slightly alkaline tartrate medium is preferable for the analytical purposes, because in this medium the interference by iron(III) is significantly suppressed. Effect of some metal ions on the d.p.p. determination of cobalt(II) is given in Table 1. Serious interference by copper(II) was found, which is due to the overlapping of the reduction peak of the copper(II)–nitrosonaphthol complex with the cobalt(II) peak. Improvement of selectivity of the method may be achieved by selective extraction of the cobalt complex in organic solvents. The extract may be directly subjected to polarographic measurements. Further study is under way.

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