Polarographic Studies on α -Pyridylazo-Resorcinol and its Cobalt(II) Chelate in N,N-Dimethylformamide-Water Mixture

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Introduction

Willard and Dean¹⁾ firstly used a di-o-hydroxyazo dye for the polarographic determination of aluminum. In an acetate buffer of pH 4.6, Eriochrome Violet B exhibited a single, well-defined reduction wave. In the presence of aluminum this step was reduced in height and a new step appeared at a more negative potential. The height of this second step was proportional to the aluminum concentration. Eriochrome Violet B or similar dyes have been used also for the polarographic determination of Th³⁾, Zr^{2, 3)}, Ga⁵⁾, In⁵⁾, U³⁾ Cr⁴⁾ and Lanthanides.^{6, 7)}

Although the use of α -pyridylazo-resorcinol (PAR) as a chelating agent in spectrophotometric determination^{8~10)} and as a metal indicator in chelometric titration^{11, 12)} has been proposed, the polarographic behaviors of mono-o-hydroxyazo dyes such as PAR and their metal chelates have not yet been reported.

However, it is to be noted that the polarographic behavior of mercuric diethyldithiocarbamate in N,N-dimethylformamide (DMF)-water mixture was reported recently.¹³⁾

The present paper concerns a detailed polarographic investigation of PAR and its cobalt(II) chelate in DMF-water mixture.

Experimental

A Yanagimoto PA 102 recording polarograph was used for current and potential measurements. Unless otherwise stated, all polarograms were recorded at $25 \pm 0.3^\circ\text{C}$. All potentials reported were measured with reference to a saturated calomel electrode (SCE). A conventional H-type cell with an external electrode was used. Pure nitrogen gas passed through the basal solution was used to remove dissolved oxygen from the electrolytic solution before polarographic runs. Characteristic of the capillary used were $m = 0.764$ mg/sec and $t = 3.61$ sec/drop at -0.45 V. in electrolytic solution composed of $2 \times 10^{-4} M$ PAR, $0.1 M$ HOAc- $0.1 M$ NaOAc buffer solution, 20 volume % DMF and 0.005% polyacrylamide (PAA). The pH measurements were made with a Toa Denpa glass electrode pH meter.

The PAR used in this investigation was purified by recrystallization from water-ethanol mixture, and the purified material thus obtained was analysed for nitrogen, hydrogen and carbon. PAR solution was standardized by photometric titration with a standard copper sulfate solution. Cobalt sulfate solution was standardized by chelometric titration with

murexide metal indicator. Acetate, phosphate and ammonia-ammonium salt buffer solutions were used to control the pH. All other chemicals were of reagent grade. PAA was used as a maximum suppressor only in the investigation by direct current polarography.

Results and Discussion

1) Direct Current Polarography

Experimental procedures were as follows. 5 ml of 1M NaOAc or 10 ml of 0.5M Na_2HPO_4 -0.5M NaH_2PO_4 buffer solution was placed in a 50 ml measuring flask with 10 ml of $2 \times 10^{-3}M$ PAR followed by adding the requisite volume of CoSO_4 solution, 1 ml of 0.5% PAA and 10 ml of DMF. The solution was then carefully made up to the mark at 25°C. An aliquot was transferred to the H-type cell, deoxygenated for at least 15 minutes by purified nitrogen gas and polarographed over the potential range of +0.5 to -1.0 V.

Fig. 1 shows DC and AC polarograms of (1) free PAR in an acetate buffer of pH 5.5 and (2) PAR plus cobalt in the same buffer solution.

The reduction wave of PAR was well-defined at about -0.2V. and its half-wave potential was pH-dependent. On addition of cobalt, the height of PAR reduction wave was lowered, the decrease being dependent on the concentration of cobalt, while a second wave appeared at a potential of 0.15 V. more negative than the reduction wave of PAR itself and the wave-height was proportional to the cobalt concentration. Although the height of these waves were pH-dependent, they were independent of the time elapsing between the preparation of the solution and the polarographic measurement.

Fig. 1. DC and AC Polarogram.
0.1M HOAc-0.1M NaOAc, 20 Vol% DMF-water mixture, 0.005% PAA
(A) PAR $4 \times 10^{-4}M$, (B) PAR $4 \times 10^{-4}M$ + CoSO_4 $10^{-4}M$, (B') AC polarogram of (B),
(C) AC polarogram of 4×10^{-5} PAR

Fig. 2 shows the effect of pH on the diffusion current of PAR and Co-PAR complex. Diffusion current of Co-PAR was found to be almost constant in the pH range from 5.2 to 6.5. The half-wave potentials of the first and the second waves were measured in solutions of various pH values. The relation of half-wave potential ($E_{1/2}$) to pH was almost linear, $E_{1/2}$ being given by the following empirical equations:

$$E_{1/2} = 0.26 - 0.092 \text{ pH (PAR)}$$

$$E_{1/2} = 0.04 - 0.076 \text{ pH (Co-PAR)}$$

The first and the second waves overlap each other above pH 6.8. Therefore, the determination of cobalt should be performed at the pH range from 5.4 to 5.8.

Although the reduction of azobenzene to hydrazobenzene has been shown to be a reversible, two electron process, the reduction of PAR proceeds irreversibly. The diffusion coefficient calculated for PAR, $D = 0.36 \times 10^{-5} \text{ cm}^2/\text{sec.}$, is com-

Fig. 2. Effects of pH on diffusion current. Acetate or phosphate buffer was used to control pH.
0.005% PAA
20 Vol% DMF-water mixture
(A) $4 \times 10^{-4} M$ PAR
(B) $4 \times 10^{-4} M$ PAR + $10^{-4} M$ CoSO₄

Fig. 3. Effect of temperature on i_d of
(A) PAR and (B) Co(II) PAR.
0.4 mM PAR + 0.1 mM CoSO₄
0.1M HOAc-0.1M NaOAc, 0.005%
PAA
20 Vol.% DMF-water mixture

Table 1. Effect of the height of the mercury reservoir on the limiting current of PAR and its cobalt complex for solutions of 0.4 mM PAR and 0.4 mM PAR + 0.1 mM CoSO₄ in 20 vol.% DMF-water mixture containing 0.1M HOAc-0.1M NaOAc (pH 5.5)

A) PAR

h (corr.) (cm)	i_d (μA)	i_d/h (corr.)
69.85	0.97	0.116
65.05	0.92	0.114
60.75	0.89	0.114
56.35	0.86	0.115

B) PAR + Co

1. PAR

h (corr.) (cm)	i_d (μA)	i_d/h (corr.)
69.85	0.490	0.059
64.95	0.465	0.058
60.85	0.445	0.057
56.75	0.418	0.056

2. Co-PAR

h (corr.) (cm)	i_d (μA)	i_d/h (corr.)
69.85	0.412	0.049
64.95	0.406	0.050
60.85	0.398	0.051
56.75	0.390	0.052

comparable with the published data¹⁴⁾ for azobenzene, $D = 0.41 \times 10^{-5}$ cm²/sec., the molecule of which is similar to PAR in size and structure. It may be seen from these data that the reduction of PAR corresponds to an irreversible two electron process.

The temperature coefficients of the diffusion currents of PAR and CoPAR are shown in Fig. 3. A temperature coefficient of +2.5% per degree was found for the PAR and +1.7% per degree for the Co-PAR.

A study of change in the diffusion current by changing the height of the head of mercury showed that the ratio $i_d/h^{1/2}$ was constant for both PAR and Co-PAR. The results indicate that these reduction processes are of diffusion controlled (Table 1).

In the absence of any surface active agent, a maximum was observed on the first wave, which could be suppressed by 0.008% PAA. (Fig. 4)

PAR and its cobalt complex are sparingly soluble in water. More than 10 volume % DMF should be added to dissolve PAR and Co-PAR. However, since the dissociation of Co-PAR is raised by increasing the DMF content, 20 volume % DMF was used throughout the present experiments.

Fig. 4. Effect of PAA.

0.4 mM PAR + 0.1 mM CoSO₄
0.1M HOAc-0.1M NaOAc
20 Vol% DMF-water
(A) PAA 0%, (B) 0.004%, (C) 0.008%

Fig. 5. Calibration Curve

PAR $4 \times 10^{-4}M$, PAA 0.005%
0.1M HOAc-0.1M NaOAc
20 Vol% DMF-water mixture

Solutions prepared for a calibration of Co-PAR contained constant amounts of PAR, sodium acetate-acetic acid buffer, DMF and PAA, and various amounts of cobalt. The concentrations were $4 \times 10^{-4}M$ for PAR, 0.1M for acetate buffer, 0.005% for PAA, 20 volume % for DMF, $0.5 \times 10^{-5}M$ to $2 \times 10^{-4}M$ for cobalt sulfate. The calibration curve was a straight line which intersects the current axis at a value slightly higher than the origin, as shown in Fig. 5. A linear relationship was obtained in the range from 4×10^{-5} to $12 \times 10^{-5}M$ Co at the constant concentration ($4 \times 10^{-4}M$) of PAR.

2) Alternating Current Polarography

In acetate or phosphate buffer solution, three AC waves depending on the pH of the solution were obtained. In phosphate buffer solution, the first wave appeared at about +0.2 V., the second at about 0V., and the third at a potential corresponding to that of the DC step as shown in Fig. 6. The first wave was found even in the supporting electrolyte solution itself. Therefore, this step is caused by the dissolution of mercury by the supporting electrolyte. On the other hand, the first wave diminishes with increase of the height of the second wave. This fact shows that the second step is substantially caused by the dissolution of mercury by PAR.

Although the corresponding DC anodic wave was very small, the second AC peak current was very high and the summit potential shifted to more negative side with increasing pH or with increasing PAR concentration. If the oxidation of the second step is assumed to proceed according to the equation

it can be expected that the second wave shift to more positive potential with decreasing pH or decreasing concentration of PAR. Plots of the summit potential of the second wave against pH are shown in Fig. 7. The slope of summit potential versus pH was about 0.07 volt/pH. As expected, the summit potential of the second wave shifted to more negative side with increasing concentration of PAR. (Fig. 8)

Fig. 6. DC and AC polarograms of PAR.
 $0.1M Na_2HPO_4$ - $0.1M NaH_2PO_4$
 20 Vol% DMF (pH 7.2)
 (A) PAR $4 \times 10^{-4}M$, (B) $4 \times 10^{-4}M$, (C) 0, (D)
 PAR $4 \times 10^{-4}M$

Fig. 7. Effect of pH on (A) E_p and (B)
 i_p .
 PAR $4 \times 10^{-4}M$.
 Acetate or phosphate buffer was
 used to control pH.
 20 Vol% DMF-water mixture

Fig. 8. Effect of Concentration of PAR.
 $0.1M Na_2HPO_4$ - $0.1M NaH_2PO_4$
 20 Vol% DMF-water mixture

Fig. 9. Electrocapillary Curves.
 $0.1M Na_2HPO_4$ - $0.1M NaH_2PO_4$
 20 Vol% DMF-water mixture
 (A) Absence of PAR
 (B) Presence of $4 \times 10^{-5}M$ PAR

Table 2. Comparison between peak currents
 of Pb^{2+} ion in $0.1M KCl$ and PAR in
 $0.1M HOAc$ - $0.1M NaOAc$.

Ion	Concn. (M)	D (cm^2/sec)	Peak Current (μV)
Pb^{2+}	10^{-5}	0.98×10^{-5}	20.6
PAR	10^{-5}	0.36×10^{-5}	84.0

Fig. 10. Calibration Curves.
 0.1M Na_2HPO_4 -0.1M NaH_2PO_4
 20 Vol% DMF-water mixture

Fig. 11. Titration Curve of PAR with
 CoSO_4 ($0.97 \times 10^{-3} \text{M}$)
 0.1M Na_2HPO_4 -0.1M NaH_2PO_4
 20 Vol% DMF-water mixture
 PAR $0.93 \times 10^{-4} \text{M}$
 Total Volume 50 ml

The second wave height increased with increasing pH and reached a maximum value at about pH 7.0, then fell again with further increase of pH. (Fig. 7) The second wave height was also affected by the kind of supporting electrolyte.

The effect of temperature showed that the second wave decreases with increasing temperature in the range of 30°C to 60°C. This fact shows that the alternating current component of the second wave has both faradaic and adsorptive properties.

Electrocapillary curves obtained are shown in Fig. 9. In the presence of PAR, a remarkable decrease of the drop time was observed between +0.1 and -0.1V..

The relation between the height of wave and the concentration of PAR is shown in Fig. 10. The peak height of the second wave was found to be linearly proportional to the bulk concentration of PAR over the range of 1.6 to $3.0 \times 10^{-5} \text{M}$. In more concentrated solutions, the calibration curve showed a shape of the Langmuir adsorption isotherm.

These results also support the conclusion of an adsorptive property of the second step. For further confirmation, the peak current of PAR was compared with that of a simple metal ion. AC polarogram of lead ion has been reported to be reversible.¹⁵⁾ As shown in Table 2, the peak current of PAR was much larger than that of lead ion. This fact may show that the second step corresponds to the current based upon the oxidation of the adsorbed PAR on the dropping mercury electrode.

Peak current of the second wave decreased with the addition of cobaltous solution and disappeared at the equivalence point. From this equivalence point, the molar ratio of cobalt to PAR was determined to be 1 to 2. This result is in accord with the result from the continuous variation method in spectrophotometry.^{8, 10)}

Summary

Polarographic behaviors of PAR and its cobaltous complex was analysed. In an acetate buffer solution, DC polarogram of PAR showed a single, well-defined, irreversible two electron reduction wave. In the presence of cobalt, the reduction of Co-PAR occurred at a more negative potential and the wave height was proportional to the concentration of cobalt. In a phosphate buffer solution, PAR and Co-PAR waves came to coalescence. However, the AC polarogram showed three peaks in any supporting electrolyte solutions. In the phosphate buffer, the second peak corresponded to the adsorption of PAR and its oxidation to Hg-PAR complex. From the peak current titration curve, molar ratio of PAR to Co was determined to be 2 to 1.

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ジメチルホルムアミド-水混合溶媒中の α -ピリジルアゾレゾルシノール
およびコバルトキレートのパラログラフ的研究

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20 Vol. % DMF-水混合溶媒中, 0.1M 酢酸-0.1 M 酢酸ナトリウム支持電解質, 0.005% ポリアクリルアミドの存在下で PAR は -0.2V 附近に不可逆二電子還元波を示す, 一方 Co(II)PAR は PAR 自身の還元波より約0.15V 負電位に還元波を示し, その波高は PAR $4 \times 10^{-4}M$ に対し, Co 濃度 $4 \sim 12 \times 10^{-5}M$ の濃度範囲で良好な比例性がみとめられる. PAR および Co(II)PAR の半波電位は pH によつて変化し, pH > 7 では分離波は得られない. しかし 0.1M Na_2HPO_4 -0.1M NaH_2PO_4 緩衝液, 20 Vol.% DMF-

水混合溶媒中で, PAR は 0V (対 SCE) 附近に良好な交流ピークを示す. このピーク電流は PAR の水銀溶出波であるが, その温度係数, 電気毛管曲線および Pb(II) のピーク電流値との比較より, この電極反応に吸着過程が含まれるものと考えた. またこの支持電解質中で, ピーク電流値の変化より Co(II) と PAR とのモル比を検討した所, 1:2なる結果が得られた. この結果は分光光度法による連続変化法の結果と一致した.