Polarographic Behavior of Bismuth in Quercetin Solution*

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Chelate complexes of various metal cations with flavonoids have been investigated spectrographically and polarographically.¹⁻⁹⁾ In this paper, bismuth-quercetin complex was studied by the polarographic method.

A bismuth reduction wave in H_2SO_4 solution containing 10% ethanol decreased linearly with increasing concentration of quercetin added by the precipitation of complex compound (Fig. 1). The molecular ratio of bismuth to quercetin was 1:1 (Fig. 3). It was, therefore, deduced that bismuth ion, as BiO^+ , forms a chelate complex with quercetin in which 3-hydroxy and 4-carbonyl groups are functional. The presence of ethanol more than 30% gave a second wave at more negative potentials than the first one (Tables 1, 2, and 4). It appears that the second wave is due to the reduction of the complex formed. The experimental results showed that the rate of complex formation increased with decreasing the ethanol content and the H_2SO_4 concentration (Fig. 2). Therefore, all polarograms were recorded after standing for 24 hours after the preparation of the electrolytic solution. Base solution containing 10% ethanol

Fig. 1 Influence of H_2SO_4 concentration on polarograms of $5 \cdot 10^{-4} M \text{Bi}^{3+}$ and Quercetin solution containing 30% Ethanol; 2: 0.1 N, 3: 0.5 N, 4: 1.0 N, 5: 5.0 N H_2SO_4 and 1: Bi^{3+} only in 0.1 N H_2SO_4

Table 1 Influence of H_2SO_4 Concentration on the Polarograms of $5 \cdot 10^{-4} M \text{Bi}^{3+}$ and $51 \cdot 0^{-4} M (\text{Bi}^{3+} + \text{Quercetin})$ in 30% Ethanol

H_2SO_4 N	Bi^{3+}		$\text{Bi}^{3+} + \text{Quercetin}$				
	$E_{1/2}$ V	i μA	$E_{1/2}$ (1) V	$E_{1/2}$ (2) V	i_1 μA	i_2 μA	$i_1 + i_2$ μA
0.1	0.00	3.74	0.00	—	0.10	—	0.10
0.25	0.00	3.52	0.00	—	0.20	—	0.20
0.5	0.00	3.56	-0.01	-0.25	0.28	0.26	0.64
1.0	0.00	3.52	-0.04	-0.32	0.28	0.20	0.52
2.5	-0.01	3.32	-0.10	-0.40	0.42	0.56	1.04
5.0	-0.02	3.04	-0.14	-0.50	0.60	0.72	1.44

Table 2 Influence of Ethanol Content on the Polarograms of $5 \cdot 10^{-4} M \text{Bi}^{3+}$ and $5 \cdot 10^{-4} M (\text{Bi}^{3+} + \text{Quercetin})$ in 1 N H_2SO_4

Ethanol %	Bi^{3+}		$\text{Bi}^{3+} + \text{Quercetin}$				
	$E_{1/2}$ V	i μA	$E_{1/2}$ (1) V	$E_{1/2}$ (2) V	i_1 μA	i_2 μA	$i_1 + i_2$ μA
10	0.00	4.40	-0.02	—	0.88	—	0.88
20	0.00	3.90	+0.01	—	0.60	—	0.60
30	0.00	3.52	-0.04	-0.32	0.48	0.60	1.32
40	0.00	3.28	-0.07	-0.34	0.72	0.80	1.60
50	0.00	2.96	-0.06	-0.31	1.04	0.96	2.00
60	-0.04	3.08	-0.08	-0.31	1.52	0.96	2.48
70	0.00	2.88	-0.02	-0.29	1.52	1.08	2.60

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Fig. 2 Changes in the limiting current of $5 \cdot 10^{-4} M \text{Bi}^{3+}$ in the presence of $5 \cdot 10^{-4} M$ quercetin in (a): 10% ethanol and $1.0 N \text{H}_2\text{SO}_4$ and (b): 30% ethanol and $1.0 N \text{H}_2\text{SO}_4$

Table 3 Dependence of the Limiting Currents of $5 \cdot 10^{-4} M (\text{Bi}^{3+} + \text{Quercetin})$ on the Height of Mercury Reservoir

Mercury reservoir height h cm	30% Ethanol, $0.1 N \text{H}_2\text{SO}_4$	30% Ethanol, $1 N \text{H}_2\text{SO}_4$		
	i μA	i_1 μA	i_2 μA	$i_1 + i_2$ μA
80	0.83	0.78	0.58	1.60
70	0.76	0.70	0.54	1.49
60	0.70	0.64	0.52	1.37
50	0.61	0.60	0.49	1.27
40	0.54	0.50	0.44	1.12
30	0.45	0.43	0.37	0.94
Slope ($h=50$)	0.180	0.157	0.123	0.127

Fig. 3 Relation between the quercetin concentration and the limiting current of $2.5 \cdot 10^{-4} M \text{Bi}^{3+}$ in 10% ethanol solution containing a: $0.1 N \text{H}_2\text{SO}_4$, b: $0.5 N \text{H}_2\text{SO}_4$ and c: $1.0 N \text{H}_2\text{SO}_4$, and d: A.C. polarographic peak current in $0.1 N \text{H}_2\text{SO}_4$

Table 5 Dependence of the Limiting Current of ($2.5 \cdot 10^{-4} M \text{Bi}^{3+} + 10^{-4} M \text{Quercetin}$) on the Height of Mercury Reservoir

Mercury reservoir height cm	30% Ethanol, $1 N \text{H}_2\text{SO}_4$			30% Ethanol, $0.5 N \text{H}_2\text{SO}_4$		
	i_1	i_2	$i_1 + i_2$	i_1	i_2	$i_1 + i_2$
80	1.30	0.80	2.34	1.96	—	1.96
70	1.10	0.88	2.14	1.84	—	1.84
60	0.90	0.92	2.00	1.64	—	1.64
50	0.74	0.90	1.82	1.52	—	1.52
40	0.60	0.84	1.62	1.26	0.10	1.40
30	0.50	0.76	1.40	1.06	0.30	1.18
Slope ($h=50$)	0.312		0.150			0.148

and $0.1 N \text{H}_2\text{SO}_4$ was most suitable for the amperometric titration (Fig. 3).

In the presence of equimolar quercetin to bismuth, the limiting currents of the single reduction wave and the two step waves were controlled by the diffusion process (Table 3). However, in the presence of a small amount of quercetin, the dependence of the limiting current of the first wave on the mercury reservoir height was different from that of the diffusion current (Table 5). And, in 30% ethanol and $0.5 N \text{H}_2\text{SO}_4$, where a single wave was observed, the second wave was shown at the lower height of the mercury reservoir (Table 5). A particular phenomenon was observed also in A.C. polarographic curves. It was

Table 4 Relationship Between the Limiting Current of $2.5 \cdot 10^{-4} M$ Bi^{3+} and the Concentration of Quercetin

10% Ethanol												
H ₂ SO ₄	0.1 N			0.5 N			1.0 N			5.0 N		
Quercetin ·10-4 M	i ₁	i ₂	i ₁ +i ₂	i ₁	i ₂	i ₁ +i ₂	i ₁	i ₂	i ₁ +i ₂	i ₁	i ₂	i ₁ +i ₂
0	2.32			2.14			2.28					
1.0	1.50			1.52			1.76					
2.0	0.68			0.84			1.40					
2.5	0.36			0.84			1.10					
3.0	0.36			0.86			1.14					
4.0	0.36			0.96			1.10					
5.0	0.38			1.02			1.28					

30% Ethanol												
0	1.84			1.98			1.94			1.86		
1.0	1.16			1.48	0		0.74	0.84	1.76	0.82	0.88	1.70
2.0	0.70			0.90	0.24	1.18	0.60	0.74	1.44	0.72	1.06	1.78
2.5	0.42			0.46	0.26	0.86	0.56	0.64	1.24	0.70	0.94	1.64
3.0	0.28			0.36	0.32	0.78	0.44	0.48	1.00	0.52	0.68	1.24
4.0	0.12			0.34	0.18	0.54	0.40	0.36	0.80	0.44	0.62	1.10
5.0	0.10			0.28	0.26	0.66	0.28	0.20	0.52	0.42	0.56	1.04

50% Ethanol												
0	1.40			1.70			1.64			1.58		
1.0	0.78	0.38	1.16	1.66			0.86	0.58	1.60	0.90	0.64	1.54
2.0	0.38	0.28	0.66	1.32	0.26	1.62	0.62	0.98	1.62	0.70	0.84	1.54
2.5	0.30	0.18	0.48	0.92	0.56	1.64	0.72	0.82	1.60	0.68	0.82	1.54
3.0	0.28	0.16	0.46	0.78	0.72	1.54	0.80	0.80	1.62	0.68	0.88	1.56
4.0	0.20	0.16	0.40	0.64	0.84	1.50	0.84	0.76	1.60	0.70	0.84	1.54
5.0	0.18	0.14	0.36	0.50	0.48	1.02	0.88	0.70	1.58	0.74	0.78	1.52

presumed that the adsorption plays a roll on the electrode process of bismuth ion in the presence of a small amount of quercetin.

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Polymerization of Vinyl Acetate by Silent Electric Discharge

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Recently, though many experiments have been made on the polymerization of vinyl acetate, polymerization of high polymers by silent electric discharge has simply been disregarded. The present paper is conceived with the latter, where the polymerization is accomplished by silent electric discharge. The apparatus for the measurements is as described in Tsuda's previous report (Journal of the Chemical Society of Japan 75, 383 (1954).)

- 1) Discharge voltages were 12.5, 8.25 and 4.5 kV in nitrogen, respectively.
- 2) The polymer obtained were treated according to Matsumoto's previous report (Journal of the polymer Science of Japan 12, 428 (1955).), in order to determine both conversion and degree of the polymerization.

The original written in Japanese can be seen in Denki-Kagaku 29, 389 (1961).