*Polarography of Bis(aminophenyl)arsinic Acids, Phenylarsonic Acid and Arsanilic Acids**

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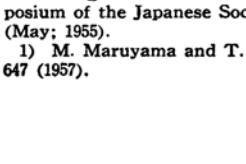
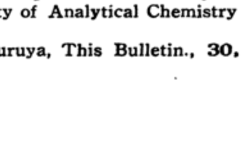
The writers stated in the preceding paper[1] that, on considering the polarographic behavior of bis(nitrophenyl)arsinic acids at the dropping mercury electrode, the 2nd wave that appears in an acid range may contain waves due to a three-electron reduction of arsenic. In order to further clarify this fact and also the polarographic behavior of organic arsenic compounds, reduction waves of bis(aminophenyl)arsinic acids, phenylarsonic acid, and arsanilic acids at the dropping mercury electrode were examined. The present paper also describes the results obtained from experiments on fundamental data for quantitative determinations.

Experimental

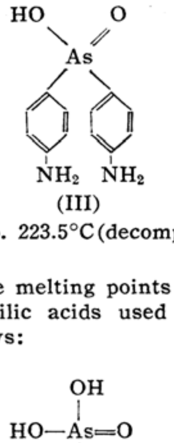
The four isomers of bis(aminophenyl)arsinic acids according to the position of the amino group, 2,2′-(I), 3,3′-(II), 4,4′-(III), and 3,4′-(IV), were used as the sample. Their respective melting points are shown with their structures:



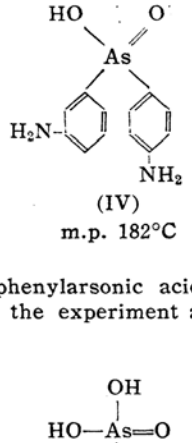
(I)
m.p. 154°C



(II)
m.p. 247°C

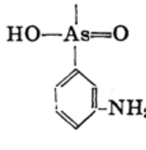


(III)
m.p. 223.5°C (decomp.)

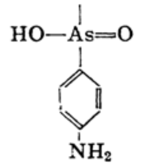


(IV)
m.p. 182°C

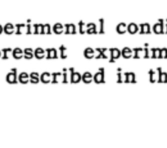
The melting points of phenylarsonic acid and arsanilic acids used for the experiment are as follows:



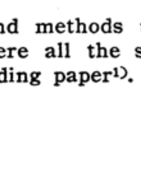
(V)
m.p. 158.5°C



(VI)
m.p. 144°C



(VII)
m.p. 207°C (decomp.)



(VIII)
m.p. 232°C

Experimental conditions and methods used in the present experiments were all the same as those described in the preceding paper[1].

* The gist of this work was presented at the symposium of the Japanese Society of Analytical Chemistry (May; 1955).

1) M. Maruyama and T. Furuya, This Bulletin., **30**, 647 (1957).

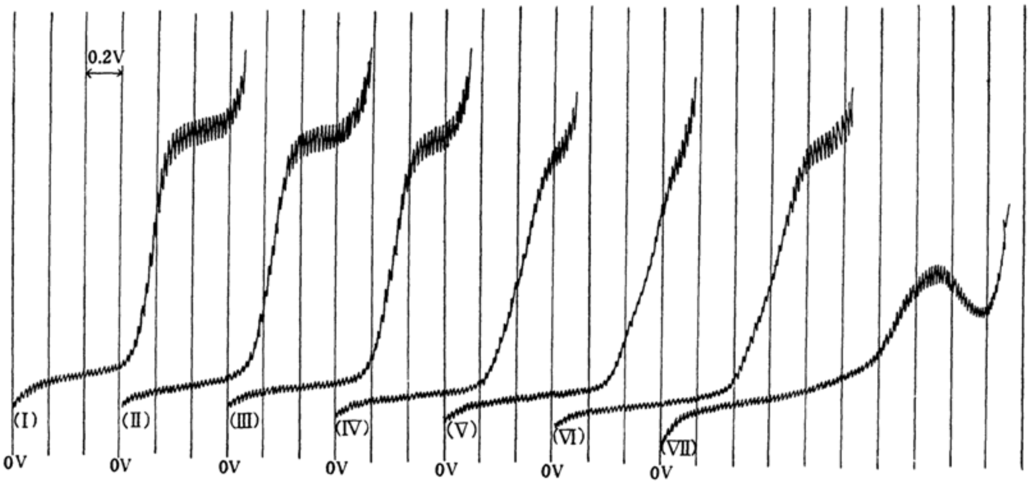


Fig. 1. Typical polarograms of 4,4′-Bis(aminophenyl)arsinic acid in buffer solution at various pH values.
(I) pH 1.04 (II) pH 2.2 (III) pH 3.0 (IV) pH 4.0 (V) pH 5.0
(VI) pH 6.0 (VII) pH 7.0

Experimental Results and Discussion

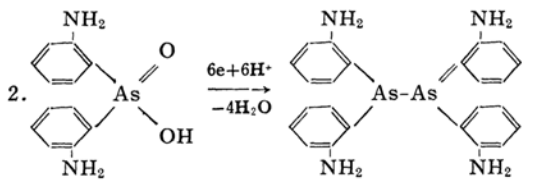
(1) **Reduction of Bis(aminophenyl) arsinic Acids in Buffers Solutions of Various pH.**—2,2′-, 3,3′-, 4,4′-, and 3,4′-Bis (aminophenyl)arsinic acids and diphenylarsinic acid show irreversible reduction wave below pH 7 (polarogram of 4,4′-compound at various pH is shown in Fig. 1 as an example). The wave form is a one-step wave at pH 1 to 3 and a complicated wave form, similar to that of diphenylarsinic acid, appears at pH 4 to 6. As was described in the preceding paper, diphenylarsinic acid shows a very similar, complicated wave form at pH 1 to 5 and an irreversible, three-electron reduction at around pH 2 to 3.

The half-wave potentials in all these compounds shift to the negative side with increasing values of pH, more markedly so in the 2,2-compound than the other isomers, and those of the other three isomers are very close together. The half-wave potentials of these compounds are indicated in Table I.

TABLE I
HALF WAVE POTENTIALS OF BIS(AMINOPHENYL)-ARSINIC ACIDS AT VARIOUS pH VALUES
$\pi_{1/2}$ mV(vs. S.C.E.).

pH	4,4′-	3,4′-	3,3′-	2,2′-
1.04	− 775	− 782	− 800	− 873
2.2	− 845	− 835	− 872	− 965
3.0	− 905	− 913	− 930	−1078
4.0	− 990	−1010	−1030	−1170
5.0	−1100	−1107	−1140	−1370
6.0	−1212	−1213	−1284	···

The wave height is approximately constant in the acid range, irrespective of pH, except for 2,2′-compound, and decreases suddenly at above pH 6. For the 2,2′-compound, the wave height tends to decrease somewhat with increasing pH values. As will be described later, the limiting current is controlled by the diffusion process and the number of electrons, *n*, taking part in the reduction, obtained by the microelectrolysis, was 3 for all the compounds at pH 2–3. These results suggest the following type as the reduction mechanism:



(2) **Effect of Various Factors on the Limiting Current of Bis(aminophenyl) arsinic Acids.**—

a) *Relationship between Concentration and Limiting Current:* The limiting current of 2,2′-, 3,3′- and 4,4′-bis(aminophenyl) arsinic acid and diphenylarsinic acid was measured in various concentrations in buffer solution of pH 2.2 and the results of 4,4′-compound and diphenylarsinic acid are presented in Table II. Other 2,2′-, 3,3′-compound had the same result.

b) *Relationship between Temperature and Limiting Current:* The results of measurement with various isomers and diphenyl arsinic acid indicate that the limiting

TABLE II

LIMITING CURRENT VS. CONCENTRATION

a) 4,4'-Bis(aminophenyl)arsinic acid

C(mM/l)	i_d(μamp.)	i_d/C(μamp./mM)
0.339	4.21	12.4
0.271	3.33	12.3
0.203	2.48	12.2
0.136	1.63	12.0
0.068	0.87	12.8
		12.35±0.41

As can be seen from Table II, a proportionality is established between the concentration and the limiting current in all these compounds.

b) Diphenyl arsinic acid

C(mM/l)	i_d(μamp.)	i_d/C(μamp./mM)
0.163	2.31	14.2
0.126	1.69	13.4
0.082	1.11	13.6
0.041	0.57	13.9
Mean		13.78±0.58

current increases in proportion to the rise of temperature and the temperature coefficients of 2, 2'-, 3, 3'-, and 4,4'-compound, dephenyl arsinic acid in this case are 1.36 %, 1.46 %, 1.39% and 1.38 %. These coefficients agree approximately with that in the case of diffusion current.

c) *The Relationship between the Height of Mercury Reservoir and Limiting Current:* The results of measurement with various isomers, (shown in Table III; the result of 4,4'-compound is shown as an example), indicate that a linear relationship exists between the limiting current and the square root of the height of the mercury reservoir, $h_{eff.}^{1/2}$, i. e. these limiting currents are controlled by the diffusion process.

TABLE III

LIMITING CURRENT VS. EFFECTIVE HEIGHT OF MERCURY RESERVOIR

4,4'-BIS(AMINOPHENYL)ARSINIC ACID

(Concn.: 3.39×10^{-4}M, pH: 2.2)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μAmp.)	4.15	4.27	4.43	4.57	4.72
$i_d/h_{eff.}^{1/2}$	0.54	0.53	0.53	0.53	0.53

(3) **Reduction of Phenylarsonic Acid and Arsanilic Acids in Buffer Solutions of Various pH.**—The reduction wave of arsanilic acids appear at pH 1 to 3 and 2-, 3- and 4-arsanilic acid and phenylarsonic acid show irreversible waves with similar wave heights and wave forms (Fig. 2).

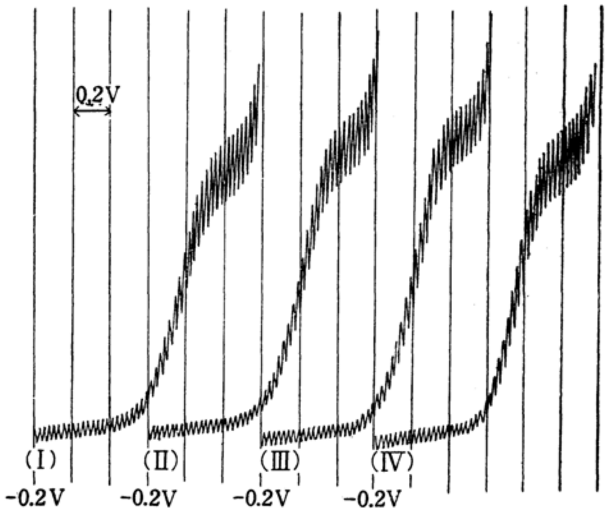


Fig. 2. Typical polarograms of arsanilic acids, phenylarsonic acid in buffer solution at pH 1.04.
(I) 2-Arsanilic acid
(II) 3-Arsanilic acid
(III) 4-Arsanilic acid
(IV) Phenylarsonic acid

The wave height is approximately constant at pH 1 to 3 but decreases rapidly at above pH 4. The half-wave potentials shift to the negative side with increasing pH values and the values tend to become negative in the order of phenylarsonic acid, and 2-, 3- and 4-arsanilic acid at the same pH, though the difference is very slight (Table IV).

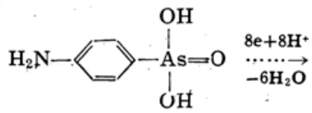
TABLE IV

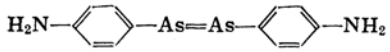
HALF-WAVE POTENTIALS OF PHENYLARSONIC ACID AND ARSANILIC ACIDS IN BUFFER SOLUTION

$\pi_{1/2}$mV. (vs. S.C.E.)

pH	Phenylarsonic acid	2-Arsanilic acid	3-Arsanilic acid	4-Arsanilic acid
1.04	− 955	− 960	− 976	− 985
2.2	−1060	−1072	−1080	−1098
3.0	−1175	−1176	−1175	−1185

The limiting current of these compounds is controlled by the diffusion process and the number of electrons, n, taking part in the reduction, obtained by the microelectrolysis, a buffer solution of pH 2.2, was approximately 4, indicating a four-electron reduction. If such is the case, the following type of reduction mechanism may be considered.





(4) Effect of Various Factors on the Limiting Current of Phenylarsonic Acid and Arsanilic Acids.—

a) *Relationship between Concentration and Limiting Current:* The results of measurement of limiting current of phenylarsonic acid and various isomers of arsanilic acid in a buffer solution of pH 2.2, at various concentrations, (as shown in Table V, the results of 4-arsanilic acid and phenyl arsinic acid are shown as an example), indicated that a linear relationship exists between concentration and limiting current.

TABLE V
LIMITING CURRENT VS. CONCENTRATION

a) 4-Arsanilic acid

C(mM)	i_d(μamp.)	i_d/C(μamp./mM)
0.538	10.67	19.8
0.428	8.42	19.7
0.321	6.27	19.5
0.214	4.17	19.5
0.107	2.08	19.4
Mean		19.59±0.20

b) Phenyl arsinic acid

C(mM)	i_d(μamp.)	i_d/C(μamp./mM)
0.520	10.30	19.8
0.416	8.42	20.2
0.312	6.17	19.8
0.208	4.07	19.6
0.104	1.94	18.7
Mean		19.61±0.77

b) *Relationship between Temperature and Limiting Current:* The results of measurement in a buffer solution of pH 2.2, indicated that the limiting current increases in proportion to the rise of temperature and the temperature coefficients of 4-, 3- and 2- arsanilic acid and phenyl arsinic acid are 1.27 %, 1.39 %, 1.28 % and 1.52 %. These coefficient agreed approximately with that in the case of diffusion current.

c) *Relationship between the Height of the Mercury Reservoir and Limiting Current:* The results obtained from the measurement in a buffer solution of pH 2.2,(shown in Table VI) (only 4-arsanilic acid and phenyl arsinic acid), indicate that a linear relationship is established between the square root of the height of the mercury reservoir, $h_{eff.}^{1/2}$ and the limiting current. Therefore, the limiting current does not contain a kinetic current but is controlled by the diffusion process.

TABLE VI
LIMITING CURRENT AND EFFECT HEIGHT OF MERCURY RESERVOIR

a) 4-Arsanilic acid
(Conc.: 3.21×10^{-4}M)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μamp.)	5.69	5.96	6.26	6.36	6.60
$i_d/h_{eff.}^{1/2}$	0.74	0.74	0.75	0.73	0.74

b) Phenyl arsonic acid
(Concn.: 3.12×10^{-4}M)

$h_{eff.}^{1/2}$(h: cm.)	7.75	8.06	8.37	8.66	8.94
i_d(μamp.)	5.18	5.63	5.79	5.93	6.09
$i_d/h_{eff.}^{1/2}$	0.67	0.70	0.69	0.69	0.68

(5) Determination of Bis(aminophenyl)arsinic Acids in Arsanilic Acid.—The foregoing facts indicate that it is possible to determine bis(aminophenyl) arsinic acids and arsanilic acids individually by polarography but separatory determination of their isomers is impossible, considering the wave form and the half-wave potential of the reduction wave.

The problem in industrial process is the determination of bis(aminophenyl)arsinic acids in 4-arsanilic acid, the former being often present as an impurity in the latter during synthetic process. There has been no suitable method of determining this compound and some difficulties have been experienced.

However, the foregoing facts suggest the possibility of the utilization of polarographic method for this purpose. Actually, reduction at the dropping mercury electrode gives a separate wave (occurs first) by bis(aminophenyl)arsinic acids and its determination in 4-arsanilic acid is possible from this wave height.

Analytical results obtained with several kinds of synthetic sample are presented in Table VII.

TABLE VII
DETERMINATION OF BIS(AMINOPHENYL)ARSINIC ACID IN 4-ARSANILIC ACID

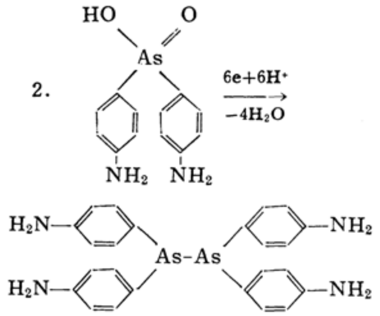
No.	Calculated Value (%) 4-Arsanilic acid	Calculated Value (%) Bis(aminophenyl) arsinic acid	Observated Value (%) Bis(aminophenyl) arsinic acid
1	85.0	15.0	14.0
2	70.0	30.0	30.1
3	60.0	40.0	41.7
4	40.0	60.0	56.0
5	20.0	80.0	76.0

Summary

1) Polarographic behaviors of bis (aminophenyl)arsinic acids, phenylarsonic

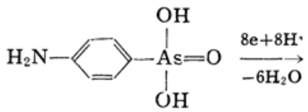
acid and arsanilic acids, were examined with dropping mercury electrode.

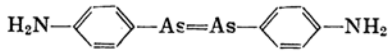
2) The reduction wave of bis(aminophenyl)arsinic acids appearing on the acid side is an irreversible three-electron reduction and this reduction mechanism is considered to be of the following type.

2. 

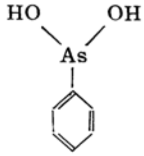
3) An assumption was forwarded in the preceding paper that the 2nd wave shown by bis(nitrophenyl)arsinic acids on the acid side may contain a reduction wave owing to the reduction of arsenic and that it is more likely to be a three-electron rather than a 4-electron reduction. The foregoing results obtained with bis(aminophenyl)arsinic acids suggest that it would be more appropriate to consider an irreversible, three-electron reduction.

4) The reduction waves shown by phenylarsonic acid and arsanilic acids on the acid side are an irreversible, four-electron reduction and the reduction mechanism may be assumed as follows:

2. 



5) Compounds like phenylarsinic acid (IX) do not exhibit a reduction wave at the dropping mercury electrode.



(IX)

6) Summarizing the foregoing facts, it may be concluded that these organic arsenic compounds which show a reduction wave at the dropping mercury electrode are quiquevalent arsenic compounds, the reduction wave is that of quinquevalent to tervalent, and that the compounds not possessing As=O are not reduced.

7) The limiting current of these compounds in the acid side is controlled by the diffusion process and is in proportional relationship with the concentration, so that it can be utilized for quantitative analysis.

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