*Polarography of Bis(nitrophenyl)arsinic Acids**

By Masao MARUYAMA and Toshiko FURUYA

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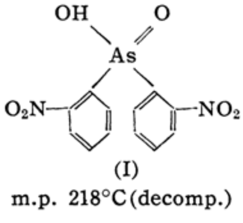
There are numerous reports on the study of polarography of aromatic nitro compounds but those on organic arsenic compounds are comparatively rare, brief reports being made on phenylarsonic acids[1,2], diphenylarsinic oxide, and dephenylarsinic acid[3]. It has been shown that phenylarsonic acids show a reduction wave with a half-wave potential of −1.25 V. vs. N.C.E. in a buffer solution of pH 2.97 but nothing has been given as to its electrolytic reduction mechanism and limiting current value, nor its proportionality with the concentration. As for diphenylarsinic oxide and acid, only brief mention is made of the fact that they show reduction waves and consequently could be utilized for indirect determination of diphenylcyanarsine.

In the present series of experiments, polarographic behavior of bis (nitrophenyl) arsinic acids, including diphenylarsinic acid, was clarified and discussions are made on the results of studies made in order to obtain some fundamental data for its utilization for quantitative determination. Further, a few examples of the determination are described.

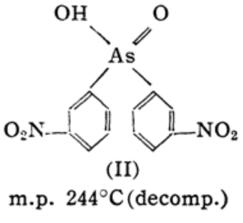
Experimental

There are six isomers of bis(nitrophenyl)arsinic acid according to the position of the two nitro groups, viz. 2,2′-(I)' 3,3′-(II), 4,4′-(III), 2,3′-(IV), 2,4′-(V), and 3,4′-(VI). These six isomers and a compound without nitro group, diphenylarsinic acid, (VII), were submitted to the experiments. The melting points of these compounds are indicated with their structures.



(I)

m.p. 218°C (decomp.)



(II)

m.p. 244°C (decomp.)

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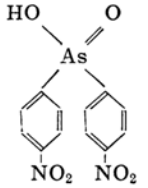
* The Gist of the present report was presented at the 8th Annual Meeting of the Chemical Society of Japan (April, 1955).

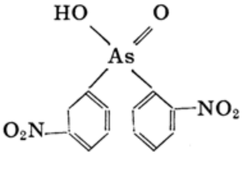
1) B. Breyer, *Ber.*, **71**, 163 (1938).

2) B. Breyer, *Biochem. Z.*, **301**, 65 (1939).

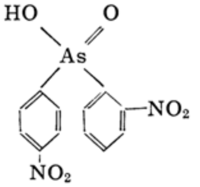
3) M. Suzuki and I. Tachi, *J. Electrochem. Soc. Japan*, **16**. 152 (1948).



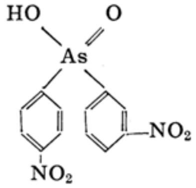
(III)
m.p. 263°C (decomp.)



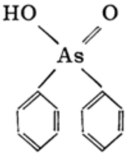
(IV)
m.p. 257°C (decomp.)



(V)
m.p. 248-250°C



(VI)
m.p. 230°C



(VII)
m.p. 167-168°C

The composition of the buffer solutions used is listed below and pH was measured with a glass electrode pH meter (manufactured by the Yamashita Denshiki Kagakukeiki Reserch Laboratory).

pH 1.04 ....0.1 N HCl
pH 2.2-7.0......McIlvaine
(0.1 M citric acid-0.2 M Na_2HPO_4)
pH 8.0-12.38...Sörensen
(0.1 M KH_2PO_4-0.05 M $Na_2B_4O_7$)
pH 13.05 ......0.1 N NaOH

All the samples were dissolved in distilled water and mixed with the buffer solution to be used as the electrolytic solution. This solution was bubbled with purified nitrogen gas and washed with chromous chloride solution, for about 15 minutes to remove dissolved oxygen.

The apparatus used was a Heyrovsky-Shikata type photo-recording polarograph (Yanagimoto Model 52). The sensitivity of the galvanometer was 1.47×10^{-9} amp./1 mm./m. and the dropping mercury cathode used had a capillary constant of m=2.35 mg./sec., t=4.26 sec./drop.

The polarographic cell used was an H-type with a ground-glass joint (universal) as shown in Fig. 1, which has long been used in this laboratory.

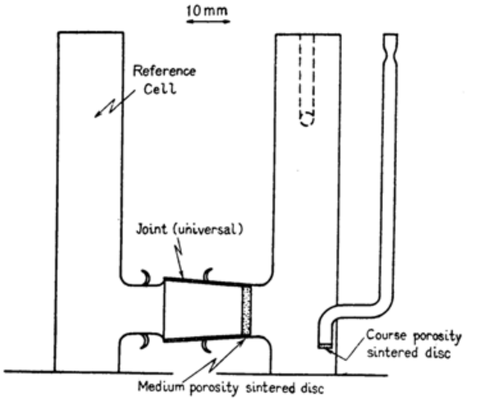


Fig. 1. H-Type-polarographic cell

Microelectrolysis was carried out in accordance with the method of Gilbert and Rideal[4]. A definite amount (0.2-0.3 ml.) of the electrolytic solution was electrolyzed at the dropping mercury electrode and the number of electrons, *n*, was calculated from the decrease in wave height in the polarogram before and after the electrolysis, according to the following equation:

$$\frac{d(\log h)}{dt}=\frac{k_2}{2.30.n.F.v.k_1}$$

All the experiments were carried out in a thermostat maintained at 25°±0.1°C.

Experimental Results and Discussion

(I) Reduction in Buffer Solutions of Various pH Values.—The polarograms of the six isomers of bis(nitrophenyl)arsinic acids in buffer solutions of various pH values show reduction waves of complicated form. Even at the same pH, different isomers show different wave forms, as indicated in Fig. 2, and the wave form changes further with changes in pH.

These complicated reduction waves were classified into two portions, designated as 1st and 2nd waves, and each was examined. The 1st wave that appears initially is composed of one or two steps, the slope is more acute than the 2nd wave, and appears in the whole range of pH 1 to 13. The complicated waves appearing at more negative potentials than the 1st wave are collectively taken as the 2nd wave.

The 1st Wave. The half-wave potential of the 1st wave tends to shift to the negative side as the pH value increases but the wave height remains almost constant for all the isomers and through all pH values. The wave form is a one- or two-step wave below pH 7 but becomes a one-step wave above pH 8 for all six isomers (Table I).

Since this 1st wave does not appear in the reduction wave of diphenylarsinic acid, it is certain that the wave is due to

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[4] G. A. Gilbert and E. K. Rideal, *Trans. Faraday Soc.*, **47**, 396 (1951).

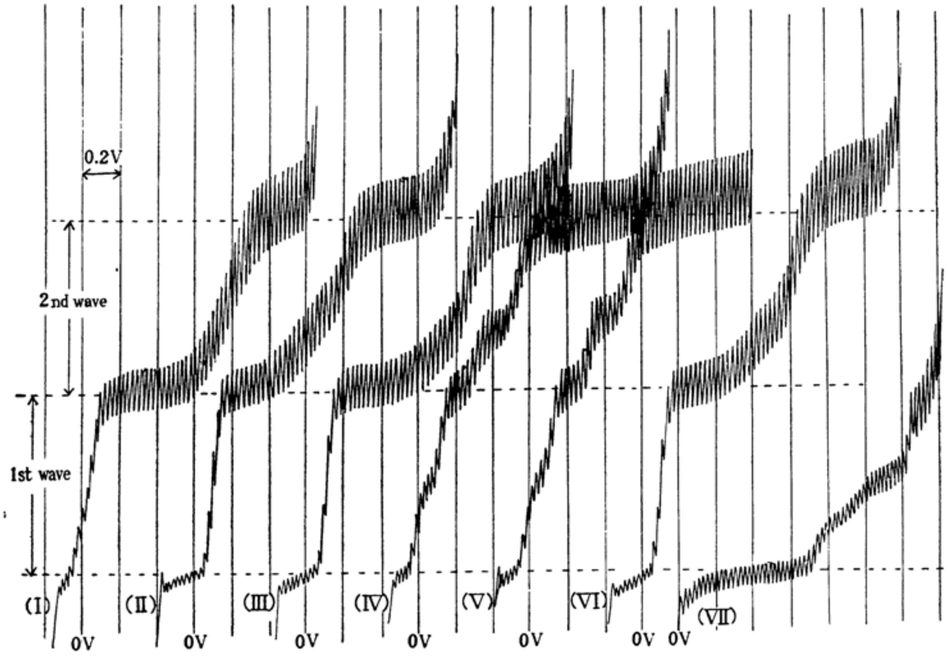


Fig. 2. Typical polarograms of Bis(nitrophenyl)arsinic acids diphenylarsinic acid in buffer solution of pH 2.2.
(I) 2,2′-compound (II) 3,3′-compound (III) 4,4′-compound
(IV) 2,3′-compound (V) 2,4′-compound (VI) 3,4′-compound
(VII) diphenylarsinic acid

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

pH	2,2′-*	3,3′-	4,4′-	2,3′-	2,4′-	3,4′-
1.04	−004	−071	−056	+046 −076	+048 −064	−062
2.2	−048	−110	−111	+008 −128	+005 −120	−111
3.0	−064	−152	−146	−030 −171	−035 −160	−152
4.0	−110	−198	−196	−070 −215	−074 −220	−200
5.0	−180	−270	−272	−174 −284	−142 −265	−270
6.0	−281	−355	−340	−243 −352	−246 −348	−338
7.0	−360	−390	−388	−324 −392	−325 −378	−384
8.0	−440	−450	−450	−430	−422	−440
9.0	−500	−494	−490	−490	−480	−492
10.0	−549	−550	−535	−544	−534	−512
11.0	−560	−586	−552	−565	−554	−528
12.38	−630	−652	−630	−650	−620	−628
13.05	−670	−660	−664	−626	−650	−664

* It was difficult to measure the half-wave potential on the acid side as a two-step wave and, therefore, it was obtained as a one-step wave.

the reduction of the nitro group. At below pH 7, the nitro group in the 2-position is reduced in a more positive potential than that in the 3- or 4-position, as was evidenced in the case of pH 2.2 shown in Fig. 2, and this results in two-step waves appearing in the 2,3- and 2,4-compounds, the ratio of wave heights being 1:1. The wave of the 2,2′-compounds, when well examined, appears to be a two-step wave and its wave height ratio is 1:3. This is assumed to be due to the fact that one of the four oxygen atoms of the two nitro groups forms a hydrogen bond with the hydrogen atom of the hydroxyl group in the molecule, so that this oxygen atom is reduced at more positive potentials than the other three oxygen atoms. But it is necessary to study this matter in detail further. A similar phenomenon was assumed to occur with 2,3′- and 2,4′-compounds but such waves could not be observed in the polarogram.

Analysis of the wave form indicated the 1st wave to be irreversible and its limiting current is controlled by a diffusion process, as will be described later. The number of electrons, *n*, taking part in the reduction in buffer solutions of pH 2.2–3.0, by microelectrolysis according to the method of Gilbert and Rideal[4] was approximately 8, n being 7.8 and 7.7 in the 2,2′-compound, 8.1 and 7.7 in the 3,3′-compound, and 8.0 and 7.8 in the 4,4′-compound. From such a fact, it may be assumed that the 1st wave of bis(nitrophenyl)arsinic acids is due to the reduction of the two nitro groups into –NHOH.

$$-NO_2 \xrightarrow[-H_2O]{4e+4H^+} -NHOH$$

The 2nd Wave. As shown by the example in Fig. 2, the 2nd wave is composed of complicated wave forms which would be difficult to analyze. The 2nd wave appears only below pH 6 in compounds not possessing $-NO_2$ group in 2-position, the wave disappearing at above pH 7. In the 2,2′-, 2,3′-, and 2,4′-compounds, however, the 2nd wave appears as a complicated wave with a maximum, even at above pH 7 up to pH 10, although the wave height decreases drastically, disappearing at above pH 11. Table II shows the relationship between pH and the 1st and the 2nd wave for all the isomers.

As was mentioned earlier, the half-wave potential of the 2nd wave is difficult to determine, wing to the complicated form of its reduction wave. Moreover, the wave form varies with pH even in one isomer so that it is impossible to compare the half-wave potential of the 2nd wave of each isomer. In each individual isomer,

TABLE II

RELATIONSHIP BETWEEN pH AND 1ST AND 2ND WAVES IN BIS(NITROPHENYL)ARSINIC ACIDS

Positions of $-NO_2$	The 1st wave	The 2nd wave
2,2′-	pH 1-7: 2-step wave with wave height 1:3 pH 8-13: 1-step wave	pH 1-10: 2nd wave observed pH 11-13: not apparent
2,3′-	pH 1-7: 2-step wave with wave height 1:1 pH 8-13: 1-step wave	—ditto—
2,4′-	—ditto—	—ditto—
3.3′-	pH 1-13: 1-step wave	pH 1-6: 2nd wave observed pH 7-13: not apparent
3,4′-	—ditto—	—ditto—
4,4′-	—ditto—	—ditto—

TABLE III

WAVE HEIGHT OF 1ST AND 2ND WAVE AND THEIR RATIO OF BIS(NITROPHENYL)ARSINIC ACIDS

(Sample concentration: 1.14×10^{-4}M/l)

position of $-NO_2$		pH 1.04	pH 2.2	pH 3.0	pH 4.0	pH 5.0	Mean
2,2′-	1st wave	3.63	3.60	3.71	3.62	…	3.64
	2nd wave	3.32	3.35	3.24	2.80	…	3.18
	ratio	8 : 7.3	8 : 7.5	8 : 7.0	8 : 6.2	…	8 : 7.0
3,3′-	1st wave	3.38	3.36	3.36	3.33	3.29	3.34
	2nd wave	3.10	3.13	3.11	2.93	2.90	3.03
	ratio	8 : 7.3	8 : 7.4	8 : 7.4	8 : 7.0	8 : 7.0	8 : 7.3
4,4′-	1st wave	3.54	3.35	3.34	3.33	3.32	3.38
	2nd wave	3.18	3.23	3.23	3.12	3.09	3.17
	ratio	8 : 7.2	8 : 7.7	8 : 7.7	8 : 7.5	8 : 7.5	8 : 7.5
2,3′-	1st wave	3.39	3.45	3.57	3.29	3.43	3.43
	2nd wave	2.94	2.96	3.08	2.90	2.87	2.95
	ratio	8 : 6.9	8 : 6.9	8 : 6.9	8 : 7.1	8 : 6.9	8 : 6.9
2,4′-	1st wave	3.50	3.55	3.51	3.64	3.60	3.56
	2nd wave	3.26	3.09	3.98	3.23	3.07	3.13
	ratio	8 : 7.5	8 : 7.0	8 : 6.8	8 : 7.1	8 : 6.8	8 : 7.4
3,4′-	1st wave	3.64	8.64	3.72	3.37	3.33	3.54
	2nd wave	3.43	3.65	3.60	2.89	2.80	3.27
	ratio	8 : 7.5	3 : 8.0	8 : 7.8	8 : 6.9	8 : 6.7	8 : 7.4
Mean	1st wave	3.50	3.48	3.51	3.41	3.37	
	2nd wave	3.20	3.24	3.22	3.00	2.98	
	ratio	8 : 7.3	8 : 7.5	8 : 7.3	8 : 7.0	8 : 7.0	8 : 7.2

however, the reduction potential tends to shift to the negative side with the increasing pH. As a replacement of comparing the half-wave potential, comparison was made of the potential from the initial portion of the reduction potential to the point of inflexion to the latter stationary phase. As indicated in Fig. 3, the compounds possessing $-NO_2$ group in 2-position give reduction waves in narrower range of potentials than other isomers and the reduction potential shifts to the negative side in the order 2,3′-, 2,4′-, 3,3′-, 3,4′-, 4,4′-, 2,2′-, and diphenylarsinic acid.

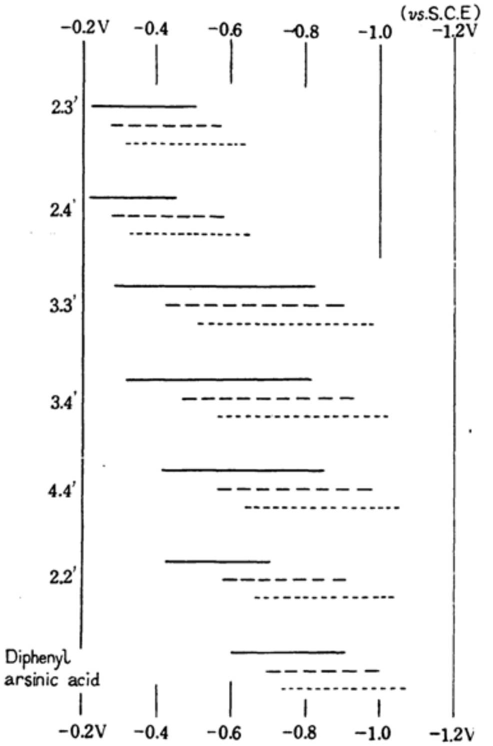
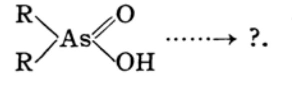


Fig. 3. Relative positions of reduction potential of the 2nd wave in Bis(nitrophenyl)arsinic acids
—— pH 1.04 - - - pH 2.2 ······ pH 3.0

Reduction mechanism of the 2nd wave will next be considered. As will be seen from Table III, the wave height of the 2nd wave is somewhat lower than that of the 1st wave on the acid side and the reduction that could be assumed for the 2nd wave will be in the reduction step of $-NO_2$ group,

$$-NHOH \xrightarrow[-H_2O]{2e+2H^+} -NH_2$$

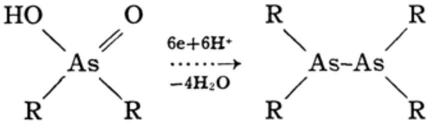
and



$$R_2As(=O)OH \longrightarrow ?.$$

Considering the complicated wave form of the 2nd wave, these reactions must occur one after the other and the degree of duplication results in the variation of the breadth of the reduction wave potential, as shown in Fig. 3, and in the variation of wave form.

The number of electrons, n, taking part in the reduction was calculated according to the method of Gilbert and Rideal for the 2nd wave and the value of 7.3 for pH 2.2 was obtained in the 2,2′-compound. This result seems to indicate a seven-electron reduction but this is not necessarily conclusive. The value of n calculated for diphenylarsinic acid, without any $-NO_2$ group, was 3.2 and 3.3 at pH 2.2, indicating it to be a three-electron reduction. Since diphenylarsinic acid has the same structure as bis(nitrophenyl)-arsinic acids, with the exception of the absence of $-NO_2$ group, it was assumed that their diffusion coefficients would be approximately equal, and the polarogram of diphenylarsinic acid was taken under identical conditions as those for bis(nitrophenyl)arsinic acids. Subtraction of its wave height from that of the 2nd wave of bis(nitrophenyl)arsinic acids gave a value one-half of that of their 1st waves, i.e. corresponding to a 4-electron reduction from two $-NHOH$ to NH_2. Summarizing these facts, it may be assumed that the 2nd wave consists of four-electron reduction of two $-NHOH$ to $-NH_2$ and a three-electron reduction of arsenic. The following type may be considered for the reduction of arsenic:

2.


$$(HO)(O{=})AsR_2 \xrightarrow[-4H_2O]{6e+6H^+} R_2As{-}AsR_2$$

However, the state of reduction of diphenylarsinic acid may be vastly different and it would be too dangerous to conclude from these results that the foregoing facts indicate a three-electron reduction of arsenic. Further studies on this matter seem to be necessary.

(2) Effect of Various Factors on the Limiting Current of Bis(nitrophenyl)-arsinic Acids.

a) Relationship between Concentration and Limiting Current.—Polarograms of 2,2′-, 3,3′-, and 4,4′-compounds were taken in a buffer solution of pH 2.2 in various concentrations and the wave height of 1st and 2nd waves were measured. For example, the result of 2,2′-compounds is presented in Table IV.

It is seen that there is a proportionality between the concentration and the limiting current in both the 1st and the 2nd wave in each of these compounds and i_d/C of the 1st and the 2nd wave in these compounds seem to be approximately equal.

TABLE IV

LIMITING CURRENT VS. CONCENTRATION

2,2′-Bis(nitrophenyl)arsinic acid

Concentration (mM/l)	1st wave i_d (μamp.)	 i_d/C (μamp,/mM)	2nd wave i_d (μamp.)	 i_d/C (μamp,/mM)
0.034	1.15	33.8	0.96	28.2
0.046	1.50	32.6	1.23	26.7
0.068	2.19	32.2	1.89	27.8
0.080	2.45	30.6	2.13	26.6
0.091	3.10	34.1	2.77	30.4
0.102	3.38	33.0	2.90	28.4
0.114	3.79	33.2	3.39	29.7
0.123	4.13	33.0	3.84	30.7
0.136	4.52	33.2	3.99	29.3
0.148	4.81	32.5	4.35	29.4
0.159	5.10	32.1	4.61	29.0
Mean		32.75±0.81		28.74±0.94

b) Relationship between Temperature and Limiting Current.—Limiting current of the 1st and the 2nd wave was determined from the polarograms of 2,2′-, 3,3′- and 4,4′-compounds in a buffer solution of pH 4.0, sample concentration being 2×10^{-4} M, at 30°, 25°, 20°, 15° and 10°C. The results obtained from the 1st wave indicate that there is a proportionality between the temperature and the limiting current in both 3,3′- and 4,4′-compound in this temperature range. The temperature coefficients of 3,3′ and 4,4′-compounds in this case are 1.59 % and 1.61 %. These coefficients are appoximately equal to that in the case of ordinary diffusion current. The measurement was impossible with the 2,2′-compound since the solubilities decrease below 20°C, at this concentration and pH, and the compound precipitates out.

$$\left\{\left(\frac{i_d(t_1)}{i_d(t_2)}\right)^{1/t_2-t_1}-1\right\}\times100\%$$

c) Relationship between the Height of Mercury Reservoir and Limiting Current.—Polarograms of 2,2′-, 3,3′- and 4,4′-compounds in a buffer solution of pH 2.2, in a concentration of 1.14×10^{-4} M, with varying heights of the mercury reservoir and the wave heights of the 1st and the 2nd wave were measured. As indicated in Table V, the results of 2,2′-compound and diphenyl arsinic acid are presented only, a linear relationship was found to hold between the limiting current and the square root of the height of mercury reservoir $h^{1/2}{}_{eff.}$ In other words, these limiting currents do not contain any kinetic current but are controlled by the diffusion process.

(3) Determination of Bis(nitrophenyl)arsinic Acid Mixture.—As was

TABLE V

LIMITING CURRENT VS. EFFECTIVE HEIGHT OF THE MERCURY RESERVOIR 2,2′-BIS (NITRO PHENYL) ARSINIC ACID

$h_{eff.}{}^{1/2}$ (h:cm.)	1st wave i_d (μamp.)	 $i_d/h_{eff.}{}^{1/2}$	2nd wave i_d (μamp.)	 $i_d/h_{eff.}{}^{1/2}$
9.19	5.66	0.63	4.98	0.54
8.63	5.29	0.61	4.61	0.53
8.03	4.99	0.62	4.41	0.55
7.38	4.58	0.62	4.04	0.55
6.67	4.18	0.63	3.57	0.54
5.87	3.71	0.63	3.20	0.55

Diphenyl arsinic acid
(concn.:2×10^{-4}M/l)

$h_{eff.}{}^{1/2}$ (h:cm.)	i_d (μamp.)	$i_d/h_{eff.}{}^{1/2}$
8.91	4.40	0.49
8.03	3.94	0.49
7.38	3.55	0.48
6.28	3.00	0.48

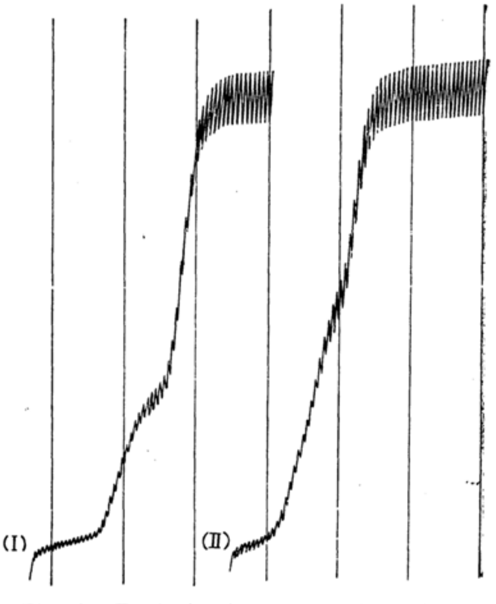


Fig. 4. Typical polarograms of synthetic mixtures of Bis(nitrophenyl)arsinic acids.
(I) 2,2′- : 3,3′-=30 : 70(wt %)
(II) 2,2′- : 4,4′-=50 : 50(,,)

mentioned earlier, the compounds possessing $-NO_2$ group in 2-position exhibit a reduction wave of the 1st wave in a more positive potential range than those with $-NO_2$ group in other positions and consequently show a divided wave (Fig. 4).

It follows, therefore, that the determination of a mixture of 2,2′- and 3,3′- or 4,4′-bis(nitropenyl)arsinic acid can be made concurrently by determining the 2,2′-compound from the 1st step in the 1st wave and 3,3′- or 4,4′-compound from the 2nd step wave that appears next. Tables VI and VII give results of determination carried out on several mixed samples by the standard addition method.

TABLE VI

DETERMINATION OF A SYNTHETIC MIXTURE OF 2,2′- AND 3,3′-BIS(NITROPHENYL)ARSINIC ACIDS

No.	Calculated Value (wt. %)		Observated Value (wt. %)	
	2,2′-	3,3′-	2,2′-	3,3′-
1	10.0	90.0	10.1	89.9
2	20.0	80.0	19.5	80.5
3	30.0	70.0	30.4	69.6
4	40.0	60.0	39.5	60.5
5	50.0	50.0	49.8	50.2
6	60.0	40.0	60.0	40.0
7	70.0	30.0	69.2	30.8
8	80.0	20.0	78.8	21.2
9	90.0	10.0	85.6	14.4

TABLE VII

DETERMINATION OF A SYNTHETIC MIXTURE OF 2,2′- AND 4,4′-BIS(NITROPHENYL)ARSINIC ACIDS

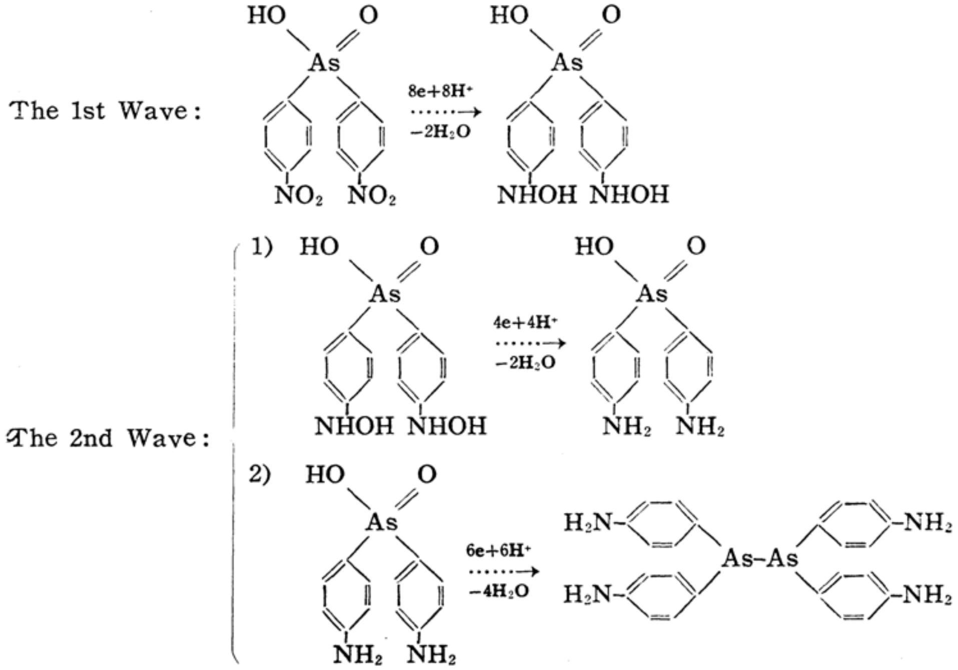
No.	Calculated Value (wt. %)		Observated Value (wt. %)	
	2,2′-	4,4′-	2,2′-	4,4′-
1	20.0	80.0	20.4	79.6
2	50.0	50.0	48.3	51.7
3	70.0	30.0	69.3	30.7

Separatory determination of a mixture of 3,3′- and 4,4′-bis(nitrophenyl)arsinic acids is impossible since such a mixture does not exhibit separate waves but the value of i_d/C is approximately equal in the two compounds so that the approximate value of the content can be obtained.

Mixtures of non-symmetrically substituted 2,3′-, 2,4′-, and 3,4′-compound cannot be determined although the presence of a compound with $-NO_2$ group in the 2-position can be detected from their 1st wave, as is evident from their reduction wave.

Summary

1) Polarographic behavior of the six isomers of bis(nitrophenyl)arsinic acid was considered and the waves can roughly be divided into 1st and 2nd waves in acid range at the dropping mercury electrode.



2) The limiting current is controlled by the diffusion process and the Ilkovič equation is applicable.

3) The electrolytic reduction mechanisms of the 1st and 2nd waves are considered to be in the following manner, taking that of 4,4′-bis(nitropenyl)arsinic acid as an example: (see the figure of the preceding page).

4) By the utilization of the 1st wave, polarography can be used for the determination of bis(nitrophenyl)arsinic acids, especially those with the nitro group in 2-position.

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Engineering Research Institute
Faculty of Engineering
University of Tokyo
Hongo, Tokyo