Effect of Gelatin on the Polarographic Waves of *p*- and *o*-Nitroanilines

By Nobuyuki TANAKA and Masako KOBAYASHI

(Received March 12, 1951)

Several literatures have been published on the studies on polarographic reduction waves of nitroanilines. In 1932, M. Shikata and E. Taguchi[1] reported on the reduction potentials of *o*-, *m*- and *p*-nitroanilines measured by the 45° tangent method in a wide range of *p*H with buffered and non-buffered solutions, and they discussed the relation between the reduction potentials and the constitutions. Recently O. D. Shreve and E. C. Markham[2] reported on the effect of ethyl alcohol on the polarographic waves of nitroanilines. Y. Yasumori[3] tried to apply the polarographic waves of *p*- and *o*-nitroanilines to the simultaneous determination of these compounds in their mixtures, when he employed the double waves of these compounds which were obtained in supporting electrolyte of a suitable *p*H and a suitable concentration of ethyl alcohol. However, these researchers told of nothing concerning the effect of gelatin on the reduction waves of these compounds.

In the present paper are reported the effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines and its application to the determination of these compounds. The experiments and discussions on the characteristics of the polarographic waves themselves of these compounds and the reduction mechanisms will be reported elsewhere.

(1) M. Shikata and E. Taguchi, *J. Agricul. Soc. Japan*, **8**, 1225 (1932).

(2) O. D. Shreve and E. C. Markham, *J. Am. Chem. Soc.*, **71**, 2993 (1949).

(3) private communication.

Experimental

Apparatus.—A Heyrovsky-Shikata type polarograph was employed. A dropping mercury electrode was employed for the cathode, and a normal calomel electrode, for the anode. The capillary constant, $m^{2/3}\ t^{1/6}$, was 1.124 (mg.$^{2/3}$ sec.$^{-1/2}$), measured in distilled water free from oxygen without applied potential. All measurements were carried out in a thermostat of 25° or 30°.

Reagents.—*p*- and *o*-Nitroanilines were kindly given by Nippon Kasei Chemical Industries Limited, which have the melting points of 148.0-148.5° and 72.0-72.5° respectively. Their standard solutions were prepared by dissolving them in distilled water, the concentrations of which were about 1 millimol per liter.

The Clark and Lub's buffer of *p*H 9.0 was used as a supporting electrolyte solution, its actual *p*H value being 8.8 determined with an antimony electrode.

Results and Discussion

The polarographic waves of *p*- and *o*-nitroanilines measured in the supporting electrolyte containing no gelatin are shown in Fig. 1, on which distinct maxima appeared. These maxima were suppressed by adding 0.005-0.01% of gelatin to the supporting electrolyte. When

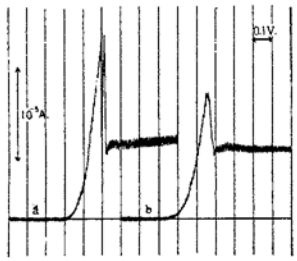

Fig. 1.—Polarograms of *p*- and *o*-nitroanilines in the supporting electrolyte containing no gelatin; (a) *p*-nitroaniline ($0.5\times10^{-5}M$), (b) *o*-nitroaniline ($0.5\times10^{-3}M$). Each poralogram beings at −0.4 volt *vs.* N. C. E.

the concentration of gelatin increased more than about 0.01%, it was found that the wave of nitroaniline splitted into two waves. The total height of the double wave was almost constant independently of the concentration of gelatin. The ratio of the wave height of the second wave to the first one became greater with the increase of the concentration of gelatin contained in supporting electrolyte. These phenomena are shown in Figs. 2 and 3.

In addition to the fact it became clear that the ratio of the second wave to the first one was different between *p*- and *o*-compounds when the supporting electrolyte contained the

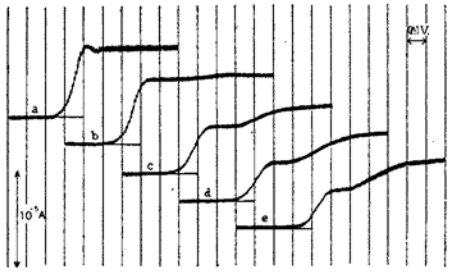

Fig. 2.—Polarograms of *p*-nitroaniline ($0.5\times10^{-3}M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02%, (d) 0.05% and (e) 0.1%. Each polarogram begins at −0.4 volt *vs.* N. C. E.

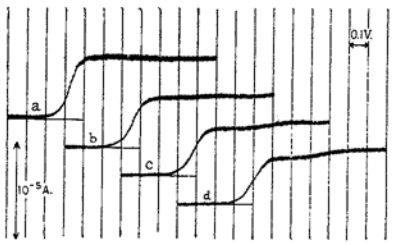

Fig. 3.—Polarograms of *o*-nitroaniline ($0.5\times10^{-3}M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02% and (d) 0.1%. Each polarogram begins at −0.4 volt *vs.* N. C. E.

same concentration of gelatin.

The linear relations were held between the concentrations and the wave heights of both the first and the second waves of each compound, as shown in Figs. 4 and 5. Therefore,

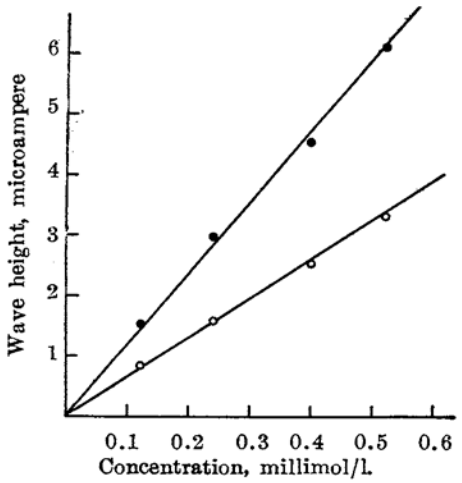

Fig. 4.—Relation between the wave height and the concentration of *p*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

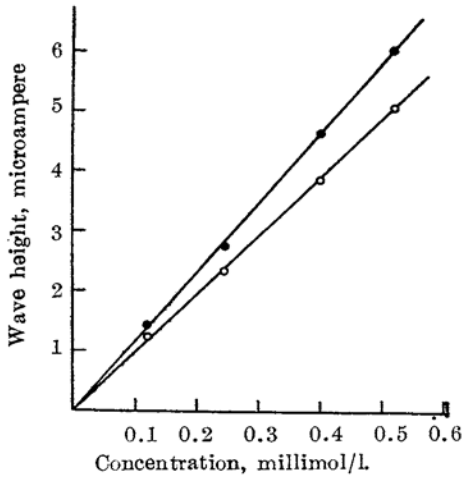

Fig. 5.—Relation between the wave height and the concentration of *o*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

these double waves seemed possible to be applied to the simultaneous determination of both compounds, which will be described later.

The relations of $\log I/I_d-I$ *vs.* V held straight lines, but their slopes were far less than those expected from the reversible reduction. They should hold straight lines with slopes of about 10 millivolts, if the reduction proceeded reversibly and if the numbers of electrons necessary to the reduction were six as reported by Shreve and Markham and as confirmed by the authors.

The half-wave potentials were almost independent of the concentration of the reducible substances, but shifted to negative potential with increasing concentration of gelatin, which are indicated in Tables 1 and 2.

Table 1

Half-wave Potentials and Slopes of $\log I/(I_d-I)$ *vs.* V of the First Waves of *p*- and *o*-Nitroanilines in Various Concentrations

Concentration, milllmol/l.	*p* or *o*	$V_{1/2}$ *vs.* N.C.E., volt	Slope of $\log I/(I_d-I)$ *vs.* V, volt
0.12	*p*	−0.820	0.062
	o	−0.791	0.066
0.24	*p*	−0.814	0.061
	o	—0.785	0.068
0.40	*p*	−0.821	0.062
	o	−0.789	0.068
0.52	*p*	−0.828	0.071
	o	−0.797	0.073

Supporting electrolytes contained 0.1% of gelatin.

Table 2

Half-wave Potentials and Slopes of $\log I/(I_d-I)$ *vs.* V of the First Waves with the Change in the Concentration of Gelatin

Concentration of gelatin, %	*p* or *o*	$V_{1/2}$ *vs.* N.C.E., volt	Slope of $\log I/(I_d-I)$ *vs.* V, volt
0.005	*p*	(−0.74)	—
	o	(−0.73)	—
0.01	*p*	−0.750	0.057
	o	−0.756	0.069
0.02	*p*	−0.772	0.064
	o	−0.780	0.076
0.05	*p*	−0.795	0.068
	o	−0.787	0.075
0.1	*p*	−0.815	0.069
	o	−0.801	0.078

Concentration of *p*- and *o*-nitroanilines are 0.5 millimol per liter.

The numbers of electrons necessary to the reduction were calculated from the polarogram by means of the Ilkovič equation and the diffusion constant. For the latter, 8.79×10^{-6} cm.^{2}sec.$^{-1}$, the value given by Shreve and Markham, was employed. The result showed that the reduction of *p*- and *o*-nitroanilines, including the second wave if the wave splitted into two waves, was of the six-electron reduction, as the same as reported by Shreve and Markham.

It seems important to answer the problems of why the wave splits by the addition of gelatin and of why the ratio of the wave height of the second wave to the first one increases with the increase of the concentration of gelatin. It has been reported that nitro compound often gives a double wave in the certain condition. Being the case, the first wave corresponds to the reduction of nitro compound to hydroxylamine, (that is, a four-electron reduction), while the second wave corresponds to the reduction of hydroxylamine (that is, a two-electron reduction).

The present case, no doubt, did not correspond to such a case, because the ratio of both waves changed continuously with increasing concentration of gelatin. The authors would like to infer that some changes at the electrode interface occurring by the addition of gelatin caused the wave splitting. Such a case has been recently reported by E. L. Colichman[4] in regard to the reduction waves of the several inorganic compounds, which are greatly influenced by surface active substances, such as gelatin and cetyltrimethylammonium bromide.

(4) E. L. Colichman, *J. Am. Chem. Soc.*, **72**, 4086 (1950).

In the present study, however, the authors could not confirm the idea, but as the result of some experiments, they did not prove the phenomenon to be explained by the idea of the formation of intermediate reduction substances and also by that of kinetic current.

Analytical Application

Since it was found out that the wave heights are proportional to the concentration and that the ratio of wave height of the second wave to the first one is different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin, the double waves were applied to the simultaneous determination of these compound. The concentration of gelatin contained in the supporting electrolyte was decided to be 0.1%, considering that, in the case, the difference of the ratio of the second wave to the first one was the greatest between *p*- and *o*-compounds. The relations of the wave heights and the concentrations were obtained in this condition, as shown in Figs. 4 and 5. From the result the following equations were obtained to express the concentration of each of these compounds contained in the solution electrolyzed.

Table 3

Simultaneous Determination of Synthetic Samples

Ratio of *p*:*o* in synthetic samples, (*p* : *o*)		Concentration present, millimol/l.	Concentration found, millimol/l.
1 : 1	*p*	0.24	0.27
	o	0.24	0.18
2 : 1	*p*	0.32	0.35
	o	0.16	0.18
4 : 1	*p*	0.32	0.32
	o	0.08	0.06
5 : 1	*p*	0.40	0.46
	o	0.08	0.09
1 : 2	*p*	0.16	0.17
	o	0.32	0.27
1 : 3	*p*	0.08	0.08
	o	0.24	0.23
1 : 5	*p*	0.08	0.10
	o	0.40	0.39

$$C_p = \frac{7.9\,h_2 - 11.6\,h_1}{38.3} \quad \text{(millimol/l.)}$$

$$C_o = \frac{11.6\,h_1 - 6.4\,h_2}{38.3} \quad (\quad ,, \quad),$$

where C_p and C_o represent the concentrations of *p*- and *o*-nitroanilines and h_1 and h_2, the first wave height and the total wave hight both measured in microampere.

Some synthetic samples were analyzed with the procedure with the results shown in Table 3. The results were not so good, but it was concluded that an approximate content of each compound can be estimated with the procedure.

Summary

The effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines has been investigated,

(1) Maxima of the polarographic waves of these compounds which occur in the supporting electrolyte without gelatin were supressed by adding 0.005-0.01% of gelatin to the supporting electrolyte.

(2) The wave of each of these compounds splitted into two waves when the supporting electrolyte contained more than 0.01% of gelatin.

(3) The ratio of the wave heights of the second wave to the first increased with increasing concentration of gelatin, and it was different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin.

(4) The wave heights of the first and the second waves of each compound were proportional to the concentration.

(5) These double waves were applied to the simultaneous determination of both compounds, with the result that the procedure was available for rough estimation of content.

The authors are grateful to Nippon Kasei Chemical Industries Limited that gave them purified samples of *p*- and *o*-nitroanilines. The cost of this study has been partly defrayed from the Grant in Aid from the Ministry of Eduaction.

Institute of Science and Technology, the University of Tokyo, Tokyo