Simultaneous Polarographic Determination of a System of o-Nitroanisole, o-Chloronitrobenzene and o-Nitrophenol

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o-Nitroanisole is industrially synthesized as a dyestuff intermediate by the reaction of *o*-chloronitrobenzene, sodium hydroxide and methanol. In this process, *o*-nitrophenol is often formed as a by-product. The final solution thus contains *o*-nitroanisole, unreacted *o*-chloronitrobenzene and *o*-nitrophenol as a by-product. From the industrial point of view, it is desired to determine these three compounds in the final solution with the greatest possible simplicity and rapidity. The present study deals with the polarographic method applied to the above determination.

In general, the aromatic nitro compounds are easily reduced at a dropping mercury electrode and numerous investigations upon each of these compounds have already been reported. *o*-Nitroanisole in 10% ethanol-buffer or 30% methanol-buffer solutions of various pH values[1,2], *o*-chloronitrobenzene in 50% ethanol-buffer or 30% methanol-buffer solutions[3,2] and *o*-nitrophenol in ethanol-buffer[4,5] or tetraethylammonium bromide solution[6] have been studied polarographically. It is accordingly known that they can be determined independently, but in the case they are mixed, the condition becomes quite different. As was expected, the half-wave potentials of such compounds are so close that their waves often overlap each other and it seems difficult to get their well-defined waves with good separation. The chief efforts of the present study were exerted to find out the optimum condition of the supporting electrolytes under which the waves of three compounds might be obtained with satisfactory separation.

From this point of view, the effects of pH and various kinds of electrolytes, such as the components of buffer solutions, the effect of mixing of organic solvents such as methanol, ethanol and acetone were thoroughly investigated. The optimum condition is obtained with sodium hydroxide-methanol solution in which the wave of *o*-nitrophenol is so well separated from those of the others that it can easily be determined. The separation of the waves of *o*-nitroanisole and *o*-chloronitrobenzene in this solution is not, however, satisfactory, though better than in other solutions. To improve the wave form, the compensation of residual current was then tried and it was found that by passing the compensating current very excessively, the separation of two reduction waves became distinct.

Expriemental

Three nitro compounds were obtained from Toa Gosei Company and were further purified. *o*-Nitroanisole the purity of which was more than 99% was redistilled under reduced pressure. *o*-Chloronitrobenzene and *o*-nitrophenol were recrystallized from methanol of which m. p.'s were 33.0 and 45.7°C respectively. 0.01M ethanol, methanol and acetone solutions of each compound were prepared as master solutions. Sørensen's borate-citrate and phosphate buffer solutions of various pH values ranging from 1.17 to 12.16 and other indifferent electrolyte solutions, were also prepared from reagents of analytical grade. The sample solution to be electrolyzed was prepared by mixing the master solution and the indifferent salt solution in an appropriate ratio. Inactive gelatin was added till it was 0.01% of the solution. To remove oxygen, nitrogen was passed through the solution.

The electrolysis was carried out in a liquid paraffin bath which was regulated at 25°C. Both the photographic methods using a Yanagimoto's polarograph apparatus and the pen-writing method using a direct-current amplifier which had been conceived in this laboratory[7] were used. The compensating method of residual current was also applied in further studies by using the circuit proposed by Ishibashi, Shinagawa and Sasabe[8].

Results

As the results of the preliminary experiments treating the solutions of three components in

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[1] J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. & Colloid. Chem.*, **53**, 545 (1949).

[2] H. Iida and K. Kayahara, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 289 (1957).

[3] S. F. Dennis, A. S. Powell and M. J. Astle, *J. Am. Chem. Soc.*, **71**, 1484 (1949).

[4] J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948).

[5] M. J. Astle and W. V. McConnell, *J. Am. Chem. Soc.*, **65**, 35 (1943).

[6] E. Gergely and T. Iredale, *J. Chem. Soc.*, **1953**, 3226.

[7] S. Kikuchi, Y. Sakaguchi and K. Honda, This Bulletin, **25**, 98 (1952).

[8] M. Ishibashi, M. Shinagawa and T. Sasabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **64**, 1441 (1943).

an arbitrary ratio, it was confirmed that the reduction waves appear in the order of *o*-chloronitrobenzene, *o*-nitroanisole and *o*-nitrophenol and the latter can easily be measured because its wave is distinctly separated from those of the two others in most of the tested solutions (Fig. 1). But the reductions of *o*-chloronitrobenzene and *o*-nitroanisole take place at such close potentials that their waves appear to coincide considerably. Hence it seems difficult to determine them directly on a polarogram. The problem is, therefore, reduced to the polarographic determination of the system of *o*-nitroanisole and *o*-chloronitrobenzene.

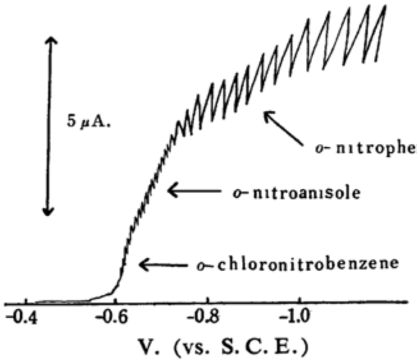

Fig. 1. Polarogram of *o*-nitroanisole (5×10^{-4}M/l.), *o*-chloronitrobenzene (5×10^{-4}M/l.) and *o*-nitrophenol (2×10^{-4}M/l.) in 1 N NaOH-methanol (4 : 1).

The System of *o*-Nitroanisole and *o*-Chloronitrobenzene. — Müller[9] described that when two components in a solution the waves of which are assumed to be reversible, are both measurable, their half-wave potentials must differ at least by $(RT/nE)\ln 1000$. In general it would be unwise to presume the separation of waves from the reported values of half-wave potentials of the components to be reduced. It seems desirable to examine the above system under every possible condition.

Here the system of two compounds in mole ratio of 1 : 1 in various electrolyte solutions was investigated to observe the feature of overlapping of waves. In the solutions of various pH values ranging from 1 to 12, containing methanol, ethanol or acetone 2∼50%, their reduction waves overlap completely and there is no possibility of determining them directly. In the case of strong basic solutions, the overlapped wave shows a slight tendency to split into two parts, which indicates the possibility of simultaneous determination. Further investigation was then carried out, varying the alkaline concentration and the ratio of organic solvent. The results are summarized in Table I.

TABLE I. SEPARATION OF REDUCTION WAVES OF *o*-NITROANISOLE AND *o*-CHLORONITROBENZENE IN VARIOUS ELECTROLYTE SOLUTIONS

Concentration of NaOH	Solvent		Separation of waves
N		%	
0.1	Methanol	10	**
1	Acetone	2	*
	〃	10	**
	〃	20	*
	Methanol	40∼50	**
	〃	10∼30	***
	〃	2∼ 5	*
2	Acetone	20	No separation
	Methanol	50	**
	〃	20∼30	***
	〃	5∼10	**
3	Methanol	50	**
	〃	5∼30	***
4	Methanol	50	*
	〃	20∼30	**
	〃	10	*
5	Methanol	30	*
10	Methanol	20∼50	*

*** ; favorable
** ; fairly good
* ; not good

By examining the results in Table I and considering the practical condition, a solution of four parts of 1 N sodium hxdroxide and one part of methanol was selected as the most suitable solution. In Fig. 2, curve (a) shows an overlapped wave and curve (b) the separated wave.

Use of the Compensating Method of Residual Current.—As mentioned above, it is possible to determine *o*-nitroanisole and *o*-chloronitrobenzene in the solution hitherto described when their molar concentrations are equal or nearly equal. But with the increase of differences of their concentrations, the separation of waves becomes again unsatisfactory and it cannot be expected to obtain accurate results. To resolve this difficulty, the compensating method of residual current was tested and it was found that the current compensation gave rise to an apparent separation of waves. For the present purpose, the compensating current must be applied so excessively that the zero-current inclines downwards with the potential increase, resulting in an abnormal form of polarogram. The shape of the polarogram is shown in Fig. 2, curve (c).

By the application of this method, the difference of concentrations of both compounds may

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[9] O. H. Müller, "The Polarographic Method of Analysis", Chemical Education Co., Easton, Pa. (1950), p. 156.

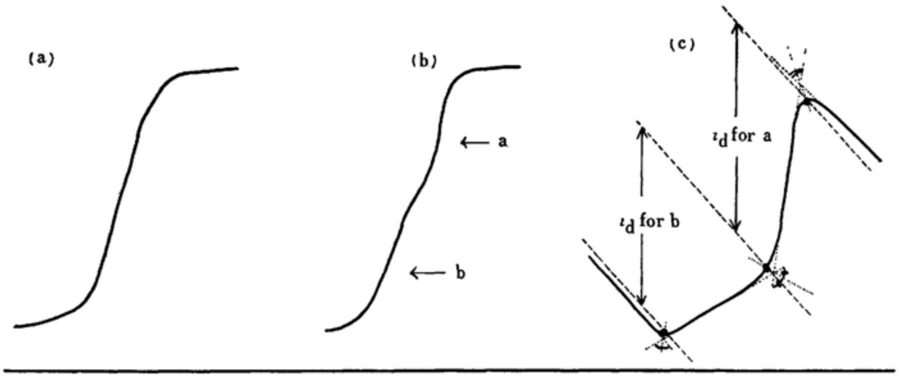

Fig. 2. Wave forms of *o*-nitroanisole (a) and *o*-chloronitrobenzene (b):
(a) in neutral media, (b) in alkaline media,
(c) in alkaline media, compensating current is passed excessively.

be extended over a considerable range. The separation of the waves is noticeable even when their concentration ratio is 10 : 1 and vice versa. A calibration curve must be made for each compensating condition, because the wave-height of this abnormal polarogram measured by an appropriate drawing method usually presents a little lower value than that of a normal polarogram. The relation between the concentrations of *o*-nitroanisole and *o*-chloronitrobenzene in 1 N sodium hydroxide-methanol (volume ratio 4 : 1) and their wave-heights are shown in Tables II and Fig. 3.

TABLE II. CONCENTRATIONS AND WAVE-HEIGHTS (i_d) FOR THE 1 N SODIUM PYDROXIDE METHANOL (4 : 1) SOLUTIONS OF *O*-NITROANISOLE AND FOR THAT OF *O*-CHLORONITROBENZENE

Concentration C	*o*-Nitroanisole		*o*-Chloronitrobenzene	
	i_d	$i_d/Cm^{2/3}t^{1/6}$	i_d	$i_d/Cm^{2/3}t^{1/6}$
M/l.	μA.		μA.	
10×10^{-4}	6.1_3	5.92	5.7_3	5.53
8×10^{-4}	4.7_8	5.77	4.9_1	5.93
6×10^{-4}	3.7_3	5.99	3.5_8	5.77
4×10^{-4}	2.5_3	6.10	2.2_0	5.32
2×10^{-4}	1.1_3	5.45	1.1_8	5.69

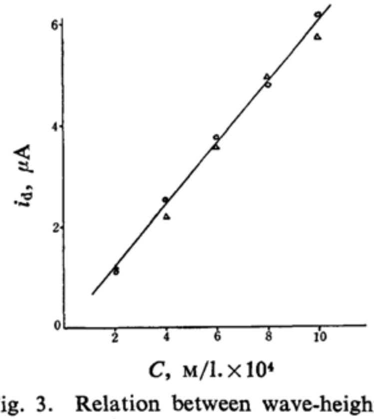

Fig. 3. Relation between wave-heights and concentrations.
○ *o*-Nitroanisole
△ *o*-Chloronitrobenzene

System of Three Components.—As described before, *o*-nitrophenol can be determined directly on the ordinary polarogram. The relation between concentrations and wave-heights is shown in Table III and Fig. 4. Once *o*-nitrophenol is determined by the usual polarography, the electrolysis is repeated, using the compensating current. On this second polarogram *o*-nitroanisole and *o*-chloronitrobenzene are

TABLE III. CONCENTRATIONS AND WAVE-HEIGHTS (i_d) FOR THE 1N SODIUM HYDROXIDE METHANOL (4 : 1) SOLUTIONS OF *O*-NITROPHENOL

Concentration, C	i_d	$i_d/Cm^{2/3}t^{1/6}$
M/l.	μA.	
10×10^{-4}	8.1_4	7.76
5×10^{-4}	4.1_8	7.84
2×10^{-4}	1.8_4	8.88
5×10^{-5}	0.4_9	9.45

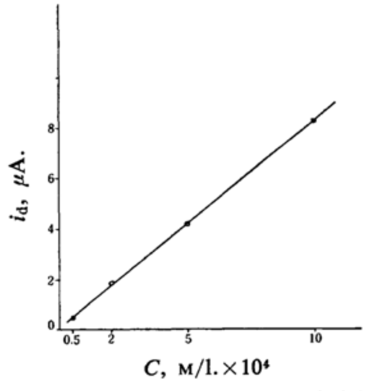

Fig. 4. Relation between wave-heights and concentrations of *o*-nitrophenol.

determined by reference to the data of Table II. Experiments are carried out, varying the concentration of one of three components, while those of two others remain constant. The results, summarized in Table IV, are, therefore, classified in three groups according to the compound of which the concentration is varied.

TABLE IV. SIMULTANEOUS DETERMINATION OF *o*-NITROANISOLE (a), *o*-CHLORONITROBENZENE (b) AND *o*-NITROPHENOL (c)

(1) Concentration of a is varied, while those of b and c remain constant.

Concentration, calculated M/l.	Wave-height μA.	Concentration, found M/l.	Difference %
a 8×10^{-4}	4.7	7.9×10^{-4}	− 1.5
b 1×10^{-3}	4.8	8.4×10^{-4}	−16
c 2×10^{-4}	1.8	2.0×10^{-4}	− 2
a 6×10^{-4}	3.3	5.3×10^{-4}	−11
b 1×10^{-3}	4.9	8.6×10^{-4}	−14
c 2×10^{-4}	1.9	2.1×10^{-4}	+ 3
a 4×10^{-4}	2.7	4.2×10^{-4}	+ 6
b 1×10^{-3}	4.9	8.6×10^{-4}	−14
c 2×10^{-4}	1.7	1.8×10^{-4}	− 9
a 2×10^{-4} b 1×10^{-3}	Measurement is not possible		
c 2×10^{-4}	1.7	1.8×10^{-4}	− 9

(2) Concentration of b is varied, while those of a and c remain constant.

Concentration, calculated M/l.	Wave-height μA.	Concentration, found M/l.	Difference %
a 1×10^{-3}	6.1	9.9×10^{-4}	− 1
b 8×10^{-4}	3.7	6.3×10^{-4}	−22
c 2×10^{-4}	1.9	2.1×10^{-4}	+ 4
a 1×10^{-3}	6.4	1.1×10^{-3}	+ 8
b 5×10^{-4}	2.5	4.2×10^{-4}	−16
c 2×10^{-4}	1.8	2.0×10^{-4}	− 2
a 1×10^{-3}	5.6	9.2×10^{-4}	− 8
b 3×10^{-4}	1.5	2.7×10^{-4}	− 9
c 2×10^{-4}	1.9	$2.0_6\times10^{-4}$	+ 3
a 1×10^{-3}	5.8	9.4×10^{-4}	− 6
b 2×10^{-4}	0.9	1.5×10^{-4}	−24
c 2×10^{-4}	1.7	1.8×10^{-4}	−11

(3) Concentration of c is varied, while those of a and b remain constant.

Concentration, calculated M/l.	Wave-height μA.	Concentration, found M/l.	Difference %
a 5×10^{-4}	2.6	4.2×10^{-4}	−16
b 5×10^{-4}	2.7	4.2×10^{-4}	−16
c 1×10^{-3}	8.6	$1.0_5\times10^{-3}$	+ 5
a 5×10^{-4}	2.6	4.1×10^{-4}	−17
b 5×10^{-4}	2.3	3.9×10^{-4}	−23
c 5×10^{-4}	4.0	4.8×10^{-4}	− 4
a 5×10^{-4}	2.7	4.3×10^{-4}	−15
b 5×10^{-4}	2.3	3.8×10^{-4}	−24
c 2×10^{-4}	1.7	1.8×10^{-4}	−10
a 5×10^{-4}	2.8	4.5×10^{-4}	−11
b 5×10^{-4}	2.4	4.1×10^{-4}	−18
c 5×10^{-5}	0.4_4	4.5×10^{-5}	−10

Summary

1) The solution of *o*-nitroanisole, *o*-chloronitrobenzene and *o*-nitrophenol is investigated polarographically with the intention of their simultaneous determination.

2) The most suitable supporting electrolyte solution for the above object is the mixture of 4 parts of 1 N sodium hydroxide and 1 part of methanol.

3) Although this solution is not buffered, the variation of concentration of one component does not exert appreciable influence upon the wave-heights and the relative positions of the waves of other two components.

4) *o*-Nitrophenol can be determined directly from the ordinary polarogram. The accuracy of determination is under ±10%.

5) The residual current compensation gives aid to the determination of *o*-nitroanisole and *o*-chloronitrobenzene. By passing the compensating current very excessively, their reduction waves become better defined. The accuracy of determination is +8∼−17% for *o*-nitroanisole and −24∼−9% for *o*-chloronitrobenzene.

6) The half-wave potentials of three compounds, 5×10^{-4} M/l. in 1 N sodium hydroxide-methanol (4:1) solution are as follows;

	$E_{1/2}$(vs. S.C.E.) V.	Difference V.
o-Chloronitrobenzene	−0.645	
		0.114
o-Nitroanisole	−0.759	
		0.179
o-Nitrophenol	−0.938	

These values would give some indications for the estimation of the separation of waves.

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