*Polarographic Behavior of Nitroammonocarbonic Acids in Aqueous Media. II. Nitroguanidine**

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In the preceding paper [1], the polarographic behavior of nitrourea in aqueous media was reported. We extended this study to the behavior of nitroguanidine, and obtained complicated results in this case as well as in the case of nitrourea. This report mainly consists of the experimental results.

Experimental

The experimental method was described in Part I. Nitroguanidine, prepared through the dehydration of guanidine nitrate in concentrated sulfuric acid[2] and purified by recrystallization from water several times, was composed of colourless needles, m.p., 230°C (decomp.) (Found: N, 53.85. Calcd. for $CH_4N_4O_2$: N, 53.85%).

Experimental Results and Discussion

1) Effects of pH upon the Half-Wave Potential ($E_{1/2}$) and the Limiting Current (i_l).—Polarographic waves at various pH are reproduced in Fig. 1. The relationship of

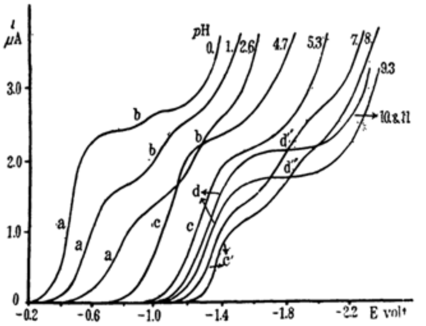

Fig. 1. Polarograms of 1×10^{-4} mol./l. Nitroguanidine.

pH-$E_{1/2}$ (vs. S.C.E.) and of pH-i_l is shown in Figs. 2 and 3, respectively. From these data, we can make the following summary:

a)	in range of pH 0–3	double wave: (a) and (b) waves
b)	in range of pH 4–5	single wave: (c) wave
c)	in range of pH 5.6–8	double wave: (c′) and (d′) waves
d)	above pH 9.3	single wave: (d) wave

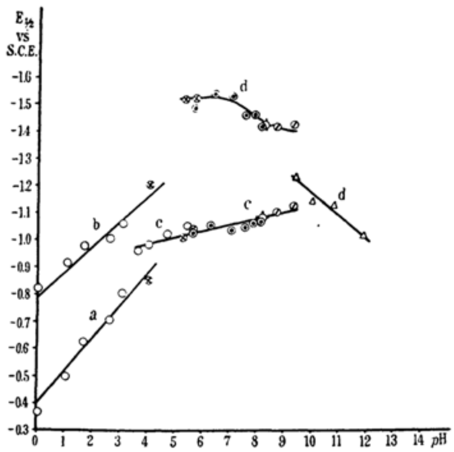

Fig. 2. Nitroguanidine: Relationship between pH and $E_{1/2}$ (vs. S.C.E.)

Species of buffer solution

○ Wolpole (1N-HCl & 1N-CH_3COONa)
⊗ Kolthoff (M/10-Citric Acid & M/5-Na_2HPO_4)
⊙ Sφrensen (M/15-KH_2PO_4 & M/15-Na_2HPO_4)
-ọ- Kolthoff (M/20-Borax & M/10-KH_2PO_4)
⊘ Sφrensen (M/20-Borax & N/10-HCl)
△ Sφrensen (M/20-Borax & N/10-NaOH)

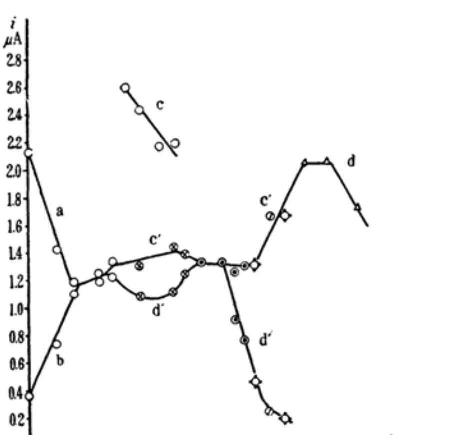

Fig. 3. Nitroguanidine: Relationship between pH and i_l (conc. 1×10^{-4} mol./l.)

* The main part of this paper was presented at the 1st Symposium on Polarograph on Nov. 17, 1954, Kyoto.

1) K. Namba and K. Suzuki, This Bulletin, 28, 620 (1955).

2) T.L. Davis, "The Chemistry of Powder and Explosives", John Wiley and Sons, Inc., New York, N. Y., (1943), p. 380.

Whether the wave is single or double in its shape depended upon the species of buffer solution as found in the range of pH 4–5 and at pH 9 in Fig. 2. The single wave obtained in the range of pH 4–5 in the Walpole solution will be the duplicated wave of the 1st and 2nd waves, due to the vicinity of reduction potential for both waves, while the total value of i_l of the double wave in acidic media is almost the same. When we examined the polarogram of guanidine nitrate under the same condition, no reduction wave was found. From this fact, all reduction waves found are considered to be those of $N\text{-}NO_2$ radical.

In the previous paper[3], we examined the influence of concentration upon the limiting current and of temperature on the stability. A linear relationship between the limiting current and concentration was obtained over the concentration range of $1\text{–}10\times10^{-4}$ mol./l. in acidic media, where the nitroguanidine was stable.

2) Effects of the Height of Mercury Reservoir and of Temperature upon the Limiting Current.—Table I represents the relationship between the effective height of mercury reservoir, h_{eff}, and the limiting current.

TABLE I

DEPENDENCE OF THE EFFECTIVE HEIGHT OF MERCURY RESERVOIR ON THE LIMITING CURRENT OF 1×10^{-4} mol./l. NITROGUANIDINE

Temperature 25°C

		pH 1.05				pH 3.49	
		(a)		(b)		(c)	
h_{eff}	$h_{eff}^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$
cm.		μa.		μa.		μa.	
57	7.55	1.80	2.38	1.25	1.66	3.47	4.60
47	6.86	1.63	2.38	1.02	1.49	3.04	4.43
37	6.08	1.48	2.43	0.86	1.41	2.94	4.83
27	5.20	1.25	2.40	0.71	1.37	2.32	4.46
22	4.69	1.11	2.37	0.67	1.43	2.10	4.48
17.5	4.18	1.02	2.44	0.61	1.46	1.82	4.36

		pH 5.10			
		(c′)		(d′)	
h_{eff}	$h_{eff}^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$
cm.		μa.		μa.	
57	7.55	1.69	2.24	1.74	2.31
47	6.86	1.48	2.16	1.48	2.16
37	6.08	1.30	2.14	1.32	2.17
27	5.20	1.05	2.02	1.09	2.10
22	4.69	0.96	2.05	1.02	2.18
17.5	4.18	0.82	1.96	0.91	2.18

		pH 7.01				pH 9.30	
		(c′)		(d′)		(d)	
h_{eff}	$h_{eff}^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$	i_l	$i_l/h^{1/2}$
cm.		μa.		μa.		μa.	
57	7.55	1.50	1.99	1.58	2.09	2.65	3.51
47	6.86	1.39	2.03	1.49	2.17	2.30	3.36
37	6.08	1.21	1.99	1.27	2.09	1.98	3.26
27	5.20	1.03	1.98	1.11	2.13	1.73	3.33
22	4.69	0.93	1.98	1.00	2.14	1.55	3.31
17.0	4.12	0.77	1.87	0.90	2.18	1.33	3.18

The fact that the limiting current at pH 1.05, 3.49, 5.10, 7.01 and 9.30 are proportional to $h^{1/2}$ means that these currents are controlled by the diffusion process.

The relationships between the temperature and the limiting current at pH 2.20, 5.05, 8.16 and 10.82 are shown in Table II.

TABLE II

INFLUENCE OF THE TEMPERATURE ON THE LIMITING CURRENT OF 1×10^{-4} mol./l. NITROGUANIDINE

	pH 2.20			
	(a)		(b)	
t, °C	i_l, μa.	Temp. coeff., %	i_l μa.	Temp. coeff., %
26.2	1.22	av. 1.14	1.17	av. 1.65
35.8	1.42		1.35	
45.3	1.69		1.44	
53.9	1.86		1.62	

	pH 5.05			
	(c′)		(d′)	
t, °C	i_l, μa.	Temp. coeff., %	i_l, μa.	Temp. coeff., %
22.5	1.41	av. 1.47	1.03	av. 2.03
35.0	1.65		1.38	
44.5	2.03		1.60	
54.2	2.23		1.85	

	pH 8.16			
	(c′)		(d′)	
t, °C	i_l, μa.	Temp. coeff., %	i_l, μa.	Temp. coeff., %
26.7	1.41	av. 1.32	0.51	av. 1.73
36.0	1.60		0.64	
45.5	1.86		0.74	
52.6	1.93		0.80	

pH 10.82

t. °C	i_l, μa.	Temp. coeff., %
26.0	2.12	
35.1	2.40	1.45
43.0	2.83	2.53
53.2	2.96	4.50

The temperature coefficient of (a) wave at pH 2.20 was comparatively less than those of other waves. In acidic and neutral solu-

3) K. Namba and K. Suzuki, *Journal of the Industrial Explosives Society*, Japan, 15, 171 (1954).

tion, since we obtained reasonable values in the temperature coefficient, the limiting current seems to follow the diffusion law. However, at pH 10.82, as shown in Table II, the above value increases in proportion to temperature, acceleratively, and the limiting current at lower temperature seems to be controlled kinetically. It is easily assumed that a slight decomposition[3] will exist above 45°C through the character of nitroguanidine.

3) Calculation of the Electron Number for Reduction (n).—We could not find out the proper value of diffusion coefficient of anion such as $\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>C=N\cdot COO^-$, whose molecular size and weight are almost similar to those of nitroguanidine. We chose anion of malonamic acid as the most adequate anion as we did in the case of nitrourea[1], the diffusion coefficient of which was estimated to be 9.49×10^{-6} cm^2 sec^{-1}. The calculated value of n by this method, n_A, was 2.64 for the 1st and 2.80 for the 2nd wave at pH 1.65, 3.08 for the 1st and 2.89 for the 2nd wave at pH 5.63 and 4.74 at pH 10.7.

From the application form of Stokes-Einstein's equation[4], by using the value of true density of nitroguanidine which was estimated to be 1.78[5], we obtained 8.55×10^{-6} cm^2 sec^{-1} as the D value. The calculated n_B by this method was 2.78 for the 1st and 2.96 for the 2nd wave at pH 1.65, 3.25 for the 1st and 3.20 for the 2nd wave at pH 5.63, and 5.00 at pH 10.7.

The total height of the 1st and 2nd wave in acidic solution is almost constant as was found in Fig. 3. It is also found that the total height in alkaline was less than in acidic. Since the (d) wave shown in Fig. 2 is completely different from the (a), (b), (c), (c′) and (d′) waves, the reduction mechanism of (d) wave must be considered in another aspect.

From the above results, the calculated n was three for the 1st and 2nd wave at pH 1.65 and 5.63, respectively, and five at pH 10.7.

Assuming the mechanism of reduction of nitroguanidine with three electrons in acidic media, and with five electrons in alkaline media, we must imagine tetrazene compounds such as those shown in the following formula.

In acidic media:

(a) and (c′)
$$2NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot NO_2+6H^{+}+6e$$
$$=NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot N:\underset{\overset{\downarrow}{O}}{N}\cdot NH\cdot\overset{NH}{\ddot{C}}\cdot NH_2+3H_2O$$

(b) and (d′)
$$NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot N:\underset{\overset{\downarrow}{O}}{N}\cdot NH\cdot\overset{NH}{\ddot{C}}\cdot NH_2+6H^{+}+6e$$
$$=2NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot NH_2+H_2O$$

In alkaline media:

(d)
$$2NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot NO_2+10H^{+}+10e$$
$$=NH_2\cdot\overset{NH}{\ddot{C}}\cdot NH\cdot N:N\cdot NH\cdot\overset{NH}{\ddot{C}}\cdot NH_2+4H_2O$$

However, such a tetrazene compound would be too unstable to exist, though one such tetrazene compound, the so-called "Tetracene", prepared by the interaction of aminoguanidine nitrate with natrium nitrite in neutral media, was used as initiators. Further investigation on this problem by another method will be necessary.

Summary

1) The relationships of pH–$E_{1/2}$ (vs. S.C.E.) and of pH–i_l of nitroguanidine under the dropping mercury electrode were studied.

2) From results about the influence of the effective height of mercury reservior and temperature upon i_l, it was found that i_l will follow the diffusion law, and that the Ilkovič equation is applicable in this case.

3) Although the electron number consumed for reduction (n) was calculated by assuming a diffusion coefficient these were insufficient in discussion of reduction mechanism. Further investigation will be necessary.

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4) I.M. Kolthoff and J.J. Lingane, "Polarography", Interscience Publishers, New York, N.Y., (1952), p. 57.

5) W.C. McCrone, *Anal. Chem.*, **23**, 205 (1951).