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## HYDROGEN ELECTRODE REACTION IN ALKALINE SOLUTION

### II Discharge of tetramethylammonium ion on mercury cathode

By

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#### Abstract

Cathodic process on mercury was studied in an alkaline solution of tetramethylammonium hydroxide (TMA-OH) under atmospheric hydrogen pressure at  $25 \pm 0.05^\circ\text{C}$ . Experimental results obtained by the galvanostatic pulse and potential sweep methods lead to the following conclusions: (1) Tetramethylammonium ion ( $\text{TMA}^+$ ) discharges with the relation,

$$-V(\text{volt, NHE}) = (2.10 \pm 0.34) + (0.217 \pm 0.032) \{ \log i - \log [\text{TMA}^+] \},$$

and the discharged substance accumulates on the electrode surface at potentials more negative than  $-1.8 \text{ v}$  (NHE). (2) The Tafel line at potentials more positive than  $-1.8 \text{ v}$  ( $i < ca. 2 \text{ mA/cm}^2$ ) is the same with that in NaOH solution, *i. e.*,  $\eta$  (overvoltage, volt) =  $1.36 + 0.15 \cdot \log i$ , and is attributed to the hydrogen electrode reaction (h. e. r.). (3) The activity of mercury for the h. e. r. is  $10^2 \sim 10^3$  times larger in alkaline solution than in acidic solution.

#### Introduction

Previous study on the cathodic process at Hg electrode in NaOH solution (Part I<sup>1)</sup>) clarified impossibility of determining the activity of Hg itself for the hydrogen electrode reaction (h. e. r.), since  $\text{Na}^+$  ion discharges much faster than the hydrogen evolution, and the deposited sodium accumulates significantly at potential more negative than  $-1.6 \text{ v}$  (NHE), so that the surface state completely changes from that of Hg itself.

Tetramethylammonium hydroxide (TMA-OH) on the other hand is known as a strong organic base and its cation ( $\text{TMA}^+$ ) is much more stable than  $\text{Na}^+$  in aqueous solution as seen from the difference of the half wave potentials of polarogram.<sup>2)</sup> Thus, one can expect a possibility of observing the h. e. r. on Hg itself without the accumulation of the discharged substance from  $\text{TMA}^+$  ion.

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Present work is performed to clarify the electrochemical behaviour of TMA<sup>+</sup> ion on Hg cathode and to determine experimentally the activity of Hg for the h. e. r. in alkaline solution.

## § 1 Experimental

Experimental apparatus and procedure were the same as reported in Part I.<sup>1)</sup> Electrolyte solutions were prepared from TMA-OH or (CH<sub>3</sub>)<sub>4</sub>NI (TMA-I) of special grade (Wako Chemical Industries Ltd., Osaka, Japan) and conductivity water. Solutions were then purified by pre-electrolysis for a few days with current of 3 mA/cm<sup>2</sup> under bubbling a purified hydrogen, except for the solution of pH less than 12, where the pre-electrolysis is expected to affect pH value. In the latter solution no purification was conducted.

Measurements were carried out on hanging drop electrode by the galvanostatic pulse and potential sweep methods. The Tafel relation is often abnormal in the first measurement, the slope being extraordinarily large. Hence, only the reproducible relations, obtained usually in the second or the third measurement, are recorded. Current-potential transient (*I-V* curve) by the potential sweep method was observed as a function of potential range and sweep rate. A series of measurements mentioned above is repeated by changing solution pH by addition of conc. HI or H<sub>2</sub>SO<sub>4</sub>.

All measurements were conducted at 25±0.05°C. Potentials are presented on the normal hydrogen electrode scale (NHE) in the text.

## § 2 Results

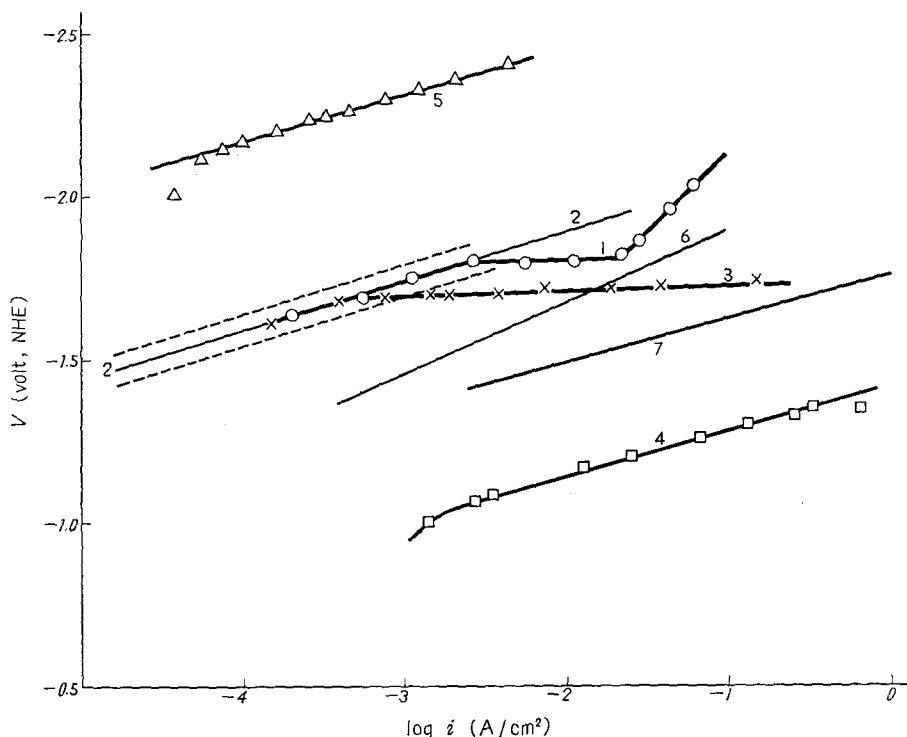
### 2-1 The Tafel relation

2-1-1 The Tafel relations are illustrated in Fig. 1. Curve 1 (○) represents a typical Tafel relation in 1N TMA-OH obtained by the galvanostatic pulse method. The potential first changes linearly with log *i* with a slope of *ca.* 0.15 v (the first region), then stays almost constant (the second region) and finally changes with large slope (the third region). The second region appears at *ca.* -1.8 v. Curve 2 obtained from *I-V* curve by the potential sweep method, reproduced the first region of curve 1 without showing the second region at the potential, -1.8 v. Dotted lines in the figure indicate the limit in fluctuation of Tafel relations observed. The first region of curve 1 is expressed as,

$$V(\text{volt, NHE}) = -2.20 - 0.15 \log i + 0.11 \log [\text{TMA-OH}]$$

at  $V > -1.8$  v, (1)

where the last term arises from the results described in the next section. Curve 3 (×) represents the Tafel relation in 1N NaOH quoted from Part 1.<sup>1)</sup> It is interesting to see that at low current densities, curve 3 is coincident with curves 1 and 2, whereas the horizontal region appears at the potential



**Fig. 1.** Tafel relations on Hg in alkaline and acidic solutions at  $25 \pm 0.05^\circ\text{C}$   
 1, 1N TMA-OH (galvanostatic); 2, 1N TMA-OH (potential sweep);  
 3, 1N NaOH<sup>1)</sup>; 4, 1N H<sub>2</sub>SO<sub>4</sub><sup>1)</sup>; 5, 0.1N TMA-OH on dropping Hg by  
 JOFA *et al.*<sup>3)</sup>; 6, the Tafel relation for TMA<sup>+</sup> ion discharge at [TMA<sup>+</sup>]  
 = 1N; 7, the Tafel relation for Na<sup>+</sup> ion discharge at [Na<sup>+</sup>] = 1N.<sup>1)</sup>

0.1 v more positive than that of curve 1. The appearance of the horizontal region in curve 3 was attributed to the accumulation of sodium on electrode surface.<sup>1)</sup> Curve 4 shows the results in 1N H<sub>2</sub>SO<sub>4</sub>.<sup>1)</sup> No break is observed, though the depolarization at low current density appears.

**2-1-2** Effect of TMA-OH concentration, [TMA-OH], on the Tafel relation was studied in 0.01, 0.1 and 1N solutions. Results are shown in Fig. 2. The effect of [TMA-OH] on  $V$  is estimated on an average as  $(\partial V / \partial \log [\text{TMA-OH}])_i = -0.11$  v at low current densities. At high current densities, however, the Tafel relation for 0.01 and 0.1N solutions shows a steep linear line without the second region as for 1N solution. The break potential shifts in the negative direction with decrease of [TMA-OH], *e.g.*, -1.9 v in 0.1N TMA-OH.

**2-1-3** Effect of pH on the Tafel relation was studied by adding successively

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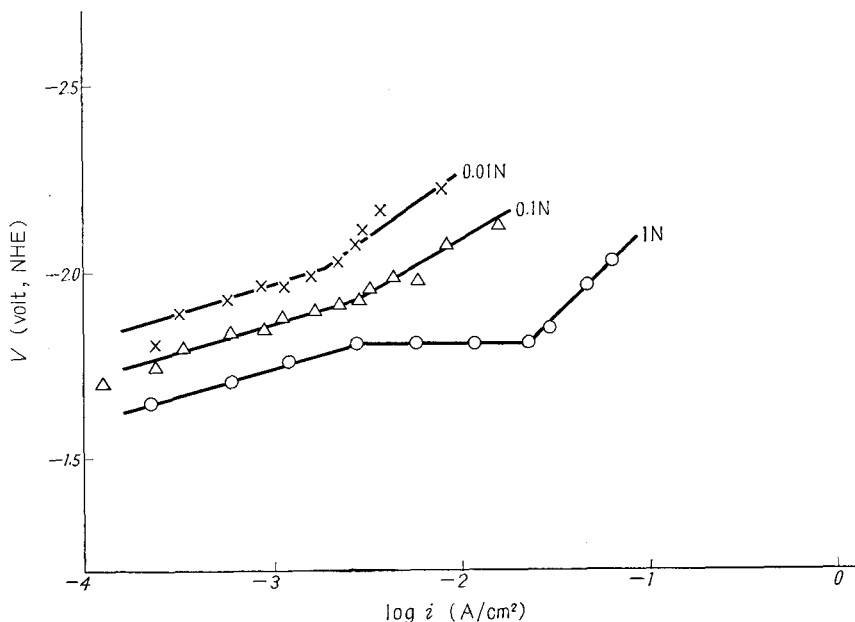


Fig. 2. The Tafel relation on Hg in TMA-OH solutions of different concentration at  $25 \pm 0.05^\circ\text{C}$ .

a small quantity of conc. HI or 1N TMA-OH into the solution of 0.1N TMA-OH or 0.1N TMA-I, respectively. Concentration of  $\text{TMA}^+$  ion  $[\text{TMA}^+]$ , was practically constant during these additions. Results show that the pH effect on  $V$  at a constant current density is very similar to the effect of  $[\text{TMA-OH}]$  on  $V$  and hence that the value of  $(\partial V / \partial \log [\text{TMA-OH}])_i = -0.11 \text{ v}$  in TMA-OH solution is mainly attributed to the pH effect. Absence of  $[\text{TMA}^+]$  effect or minor one, if any, is also supported by the agreement of the Tafel relation observed in NaOH with that in TMA-OH solution (Fig. 1) at low current densities.

## 2-2 Galvanostatic transient

Three regions of potential mentioned above (curve 1 in Fig. 1) are now investigated in detail by observing the galvanostatic transients.

2-2-1 Figure 3 shows galvanostatic charging curves obtained in 1N TMA-OH with representative current densities for the first and third regions of the Tafel relation, *i. e.*,  $i = 0.375$  (curve, a) and  $46.7$  ( $\text{mA}/\text{cm}^2$ ) respectively. Curve a indicates a small halt at the beginning, whereas curve b shows another much more definite halt before the steady state is reached (called the first and second halt respectively). The potential of the inflexion point

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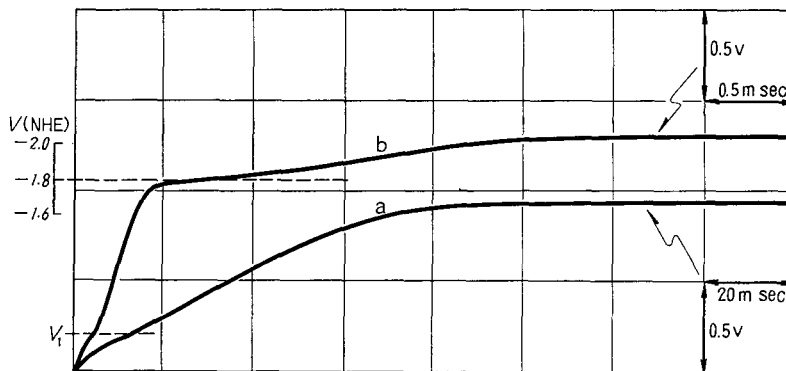


Fig. 3. Charging curve in 1N TMA-OH at constant current densities ( $25 \pm 0.05^\circ\text{C}$ ) a,  $i = 0.375 \text{ mA/cm}^2$ ; b,  $i = 46.7 \text{ mA/cm}^2$ .

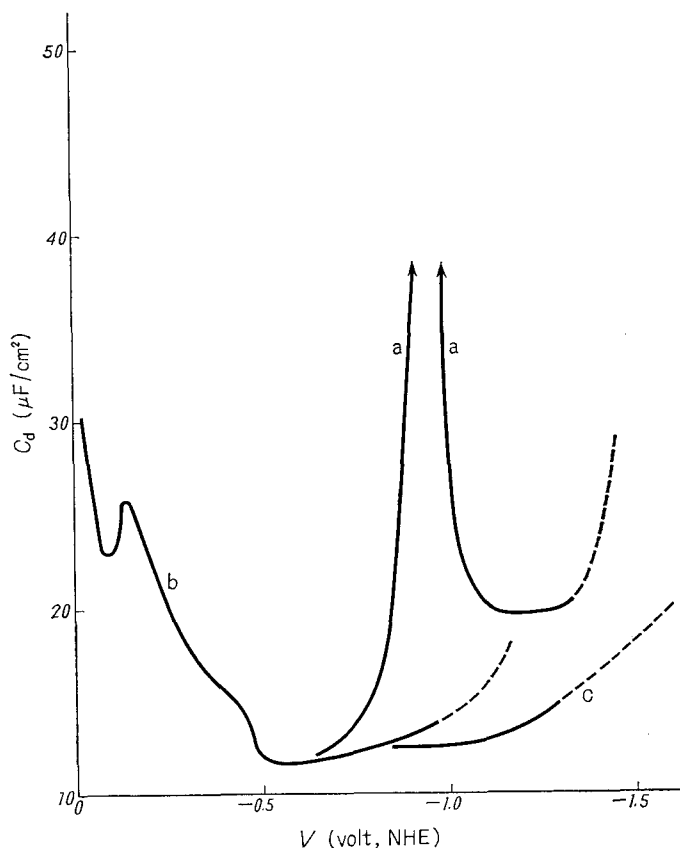
TABLE 1. Value of  $V_1$  and  $q_1$  on Hg as a function of pH and current density in 1N TMA<sup>+</sup> at  $25 \pm 0.05^\circ\text{C}$

pH	$i$	$V_1$	$q_1$	Solution
	(mA/cm <sup>2</sup> )	(v, NHE)	(Coul./cm <sup>2</sup> )	
13.9	0.576	-1.10	$4.3 \times 10^{-6}$	1N (CH <sub>3</sub> ) <sub>4</sub> NOH
"	5.69	-1.01	3.1 "	"
"	56.5	-1.14	4.8 "	"
13.5	2.79	-1.22	1.8 "	~1N (CH <sub>3</sub> ) <sub>4</sub> NOH
"	5.69	-1.15	6.3 "	+ conc. H <sub>2</sub> SO <sub>4</sub>
12.6	0.576	-1.20	8.1 "	"
"	5.69	-1.24	9.1 "	"
11.3	"	-0.97	4.0 "	"
"	0.576	-1.15	7.3 "	"
10.5	"	-1.06	5.6 "	"
"	5.69	-1.08	5.8 "	"
9.8	"	-1.04	11.7 "	"
13.4	0.392	-0.94	5.7 "	~1N (CH <sub>3</sub> ) <sub>4</sub> NOH
"	1.08	-0.91	2.4 "	"
"	2.24	-0.96	6.3 "	"
"	4.15	-0.98	5.2 "	"
"	5.23	-0.99	5.8 "	"
"	10.7	-1.06	"	"
"	21.0	-0.95	3.1 "	"
"	42.0	-0.99	4.5 "	"

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of the first halt,  $V_1$ , and the electricity consumed up to  $V_1$ ,  $q_1$  (Coulomb/cm<sup>2</sup>), were found independent of pH and current density (Table 1). The first halt, however, is very sensitive to [TMA<sup>+</sup>]. It appears only to a noticeable extent in 0.5N TMA<sup>+</sup> solution but does not in 0.1 and 0.01N TMA<sup>+</sup> solutions.

Differential capacity in 1N TMA-OH was estimated as a function of potential from a slope of the charging curve and the current density used, by the equation,  $C_d = i/(dV/dt)$ . Figure 4, represents the result at  $i = 1$  mA/cm<sup>2</sup> (the first region) in 1N TMA-OH in comparison with those in 1N H<sub>2</sub>SO<sub>4</sub> and 1N NaOH.  $C_d$ - $V$  curve in 1N TMA-OH (curve, a) shows a maximum at  $V = -0.9 \sim -1.0$  v, as expected from the charging curve (Fig. 3, curve a,  $V_1$ ),



**Fig. 4.** Differential capacity on Hg estimated from charging curves in alkaline and acidic solutions as a function of potential ( $25 \pm 0.05^\circ\text{C}$ ).  
 a, 1N TMA-OH; b, 1N H<sub>2</sub>SO<sub>4</sub><sup>(1)</sup>; c, 1N NaOH<sup>(1)</sup>.  
 Charging curves are taken at  $i = 1$  mA/cm<sup>2</sup>.

whereas in  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  solutions, no maximum was observed<sup>1)</sup> at the potential mentioned above (curves b and c). Such a contrast and the dependence of the first halt on  $[\text{TMA}^+]$  clearly indicate that the  $\text{TMA}^+$  ion plays an important role in the charging process. Maximum value of  $C_d$  was not obtained with certainty because of difficulty in accurate determination of  $dV/dt$  at around the inflexion point. Final increase of  $C_d$  as indicated by dotted lines in the figure is due to the approach of potential to the steady value. The second halt in the charging curve is found at potential much more negative than  $V_1$ . The potential value at the second inflexion point,  $V_2$ , is close to the potential,  $-1.8$  v, of the second region mentioned above (1N TMA-OH).  $V_2$  values in 0.1 and 0.01N TMA-OH are not so definite as in 1N solution but seem to be almost the same with the break potential in the Tafel relation for the respective solutions (Fig. 2). The electricity consumed at the halt was roughly estimated as  $2 \times 10^{-6} \sim 2 \times 10^{-5}$  Coulomb/cm<sup>2</sup>. Its dependence on current density and  $[\text{TMA-OH}]$  is not clear at the present time. In 1N TMA-OH, the charging curve with a current density corresponding to the second region, reveals the steady potential at the second halt.

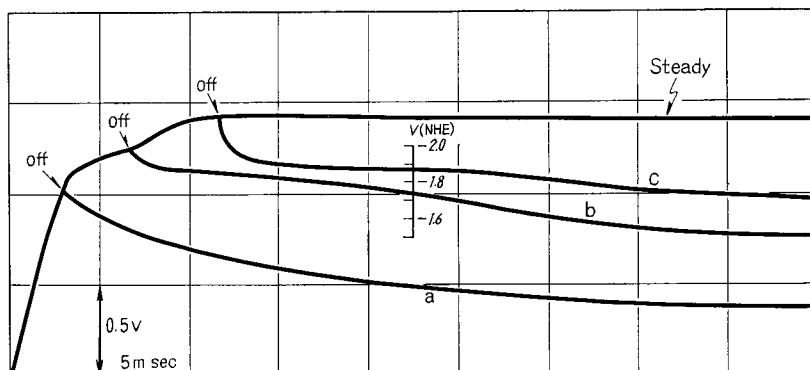


Fig. 5. Decay curves with different potentials at switching off the current ( $i=5.85$  mA/cm<sup>2</sup>, 0.1N TMA-OH,  $25 \pm 0.05^\circ\text{C}$ ).

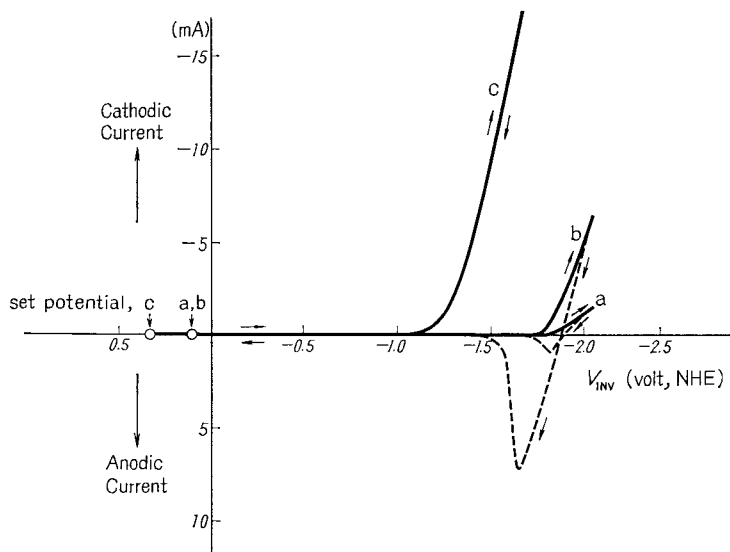
2-2-2 Figure 5 illustrates decay curves of the galvanostatic transient at  $i=5.85$  mA/cm<sup>2</sup> in 0.1N TMA-OH. The curve a, of which potential before cutting off the current,  $V_s$ , is more positive than  $-1.9$  v, shows a smooth potential decay but with extremely slow rate in comparison with that in acidic solution<sup>1)</sup>. Curves b and c with  $V_s$  more negative than  $-1.9$  v show a stagnation of potential at ca.  $-1.9$  v and then a gradual decay. The potential at the stagnation is nearly same with the potential of the second region (1N TMA-OH) or the break (0.1, 0.01N TMA-OH) of the Tafel

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relation and of the second halt in the charging curve. In 1N TMA-OH, the decay curve with  $V_s$  more negative than  $-1.8$  v shows a markedly irregular potential variation after its stagnation at *ca.*  $-1.8$  v, as observed in NaOH solution.

### 2-3 Potential sweep transient

We now applied a potential sweep to the electrode, where potential was swept proportionally to the time, first from a set potential in the negative direction and then inverted at a potential,  $V_{INV}$ , towards the set value. The set potential was the rest potential in the most cases. Figure 6 shows typical



**Fig. 6.**  $I$ - $V$  curves on Hg by the potential sweep method in alkaline and acidic solutions ( $25 \pm 0.05^\circ\text{C}$ ).  
a, 1N TMA-OH; b, 1N NaOH<sup>1)</sup>; c, 1N H<sub>2</sub>SO<sub>4</sub><sup>1)</sup>;  
Sweep rate, 4v/1.1 min.

$I$ - $V$  curves in 1N TMA-OH, 1N NaOH and 1N H<sub>2</sub>SO<sub>4</sub>, respectively. Curve a in 1N TMA-OH reveals a hysteresis, which clearly supports the presence of the discharged substance, as in the case of NaOH solution<sup>1)</sup> (curve, b). No hysteresis is observed in 1N H<sub>2</sub>SO<sub>4</sub><sup>1)</sup> (curve, c). The  $I$ - $V$  curve was now investigated as a function of  $V_{INV}$ , sweep rate, pH and [TMA-OH], respectively.

#### 2-3-1 Effect of $V_{INV}$

Figure 7 shows  $V_{INV}$  effect on the  $I$ - $V$  curve at a constant sweep rate of 4 v/1.1 min in 1N TMA-OH. Curve a with  $V_{INV} \sim -0.9$  v indicates a small but definite hysteresis. Curve b with  $V_{INV} \sim -1.5$  v, on the other hand, shows

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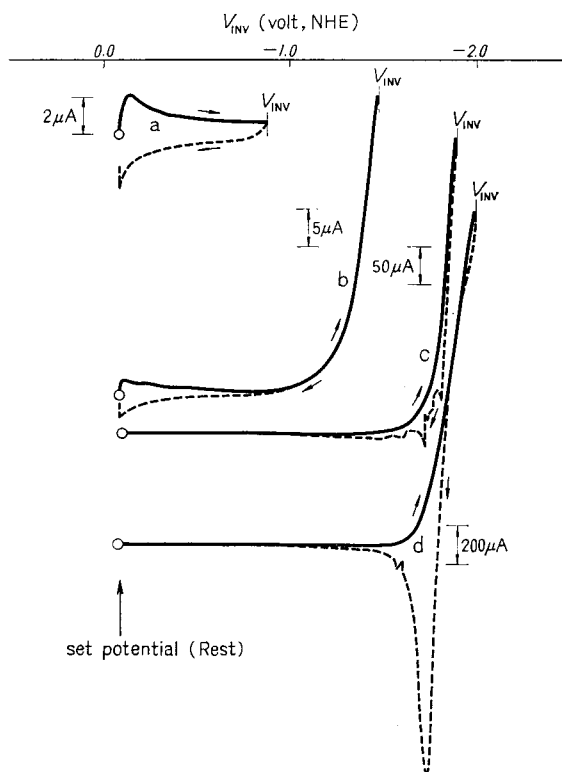


Fig. 7.  $I$ - $V$  curves on Hg as a function of  $V_{INV}$  in 1N TMA-OH. Sweep rate, 4 v/1.1 min; Temp.,  $25 \pm 0.05^\circ\text{C}$ .

almost reversible behaviour except for the part of small current mentioned above. When  $V_{INV}$  is shifted to more negative value, *e.g.*,  $-1.9 \sim -2.0$  v, other hysteresis appears (curves c and d). The latter hysteresis is observed to commence at  $V_{INV} = -1.8$  v in 1N TMA-OH and become increasingly large with decrease of  $V_{INV}$ .

Now we define the electricity,  $Q$ , as<sup>1)</sup>

$$Q = \frac{1}{2}(Q_c - Q_a), \quad (3)$$

where  $Q_c$  and  $Q_a$  are the electricity for the area of  $I$ - $V$  curve before and after the potential inversion. They are taken positive for the negative charge. The factor 1/2 in Eq. (3) arises from the assumptions that the substance accumulated during the forward cathodic sweep, dissolves into the solution giving back the electron to the electrode during the anodic sweep, and that

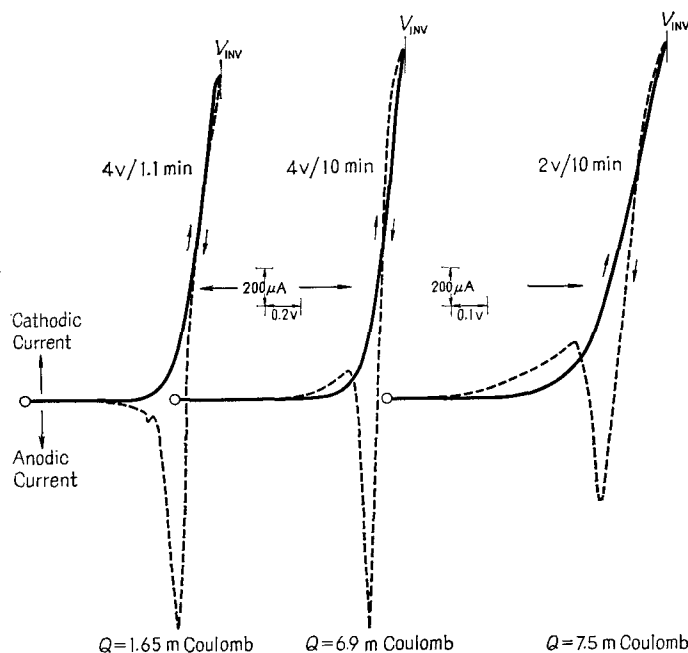
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the contribution of the h.e.r. to  $Q_c$  and  $Q_a$  is same.

### 2-3-2 Effect of the sweep rate on $Q$

A series of  $I$ - $V$  curves was observed as a function of the sweep rate in 1N TMA-OH, keeping the value of  $V_{INV}$  constant.

With regard to the first small hysteresis,  $Q$  was approximately independent of the sweep rate studied, (4 v/1.1 min  $\sim$  1 v/10 min) and of [TMA-OH]. The second large hysteresis, on the other hand, shows a sweep rate dependence; namely, the  $Q$  decreases with increase of the sweep rate in



**Fig. 8.**  $I$ - $V$  curves on Hg as a function of the sweep rate in 1N TMA-OH ( $25 \pm 0.05^\circ\text{C}$ ).

1N TMA-OH as shown in Fig. 8. Figure 9 represents the dependence of  $Q$  on the time required for the attainment of the potential change of one volt. Experimental points are not enough in number but from the analogy with the case of  $\text{Na}^+$  ion discharge<sup>1)</sup>, the  $Q$  seems to increase proportionally to the time or inversely proportionally to the sweep rate at a rapid scanning, *i. e.*,

$$Q \propto 1/v \quad \text{at const. } V_{INV} \text{ and 1N TMA-OH,} \quad (4)$$

where  $v$  is the sweep rate.

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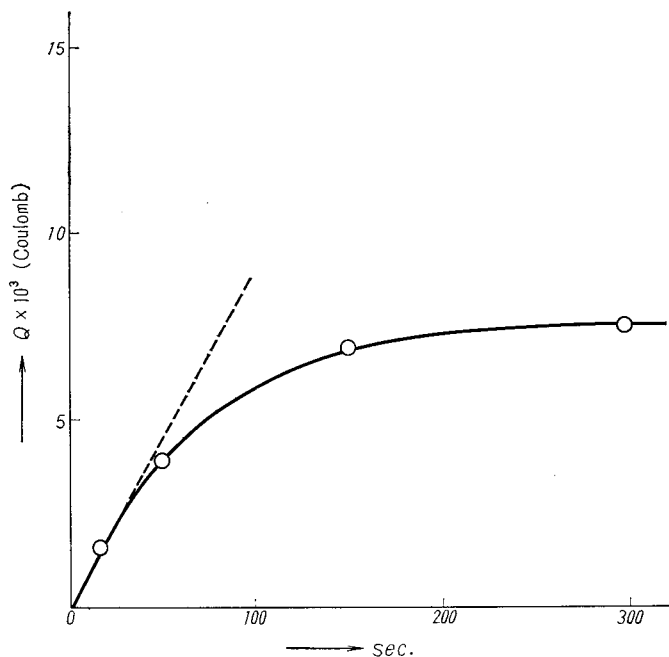


Fig. 9.  $Q$  as a function of the time required for the attainment of the potential change of one volt in 1N TMA-OH at  $25 \pm 0.05^\circ\text{C}$ .

### 2-3-3 Effect of pH and $[\text{TMA}^+]$ on $Q$

Results of  $Q$  at different pH's and  $[\text{TMA}^+]$ 's are summarized as a function of  $V_{\text{INV}}$  in Fig. 10. The figure is discussed as follows.

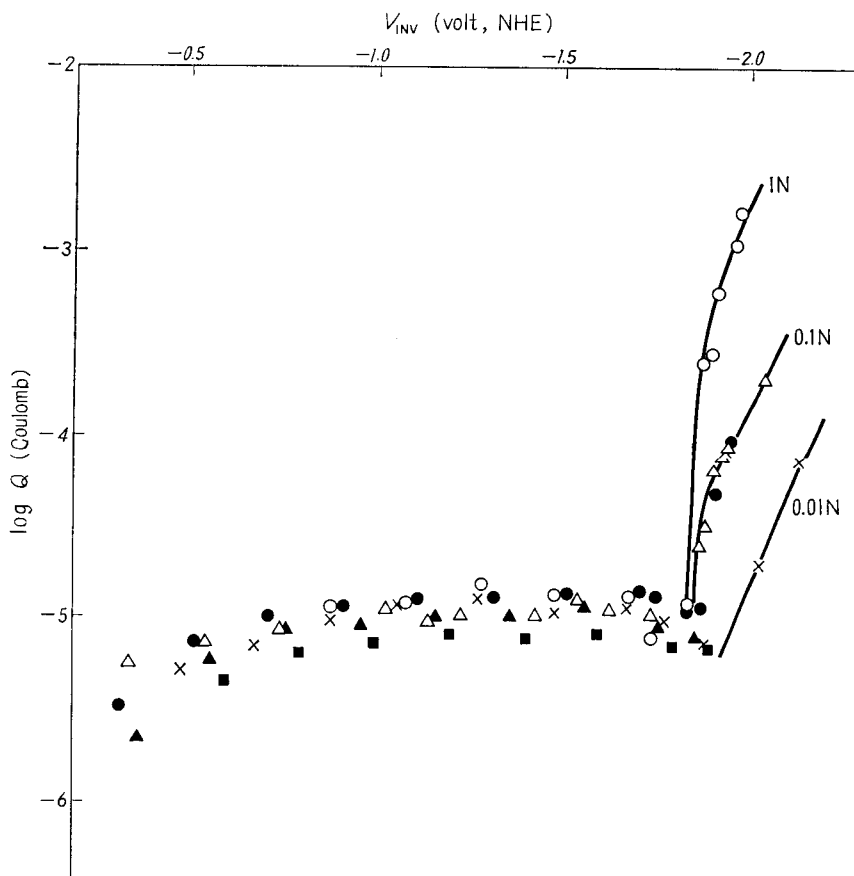
a) At  $V_{\text{INV}}$  more negative than  $-1.9$  v (A region), logarithm of  $Q$  increases almost linearly with decrease of  $V_{\text{INV}}$  at constant  $[\text{TMA-OH}]$ . Log-log plot of  $Q$  against  $[\text{TMA-OH}]$  at constant  $V_{\text{INV}}$  yields a straight line with a slope of unity. Thus,  $Q$  is proportional to  $[\text{TMA-OH}]$ . The curve, 0.1N, in Fig. 10 includes the results obtained in solutions of 0.1N  $\text{TMA}^+$  with different pH's, *i.e.*, the symbols,  $\triangle$  and  $\bullet$ , represent the data for 0.1N TMA-OH and 0.1N TMA-I, respectively. They fall into one and the same line, which shows the absence of pH effect. Consequently,  $Q$  is expressed from the figure as,

$$Q = k \cdot [\text{TMA}^+] \cdot \exp(-\alpha FV/RT), \quad (5)$$

where  $k$  is a constant at a given sweep rate and  $\alpha$  is  $0.27 \pm 0.03$  on an average.

b) In the region of  $-1.0 > V_{\text{INV}} > -1.8$  v (B region),  $Q$  is very small compared with that of A region and almost constant, *ca.*  $10^{-5}$  Coulomb, being independent of  $V_{\text{INV}}$  and  $[\text{TMA}^+]$ .

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**Fig. 10.**  $\log Q$  vs  $V_{INV}$  curves as a function of pH and the concentration of TMA<sup>+</sup> ( $25 \pm 0.05^\circ\text{C}$ ).

Sweep rate, 4 v/1.1 min: ○, 1N TMA-OH; △, 0.1N TMA-OH; ×, 0.01N TMA-OH; ●, 0.1N TMA-I; ▲, 0.1N TMA-I+TMA-OH (pH=12.1); ■, 0.1N TMA-I+TMA-OH (pH=12.7).

c) At  $V_{INV} > -1.0$  v, a tendency of  $Q$  becoming smaller with increase of  $V_{INV}$  is noticed.

#### 2-4 Rest potential

Present authors concluded that an open circuit potential, *i.e.*, the rest potential,  $V_r$ , of Hg in NaOH solution is determined by the presence of HgO on the electrode surface. Its presence in TMA-OH solution is also confirmed as shown in Fig. 11. The  $I$ - $V$  curve shows large anodic and cathodic current peaks, which located in the right and left hand sides respectively of

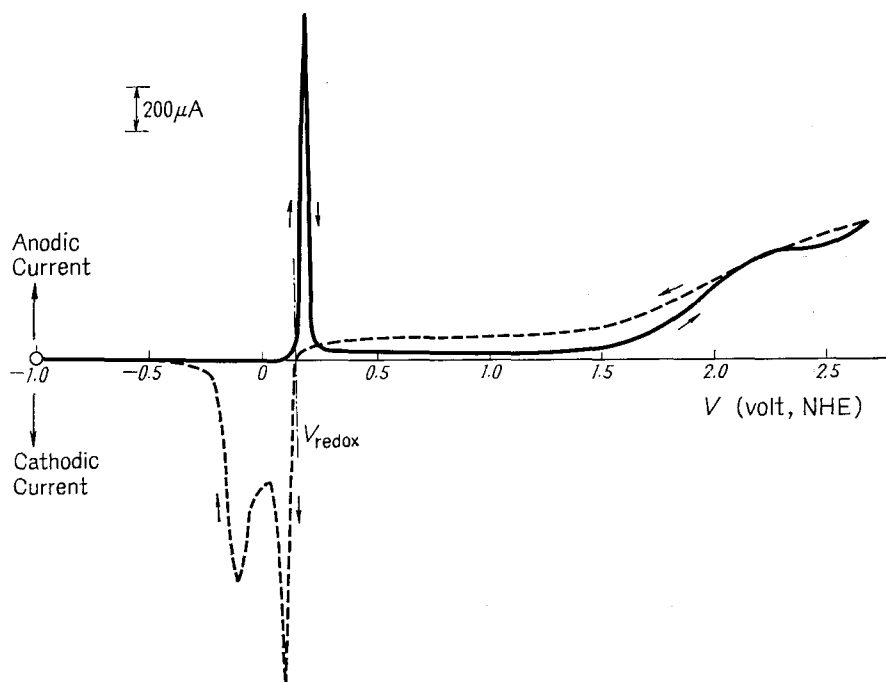


Fig. 11.  $I$ - $V$  curve on Hg by the potential sweep of anodic polarization in 1N TMA-OH at  $25 \pm 0.05^\circ\text{C}$ . Sweep rate, 4 v/1.1 min.

the potential designated as  $V_{\text{redox}}$ . The latter potential is in agreement with the equilibrium potential of the reaction,  $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + e^-$ , at given experimental conditions. The fact that  $V_r$  observed is very close to  $V_{\text{redox}}$ , leads to the conclusion that the rest potential is also determined in TMA-OH solution by the presence of HgO on mercury electrode surface.

### § 3 Discussion

#### The Tafel relation

Present Tafel relation is essentially different from that observed by JOFA *et al.*<sup>3)</sup> on dropping mercury electrode in 0.1N TMA-OH (curve 5 in Fig. 1). In the present case, the Tafel relation consists of three linear parts and overvoltage is much smaller than JOFA's. We used several TMA-OH of special grade supplied from different companies but could not find any difference in the results. Further, we carried out experiments on dropping mercury electrode instead of the hanging one, which showed no difference between them. Thus, we could not reproduce JOFA's Tafel relation. It must be mentioned here that the Tafel relation observed by JOFA *et al.* is located in the potential

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region more negative than  $-1.8$  v, where the electrode surface is expected to be much disturbed by the accumulation of the discharged substance of  $\text{TMA}^+$  ion.

**Activity of Hg for the hydrogen electrode reaction**

Coincidence of the first region of the Tafel relation in 1N TMA-OH with that in 1N NaOH (Fig. 1) is one of the evidences that the Tafel relation at these low current densities represents the kinetics of the h.e.r. itself. Thus, we can estimate the activity of Hg for the hydrogen electrode reaction in alkaline solution as follows. The first region is expressed in terms of overvoltage,  $\eta$ , and current density as,

$$\eta = 1.36 + 0.15 \cdot \log i$$

at unit concentration of alkaline solution. The overvoltage is defined here as the minus of the test electrode potential referred to the reversible hydrogen electrode in the same environment. Exchange current density,  $i_0$ , which is taken as the measure of the activity, is estimated from the above equation as  $8.5 \times 10^{-10}$  A/cm<sup>2</sup>. This value is about  $10^2 \sim 10^3$  times larger than that in acidic solution<sup>4)</sup>.

**Discharge of  $\text{TMA}^+$  ion**

Abnormal behaviours observed around  $-1.8$  v, *i.e.*, (i) the appearance of the second region in the Tafel relation, (ii) the second halt in charging curve, (iii) the potential stagnation in decay curve, and (iv) the hysteresis in  $I$ - $V$  curve, lead to the conclusion that the  $\text{TMA}^+$  ion discharges and the discharged substance accumulates on the electrode surface at potentials more negative than  $-1.8$  v. Since  $Q$  of Eq. (5) is the integrated quantity of the electricity consumed for the accumulation up to the potential,  $V_{\text{INV}}$ , the differentiation of  $Q$  with respect to  $V_{\text{INV}}$  and simple transformation of  $dQ/dV$  to  $(dQ/dt) \times (dt/dV)$  yield

$$i = (kv/A) \cdot [\text{TMA}^+] \cdot (-\alpha F/RT) \cdot \exp(-\alpha F/RT),$$

where the subscript INV was omitted, and

$$i = dQ/dt$$

$$v = dV/dt \quad (\text{Sweep rate of potential})$$

$$A; \quad \text{Surface area.}$$

The first factor of the right hand side of the above equation,  $(kv/A)$ , is constant independent of  $v$ , since  $k$  is inversely proportional to  $v$  according to Eq. (4) where  $Q$  is equal to  $k$ . Thus, we have

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$$i = i_0 \cdot [\text{TMA}^+] \cdot \exp(-\alpha FV/RT),$$

where  $i_0 (= -kv\alpha F/ART)$  is estimated from Fig. 10 as  $(2.14 \pm 0.52) \times 10^{-10}$  A/cm<sup>2</sup>, or

$$-V(\text{volt, NHE}) = (2.10 \pm 0.34) - (0.217 \pm 0.032) \{ \log [\text{TMA}^+] - \log i \}. \quad (6)$$

Equation (6) is compared with the Tafel relation observed and that of Na<sup>+</sup> ion discharge in Fig. 1 (curves, 6 and 7). One can see that the TMA<sup>+</sup> ion discharge is much faster than the h.e.r. though slower than Na<sup>+</sup> ion discharge.

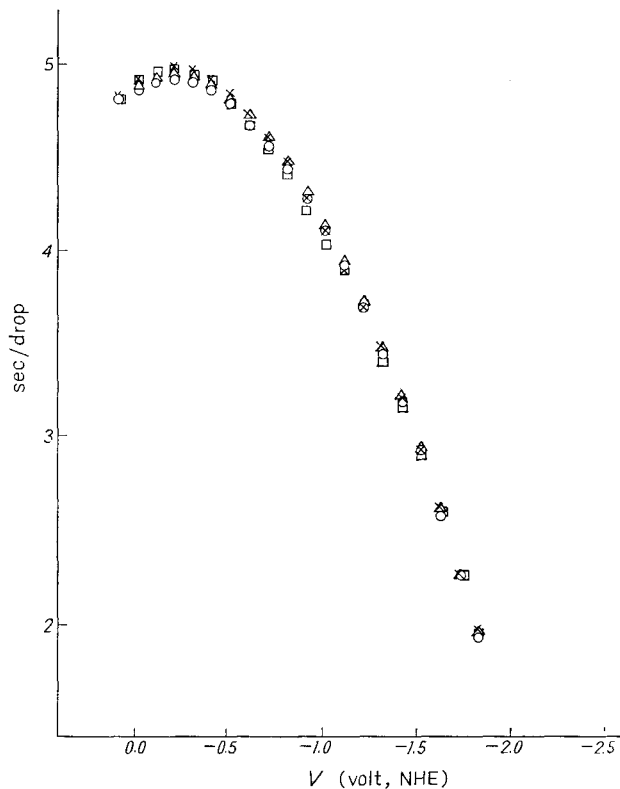
It is thus expected as in the case of Na<sup>+</sup> ion that the discharge of TMA<sup>+</sup> ion is the first step of the h.e.r. in alkaline solution if Eq. (6) holds in the first region of potential. Discharged substance will then react with water molecule, resulting in the formation of hydrogen molecule. In this case, the latter process includes the rate-determining step of the h.e.r.. Effect of aliphatic quaternary ammonium salts on the h.e.r. has been studied by several authors. ANDREEVA<sup>6)</sup> reported no effect of TMA<sup>+</sup> ion on the hydrogen overvoltage in 1 and 6.8N HCl solutions. This result is expected from the present study, since the TMA<sup>+</sup> ion discharge cannot be the elementary step of the h.e.r. in acidic solution because of its slow rate as seen from Fig. 1. The h.e.r. will take place *via* H<sup>+</sup> discharge with much faster rate in acidic solution.

In the first region of the Tafel relation, surface concentration of the reaction intermediate (*i.e.*, the discharged substance) will be determined by the steady state condition and will increase with increase of current density. Appearance of the second region at  $-1.8$  v may be understood owing to the formation of new surface state as a result of the accumulation, *e.g.* amalgam formation<sup>7)</sup> or coagulation of the substance. Absence of the second region in curve 2 (Fig. 1) obtained by the potential sweep method may be attributed to the shortcoming of time for the discharged substance to accumulate enough to change the surface state. Similarly, the absence of the second region in 0.1 and 0.01N TMA-OH solutions (Fig. 2) is attributed to the decrease in the rate of TMA<sup>+</sup> ion discharge in accordance with Eq. (5). One of the possible explanations for the appearance of the third region is the switch of the electrode reaction from the h.e.r. to another one, for instance, electrochemical reduction of TMA<sup>+</sup> ion on mercury (dilute solutions in Fig. 2) or on the above mentioned new surface in 1N TMA-OH. Further study will be required to clarify the situation.

#### The first halt, capillary curve and Q of the B region (Fig. 10)

Dependence of  $q_1$  on [TMA-OH] clearly suggests that the first halt of the charging curve be connected to the behaviour of TMA<sup>+</sup> ion at the inter-

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**Fig. 12.** Dropping time *vs* potential in various alkaline solutions.  
 ○, 1N KOH, △, 0.999N KOH+0.001N TMA-OH;  
 ×, 0.95N KOH+0.05N TMA-OH; □, 0.8N KOH +  
 0.2N TMA-OH.

face. Its value of  $ca. 5 \times 10^{-6}$  Coulomb/cm<sup>2</sup> in 1N TMA-OH (Table 1) corresponds to the formation of  $3 \times 10^{13}$  species/cm<sup>2</sup>, assuming adsorption *via* a single electron transfer to TMA<sup>+</sup> ion. If the latter assumption is valid, one can expect a difference in the electrocapillary curve by the introduction of TMA<sup>+</sup> ion into the solution. Figure 12 shows the electrocapillary curves in 1N KOH (○) and KOH+TMA-OH (other symbols), where the dropping time is plotted against the potential. The zero charge potential in 1N KOH reproduced the reported value.<sup>8)</sup> No difference is noticed in data upon the introduction of TMA<sup>+</sup> ion within an experimental error.\*<sup>3)</sup> Thus, we cannot explain the first halt by the adsorption phenomena.

\*<sup>3)</sup> Depression of the surface tension caused by the presence of TMA<sup>+</sup> has been reported<sup>9)</sup> in contrast to the present case, though the solution is neutral.

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$Q$  value defined by Eq. (3), on the other hand, reaches the value, *ca.*  $10^{-5}$  Coulomb/drop or  $3 \times 10^{-4}$  Coulomb/cm<sup>2</sup> at a potential of *ca.*  $-1.0$  v and stays constant up to  $-1.8$  v (B region in Fig. 10). The electricity required for charging up the double layer during the potential sweep (from the rest potential,  $0.08$  v in 1N TMA-OH, to  $-1.0$  v) is estimated in order of magnitude as  $10^{-5}$  Coulomb/cm<sup>2</sup> by using curves *b* and *c* of Fig. 4. Hence, the contribution of the charging process to  $Q$  is negligible. It must be mentioned here that  $Q$  value is the right order for a monolayer quantity of adsorbate assuming  $10^{15}$  adsorption sites per unit area. Since the rest potential was concluded as determined by the presense of HgO, the above  $Q$  value might be attributed to the reduction of HgO present on the surface.

#### Literatures

- 1) H. KITA and T. KURISU, This Journal, **18**, 1, (1970).
- 2) J. HEYROVSKY, *Polarographie*, Wien, Springer (1941).
- 3) S. JOFA, A. N. FRUMKIN and E. MASNICHENKO, Zhur. Fiz. Khim., **31**, 2042 (1957).
- 4) H. KITA, J. Electrochem. Soc., **113**, 1095 (1966).
- 5) A. N. FRUMKIN, *Adv. in Electrochemistry and Electrochemical Engineering*, vol. 1 Ed. P. DELAHAY and C. W. TOBIAS, Interscience Publishers, New York, London, (1961).
- 6) E. ANDREEVA, Zhur. Fiz. Khim., **29**, 699 (1955).
- 7) B. N. KABANOV, I. I. ASTAKHOV, I. G. KISELEVA, Uspekhi Khim., **34**, 1813 (1965).
- 8) D. C. GRAHAME, Chem. Rev., **41**, 441 (1947).
- 9) N. K. ADAM, "The physics and chemistry of surfaces" 3rd Ed. Oxford Univ. Press, London (1941).