Studies on the Vibrated Dropping Mercury Electrode. II. Electrocapillary Characteristics of the Current-Voltage Curve

By Hideo IMAI, Shōkichi CHAKI and Senkichi INOUYE

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The theory of the limiting current of the vibrated dropping mercury electrode (VDME) has been given in the previous report[1], and it was shown that the limiting current increases about ten times when the mean velocity of the vibration is of the order of several centimeters per second. This result suggests the potentiality of the "VDME" method for improving the sensitivity of polarographic determinations. The surface charge density of the dropping mercury electrode (DME), however, exerts an influence on the velocity of the vibration, and accordingly, it controls the limiting current. Thus, the linear relation of the limiting current with the depolarizer concentration was not always obtained. Moreover, the remarkable effect of surface active materials on the limiting current and the effect of the vibration on the summit potential of a polarographic maximum or on potential of the electrocapillary maximum (the Lippmann-potential) were observed. These results are presented and discussed in this report.

Experimental

The apparatus used was described in the previous report[1] and was not modified in any detail.

All the reagents were of analytical grade, and were used after the recrystallization. The test solution was prepared in the same way as that described in the previous report[1].

When the reduction potential of a depolarizer was adjoining the Lippmann-potential, the plateau of the limiting current was not well-defined. On this occasion, the limiting current was measured at a potential optionally determined.

The increase in the current-sensitivity owing to the vibration was expressed by the ratio, (i_l/i_d), of the limiting current against the diffusion-controlled current measured at the same potential. All measurements were made at 25.0±0.1°C.

Results and Discussion

1. Variation of Limiting Current with Depolarizer Concentration.—This relation was investigated in the cases of the mercuric, thallous, cadmium, nickel and zinc ions. The concentration ranged from 0.005 to 10 mF. The test solution contained 0.1 F potassium chloride or potassium nitrate as the supporting electrolyte, and a small

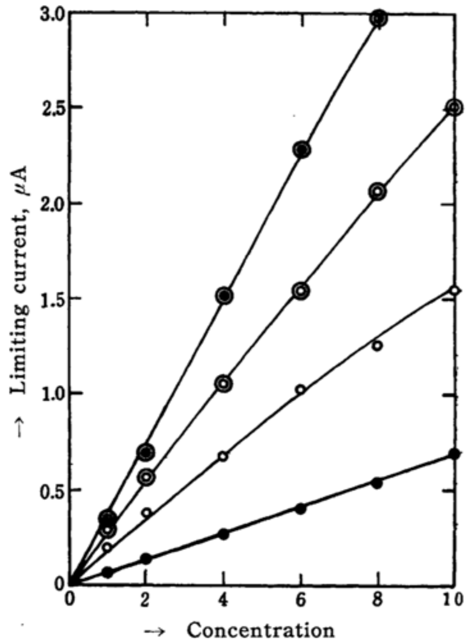

Fig. 1. The variation of the limiting current with the concentration of the zinc ion.
● : i_d of 10^{-3}, 10^{-4} and 10^{-5} F order
○ : i_l of 10^{-3} F order
◎ : i_l of 10^{-4} F order
◉ : i_l of 10^{-5} F order
The value of the current in the ordinate must be multiplied by the factor of 100, 10 and 1 μA for the concentration order of 10^{-3}, 10^{-4} and 10^{-5} F, respectively. E= 0.38 V./cm. (25 c. p. s.). m=1.81 mg./sec. t=4.1$_9$ sec. (open circuit). The supporting electrolyte=0.1 F KCl. The limiting current was evaluated at −1.2 V. vs. S. C. E.

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[1] H. Imai, S. Inouye and S. Chaki, This Bulletin, 32, 994 (1959).

TABLE I. THE VARIATION OF THE RATIO, i_l/i_d, WITH THE DEPOLARIZER CONCENTRATION (25°C)

Depolarizer concentration, mF	i_l/i_d				
	Hg^{2+} in KCl	Tl^+ in KNO_3	Cd^{2+} in KCl	Ni^{2+} in KNO_3	Zn^{2+} in KNO_3
10	—	—	—	—	2.0
5	—	—	—	—	2.5
1	5.7	3.0	3.2	3.3	3.5
0.5	5.6	2.8	3.4	3.8	4.3
0.1	5.7	2.8	3.3	4.0	5.0
0.05	5.6	2.7	3.2	4.3	6.0
0.01	—	2.8	3.2	4.6	7.0
0.005	—	2.6	3.4	4.8	—
E, V./cm.	0.4	0.38	0.38	0.38	0.38
t, sec.	8.3	6.2	6.2	6.1	4.2
m, mg./sec.	0.74	1.33	1.34	1.48	1.81

E is the intensity of the a. c. electric field (25 c. p. s.), t is the life-time of the DME and m is the rate of mercury flow.

quantity of the sodium sulfite solution was added to remove the trace of dissolved oxygen.

In the cases of the mercuric ion, the thallous ion and the cadmium ion, the plateau of the limiting current was not obtained. This is because the surface charge density of the DME markedly varies near Lippmann-potential which is adjacent to the reduction potential of the depolarizer in question. On the contrary, the nickel ion and the zinc ion developed a fairly well-defined wave except for the increase of the residual current.

The variation of the ratio, i_l/i_d, with the depolarizer concentration is given in Table I.

In the former three depolarizers of Table I, the value of i_l/i_d does not appreciably change with the depolarizer concentration. On the contrary, the value of i_l/i_d is inversely proportional to the depolarizer concentration in the latter two depolarizers, and a curvilinear plot of the limiting current versus the concentration is obtained as is shown in Fig. 1.

In this connection, the variation of the life-time of the DME with the depolarizer concentration was investigated, and the result is illustrated in Table II.

TABLE II. THE VARIATION OF THE LIFE-TIME OF THE DME WITH THE CONCENTRATION OF THE ZINC ION (25°C)

Concentration of the zinc ion, mF	Life-time of the DME, sec.	
	Open circuit	At −1.2 V. vs. S. C. E.
8	4.5_6	4.4_2
1	4.5_6	4.3_7
0.2	4.5_7	4.3_4
0.01	4.5_7	4.2_4
0.001	4.5_7	3.8_4

In Table II the life-time measured in the open circuit is independent of the depolarizer concentration, while the life-time measured at the more negative potential than the reduction potential of the zinc ion increases as the depolarizer concentration is increased.

The increase of the life-time can be assigned to the increase of the surface tension of the DME.

The surface tension increases as the surface-charge density decreases and the decrease of the surface charge density results in the retardation of the vibration. Thus, the curvilinear relation of Fig. 1 is attributable to the effect of the reductant on the surface charge density of the DME.

2. Effect of Surface Active Materials.— *2-i. Variation of limiting current with concentration of surface active materials.*—The variation of the limiting current of 1 mF zinc ion with the concentration of the surface active material such as gelatine, methyl cellulose or polyoxyethylene lauryl ether (LEO, the mean molecular weight= 862) was investigated. The result is illustrated in Fig. 2. In every case the effect of the vibration diminishes by the addition of the surface active material, the limiting current being reduced to the value of the diffusion-controlled current by the addition up to about 0.01%. This effect is attributable to the retardation of the vibration due to the decrease of the surface-charge density. The effect of gelatine is more pronounced than that of methyl cellulose, and the difference of the curvilinear relation in Fig. 2 seems to relate to the adsorption mechanism of the surface active material on the mercury surface.

2-ii. Current-voltage curve accompanied with adsorption and desorption of surface acitve material. — The effect of *n*-octyl alcohol on the current-voltage curve of 1 mF mercuric ion in 0.1 F potassium chloride was investigated. The limiting current markedly changes at two potentials which lie in the region of the anodic polarization and in the region of the cathodic polarization as is illustrated in Fig. 3. The potential of the current change at about −0.2 V. vs. S. C. E. and that of the current change at about −1.5 V. vs. S. C. E. correspond to the potential of the adsorption and that of the desorption of *n*-octyl alcohol, respectively, as is seen in comparison with the tensammetric curve appended in Fig. 3. From the fact that the limiting current changes with the adsorption or the desorption of the surface active material as is previously described in *2-i*, it is concluded that the change of the limiting current at about −0.2 V. vs. S. C. E. and that at about −1.5 V. vs. S. C. E. correspond to the decrease of the anodic current of the chloride ion owing to the adsorption of *n*-octyl alcohol and to the increase of the cathodic current of the mercuric ion owing to the desorption of *n*-octyl alcohol, respectively.

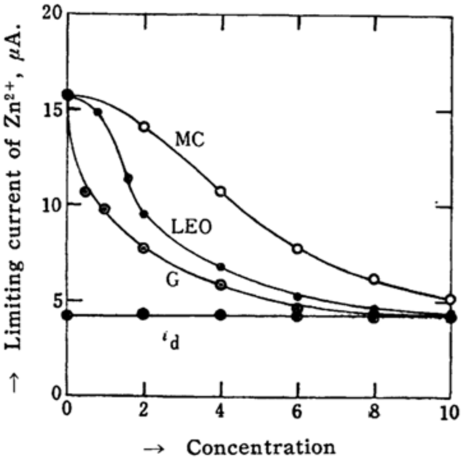


Fig. 2. The variation of the limiting current of the zinc ion with the concentration of the surface active material. The value of the concentration in the abscissa must be multiplied by the factor of 10^{-3} % for gelatine (curve G) and methyl cellulose (curve MC) or by the factor of 2.5×10^{-6} F for LEO. $(Zn^{2+})=1\times10^{-3}$ F. Refer the illustration given in Fig. 1 to the other experimental conditions.

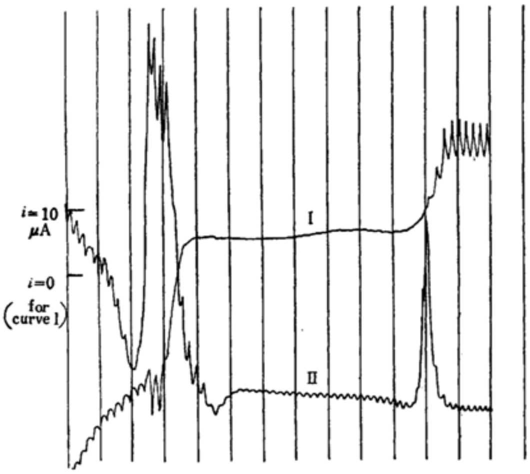


Fig. 3. The "VDME" current-voltage curve of the mercuric ion in the presence of *n*-octyl alcohol (curve I). $(Hg^{2+})=1\times10^{-3}$ F. The supporting electrolyte=0.1 F KCl. Curve II is the tensammetric curve of the same solution. The applied voltage starts from +0.2 V. vs. S. C. E., and each voltage interval corresponds to 0.15 V.

2-iii. Dependence of limiting current to frequency of vibration and to concentration of

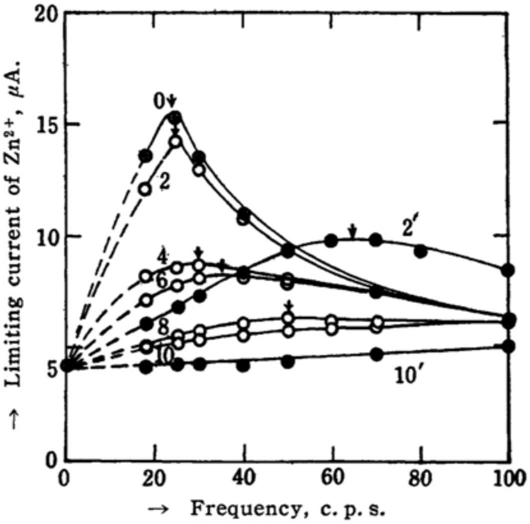


Fig. 4. The effect of the frequency of the a. c. electric field on the limiting current of the zinc ion in the presence of the surface active material. Curve 0 is obtained in the absence of the surface active material. Curves 2, 4, 6, 8 and 10 correspond to the concentration of methyl cellulose as great as 0.002, 0.004, 0.006, 0.008 and 0.01%, respectively. Curves 2′ and 10′ correspond to the concentration of gelatine as great as 0.002 and 0.01%, respectively. The maximum point of curve 10′ appears at about 200 c. p. s. $(Zn^{2+})=1\times10^{-3}$ F. Refer the illustration given in Fig. 1 to the other experimental conditions.

surface active material.—The dependence of the limiting current of the zinc ion to the frequency of the vibration was investigated in the presence of gelatine or methyl cellulose of various concentrations. The result is illustrated in Fig. 4. Under the vibration of the frequency less than 20 c. p. s., the mercury droplet is shaken off by the violent vibration in the absence of the surface active material, and the effect of the vibration on the limiting current gradually decreases as the frequency of the vibration increases. Thus, the limiting current gives a maximum at about 25 c. p. s. In the presence of the surface active material, the frequency of the vibration, which gives the maximum limiting current, shifts toward higher frequencies as the concentration of the surface active material increases. In connection with this effect, the difference between gelatine and methyl cellulose is noticeable as is pointed out in *2-ii*.

3. Effect of Vibration on Maximum Wave.—It was found that the summit potential of the polarographic maximum of the first kind shifts toward more negative potentials by the vibration.

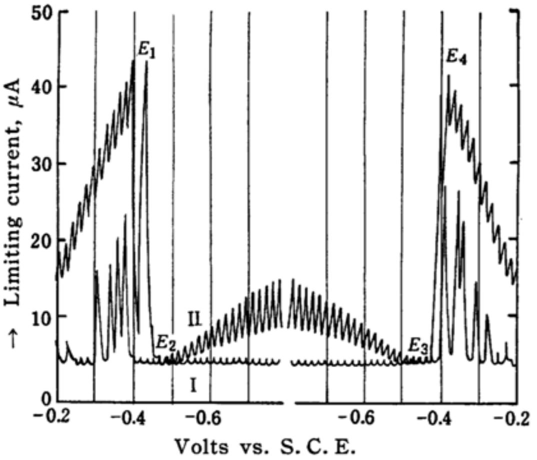
The test solution contained 1 mF mercuric ion in 0.01 F sodium sulfate solution, and the DME with the comparatively short life-time was preferable in order to obtain reproducible data. The effect of the vibration on the maximum wave of the mercuric ion is illustrated in Fig. 5, and the variation of the summit potential with the intensity of the a. c. electric field is given in Table III.

TABLE III. THE VARIATION OF THE SUMMIT POTENTIAL OF THE POLAROGRAPHIC MAXIMUM WITH THE INTENSITY OF THE a. c. ELECTRIC FIELD (E_1, E_2, E_3 and E_4 represent the potential given in Fig. 5.)

The intensity of the electric field, V./cm.	E_1	E_2	E_3	E_4
		V. vs. S. C. E.		
0	-0.37_5	-0.44_8	-0.43_5	-0.36_7
0.16	-0.39_2	-0.48_0	-0.44_2	-0.37_6
0.25	-0.43_0	-0.50_3	-0.47_7	-0.41_3
0.34	-0.49_5	-0.56_1	-0.56_5	-0.50_2

(25 c. p. s. square wave, $t=5.5_6$ sec.)

According to the theory[1] previously reported, the velocity of the vibration is a linear function of the intensity of the a. c. electric field. Accordingly, it seems to be probable that the velocity of the vibration pertains to the shift of the summit potential. In this connection, Heyrovsky and Vascautzanu[2] have pointed out the fact that the summit potential is shifted toward more negative potentials by increasing the mercury head. The authors' observation coincides with this



(A) (B)

Fig. 5. The effect of the vibration on the summit potential of the maximum wave of 1×10^{-3} F Hg^{2+} in 0.01 F Na_2SO_4. The applied voltage is scanned from −0.2 V. to −0.8 V. vs. S. C. E. (A) or from −0.8 V. to −0.2 V. vs. S. C. E. (B). Curves I and II correspond to the cases when the intensity of the applied a. c. electric field is 0 and 0.34 V./cm., respectively. $t=8.0$ sec.

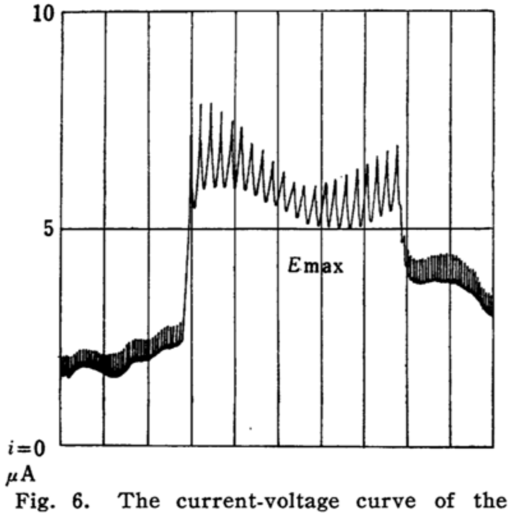


Fig. 6. The current-voltage curve of the mercuric ion under the violent vibration. The voltage starts from 0 V. vs. S. C. E. and each voltage interval corresponds to 0.1 V. $(Hg^{2+})=1\times10^{-4}$ F. The supporting electrolyte=0.1 F KCl. $E=0.38$ V./cm. $t=7$ sec. (open circuit).

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[2] J. Heyrovsky and E. Vascautzanu, *Collection Czechoslov. Chem. Communs.*, **3**, 418 (1931).

effect with respect to the point that the possible change of the ζ-potential due to the movement of the surface of the mercury droplet results in the shift of the summit potential of the maximum.

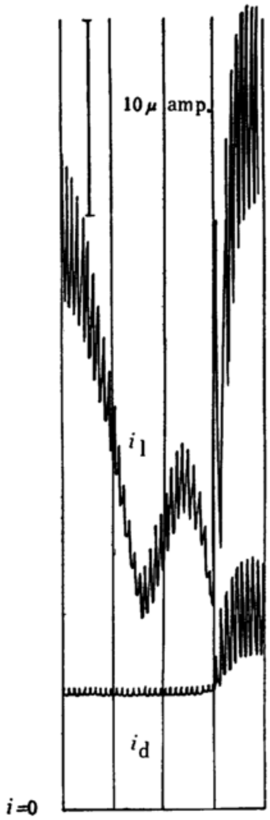

Fig. 7. The "VDME" current-voltage curve of the mercuric ion under the high rate of mercury flow. i_d is the diffusion-controlled current and i_l is the limiting current. $t=5.4_4$ sec. (open circuit). $m=1.34_7$ mg./sec. $(Hg^{2+})=1\times10^{-3}$ F. The supporting electrolyte=0.1 F KCl. The applied voltage starts from −0.7 V. vs. S. C. E. and each voltage interval corresponds to 0.1 V.

4. Anomalous Effect of Vibration on Current-Voltage Curve. — *4-i. Effect of violent vibration.*—The abrupt change of the limiting current was observed in the current-voltage curve of the mercuric ion under the application of the intense a. c. electric field (cf. Fig. 6). This change is caused by the change of the life-time of the DME. The mercury droplet is attached to the capillary orifice counteracting to the gravity and the vibration, and it is shaken off by the violent vibration caused by the coupled effect of the intense a. c. electric field and the increase of the surface charge density which is a function of the applied potential. Tachi and Okuda[3] have reported a similar phenomenon in the alternating current polarography.

4-ii. Effect of rapid rate of mercury flow. —Under the slow rate of the mercury flow, a minimum in the current-voltage curve is observed at the Lippmann-potential by the " VDME " method (cf. **1** and **4**). Under the rapid rate of the mercury flow, however, two minima were observed, the Lippmann-potential lying between them (cf. Fig. 7). It seems to be probable that this effect will be assigned to the variation of the ζ-potential at the mercury-solution interface with the flow of mercury on the surface of the DME.

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Laboratory of Chemistry
Minami College
Hiroshima University
Minami, Hiroshima

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[3] I. Tachi and M. Okuda, This Bulletin, 27, 310 (1954).

[4] H. Imai, S. Inouye and S. Chaki, ibid., 31, 767 (1958).