Studies on the Vibrated Dropping Mercury Electrode. I. The Theory of the Limiting Current and its Application to the Electrocapillarity

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When the dropping mercury electrode is vibrated by the application of an a. c. electric field, the limiting current of a depolarizer is augmented, the convection current being super-induced on the diffusion-controlled one. We called this new technique for improving the sensitivity of polarographic determinations the "VDME" method, and it was briefly reported in the previous communication[1]. Since the increment of the limiting current beyond the diffusion-controlled one depends upon the electric charge of the mercury-solution interface, this technique has a potentiality for the investigation of the electrocapillarity, especially for the determination of the zero-charge potential, i. e., the Lippmann-potential.

In this report, the theory of the limiting current and an accurate method for determining the Lippmann-potential are presented.

The Theory of the Limiting Current

The a. c. electric field exerts a moment of force as great as $q\cdot E\sin(\omega t)\cdot r\cdot\cos\theta$* on the center of the DME, and causes the forced vibration of the DME about the orifice of the capillary electrode (cf. Fig. 1). Counteracting this vibration, there exists the resistance due to the viscosity of the solution and the restoration of the displacement owing to gravity. Supposing that the former obeys Stokes's law, the moment of force is evaluated as great as $6\pi\eta r\cdot r\cdot r\, d\theta/dt$. The latter moment of force is equal to $Mg\cdot r\cdot\sin\theta$. Hence, one obtains the following equation of the vibration.

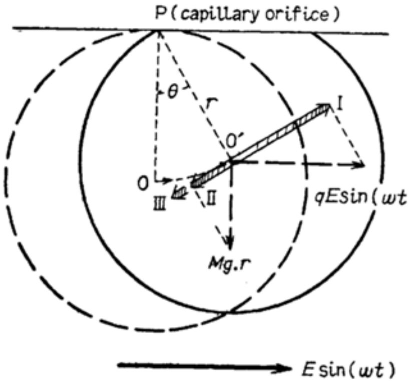

Fig. 1. The schematic representation of the forced vibration of the VDME: The moment of inertia, i, is equal to $q\cdot E\sin(\omega t)\cdot r\cos\theta$, ii is equal to $Mgr\cdot\sin\theta$ and iii is equal to $6\pi\eta r\cdot r\cdot r\, d\theta/dt$.

$$I\, d^2\theta/dt^2 = q\cdot E\sin(\omega t)\cdot r\cdot\cos\theta - Mg\cdot r\cdot\sin\theta - 6\pi\eta r\cdot r\cdot r d\theta/dt \tag{1}$$

where the moment of inertia, I, is nearly equal to $2\pi r^2/5$. In Eq. 1, $\cos\theta$ and $\sin\theta$ can be exchanged for one and θ, respectively, provided the amplitude of the vibration is small. It is noteworthy that Eq. 1 holds only in approximation; the reason is that the sphere of the DME may be deformed by the vibration.

The solution of Eq. 1 is given in the following, the term of damped vibration being neglected.

$$\theta = \alpha\{(\beta-\omega^2)\sin\omega t - \gamma\omega\cos\omega t\}/\{(\beta-\omega^2)^2+\gamma^2\omega^2\} \tag{2}$$

where $\alpha = qEr/I, \quad \beta = Mgr/I$

and $\gamma = 6\pi\eta r^3/I$ (3)

Hence, the center of the DME moves at the velocity of

$$r d\theta/dt = \alpha r\{(\beta-\omega^2)\omega\cos\omega t + \gamma\omega^2\sin\omega t\}/\{(\beta-\omega^2)^2+\gamma^2\omega^2\} \tag{4}$$

The mean velocity acquired during the motion from the site right under the capillary orifice to the site of the maximum

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[1] H. Imai, S. Inouye and S. Chaki, This Bulletin, 31, 767 (1958).

* The symbols used in this paper are listed below.
q=the surface charge of the DME.
E=the intensity of the a. c. electric field.
ω=the circular frequency of the a. c. electric field.
M=the mass of the DME.
g=the acceleration of gravity.
r=the radius of the DME.
η=the viscosity coefficient of the solution.
I=the moment of inertia of the DME.

amplitude can be evaluated by Eq. 5, i. e.,

$$(r\,\mathrm{d}\theta/\mathrm{d}t)_{\mathrm{mean}}=T/4\cdot\int_0^{T/4}(r\,\mathrm{d}\theta/\mathrm{d}t)\,\mathrm{d}t$$
$$=2\omega\alpha r(\beta-\omega^2+\gamma\omega)/\{(\beta-\omega^2)^2+\gamma^2\omega^2\} \quad (5)$$

where T is the period of the vibration.

Assuming that the concentration of the depolarizer at the vicinity of the electrode surface does not vary owing to the successive vibration, the treatment of Okinaka-Kolthoff's theory[2] developed for the limiting current of the rotated dropping mercury electrode can be applied to this case.

Thus, the following equation is given for the mean limiting current of the VDME;

$$\bar{i}_l=\bar{i}_d+knCD^{1/2}(m\tau)^{1/2}(r\mathrm{d}\theta/\mathrm{d}t)^{1/2}{}_{\mathrm{mean}} \quad (6)$$

where $\bar{i}_d$ is the mean diffusion-controlled current in μA, n is the number of electrons transferred per an ion, C is the bulk concentration of the depolarizer in mF, D is the diffusion constant in cm^2/sec., τ is the life-time of the DME in sec. and k is a numerical constant. In Eq. 6, it is assumed that the streaming velocity of the solution on and near the electrode surface is proportional to the velocity of the vibration. It is noteworthy that the actual surface velocity, and accordingly, the constant, k, are unknown.

Combining Eqs. 3, 5 and 6, one can obtain an expression for the relation between the limiting current and the surface charge of the DME;

$$\bar{i}_l=\bar{i}_d+k'(qE)^{1/2} \quad (7)$$

where k' is a proportionality factor.

The surface charge, q, of the DME in Eq. 7 can be evaluated by the following equation. Assuming Helmholtz's electrical double layer, we get

$$q=\varepsilon\varphi/4\pi\delta \quad (8)$$

where ε is the dielectric constant, φ is the potential of the DME and δ is the thickness of the electrical double layer.

Eqs. 7 and 8 lead to the following expression:

$$\bar{i}_l-\bar{i}_d=k''E^{1/2}(\varphi_{\mathrm{DME}}-\varphi_{\max})^{1/2} \quad (9)$$

where k'' is a proportionality factor, φ_{DME} is the potential of the DME and $\varphi_{\max}$ is the potential of the electrocapillary maximum.

From Eq. 9 it can be forecast that $(\bar{i}_l-\bar{i}_d)$ becomes practically zero at the potential of the electrocapillary maximum, and that the current-voltage curve of the VDME consists of two parabolas which intersect at the potential of the electrocapillary maximum. This curvilinear relation of the current and the potential can be transferred to the linear relation by plotting the square of the $(\bar{i}_l-\bar{i}_d)$ versus the potential of the DME.

The accurate determination of the Lippmann-potential will be carried out by evaluating the intersecting point of two straight lines of the $(\bar{i}_l-\bar{i}_d)^2$ versus φ_{DME} plot in the positive polarization and in the negative polarization, respectively.

Experimental

The current-voltage curve was recorded by a Shimadzu Model RP-2 polarograph. The DME used was of an appreciably long life-time and of the slow rate of mercury flow (τ=ca. 10 sec., $m\leq1$ mg./sec.). It is because the mercury flow on the surface of the DME owing to the rapid growth of the mercury droplet presumably affects the ζ-potential of the mercury-solution interface.

The a. c. source was supplied from a C-R oscillater, and was amplified by a power tube (6L6G) and the cathode-follower out-put was applied to the platinum plate electrodes (Fig. 2).

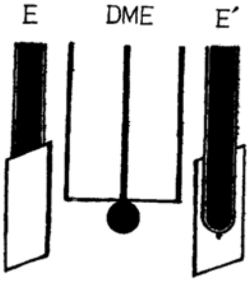

Fig. 2. VDME: E and E′ are the platinum plate electrodes to which the a. c. voltage is applied.

Since the impedance of the solution was small, the cathode resistor as small as 30 ohms was used in order to avoid the voltage drop of the out-put. The a. c. voltage was measured by a vacuum tube voltmeter.

All the reagents were of analytical grade. The test solution contained 10^{-3} F Hg^{2+} as the depolarizer. The concentration of the supporting electrolyte ranged from 10^{-3} to 1 F. In the case of the low saline concentration, the depolarizer concentration as small as 10^{-4} F was preferable in order to avoid the migration current. Under these conditions the mercuric ion develops a well-defined wave by a conventional polarograph, and the diffusion-controlled current gives a plateau ranging from -0.1 to -1.7 volts vs. S. C. E. The trace of dissolved oxygen was carefully removed by adding a small quantity of the sodium sulfite solution after the sufficient

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[2] Y. Okinaka and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 3326 (1957).

bubbling of purified nitrogen. The presence of trace oxygen in the test solution causes the fatal deformation of the current-voltage curve, especially near the potential of the electrocapillary maximum in question.

Results and Discussion

The current-voltage curve of 0.77×10^{-3} F Hg^{2+} in 0.1 F KCl is illustrated in Fig. 3. In Fig. 3 the diffusion-controlled current gives a plateau covering the whole voltage span recorded.

In the region of the positive polarization, the vibration of the DME is gradually retarded as the applied potential is shifted toward more negative potentials, corresponding to the decrease of the surface charge of the DME, and this effect results in the decrease of the limiting current. At the zero-charge potential, that is, the potential of the electrocapillary maximum, the vibration entirely ceases, and accordingly the limiting current will be solely controlled by the diffusion of the depolarizer. Under the appreciably low intensity of the a. c. electric field, the limiting current coincides with the diffusion-controlled one at the potential of the electrocapillary maximum, while it is not so under the sufficiently intense electric field as is illustrated in Fig. 3. This reason is attributable to the fact that the rapid variation of the current at the potential close to the electrocapillary maximum can not be followed by the recorder owing to its damping. In the region of the negative polarization, the limiting current reincreases as the applied potential is shifted toward more negative potentials, corresponding to the increment of the surface charge of the DME. Thus, the limiting current gives a minimum at the potential of the electrocapillary maximum.

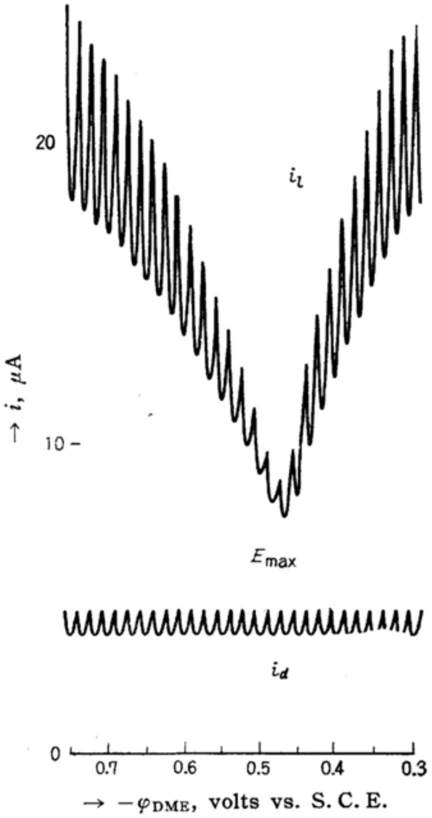

Fig. 3. The VDME current-voltage curve of 0.77×10^{-3} F Hg^{2+} in 0.1 F KCl. The a. c. frequency=25 c. p. s. The intensity of the electric field=0.55 volts/cm. $\tau=9.9_4$ sec. (open circuit). $m=0.85_5$ mg./sec. Temperature=25°C. (The intensity of the a. c. electric field can be lowered when the trace of surface active materials is removed by adding active charcoal).

The square of $(\bar{i}_l-\bar{i}_d)$ is plotted versus the potential of the DME in Fig. 4. In Fig. 4, the parabolic curvilinear relation of the current-voltage curve in Fig. 3 is transferred to the linear relation as is predicted in Eq. 9. The mean value** of the potential at the intersecting point of

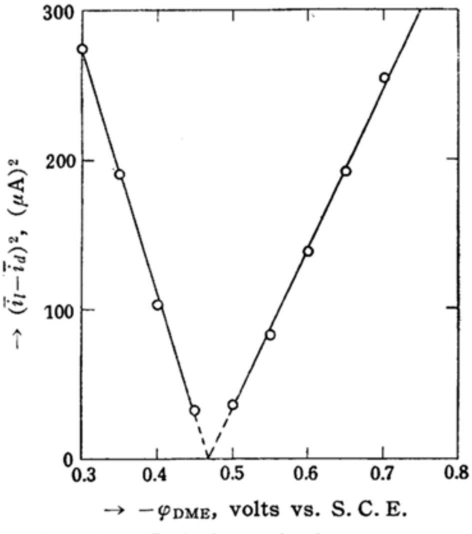

Fig. 4. Variation of the square of $(\bar{i}_l-\bar{i}_d)$ with the potential of the DME. The current was evaluated at the middle point of the saw-tooth oscillation in Fig. 3.

** This value was evaluated as the mean of the data obtained when the applied voltage sweeps toward more negative potentials and when the applied voltage sweeps toward less negative potentials.

two straight lines is -0.467 ± 0.001 volts vs. S. C. E. (in 0.1 F KCl solution). This value shows a very good agreement with the datum obtained by Grahame⁽³⁾.

This method of determining the Lippmann-potential seems to be better than any other method⁽⁴⁾ from the standpoints of the ease and rapidness of the recording, and of its good reproducibility and accuracy.

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3) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

4) D. C. Grahame, R. P. Larson and M. A. Poth, *J. Am. Chem. Soc.*, **71**, 2978 (1949); T. I. Popova and T. A. Kryukova, *J. physik. Chem.*, **25**, 283 (1951); J. A. V. Butler, "*Electrocapillarity*", Methuen & Co., Ltd., London (1940), p. 56.