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Frequency Dispersion in Capacity Measurements
at a Disk Electrode

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April, 1969

Abstract

The geometry of an electrode system affects the frequency dispersion of impedance measurements if the primary current distribution on the electrode is nonuniform. This effect is treated for a disk electrode embedded in an insulating plane with the counter electrode at infinity. The apparent capacity is found to approach zero at large frequencies. The frequency dependence of the apparent capacity will be much smaller for a spherical electrode tangent to an insulating plane. The latter system is also treated briefly.

Introduction

We investigate here the alternating-current impedance of a disk electrode embedded in an infinite, insulating plane, with the counter electrode at infinity. The distribution of current over the surface of such a disk electrode is, in general, nonuniform. Figure 1 depicts equipotential surfaces in the medium near a disk, where the solution adjacent to the disk electrode is at a uniform potential; this is the so-called "primary potential distribution," for which the distribution of current on the surface of the disk is given by¹

$$i = 0.5 i_{\text{avg}} / [1 - (r/r_o)^2]^{1/2} \quad (1)$$

With an alternating current, the current can pass from the electrode to the solution either by means of a faradaic electrode reaction or by charging the double-layer capacity. Attention here is primarily focused on the double-layer capacity. The impedance can then be represented by an equivalent circuit consisting of a series combination of a resistor and a capacitor (figure 2). However, the values of the effective resistance and double-layer capacity of the equivalent circuit are not independent of frequency. Several factors may contribute to this "frequency dispersion."

If the electrode surface is rough, the peaks and valleys will be accessible to a different degree at different frequencies (see de Levie²). Secondly, if the frequency becomes large relative to the kinetics of ion sorption in the double layer, then the apparent double-layer capacity will depend on frequency (see Delahay³). The occurrence of faradaic reactions will also cause a frequency dependence of the values in the equivalent circuit in figure 2.

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Figure 1. Potential distribution near an equipotential disk in an insulating plane.

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Figure 2. Equivalent circuit of disk system. Here, C_{eff} and R_{eff} can be regarded as the apparent double-layer capacity and the apparent resistance of the electrolytic solution, if faradaic reactions are of negligible importance.

Finally, the current distribution will be different at different frequencies, and this will lead to a frequency dispersion, as suggested by Bauer, Spritzer, and Elving.⁴

The last factor is investigated theoretically here in order that an experimentally observed frequency dispersion due to this factor will not be erroneously attributed to one of the first factors mentioned. Consequently, the electrode surface is taken here to be smooth, and the true double-layer capacity (per unit area) C is taken to be independent of frequency. Except for large organic ions, the kinetics of ion sorption should not affect the double-layer capacity until frequencies of 1 megacycle are reached. The possibility of faradaic reactions will also be included, without, however, consideration of the Warburg impedance due to concentration changes near the electrode.

At low frequencies, the reactive impedance of the double layer predominates over the resistive impedance of the electrolytic solution. Consequently, the current distribution is uniform over the surface of the disk, and C_{eff} corresponds to the true double-layer capacity. At high frequencies, the reactive impedance becomes small, and the primary current distribution is a good approximation. Hence, the effective resistance approaches the value for the primary distribution:¹

$$R_{\text{eff}} \rightarrow 1/4r_0\kappa \text{ as } \omega \rightarrow \infty. \quad (2)$$

As we shall see, C_{eff} approaches zero at high frequencies, in marked contrast to the situation at a hanging mercury drop or dropping mercury electrode.

If, however, faradaic reactions can occur, the low frequency limit will no longer yield the true double-layer capacity, since the reactive impedance is large compared to the faradaic impedance with which it is in parallel. Information about the true double-layer capacity can then be obtained only at intermediate frequencies with due allowance for the nonuniform current distribution.

For rough electrodes, the low-frequency limit will yield the true electrode area if the true double-layer capacity is known (in the absence of faradaic reactions). However, the determination of the true double-layer capacity from impedance measurements at higher frequencies will not be straightforward.

This investigation is also relevant to the frequency dependence of classical conductivity cells (see, for example, Robbins⁵).

Mathematical Model

The potential in the solution satisfies Laplace's equation,

$$\nabla^2 \Phi = 0. \quad (3)$$

The potential at infinity will be taken to be zero

$$\Phi \rightarrow 0 \text{ as } r^2 + z^2 \rightarrow \infty, \quad (4)$$

and, since the current density is zero on the insulating plane around the disk electrode, the normal component of the potential gradient will also be zero there:

$$\partial \Phi / \partial z = 0 \text{ at } z = 0, r > r_0. \quad (5)$$

At the disk, the current density is given by

$$i = C \frac{\partial(V - \Phi_o)}{\partial t} + (\alpha + \beta) \frac{i_o ZF}{RT} (V - \Phi_o) = -\kappa \frac{\partial \Phi}{\partial z} \quad (6)$$

$$\text{at } z = 0, r \leq r_o,$$

where V is the potential of the electrode, Φ_o is the potential in the solution adjacent to the electrode, κ is the conductivity of the solution, C is the true double-layer capacity, and $(\alpha + \beta)i_o ZF/RT$ relates to the kinetics of the faradaic reaction, here taken to be linear. Thus double-layer charging and a faradaic reaction can both contribute to the passage of current from the electrode to the solution. The last equality relates the current density to the normal component of the potential gradient in the solution.

For an alternating current, the electrode potential can be expressed
as*

$$V = V_o e^{j\omega t}, \quad (7)$$

where V_o is the amplitude of the applied potential. Correspondingly, the potential in the solution can be expressed in terms of a complex potential U which is independent of time:

$$\Phi = V_o e^{j\omega t} U(r, z). \quad (8)$$

The results of the analysis can be expressed in terms of two dimensionless quantities:

* Strictly speaking, one takes the real part of such complex expressions:
 $V = \text{Re}\{V_o e^{j\omega t}\} = V_o \cos(\omega t).$

$$\Omega = \frac{\omega C r_o}{\kappa} \quad \text{and} \quad J = (\alpha + \beta) \frac{i_o Z F r_o}{R T \kappa} \quad (9)$$

Ω can be regarded as a dimensionless frequency and J as a dimensionless exchange current density. $\Omega = 1$ when, for example, $C = 30 \mu\text{f}/\text{cm}^2$, $r_o = 0.25 \text{ cm}$, $\kappa = 0.05 (\text{ohm-cm})^{-1}$, and $\omega = 0.67 \times 10^4 \text{ sec}^{-1}$ (or 10,500 cps). $J = 0.0194$ when, in addition, $i_o = 0.1 \text{ mA}/\text{cm}^2$ and $(\alpha + \beta)Z = 1$. The results are expressed in terms of C/C_{eff} , the ratio of the true double-layer capacity to the apparent capacity, and $4r_o \kappa R_{\text{eff}}$, the ratio of the effective resistance to the resistance for the primary distribution (see equation 2). At low frequencies, $C/C_{\text{eff}} \rightarrow 0$ unless $J = 0$, and, for small values of J , $4r_o \kappa R_{\text{eff}} \rightarrow (4/\pi)(1 + 1/J)$.

The secondary current distribution, when $\Omega = 0$, has been discussed before.⁶

Analysis

Since Φ satisfies Laplace's equation, U also satisfies Laplace's equation. In rotational elliptic coördinates η and ξ , the solution satisfying the condition at infinity and the condition on the insulating part of the disk can be expressed as⁶

$$U = \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi) \quad , \quad (10)$$

where $P_{2n}(\eta)$ is the Legendre polynomial of order $2n$ and $M_{2n}(\xi)$ is a Legendre function with known properties.⁶ Since a similar development has recently been used to treat the current distribution on a rotating disk electrode below the limiting current,⁶ these mathematical details will not be repeated here. In the present case, the coefficients B_n will be complex.

This solution allows the potential and the potential derivative near the electrode to be expressed as

$$U_0 = \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \quad (11)$$

and

$$\left. \frac{\partial U}{\partial z} \right|_{z=0} = \frac{1}{r_0 \eta} \left. \frac{\partial U}{\partial \xi} \right|_{\xi=0} = \frac{1}{r_0 \eta} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M'_{2n}(0) \quad (12)$$

Substitution into the boundary condition 6 on the disk electrode gives

$$(j\Omega + J) \left[1 - \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \right] = - \frac{1}{\eta} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M'_{2n}(0) \quad (13)$$

where the dimensionless parameters Ω and J are given by equation 9.

This approach derives its economy from the fact that equation 10 is an appropriate solution of Laplace's equation. Hence, the problem of solving a partial differential equation is reduced to the determination of the coefficients B_n from equation 13. Multiplication of this equation by $\eta P_{2m}(\eta)$ and integration with respect to η gives an infinite set of equations for this purpose:

$$B_m = - \frac{M'_{2m}(0)}{M'_{2m}(0)} (j\Omega + J) \int_0^1 \eta P_{2m}(\eta) \left[1 - \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \right] d\eta \quad (14)$$

One can truncate this set of equations by carrying only a finite number of terms in the sum in the integrand. Higher accuracy can, of course, be obtained by carrying more terms.

After the coefficients B_n have been obtained, one needs to calculate the impedance of the system. The total current is given by

$$I = \int_0^{r_0} i 2\pi r dr = -2\pi r_0^2 \kappa \int_0^1 \eta \frac{\partial \Phi}{\partial z} \Big|_{z=0} d\eta = -2\pi r_0 \kappa V_0 e^{j\omega t} B_0 M'_0(0) \quad , \quad (15)$$

where the change of variable from r to η is effected by means of the relation

$$r/r_0 = \sqrt{1-\eta^2} \text{ on the disk.} \quad (16)$$

Since, furthermore, $M'_0(0) = -2/\pi$, the impedance is

$$Z = V/I = 1/4r_0 \kappa B_0 \quad . \quad (17)$$

We wish to compare this with the impedance of the series resistor-capacitor combination given in figure 2 and supposed to represent the resistance of the solution and the capacity of the double layer. Thus

$$Z = R_{\text{eff}} + 1/j\omega C_{\text{eff}} \pi r_0^2 \quad . \quad (18)$$

Comparison with equation 17 allows us to determine R_{eff} and C_{eff} from calculated values of B_0 :

$$4r_0 \kappa R_{\text{eff}} = B_0 / (B_{\text{or}}^2 + B_{\text{oi}}^2) \quad (19)$$

and

$$C/C_{\text{eff}} = (\pi/4) \Omega B_{oi} / (B_{or}^2 + B_{oi}^2) \quad , \quad (20)$$

where B_{or} and B_{oi} represent the real and imaginary parts of B_o , respectively.

Results

Table 1 represents the effective resistance and capacity as a function of the dimensionless frequency Ω and for several values of J , the parameter describing the faradaic reactions. One sees

Table 1. Effective resistance and capacitance as a function of frequency

$\omega C r_o / \kappa$	$4r_o \kappa R_{\text{eff}}$	C/C_{eff}	$4r_o \kappa R_{\text{eff}}$	C/C_{eff}	$4r_o \kappa R_{\text{eff}}$	C/C_{eff}
	J=0		J=0.1		J=1	
0	1.08076	1.0	13.81194	0	2.34368	0
0.1	1.08073	1.00010	7.44572	0.50009	2.33106	0.00997
0.2	1.08066	1.00039	3.62593	0.80037	2.29465	0.03873
0.5	1.08013	1.00241	1.56867	0.96385	2.08868	0.20168
1	1.07835	1.00931	1.20335	0.99906	1.70571	0.50658
2	1.07234	1.03307	1.10336	1.02950	1.32015	0.82435
5	1.05205	1.12341	1.05705	1.12084	1.09978	1.06500
10	1.03344	1.23630	1.03478	1.23430	1.04657	1.20762
20	1.01945	1.37207	1.01982	1.37078	1.02312	1.35674
50	1.00875	1.57278	1.00882	1.57215	1.00943	1.56606
100	1.00461	1.73438	1.00462	1.73404	1.00480	1.73084
200	1.00238	1.90092	1.00238	1.90074	1.00243	1.89909
500	1.00098	2.12577	1.00098	2.12570	1.00099	2.12502
∞	1.0	-	1.0	-	1.0	-

that in the absence of faradaic reactions ($J=0$) the effective resistance varies by only 8 percent from the high-frequency limit to the low-frequency limit. The effective capacity gives no high-frequency limit. The presence of faradaic reactions can change considerably the character of the impedance when interpreted in terms of the equivalent circuit of figure 2.

Low-Frequency Limit

In the absence of faradaic reactions one obtains at low frequencies a uniform, imaginary current density of small magnitude. As a first approximation,

$$B_{ni} \rightarrow -\frac{\pi}{4} \frac{\Omega P_{2n}^3(0)}{(2n-1)(n+1)} (4n+1) \text{ as } \Omega \rightarrow 0. \quad (21)$$

In particular, $B_{oi} \rightarrow \pi\Omega/4$. The real components are of order Ω^2 . In particular,

$$B_{or} \rightarrow \frac{\pi^2}{4^2} \Omega^2 \sum_{n=0}^{\infty} \frac{(4n+1)P_{2n}^4(0)}{(2n-1)^2(n+1)^2}. \quad (22)$$

Substitution of these results into equations 19 and 20 gives low-frequency limits for the effective resistance and capacity which agree with the appropriate entries in table 1.

High-Frequency Limit

At high frequencies, the surface potential U_0 becomes uniform and real. $B_{or} \rightarrow 1$, and $B_{nr} \rightarrow 0$ for $n \neq 0$. The imaginary components of the B coefficients are also small. However, the primary current distribution is infinite at the edge of the disk. This is not possible at finite frequencies

on account of the impedance of the interface. Hence, a singular-perturbation problem is encountered. The situation is so severe that the value of B_{oi} cannot be determined in a straightforward manner.

Let us examine the singular nature of the problem. The primary potential distribution will be a valid approximation everywhere except in a small region near the edge of the disk. We use rotational elliptic coördinates⁶ to investigate this region:

$$r = r_o \sqrt{(1-\eta^2)(1+\xi^2)} \quad \text{and} \quad z = r_o \eta \xi \quad . \quad (23)$$

Both ξ and η are small near the edge of the disk, and we can write

$$(r-r_o)/r_o = \frac{1}{2}(\xi^2 - \eta^2) \quad \text{and} \quad z/r_o = \eta \xi \quad . \quad (24)$$

These coördinates thus reduce to parabolic coördinates in the region under consideration. (Because this region is small, results obtained for the potential distribution will also be valid near the edge of any electrode at high frequencies if the electrode is flush with an insulating surface at its edge.)

Near the edge of the disk the potential U therefore satisfies the equation

$$\frac{\partial^2 U}{\partial \eta^2} + \frac{\partial^2 U}{\partial \xi^2} = 0 \quad . \quad (25)$$

The boundary condition on the surface of the disk, $\xi = 0$, is

$$j\Omega(1-U_0) = - \frac{1}{\eta} \frac{\partial U}{\partial \xi} \Big|_{\xi=0} \quad (26)$$

Far from the disk, the potential approaches the primary distribution¹ as approximated for small ξ :

$$U \rightarrow 1 - \frac{2}{\pi} \tan^{-1} \xi \approx 1 - \frac{2}{\pi} \xi \text{ as } \xi \rightarrow \infty \quad (27)$$

Furthermore, on the surface of the insulator

$$\partial U / \partial \eta = 0 \text{ at } \eta = 0. \quad (28)$$

By defining stretched variables as follows:

$$\bar{U} = (1-U)\frac{\pi}{2} \sqrt{\Omega} \quad , \quad \bar{\eta} = \eta \sqrt{\Omega} \quad , \quad \bar{\xi} = \xi \sqrt{\Omega} \quad , \quad (29)$$

the problem in the edge region can be made independent of the parameter Ω . The problem then becomes

$$\frac{\partial^2 \bar{U}}{\partial \bar{\eta}^2} + \frac{\partial^2 \bar{U}}{\partial \bar{\xi}^2} = 0 \quad (30)$$

$$j\bar{U}_0 \bar{\eta} = \partial \bar{U} / \partial \bar{\xi} \text{ at } \bar{\xi} = 0 \quad (31)$$

$$\partial \bar{U} / \partial \bar{\eta} = 0 \text{ at } \bar{\eta} = 0 \quad (32)$$

$$\bar{U} \rightarrow \bar{\xi} \text{ as } \bar{\xi} \rightarrow \infty \quad (33)$$

From these results one can conclude that in the original coördinate system the size of this region is of order r_0/Ω , while $1-U_0$ is of order $\Omega^{-1/2}$ and the (dimensionless) current density $j\Omega(1-U_0)$ is of order $\Omega^{1/2}$.

The problem posed by equations 30 through 33 was solved by finite-difference methods by successive over-relaxation. The results for the surface potential $\bar{U}_0$, which is proportional to the current density, are given in figure 3. The current density approaches the primary distribution far from the edge of the disk, but it is more uniform in the edge region where the impedance of the interface prevents the current density from becoming infinite. However, the high currents predicted by the primary distribution are not prevented totally from reaching the disk; the current is just spread out over a larger region. The disturbance of the real component of the current density generates a comparable disturbance in the imaginary component.

The singular-perturbation treatment of the edge region at high frequencies permits these phenomena to be clarified in a definitive manner and permits an economy in the calculations by defining a problem in which no parameters appear. An accurate treatment of the edge region would otherwise require a very fine mesh if Laplace's equation were to be solved by finite-difference methods over the whole disk simultaneously.

As we have seen, the impedance of the system is tied up in the B_0 coefficient. This coefficient can be expressed as

$$1 - B_0 = \int_0^1 (1-U_0) d\eta, \quad (34)$$

and we know that $B_{0r} \rightarrow 1$ as $\Omega \rightarrow \infty$. The primary distribution (see equation 1), which applies over the central region of the disk, can be expressed as

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Figure 3. Components of surface potential expressed in stretched variables for the region near the edge of the disk at high frequencies.

$$1 - U_o = -2j/\pi\Omega\eta \quad . \quad (35)$$

We can obtain useful results by proceeding in the following manner.

The imaginary part of equation 34 is

$$B_{oi} = - \int_0^1 (1-U_o)_i d\eta = - \frac{2}{\pi\Omega} \int_0^{\sqrt{\Omega}} \bar{U}_{oi} d\bar{\eta} \quad , \quad (36)$$

where, in the last expression, we have used the variables appropriate to the edge region. We now break this up into several parts:

$$B_{oi} = \frac{-2}{\pi\Omega} \left[\int_0^b \bar{U}_{oi} d\bar{\eta} + \int_b^{\sqrt{\Omega}} (\bar{U}_{oi} + \frac{1}{\bar{\eta}}) d\bar{\eta} - \int_b^{\sqrt{\Omega}} \frac{1}{\bar{\eta}} d\bar{\eta} \right] \quad . \quad (37)$$

The last integral can be evaluated analytically. The next to the last integral has an upper limit which approaches infinity as $\Omega \rightarrow \infty$. Since $\bar{U}_{oi} \rightarrow -1/\bar{\eta}$ as $\bar{\eta} \rightarrow \infty$, it is permissible to set this limit equal to infinity.

Thus we obtain the following high-frequency limit for B_{oi} :

$$B_{oi} = \frac{4A}{\pi\Omega} + \frac{\ell n\Omega}{\pi\Omega} \quad , \quad (38)$$

where

$$A = - \frac{1}{2} \left[\int_0^b \bar{U}_{oi} d\bar{\eta} + \int_b^{\infty} (\bar{U}_{oi} + \frac{1}{\bar{\eta}}) d\bar{\eta} + \ell n b \right] \quad . \quad (39)$$

The value of A should be independent of the value of b. However, it is broken up in this way since the first integral is unbounded as $b \rightarrow \infty$ and the second integral is unbounded as $b \rightarrow 0$. Evaluation from the information plotted in figure 3 gives $A = 0.563$. The high-frequency limit for B_{or} is

$$1 - B_{\text{or}} = \frac{2}{\pi\Omega} \int_0^{\infty} \bar{U}_{\text{or}} d\bar{\eta} \quad (40)$$

Substitution of equations 38 and 40 into equations 19 and 20 gives the high-frequency limits

$$4r_0 \kappa R_{\text{eff}} \rightarrow 1 \text{ and } C/C_{\text{eff}} \rightarrow A + \frac{1}{4} \ln \Omega \text{ as } \Omega \rightarrow \infty. \quad (41)$$

This asymptotic form for C/C_{eff} and values from table 1 for $J = 0$ are plotted in figure 4. Satisfactory agreement is reached for large values of Ω .

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Figure 4. Frequency dependence of apparent capacity on a smooth disk in the absence of faradaic reactions.

Discussion and Conclusions

The most important result of this work is the fact that there is no high frequency limit for C/C_{eff} . Consequently, the apparent capacity of a disk electrode embedded in an insulating plane should be expected to vary considerably with frequency. This conclusion is related to the fact that the primary current density becomes infinite at the edge of the disk. Since this effect is related critically to the edge region, the high-frequency behavior will be affected significantly by the detailed geometry at the edge. If the disk is slightly inset in the plane, a finite limit would be obtained.

Since this effect is related to the edge region, a similar conclusion would apply to a flat electrode of any shape embedded in an insulating plane. In contrast, for a mercury drop on an insulating plane, the primary current density does not become infinite, and the frequency-dependence of C/C_{eff} is considerably less (see appendix).

A similar singular-perturbation problem in the edge region would arise at finite frequencies for large values of J . Since the behavior of the secondary current distribution in the edge region is not of critical interest, there is no compelling reason to pursue this problem. However, the correct determination of the behavior of C/C_{eff} at high frequencies required a consideration of the edge region.

Bauer, Spritzer, and Elving⁴ report impedance measurements at a pyrolytic graphite disk electrode. Their results show that the apparent capacity varies by about a factor of 2 while the apparent resistance varies by about a factor of 10. The latter result, interpreted in terms of the present analysis, suggests that faradaic reactions are not of negligible importance.

Appendix - A drop electrode on a plane

A mercury drop at the end of a capillary tube is sometimes treated as a spherical electrode tangent to an insulating plane. The frequency dependence of the apparent capacity due to shielding by the capillary tip is inherently much less than that for a disk because the primary current distribution does not become infinite anywhere. The capillary tip can, of course, be designed to minimize the shielding and thus reduce the frequency dispersion further.

Here we use tangent-sphere coordinates⁷ ν and μ :

$$r = \frac{2r_o \mu}{\mu^2 + \nu^2}, \quad z = \frac{2r_o \nu}{\mu^2 + \nu^2}, \quad (42)$$

where r and z are cylindrical coordinates, with their origin at the base of the drop. The surface of the spherical drop is then given by $\nu = 1$. The current-density relation on the surface of the drop, analogous to equation 6, 13, or 26 becomes

$$(j\Omega + J)(1 - U_o) = \frac{1 + \mu^2}{2} \frac{\partial U}{\partial \nu} \quad \text{at} \quad \nu = 1. \quad (43)$$

The solution to Laplace's equation satisfying the conditions at infinity and on the insulating plane is expressed as

$$U = (\mu^2 + \nu^2)^{1/2} \int_0^\infty G(p) \frac{\cosh p\nu}{\cosh p} J_o(p\mu) dp. \quad (44)$$

The function $G(p)$ is analogous to the B_n coefficients used for the disk, but for the drop no discrete eigenvalues are found. By substitution of this expression into the boundary condition on the drop surface, it is possible to derive a

differential equation for $G(p)$:

$$2(j\Omega + j)(G - e^{-p}) = p \tanh p \frac{d^2 G}{dp^2} + \left(\tanh p + \frac{2p}{\cosh^2 p} \right) \frac{dG}{dp} - \tanh p \left[\tanh p + p + \frac{2p}{\cosh^2 p} \right] G, \quad (45)$$

and $G = 1$ at $p = 0$ and $G = 0$ at $p = \infty$. The impedance Z of the system will then be given by

$$\frac{1}{4\pi\kappa r_0 Z} = \int_0^\infty \frac{G(p) dp}{\cosh p}. \quad (46)$$

The primary potential distribution, applicable for large values of Ω or J and corresponding to $U_0 = 1$, is given by $G(p) = e^{-p}$. The primary distribution has been treated by Maxwell⁸ and by Matyaš⁹ and has been plotted by de Levie.² The primary current distribution on the drop is

$$\frac{i}{i_{\text{avg}}} = \frac{(1+\mu^2)^{3/2}}{2\ln 2} \int_0^\infty \frac{J_0(p\mu) p dp}{\cosh p} \quad (47)$$

and is plotted by de Levie. The value of i/i_{avg} at $\mu = 0$ (the top of the drop) is here calculated to be 1.3215, in good agreement with de Levie's graph.

For high frequencies we can obtain a second approximation directly from the differential equation:

$$G(p) = e^{-p} + j(\tanh p + 2p/\cosh^2 p)/2\Omega \cosh p. \quad (48)$$

Substitution into the integral for the impedance gives the high-frequency limits for the resistance and capacitance of the equivalent circuit.

$$4\pi r_o \kappa R_{\text{eff}} = 1/\ln 2 = 1.4427 \text{ and } C/C_{\text{eff}} = 1.1352. \quad (49)$$

The value for the resistance limit can also be inferred from the results of Maxwell. The capacitance in the equivalent circuit of figure 2 should be represented by $4\pi r_o^2 C_{\text{eff}}$. Thus, C/C_{eff} is the ratio of the true double-layer capacity to the apparent double-layer capacity and has the same meaning as for the disk.

At low frequencies, the current distribution becomes uniform and $C/C_{\text{eff}} \rightarrow 1$. However, it is difficult to force the current to the surface of the drop near the point of contact, and the effective resistance might be expected to increase considerably more than was found for the disk. The solution for G at low frequencies becomes a singular-perturbation problem. Since little interest in this limit has been expressed, the problem was not pursued.

The drop problem is quite different from the disk problem. Here the high-frequency limit is relatively easy to obtain, but the low-frequency limit is difficult. For the disk the apparent capacity varies considerably with frequency; for the drop the apparent resistance varies considerably. These differences are directly related to the fact that the primary current distribution becomes infinite at the edge of the disk and becomes zero near the point of contact of the drop. Some results for intermediate frequencies are given in table 2. These values are in satisfactory agreement with the experimental results of Tessari, Delahay, and Holub.¹⁰ In particular, the factor $1/\ln 2$ gives a good account of the shielding effect of the capillary on the effective resistance.

Table 2. Effective resistance and capacitance for a drop on a plane, in the absence of faradaic reactions ($J=0$).

$\omega C r_o / \kappa$	$4\pi r_o \kappa R_{\text{eff}}$	C/C_{eff}
0	?	1.0
0.1	1.5755	1.0016
1	1.5056	1.0632
10	1.4443	1.1330
∞	1.4427	1.1352

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Nomenclature

- B_n - coefficients in series expansion of the potential.
- C - double-layer capacity (f/cm^2).
- C_{eff} - apparent double-layer capacity in the equivalent circuit.
- G - distribution function for drop.
- i - current density (A/cm^2).
- I - total current (A).
- j - $\sqrt{-1}$.
- J - dimensionless parameter for linear electrode kinetics.
- J_0 - Bessel function of order zero.
- M_{2n} - Legendre function discussed in reference 6.
- p - separation parameter for drop.
- P_{2n} - Legendre polynomial of order $2n$.
- r - radial position from axis of disk (cm).
- r_0 - radius of disk or drop (cm).
- R_{eff} - apparent resistance in the equivalent circuit (ohm).
- t - time (sec).
- U - complex potential in the solution (V).
- U_0 - value of U at the disk surface.
- V - electrode potential relative to infinity (V)
- V_0 - amplitude of applied potential.
- z - distance from plane of disk (cm).
- Z - impedance of the system (ohm).
- η - rotational elliptic coordinate.
- κ - conductivity of the solution ($ohm^{-1} - cm^{-1}$)

- μ - tangent-sphere coördinate
- ν - tangent-sphere coördinate
- ξ - rotational elliptic coördinate.
- Φ - potential in the solution (V).
- Φ_0 - value of Φ at the electrode surface.
- ω - frequency of applied potential (radian/sec).
- Ω - dimensionless frequency.

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