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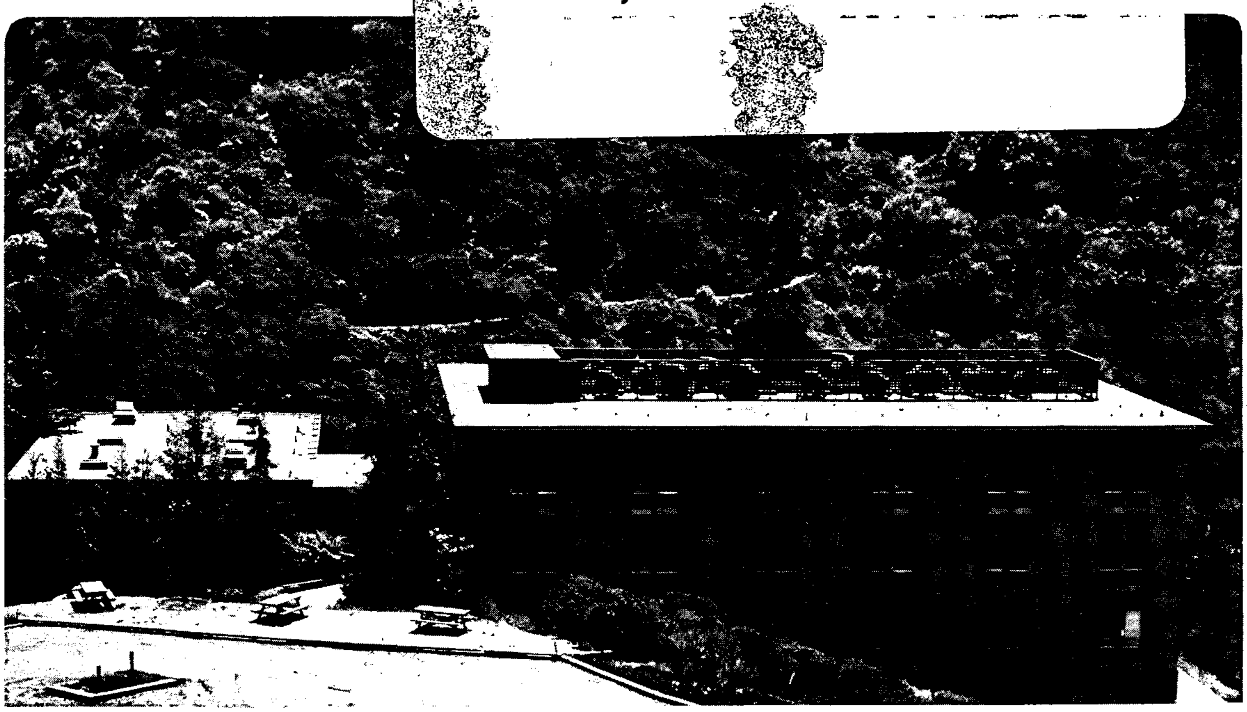

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The Kramers-Kronig Relations and Evaluation of Impedance for a Disk Electrode

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Abstract

It is shown that the Kramers-Kronig (K-K) relations for frequency dispersion (or variation with frequency) describe the impedance properties of a disk electrode. The accuracy and interpretation of impedance by the K-K relations depend on the accuracy with which one fits the functions for the capacity and effective resistance. It is also shown how to use the K-K relations to calculate the capacity from the effective resistance, and vice versa. The previously published theory of impedance at a disk electrode is thereby shown to be consistent with the Kramers-Kronig relations. The method of evaluation of the resistance and reactance for the disk electrode from the Kramers-Kronig relations is given and discussed.

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Key words: frequency dispersion, current distribution

Introduction

Since the geometry of an electrode system affects the frequency dispersion of impedance when the primary current distribution on the electrode is nonuniform, Newman(1) has solved the problem of the alternating-current impedance for a disk electrode embedded in an infinite, insulating plane, with the counterelectrode at infinity. To isolate the effects of nonuniform potential distribution on the effective resistance (R_{eff}) and double-layer capacity (C_{eff}), the electrode surface is taken to be smooth, and the true double-layer capacity (per unit area) C is assumed to be independent of frequency. In other words, all other contributions to the frequency dispersion (the roughness factor for different accessibility of peaks and valleys, the kinetic adsorption effect in the double layer, and the Warburg impedance(2-4) due to concentration changes near the electrode) have been eliminated, while the possibility of faradaic reactions has been included.

The impedance Z of a system is a complex function of the frequency ω:

$$Z(\omega) = Z_r(\omega) + i\ Z_i(\omega)\,, \qquad [1]$$

where Z_r and Z_i represent the real and imaginary parts of impedance, respectively. From this impedance we can define an auxiliary function $z(\omega)$:

$$z(\omega) = Z(\omega) - Z_\infty - \frac{i\sigma}{\omega}\,, \qquad [2]$$

where Z_∞ and σ are real constants, independent of frequency. In this way $z(\omega)$ can be endowed with the properties that $z(\omega) \to 0$ as $\omega \to \infty$ and $z(\omega)$ is well behaved near $\omega = 0$. For an electrode where faradaic reactions can occur, $\sigma = 0$. For an ideally polarizable electrode where faradaic reactions cannot occur,

$$\sigma = -1/\pi r_o^2 C\,. \qquad [3]$$

At high values of the frequency, $Z_r(\omega) \to Z_\infty$, where(5)

$$Z_\infty = 1/4\kappa r_o\,. \qquad [4]$$

The causality principle in physics leads to the result that the impedance of an electrode is analytic in the lower half of the frequency plane. Consequently, if the simple pole point $\omega_o = \omega$ is excluded from the region of integration (Figure 1a), the function $(Z(\omega_o) - Z_\infty)/(\omega_o - \omega)$ is analytic everywhere within the closed contour C, and the contour integral along C is thereby zero. The integral along the semicircle at infinity is also zero. These basic features are the main prerequisite for application of the Kramers-Kronig relations(6-8).

The objectives of the present paper are to show the applicability of the Kramers-Kronig relations for describing the behavior of impedance, to use them for calculating both the effective resistance (R_{eff}) and the effective double-layer capacity (C_{eff}) as functions of frequency, and finally, to show the consistency of the earlier theory(1) and results with the K-K relations. More specifically, the aim of the present paper is to detail the method for evaluating the effective double-layer capacity (C_{eff}) from the effective resistance (R_{eff}), and vice versa, by means of the K-K relations.

Impedances and the Kramers-Kronig Relations

Integration around the entire contour C (Figure 1a) leads to (with ω and ω_o interchanged)(8)

$$\fint_{-\infty}^{\infty} \frac{Z(\omega_o) - Z_\infty - \frac{i\sigma}{\omega_o}}{\omega_o - \omega} d\omega_o + \pi i \left[Z(\omega) - Z_\infty - \frac{i\sigma}{\omega} \right] = 0 , \qquad [5]$$

where $\fint$ denotes the Cauchy principal value of the integral. The second term results from the Cauchy integral formula for $\omega = \omega_o$. Equation 5 splits into two Kramers-Kronig relations(6,7) for the electrode impedance

$$Z_r(\omega) - Z_\infty = -\frac{1}{\pi} \fint_{-\infty}^{\infty} \frac{Z_i(\omega_o) - \frac{\sigma}{\omega_o}}{\omega_o - \omega} d\omega_o \qquad [6]$$

and

$$Z_i(\omega) = \frac{1}{\pi} \fint_{-\infty}^{\infty} \frac{Z_r(\omega_o) - Z_\infty}{\omega_o - \omega} d\omega_o + \frac{\sigma}{\omega} . \qquad [7]$$

Since $Z_r(\omega)$ is even in ω and $Z_i(\omega)$ is odd in ω, the K-K relations reduce to

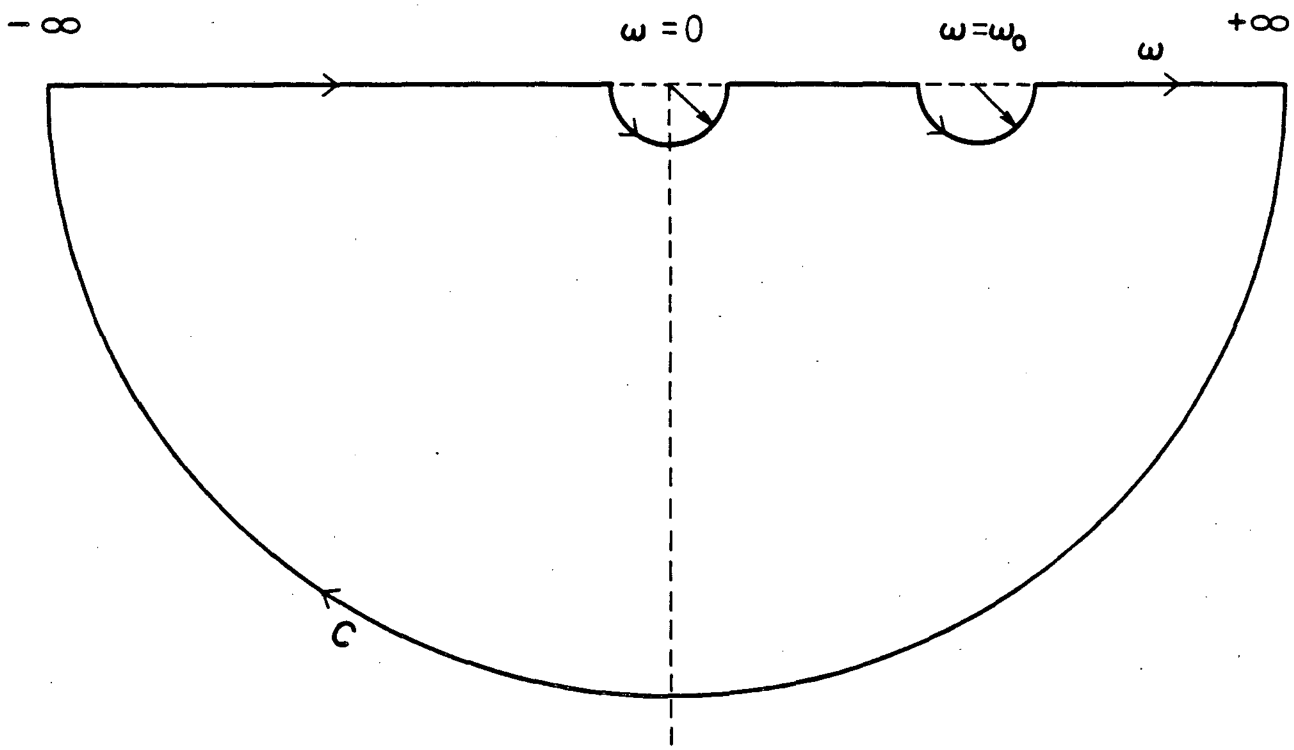

Figure 1a. Complex impedance diagram with the real and imaginary components and simple poles.

$$Z_r(\omega) - Z_\infty = -\frac{2}{\pi}\int_0^\infty \frac{\omega_o\ Z_i(\omega_o)}{\omega_o^2 - \omega^2}\,d\omega_o \qquad [8]$$

and

$$Z_i(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{Z_r(\omega_o) - Z_\infty}{\omega_o^2 - \omega^2}\,d\omega_o + \frac{\sigma}{\omega}. \qquad [9]$$

Notice that

$$\int_0^\infty \frac{d\omega_o}{\omega_o^2 - \omega^2} = 0\,. \qquad [10]$$

This last relation permits the singularities at $\omega_o = \omega$ to be avoided. This will be done in equations 14 and 15. Equation 10 also shows that no term in σ needs to be included in the integrand in equation 8. Finally, equation 10 shows that, with the Kramers-Kronig relations, a constant resistance creates no reactance through equation 9, and a constant capacitance creates no resistance through equation 8. Thus we should put the emphasis on variations in the resistance and capacitance.

According to the equivalent circuit in figure 1b, real and imaginary parts of the impedance can be related to the effective resistance and capacitance according to

$$Z_r(\omega) = R_{eff}(\omega) \qquad [11]$$

and

$$Z_i(\omega) = \frac{-1}{\pi r_o^2 \omega C_{eff}(\omega)}. \qquad [12]$$

Two dimensionless quantities have been introduced before(1,9) and are convenient in the present paper:

$$\Omega = \frac{\omega C r_o}{\kappa} \text{ and } J = (\alpha_a + \alpha_c)\frac{i_o F r_o}{RT\kappa}, \qquad [13]$$

where Ω can be regarded as a dimensionless frequency and J as a dimensionless exchange current density. By making use of these equations [10 through 13], the K-K relations take on a more suitable form for the impedance at a disk electrode:

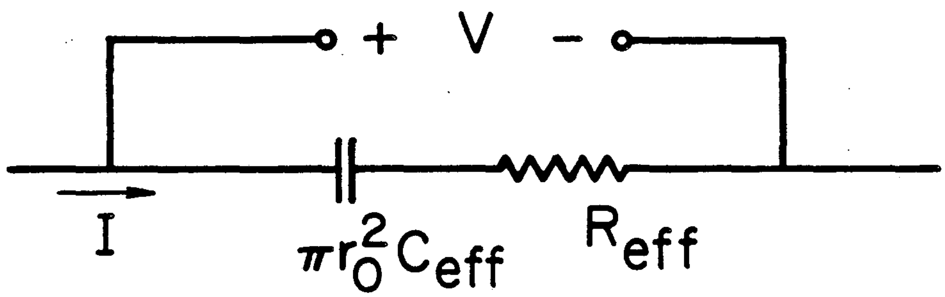

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Figure 1b. Defining equivalent circuit of the disk system, where C_{eff} and R_{eff} can be regarded as the effective double-layer capacity and the effective resistance of the electrolytic solution, respectively, if faradaic reactions are of negligible importance. More generally, R_{eff} and C_{eff} are merely alternative ways of referring to the real and imaginary parts of the impedance.

$$4\kappa r_o R_{eff}(\Omega) - 1 = \frac{8}{\pi^2}\int_0^\infty \frac{\dfrac{C}{C_{eff}(\Omega_o)} - \dfrac{C}{C_{eff}(\Omega)}}{\Omega_o^2 - \Omega^2}\, d\Omega_o \qquad [14]$$

and

$$\frac{C}{C_{eff}(\Omega)} + \pi r_o^2 C\sigma = -\frac{\Omega^2}{2}\int_0^\infty \frac{4\kappa r_o R_{eff}(\Omega_o) - 4\kappa r_o R_{eff}(\Omega)}{\Omega_o^2 - \Omega^2}\, d\Omega_o\,. \qquad [15]$$

These allow the calculation of the effective resistance from the effective double-layer capacity, and vice versa, and any singularity at $\Omega_o = \Omega$ is effectively avoided. Hence there is no longer a need to refer to the Cauchy principal value.

Figure 2 shows some of the impedance functions calculated in reference 1, specifically those for $J = 0$ and $J = 1$. C/C_{eff} increases without limit as $\Omega \to \infty$, and one might well ask how this behavior could be consistent, in view of the K-K relations, with the resistance function, which is nearly constant in this region. In the following, we shall place emphasis on the functions for the ideally polarizable electrode ($J = 0$); the curves for $J = 1$ illustrate how the behavior is markedly different at low frequencies. However, the high-frequency behavior becomes independent of J because the faradaic reaction is effectively shorted out by the double-layer capacity.

Evaluation of the Effective Resistance from the Capacitance

According to the previous paper(1), the high-frequency behavior of the effective capacitance can be expressed (for all values of J) as

$$\frac{C}{C_{eff}(\Omega)} \to 0.563 + \frac{1}{4}\ln\Omega \text{ as } \Omega \to 0\,. \qquad [16]$$

A relation which approximates the values of capacitance over the entire frequency range, for $J = 0$, is

$$\frac{C}{C_{eff}(\Omega)} = 1 + \frac{1}{8}\ln\left(1 + 0.646^8\,\Omega^2\right). \qquad [17]$$

The comparison with the theoretical values is shown in figure 3a. Substitution into the K-K relation [equation 14] gives

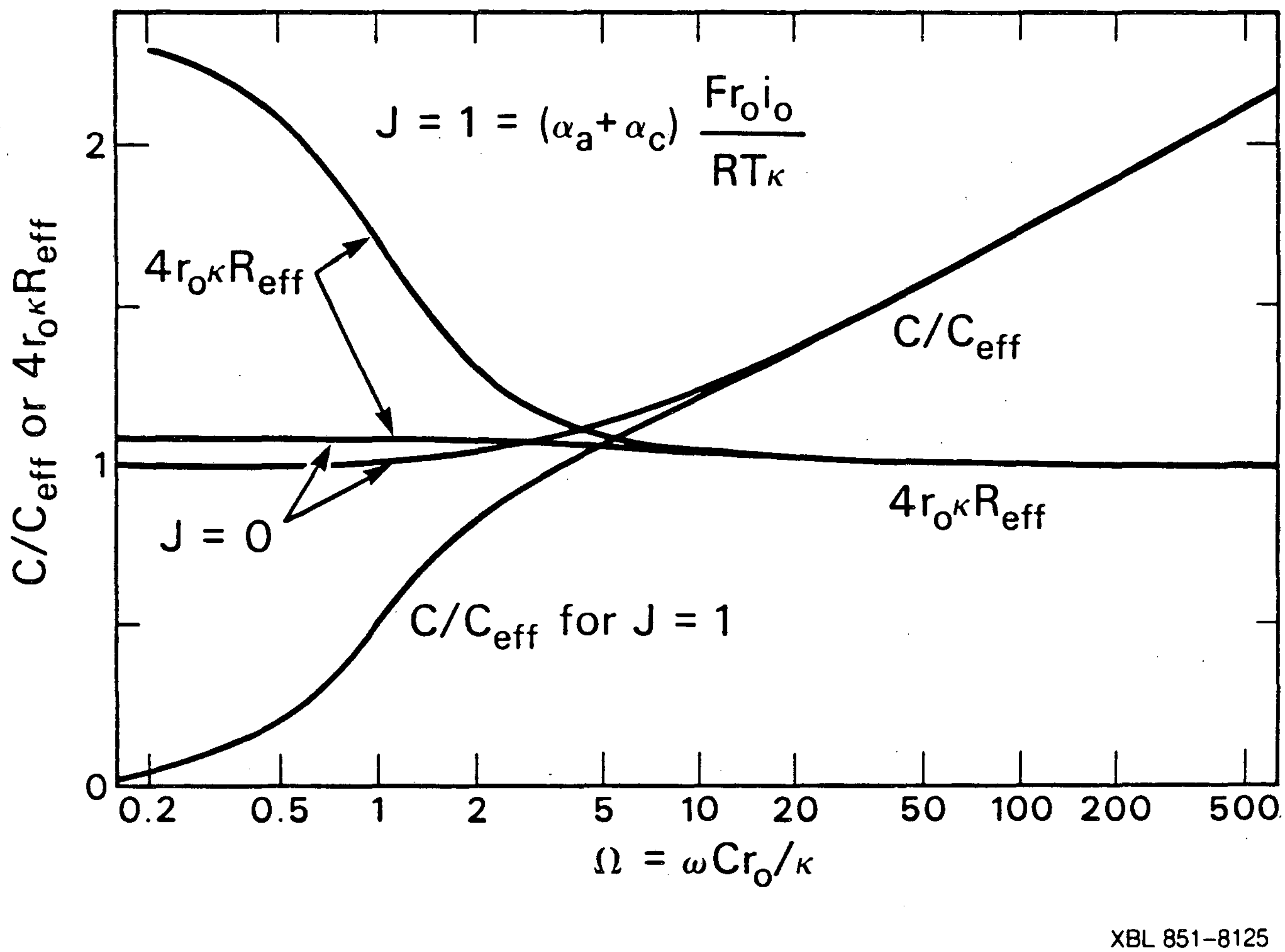

Figure 2. Dimensionless resistance and reactance for the disk-electrode system for two values of the dimensionless exchange current density (J), from reference 1.

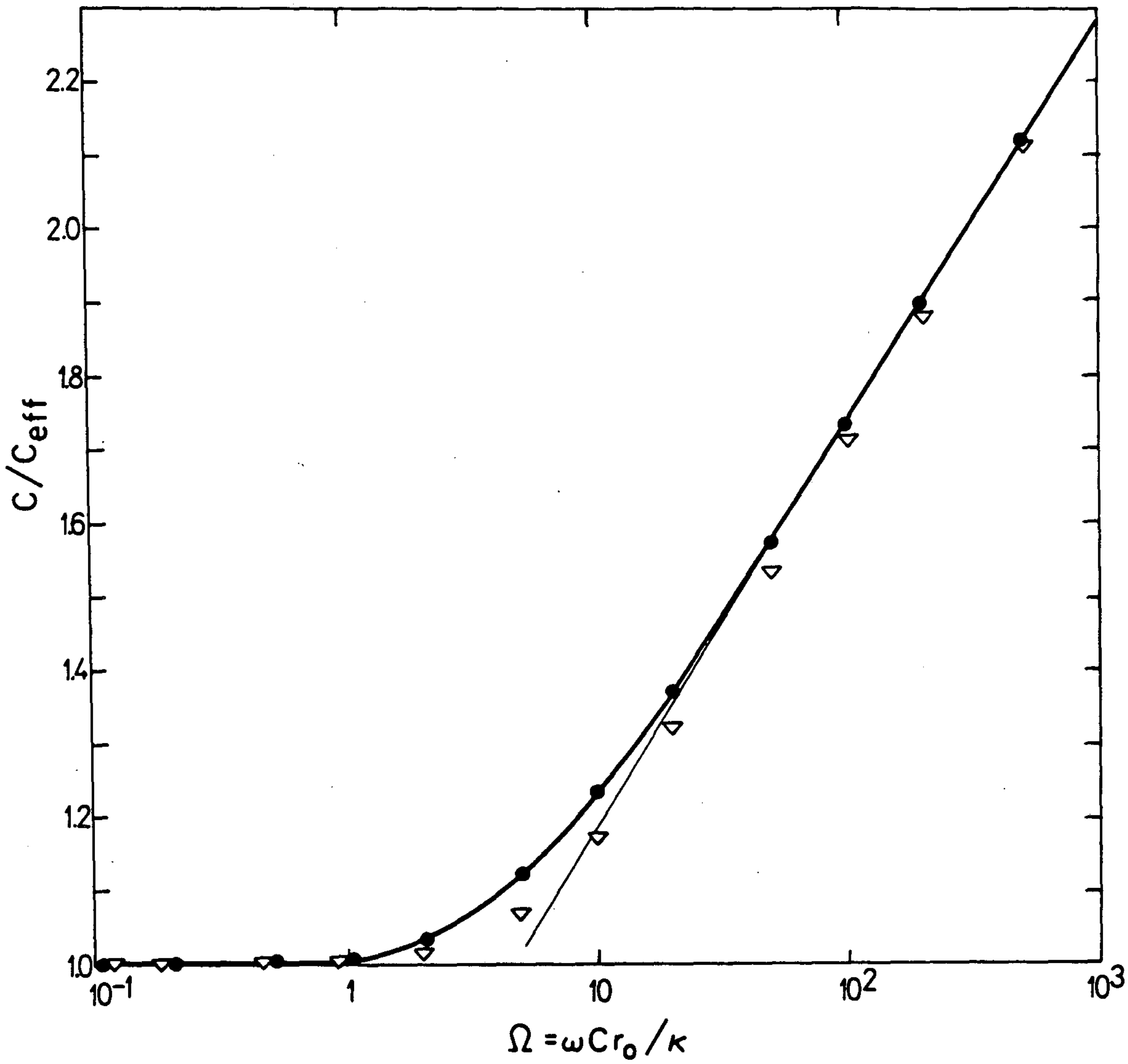

Figure 3a. Frequency dependence of the effective capacity on a smooth disk in the absence of faradaic reactions ($J = 0$):

• - values from reference 1.

∇ - values calculated from equation [17].

——- high-frequency asymptote.

$$4\kappa\tau_o R_{eff}(\Omega) - 1 = \frac{1}{\pi^2}\int_0^\infty \frac{\ln \dfrac{1 + 0.646^8\,\Omega_o^2}{1 + 0.646^8\,\Omega^2}}{\Omega_o^2 - \Omega^2}\, d\Omega_o \,. \qquad [18]$$

The values calculated from this approximation to the capacitance can be compared with the theoretical resistance values in figure 3b.

Suppose that Ω takes large values, so that the principal contribution comes when Ω_o is large compared to 1; then

$$4\kappa\tau_o R_{eff}(\Omega) - 1 \to \frac{2}{\pi^2}\int_0^\infty \frac{\ln(\Omega_o/\Omega)}{\Omega_o^2 - \Omega^2}\, d\Omega_o = \frac{1}{2\Omega} \,. \qquad [19]$$

Not only does $Z_r(\Omega) \to Z_\infty$, when $\Omega \to \infty$, but also the asymptotic behavior in equation 19 is found in the results given for the effective resistance in reference 1 for all values of J.

On the other hand, for another limiting condition, $\Omega \to 0$, equation 18 takes on the simpler form

$$4\kappa\tau_o R_{eff}(0) - 1 = \frac{1}{\pi^2}\int_0^\infty \frac{\ln(1 + 0.646^8\Omega_o^2)}{\Omega_o^2}\, d\Omega_o \,, \qquad [20]$$

for which numerical evaluation gives

$$4\kappa\tau_o R_{eff}(0) - 1 = 0.0561 \qquad [21]$$

as the first approximation to the value 0.08076 calculated in reference 1 (see also reference 10). Remember that we should put the emphasis on $4\kappa\tau_o R_{eff}(\Omega) - 1$ because it is variations in the resistance and capacitance that are important in the Kramers-Kronig relations. For $J = 0$, the resistance itself varies by only 8 percent over the whole frequency range, while the effective capacitance varies greatly.

The difference between equation 17 and the capacitance values calculated in reference 1 is displayed in figure 4. Let us now define the residual function for $C/C_{eff}(\Omega)$ as

$$\Delta(\Omega) = \frac{C}{C_{eff}(\Omega)} - 1 - \frac{1}{8}\ln(1 + 0.646^8\,\Omega^2) \,. \qquad [22]$$

Next we use the function (derived from the asymptotic behavior shown in figure 4)

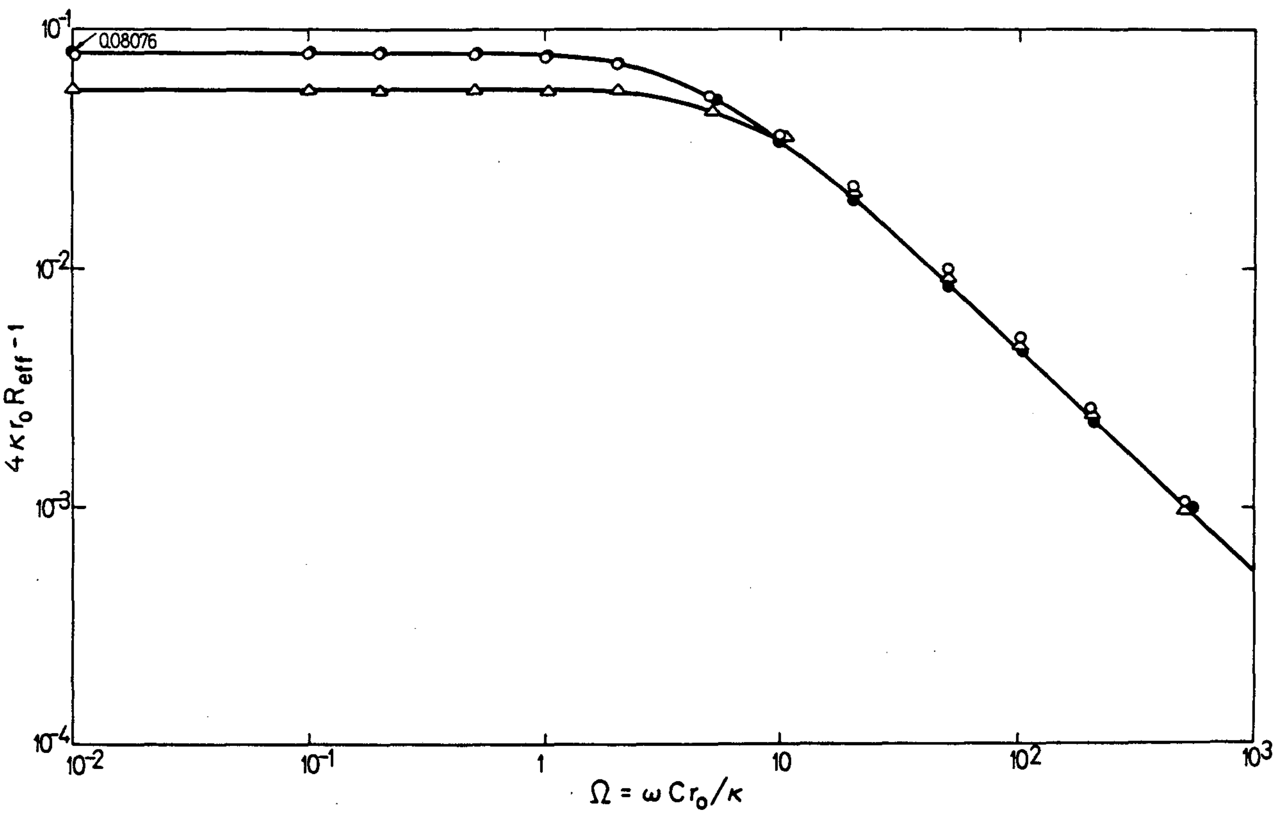

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Figure 3b. Frequency dependence of the effective resistance for $J = 0$:

• - values from reference 1.

Δ - first approximation from the K-K relation (equation [18]).

O - values calculated from the K-K relation including the residual function integration.

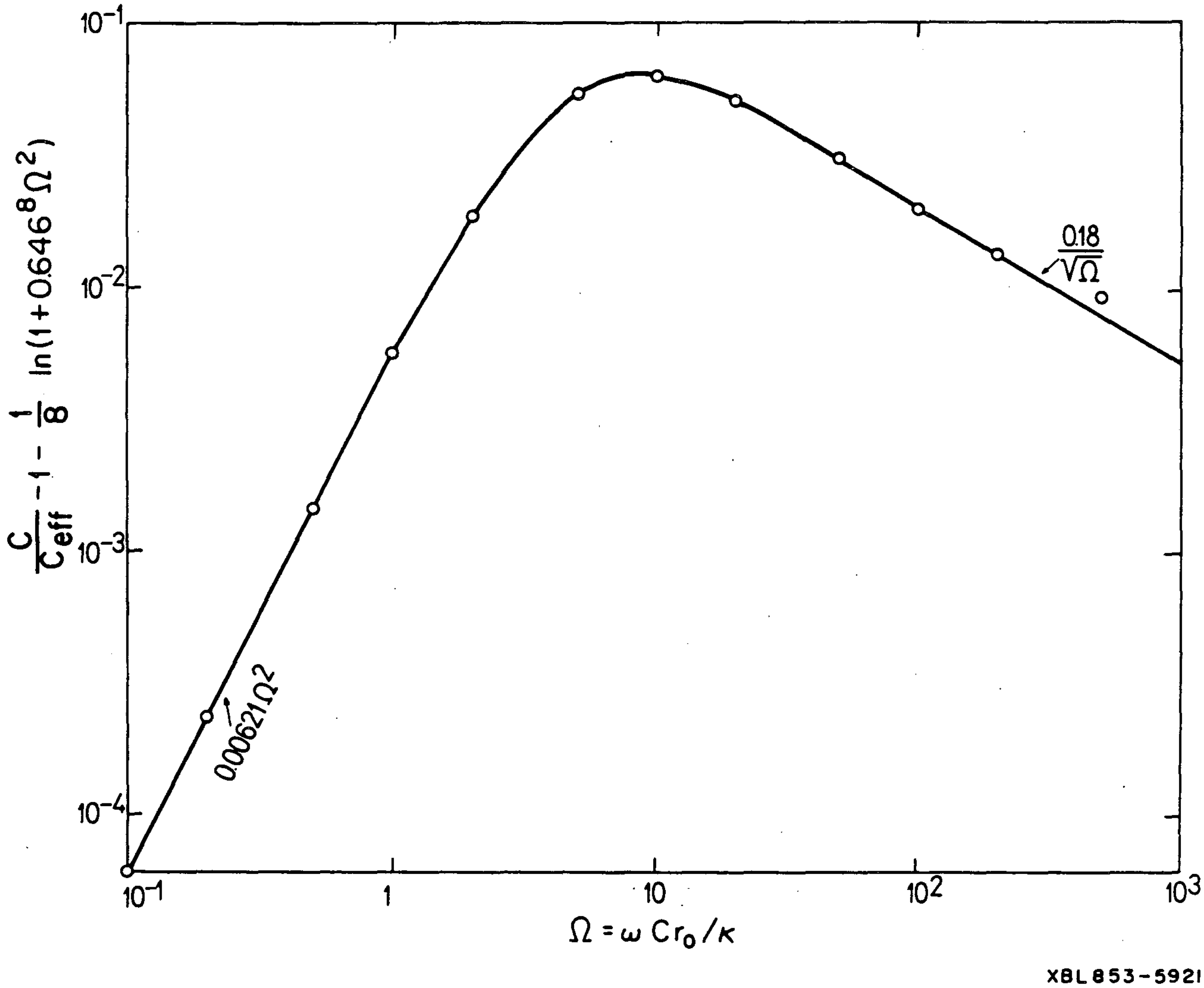

Figure 4. Frequency dependence of the residual function in the capacitance. This is used for refinement of the evaluation of the effective resistance by the K-K relation.

$$\Delta(\Omega) = \frac{1}{\dfrac{1}{0.00621\Omega^2} + \dfrac{\sqrt{\Omega}}{0.18}} . \qquad [23]$$

Now, at zero frequency, the effective resistance includes an additional contribution:

$$4\kappa\tau_o R_{eff}(0) - 1 = \frac{1}{\pi^2}\int_0^\infty \frac{\ln(1 + 0.646^6\,\Omega_o^2)}{\Omega_o^2}\,d\Omega_o + \frac{8}{\pi^2}\int_0^\infty \frac{\Delta(\Omega_o)}{\Omega_o^2}\,d\Omega_o , \qquad [24]$$

so that two numerical values (0.0561 + 0.0256 = 0.0817) now approach more closely (within 1.2%) the exactly calculated value (0.08076).

For the next approximation, let us fit the residual function by a straight line over the intervals between points on figure 4, that is

$$\Delta(\Omega) = B\,\Omega^E , \qquad [25]$$

where the B and E parameters were fitted for every interval. Now recalculation from equation 24 for the zero-frequency resistance gives $4\kappa\tau_o R_{eff}(0) - 1 = 0.0561 + 0.0244 = 0.0805$, which differs from the theoretical value by about 0.3%.

The values of the effective resistance calculated from the K-K relations are compared with the theoretical values in figure 3b. This testifies to the harmony of the theory of impedance at the disk electrode and the Kramers-Kronig relations.

Evaluation of the Capacitance from the Effective Resistance

The first approximation we use for the resistance function (for $J = 0$) is

$$4\kappa\tau_o R_{eff}(\Omega) - 1 = \frac{1}{\dfrac{1}{0.08076} + 2\Omega} = f(\Omega) . \qquad [26]$$

This expression has the correct limiting behavior at high frequencies (see equation 19) and at low frequencies, and the fit to the theoretical values is illustrated in figure 5a. When introduced into the K-K relation for the capacitance [equation 15], this form leads to an analytic approximation

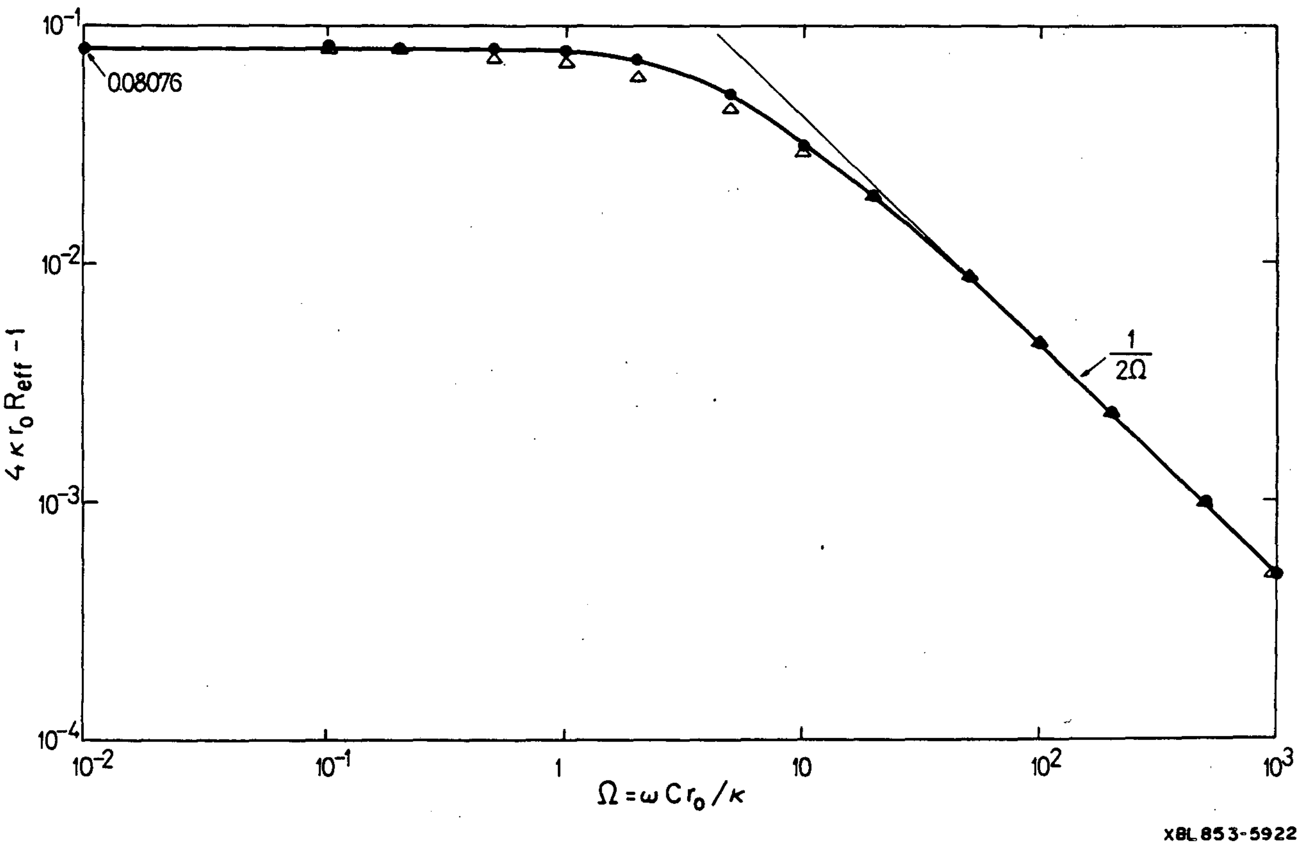

Figure 5a. Frequency dependence of the effective resistance for $J = 0$:

• - values from reference 1.

Δ - values calculated for the first approximation (equation [26]).

$$\frac{C}{C_{eff}(\Omega)} - 1 = \frac{A^2\Omega^2}{4}\frac{\ln(A\Omega)}{1 - A^2\Omega^2}, \qquad [27]$$

where $A/2 = 0.08076$. This expression roughly approximates the theoretical values in figure 5b.

Closer approach to the theoretical values has been obtained by the addition of a residual function for the resistance:

$$F(\Omega) = 4\kappa\tau_0 R_{eff}(\Omega) - 1 - f(\Omega).$$

This residual function has been fitted over each interval between theoretical points, similar to the way that equation 25 was used for the capacitance. The resulting fit was integrated according to the Kramers-Kronig relation, with the result shown in figure 5b. Apparently, every further residual correction in the K-K relations brings the numerical values closer to the theoretical capacities from reference 1 and confirms that the Kramers-Kronig relations correctly describe the impedance behavior as a function of frequency. This verification is for $J = 0$; it can be assumed that the impedance results in reference 1 for other values of J also satisfy the K-K relations.

Concluding Remarks

Landau and Lifshitz(8) write that the K-K relations are of great importance in physics for evaluation of frequency dispersion because they allow one to calculate either of two corresponding functions even when the other is known only approximately or empirically. They are also useful to test the consistency of data.

The present study shows that the impedance values from the disk electrode perfectly obey the K-K relations. An important benefit of the Kramers-Kronig relations is the ability to calculate the values of the effective resistance from the capacitance, and vice versa. The interpretation of impedance by the K-K relations depends on the functions used for the effective capacitance and resistance: the higher the accuracy, the better the agreement. However, to calculate any individual value either of the capacity, or the effective resistance, from the K-K

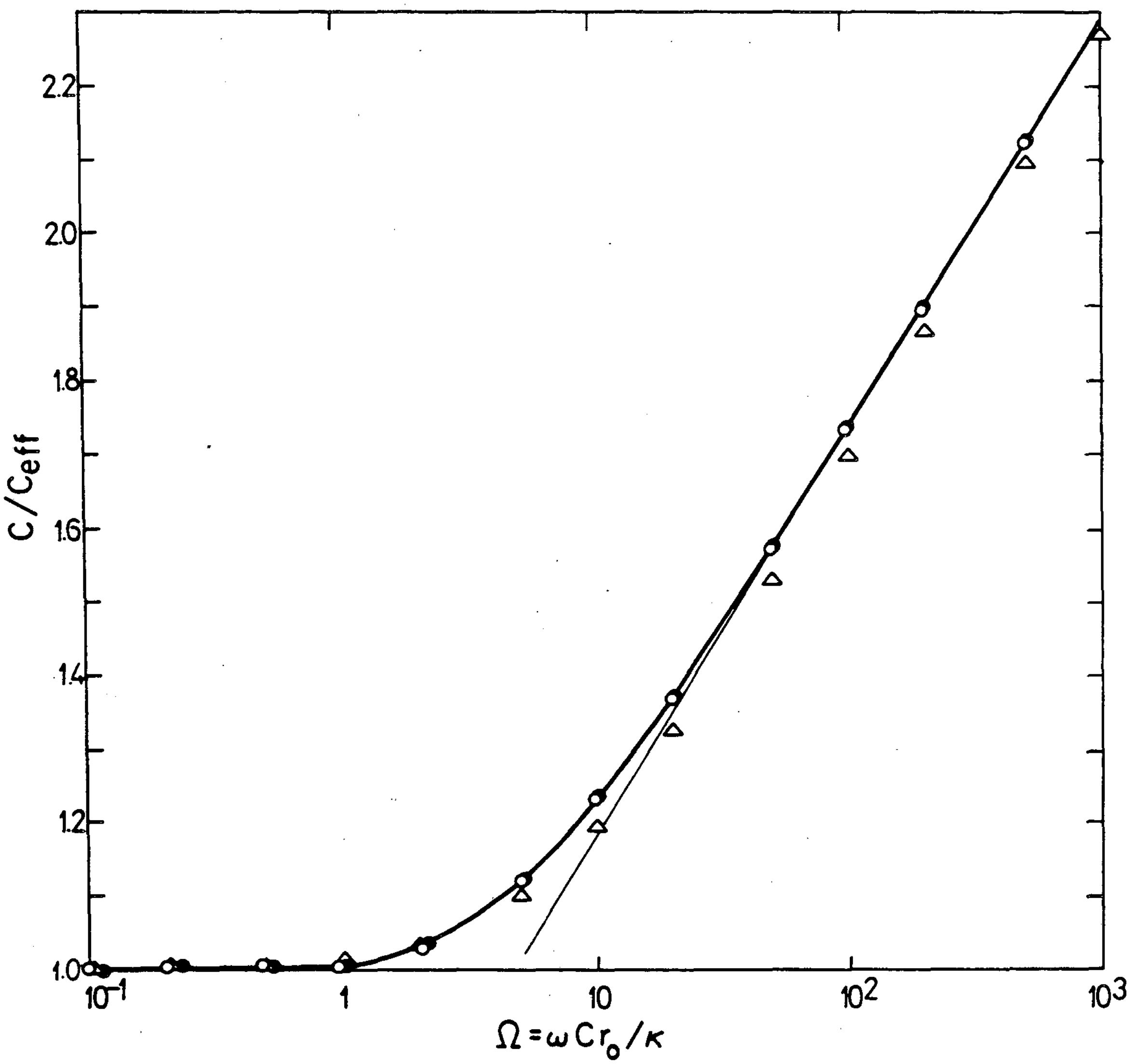

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Figure 5b. Frequency dependence of the effective capacity for $J = 0$:

• - values from reference 1.

Δ - first approximation from equation [27].

○ - values calculated from the K-K relation (equation [15]) including the residual function contribution.

relations, one must to calculate the integrals [equations 14 and 15] for the entire range of frequency from zero to infinity. Normally, the calculations, as in the present paper, have to proceed through the approximate relations, including the residual function integrals. One needs an accurate fit in the known range of frequencies and an extrapolation in frequency ranges where data are absent.

Both the real and the imaginary parts of the impedance at a given frequency can best be obtained by direct calculation(1), and not through the Kramers-Kronig relations. The same is probably true in experimental measurements. A procedure designed to measure one part of the impedance is likely to produce an accurate value for the other as well.

Acknowledgment

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Nomenclature

C double-layer capacity (F/cm^2)

C_{eff} apparent double-layer capacity in the equivalent circuit

i_o exchange current density (A/cm^2)

J dimensionless exchange current density

r_o radius of disk electrode (cm)

R_{eff} apparent (effective) resistance in the equivalent circuit (Ω)

$z(\omega)$ well behaved part of impedance function (Ω)

$Z(\omega)$ impedance of system (Ω)

$Z_i(\omega)$ imaginary part of impedance (Ω)

$Z_r(\omega)$ real part of impedance (Ω)

Z_∞ impedance at infinity frequency (Ω)

$\alpha_a + \alpha_c$ transfer coefficients in electrode kinetics

$\Delta(\Omega)$ departure function for reactance

κ conductivity of the solution (Ω^{-1} cm $^{-1}$)

σ strength of pole in impedance at zero frequency

ω frequency of applied signal (radian/s)

ω_o integration variable of frequency (radian/s)

Ω dimensionless frequency

Appendix

It is perhaps worthwhile to demonstrate that z should be analytic in the *lower* half-plane of figure 1a, since a change of sign would result in equation 5, and hence in equations 6 through 9, if we assumed that z should be analytic in the upper half-plane. Let us consider Laplace transforms of current and potential, for example,

$$\overline{V}(s) = L\{V(t)\} = \int_0^\infty e^{-st} V(t)dt \; . \qquad [A1]$$

From Ohm's law, the transfer function $Z(s)$ can be defined,

$$\overline{V}(s) = \overline{I}(s) \cdot Z(s) \; . \qquad [A2)$$

For the special case where the current is a constant,

$$\overline{I}(s) = \frac{A}{s}, \qquad [A3]$$

where A is the value of the constant current. It thus follows that $z(s)$ can be regarded as the Laplace transform of the derivative of the potential V:

$$z(s) = Z(s) - Z_\infty = \frac{1}{A} L\left\{\frac{dV(t)}{dt}\right\} = \frac{sL\{V(t)\} - V(0)}{A}, \qquad [A4]$$

where $V(0)/A$ can be identified with Z_∞ and where $z(s)$ vanishes as $s \to \infty$, as any Laplace transform must. In other words, the impedance can be considered as the Laplace transform of some function of t:

$$z(s) = Z(s) - Z_\infty = \int_0^\infty e^{-st} f(t)dt, \qquad [A5]$$

where

$$s = s_r + i\omega \,. \qquad [A6]$$

The causality principle requires t to be positive in these expressions for Laplace transforms. Furthermore, there are no poles in the right half-plane for passive systems. There could be a simple pole at $s = 0$, but it can be substracted out as was done in the body of the text. One can also note that z_r is even in ω:

$$z_r(i\omega) = z_r(-i\omega) = \int_0^\infty \cos(\omega t) f(t) e^{-s_r t} dt \,, \qquad [A7]$$

while z_i is odd in ω:

$$z_i(i\omega) = -z_i(-i\omega) = -\int_0^\infty \sin(\omega t) f(t) e^{-s_r t} dt \,. \qquad [A8]$$

Since $z(s)$ is analytic in the right half-plane, the integral of $z(s)/(s - i\omega_o)$ around any closed contour in the right half-plane will be zero. If the contour is expanded to include the entire right half-plane, the semicircle at infinity is found to contribute nothing, and there remains the integral along the imaginary axis from $\omega = -\infty$ to ∞, with integration around the pole at $s = i\omega_o$.

If we transform from the variable s to the variable $W = -is$ (so that $W_r = -i^2\omega = \omega$ and $W_i = -s_r$), we conclude that z is analytic in the lower half plane (see figure 1a).

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