



Application of Electric Circuits in Chemistry

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(Received: 15 July 2011;

Accepted: 28 May 2012)

AJC-11523

Circuit models are used to express the behaviour of the conductometric cells in the radio frequency to microwave regions. In present work complex numbers are introduced which describe the behaviour of circuit models. Theoretical and experimental results are compared to describe a simple conductometric cell.

Key Words: Conductometry, Oscillometry, Complex numbers, Electrolytes.

INTRODUCTION

Braun^{1,2} published work based on electronics for chemistry laboratory and our papers on the subjects of conductometry and oscillometry³⁻⁶ were encouraging us to work on the electric circuits for alternative current (AC), use of complex numbers and application of AC circuits in conductometry.

A sinusoidal signal has an amplitude, a frequency and a phase angle. For example in potential equal to $A \sin(\omega t + \Phi)$, A is the amplitude, ω is the angular frequency and ω is equal to $2\pi f$ where f is the frequency and Φ is the phase angle. If a potential of $A \sin(\omega t + \Phi)$ is applied across a resistor with the value of R, Ohm's law will be applicable. According to Ohm's law the current flow through the resistor is $A/R \sin(\omega t + \Phi)$ if this potential is applied across a capacitor or inductor both of them will behave as a variable resistor which is function of the frequency ω and Ohm's law is applicable. Only the difference with direct current analysis is that the operation for the AC is done in the domain of complex numbers⁷.

A complex numbers is a couple with a real and an imaginary parts. (a,b) stands for an imaginary.

Number with the real part of 'a' and the imaginary part of 'b' or it could be written as $(a+jb)$ where j is the notation for the complex number and its value is the square root of -1. That is why these numbers are called complex. Since imaginary number is a couple, X-Y axis could be used to represent them. The real part is shown on the X-axis and the imaginary part is shown on the Y-axis. Beside, a complex number could be shown with an amplitude and an angle. For example $a+jb$ could be written as $(a^2+b^2)^{1/2} \angle \tan^{-1} b/a$ where $(a^2+b^2)^{1/2}$ is the amplitude and $\tan^{-1} b/a$ is the angle. This is shown in the Fig. 1. The operations on complex number are defined as follow:

$$(a + jb) + (c + jd) = (a+c) + j(b+d)$$

$$(a + jb) - (c + jd) = (a-c) + j(b-d)$$

$$(a + jb) \cdot (c + jd) = ac + jad + jbc - bd = (ac - bd) + (ad + bc)j$$

$$(a + jb) / (c + jd) = [(a + jb) \cdot (c + jd)] / [(c - jd) \cdot (c + jd)] = \\ \frac{[(a + jb) \cdot (c + jd)]}{(c^2 + d^2)} \\ = \frac{[(ac - bd) + (ad + bc)j]}{(c^2 + d^2)}$$

For the division the denominator and the numerator are multiplied by the complex conjugate of the denominator $(c - jd)$ to make the denominator a real number. The reactance of a capacitance with a potential applied $A \sin \omega t$ is $1/j\omega C$ where C is the value of the capacitance. Ohm's law is applicable and the current is $A/1/j\omega C$ which is equal to $Aj\omega C$. For an inductance the reactance is $j\omega L$ and the current is $A/j\omega L$. A voltage divider was covered¹ for the DC (direct current) analysis. For the circuits in AC (alternative current) analysis a voltage divider is made of two resistors connected to each other in series or an inductor or a capacitor and a resistor connected in series. The later circuit in AC has a new name called filter. A filter as the name suggest, means this circuit must be transparent (or pass through) certain frequencies and block other frequencies. There are two main categories of filters low pass filter and high pass filter. A low pass filter permits the lower frequencies pass.

Through and higher frequencies are blocked. It is made of two elements, a resistor and a capacitor connected in series. This is shown in Fig. 2. By applying Ohm's law, the output potential is given as:

$$v_o = \{(1/j\omega C) / [R + (1/j\omega C)]\} v_{in}$$

Or it could be simplified to $\{1/[1 + j\omega C R]\} v_{in}$

The gain for this voltage divider or in another words low pass filter is

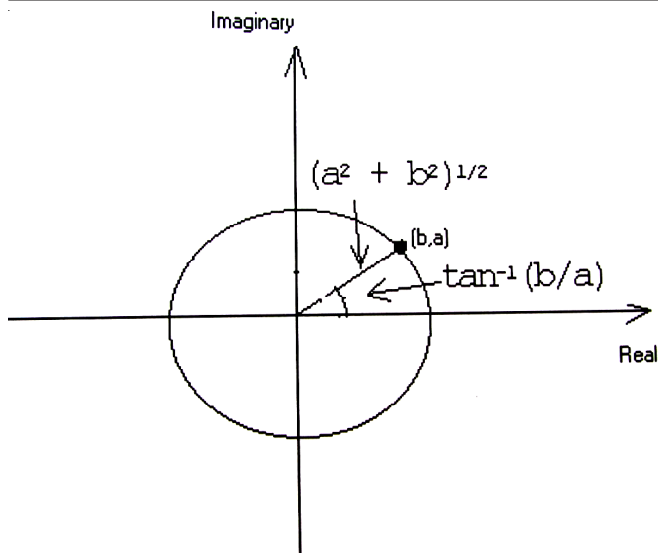


Fig. 1. Two ways representation of a complex number on X-Y axis

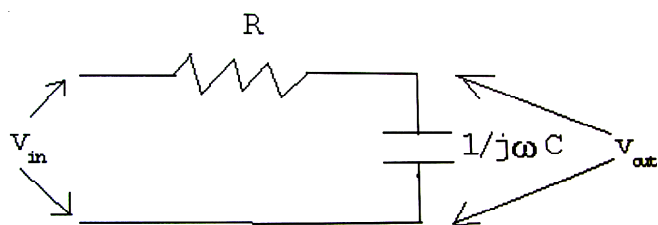


Fig. 2. An AC (alternative current) voltage divider or a low pass filter

$$(v_o / v_{in}) = [1 / (1 + j\omega RC)]$$

The expression gain is used for DC but transfer function is used for AC. This transfer function could be simplified to magnitude and angle as a function of ω .

$$Z = (v_o / v_{in}) = [(1 + \omega^2 R^2 C^2)^{1/2} / (1 + \omega^2 R^2 C^2)] \tan^{-1}(-\omega RC)$$

Figs. 3 and 4 show the plots of magnitude and phase angle as a function of frequency. Typical values of $R = 1\text{ k}\Omega$ $C = 1\text{ }\mu\text{F}$ are chosen. $1/RC$ is called the cut off frequency and has a value of 1 kHz. The plots from 1 Hz to 1 MHz are shown in Figs. 3 and 4. In Fig. 3, magnitude lower than $(1/RC) = 1\text{ kHz}$ is equal to 1 and the value of magnitude is equal to zero at higher frequencies greater than 1 kHz. The phase angle is shown in the Fig. 4 as a function of frequency.

At frequencies lower than 1 kHz the value of the phase is zero and at frequencies greater than 1 kHz the value is $-\pi/2$ or 90 degrees. These suggest this filter passes through lower frequencies, lower than 1 kHz and blocks the others. By changing the order of resistor and capacitor and measuring the potential across the resistor one gets high pass filter. The lower frequencies are blocked and higher frequencies pass though. The application of these filters are at places where there is noise present at either high or low frequencies and one likes to eliminate this noise from the signal. This may occur in electrochemical experiment. Two low and high frequencies cascaded from a band pass filter. A band pass filter passes through certain frequency range and blocks the other frequencies. This filter is used in the radios in tuning to a radio station.

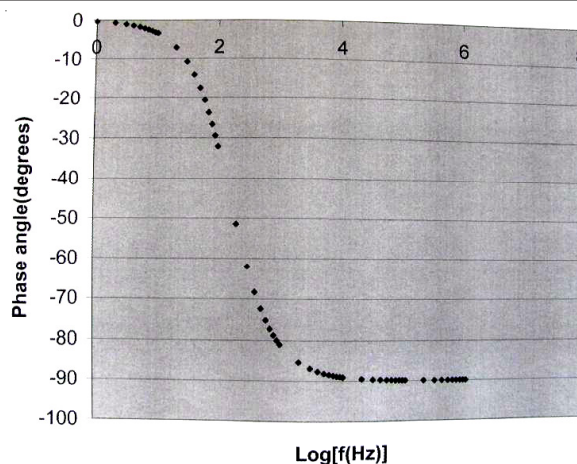


Fig. 3. Plot of the magnitude of the transfer function as a function of frequency for a low pass filter

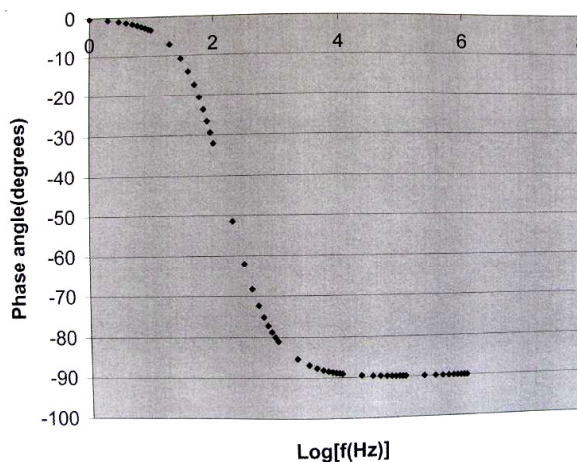


Fig. 4. Plot of the phase angle of the transfer function as a function of frequency for a low pass filter

Conductometry

A conductive type of cell is made of two electrodes in contact with an electrolyte. For the conductive type of cell an equivalent circuit is given in Fig. 5. Capacitance is mainly due to double layer and inductance is mainly wiring connecting an oscilloscope to the cell. R_1 is the voltage dividing resistor and R_2 is the resistance of the solution. The ratio of the output potential to the input potential of the circuit is

$$(v_o / v_i) = \{R_1 / [R_2 + (1 / j\omega C) + j\omega L]\}$$

where ω is the angular frequency of the field. After necessary transformation, the amplitude and phase angle are obtained

$$A(\omega) = \{R_1 / [R_2^2 + (\omega L - 1 / \omega C)^2]^{1/2}$$

$$\Phi(\omega) = \tan^{-1}(\omega L / R_2 - 1 / \omega R_2 C)$$

The curve for $A(\omega)$ is plotted in Fig. 6. Typical values of $R_1 = R_2 = 1\text{ k}\Omega$, $C = 1\text{ }\mu\text{F}$ and $L = 1\text{ mH}$ are chosen. The peak occurs at $\omega = 1/LC$. At the peak $A(\omega)$ is equal to R_1/R_2 . At $\omega = 1/LC$ where the resonance occurs, the reactance due to inductance and capacitance cancel each other and $A(\omega)$ is inversely proportional to the resistance of the solution R_2 . In another words $A(\omega)$ is proportional to conductance of the solution. By increasing concentration the conductance of the electrolyte increases and consequently the peak increases in Fig. 6.

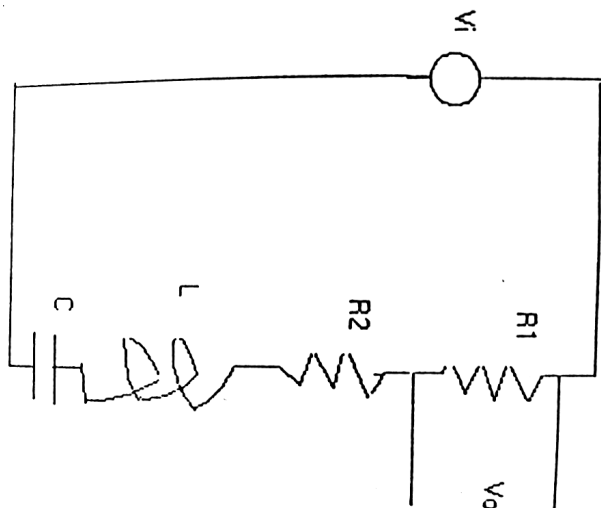


Fig. 5. An equivalent circuit model for a conductive type of cell combined with a resistor in series

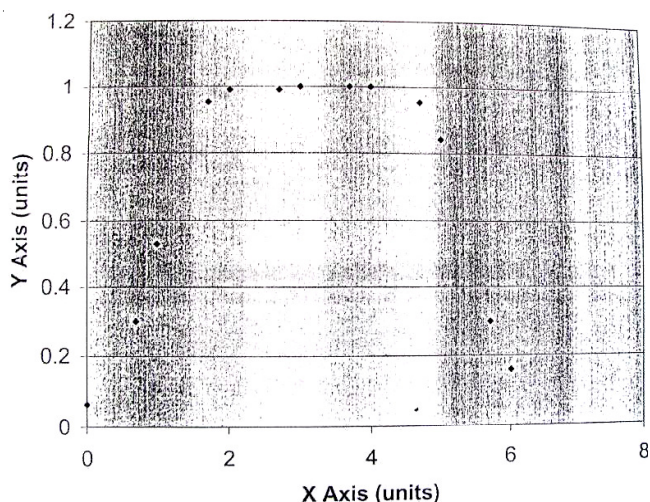


Fig. 6. Theoretical calculation of conductance *versus* frequency for a conductive type of cell

EXPERIMENTAL

A conventional two channels oscilloscope was used for the measurements. Only one channel was used. A sine wave generator was used which can apply voltages from a few hertz to 1 MHz frequency range. Non-porous platinum electrodes were used. Analytical grade hydrochloric acid was used for preparing various concentrations of hydrochloric acid. The apparatus was assembled as shown in Fig. 7. A 1 k Ω resistor is connected in series to the conductive cell. This resistor and the electrolyte cell together are considered a voltage divider. A sine wave signal was applied across both resistors by a function generator and the oscilloscope was used to measure the voltage across 1 k Ω resistor. If the current is low for the case of pure water or low concentration solutions, the potential shown across 1 k Ω resistor is low. The potential is high across

the resistor when the current is high for more concentrated solution. Fig. 8 depicts the conductances *versus* frequencies for hydrochloric acid at various concentrations. Semilog plots are used. There is a very good agreement between the theoretical (Fig. 6) and the experimental (Fig. 8).

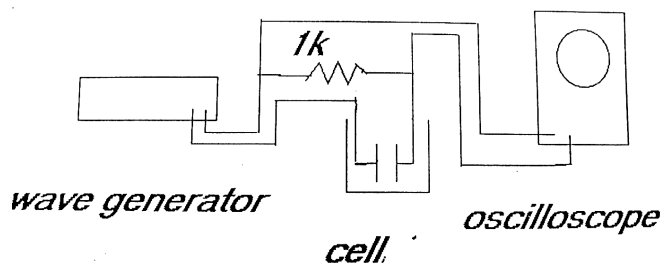


Fig. 7. Instrumental set up

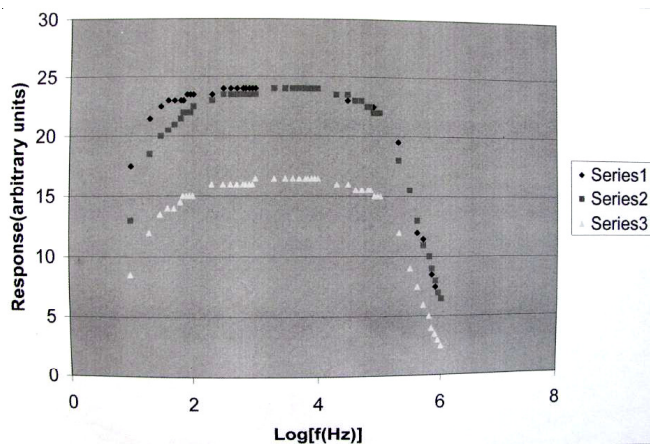


Fig. 8. Experimental measurement of the conductance for various concentration of HCl, series 1, 12 M series 2, 0.12 M series 3, 0.0012 M respectively

RESULTS AND DISCUSSION

By these presentations one learns how to handle complex numbers and how they are used in solving circuit problems. Simple equipment such as an oscilloscope and a function generator could be used to obtain valuable information about the electrolytes and the double layer, which is an interfacial phenomenon, is observed.

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