Electrolytic resistivity measurement using alternating current with high frequencies

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In this work we present resistivity measurements of saline solutions for several concentrations. We used alternating current with frequencies in the interval of 25 kHz to 90 kHz. We studied KCl and several metals for the electrodes: Cu, Fe, Al, bronze, and stainless steel. We did not use any covering on them. In our method we take the limit by extrapolation, when the frequency goes to infinity. We did not use ideal polarized electrodes. We found that our results for resistivity approximate accepted values in the literature. This tendency is present for all the materials we used. We found that from the set of metals we considered, Al is the best material for the electrodes with this method to obtain the solution resistivity. In some cases the difference between the obtained resistivity and the accepted values when Al is used, is less than 1%. For the rest of the metals considered we have differences greater than 6%.

Keywords: Physical chemistry; electrochemistry; electrolytic solutions; conductivity cell.

En este trabajo presentamos medidas de la resistividad de las soluciones salinas para varias concentraciones. Utilizamos corriente alterna con frecuencias en el intervalo de 25 kilociclos a 90 kilociclos. Estudiamos KCl y varios metales para los electrodos: Cu, Fe, Al, bronce, y acero inoxidable. No utilizamos ninguna recubierta en los electrodos. En nuestro método tomamos el límite, por extrapolación, cuando la frecuencia tiende a infinito. No utilizamos electrodos ideales polarizados. Encontramos que nuestros resultados para la resistividad se aproximan a los valores aceptados en la literatura. Esta tendencia está presente para todos los materiales que utilizamos. Encontramos que, del conjunto de metales que hemos considerado, los electrodos de *Al* son los mejores para obtener la resistividad de la solución. En algunos casos la diferencia entre la resistencia obtenida y los valores aceptados cuando *Al* se utiliza, es menor del 1%. Para el resto de los metales considerados tenemos diferencias mayores que 6%.

Descriptores: Física-química; electroquímica; soluciones electrolíticas; celdas de conductividad.

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1. Introduction

The measurement of the conductivity of an electrolytic solution is a complex process. It involves several aspects. Among these we have solution concentration, interaction of the electrodes with the solution, and the instrumentation used. These aspects have been included in a model which is an electrical equivalent circuit of a conductance cell [1]. This is shown in Fig. 1. Thus in a conductance cell there are capacitive effects, faradic impedance, Parker effect [2-4], and electrolyte resistance.

As capacitive effects we have the capacitance of the double layer on each electrode, the lead capacitance and the parallel capacitance. The faradic impedance depends on the chemical reactions of the solution with the electrodes. The Parker effect appears in high resistance solutions. In this case the impedance of the lead capacitances nearest to the electrodes becomes important.
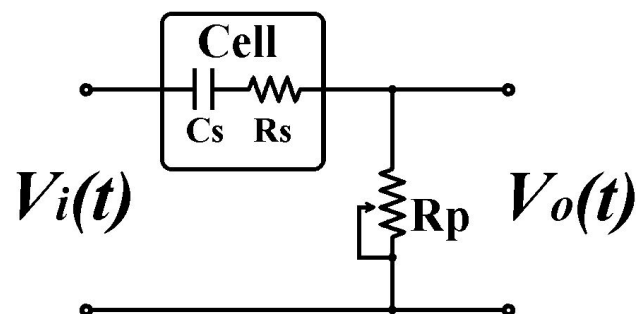

FIGURE 1. This is the electrical representation of the conductivity cell. C_s is the double layer capacity; R_s is the electrolytic solution; R_p is the variable external resistance; Vi(t) is the stimulus voltage; and $V_0(t)$ is the response voltage.
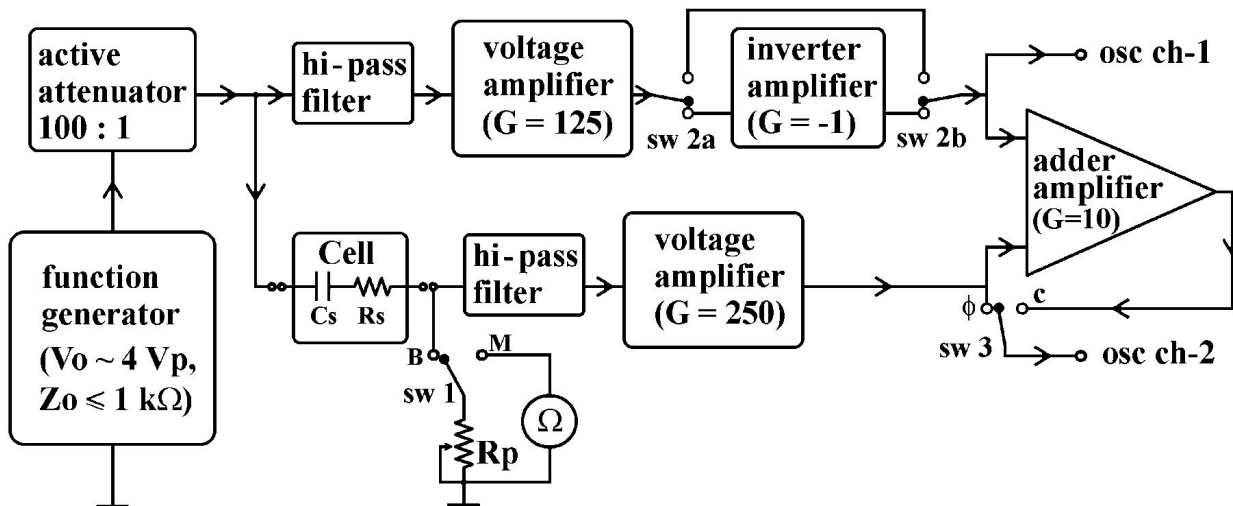
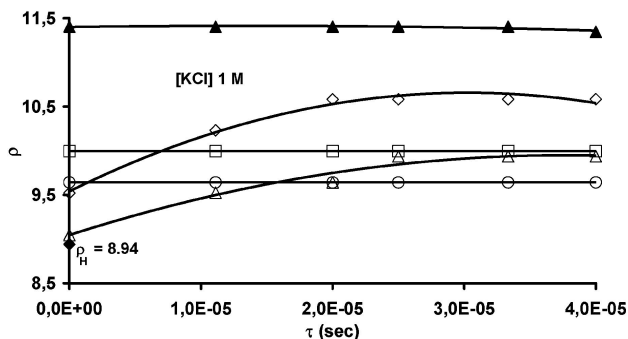FIGURE 2. Block diagram of the electronic circuit.

FIGURE 3. Curve fitting using second order expansion from Eq. (7) for the resistivity. ♦ Handbook value; △ Al; □ stainless steel; ◯ Fe; ▲ bronze; ◇ Cu.

In this work we are are interested in the resistivity of an electrolytic solution. For this purpose we used alternating currents (a.c.) to measure the resistance of an electrolytic solution. From the resistance we obtained the resistivity.

$$R = \rho(L/A), \tag{1}$$

where L/A is the cell conductivity constant.

We considered solutions of KCl at concentrations between 0.01 and 1.0 M. It is known that the impedance of the capacitive effects decreases with increasing capacitance or increasing frequency.

It is possible to minimize high frequency effects resulting from stray capacitances in leads, connections, and improper ground connections. This can be done by avoiding close placement of electrode leads and by the use of adequate ground. In this way the Parker effect is eliminated too. The conductivity cell was designed to be inserted into the connectors of the electronic board. Its volume is approximately 1 cm^3. With this design the Parker Effect was eliminated.

In this work we used polarizable electrodes made of different metals. With this kind of electrode the faradic impedance is present. With our method this impedance was eliminated. We found that our measurements converge, approximately, to the same resistivity value when the frequencies are larger than 75 kHz. This happened for all the metal electrodes we used. In Fig. 2 we show a block diagram of the electronic circuit we used in this work.

Two types of processes occur in the electrodes. The first one corresponds to a charge transfer through the interface metal-solution. In this case the electron transfer causes an oxidation or reduction. Since these reactions are ruled by Faraday's law (that is to say, "the amount of chemical reaction caused by the current flow is proportional to the amount of charge transferred"), this type of process occurs in the so-called *charge transfer electrodes* [3,4]. Electrodes with no charge transfer across the metal-solution interface potential even with the application of an external electric field are called ideal polarized electrodes (IPE). These electrodes can be used to avoid Faradaic processes.

On the other hand, the IPE electrodes contribute to the resistivity value with a capacitive reactance. This appears because of the double layer that is formed by the accumulation of charge in the proximities of the electrodes [4]. This reactance can be cancelled in the measurement of the solution resistivity using alternating currents with appropriate frequencies. We successfully used frequencies in the range from 0.05 to 100 kHz for this purpose. To avoid parasitic capacitances we mounted the cell connectors directly to the circuit board. The electrodes of conductivity cell were designed to be inserted to the circuit board connectors as shown in Fig. 3. We used an electrolytic solution of *KCl* in a cylindrical conductivity cell with a volume of around 1 cm^3.

2. Method

Figure 1 shows the electrical representation of the conductivity cell. An external, variable and known resistance, *Rp*, is used for comparison. This resistance is used to form a variable high pass filter [5, 6].

If the circuit is stimulated with a voltage sine signal, it is expected a sine voltage response is expected. This response will have amplitude no greater than the stimulus voltage and a phase difference due to the capacitive component.

Thus, if Vi(t) is the stimulus, V_1 is its amplitude and ω is its frequency:

$$Vi(t) = V_1 \sin(\omega t), \qquad (2)$$

The response, $V_0(t)$, will be:

$$Vo(t) = V_2 \sin(\omega t + \phi), \qquad (3)$$

Notice that $V_2 \leq V_1$. The phase difference is ϕ.

On the other hand it is known that for an electrical circuit such as that of Fig. 1 [7,8]:

$$\frac{V_2}{V_1} = \frac{1}{\sqrt{\left(\dfrac{Rs + Rp}{Rp}\right)^2 + \left(\dfrac{1}{\omega RpCs}\right)^2}} \qquad (4)$$

$$\phi = \arctan\left(\frac{1}{\omega Cs\,(Rp + Rs)}\right) \qquad (5)$$

where C_s is the double layer capacity; R_s is the electrolytic solution; R_p is the variable external resistance; Vi(t) is the stimulus voltage; and $V_0(t)$ is the response voltage.

If the ratio $(V_2/V_1)=1/2$, fixed, the resistance of the solution R_s is:

$$Rs = Rp\left[\sqrt{4 - \left(\frac{1}{\omega RpCs}\right)^2} - 1\right] \qquad (6)$$

Notice that if ω is very large, Rs $\approx$ Rp and $\phi \approx 0$. Otherwise, Rs will be less than Rp and $\phi \neq 0$.

3.   Experimentation

In Fig. 2 we show the block diagram of the experimental assembly. The function generator provides a sine voltage with 4 volts amplitude, frequencies from 50 Hz up to 10^5 Hz, and output impedance less than 1 KΩ. The active attenuator has three purposes. First, it eliminates any possible dc component in the signal. Second, it makes an adequate impedance coupling between the generator and the remainder circuitry. Third, it reduces the signal amplitude with a 100 to 1 factor (from 4V to 40mV). This is in order to avoid electrolysis in the cell. The generator is Philips PM 5125. The attenuator is made with a TL081 operational amplifier.

The output signal of the active attenuator is divided into two branches. The upper branch processes a reference signal, whereas the lower branch processes the measurement signal passing through the cell. Notice that a high pass filter is the first stage in both amplification branches. The output signal and the high pass filter are necessary to avoid propagation of a dc voltage. This voltage is generated in the two electrodes

of the cell. The cut-off frequency of the high pass filter is less than 1 Hz.

The upper branch is a voltage amplifier with a gain of 125 and 100 kHz bandwidth. This amplifier has the possibility of changing the phase for the final reference signal 180°. This final reference signal is displayed on the oscilloscope. The voltage amplifier is made with four stages of TL072 operational amplifiers.

The lower branch is formed by the conductivity cell, Rp, and a voltage amplifier with a gain of 250. When voltage V_1 is applied, Rp can be adjusted to obtain the condition $V_2/V_1 = 1/2$ [see Eq. (4)]. The value of V_1 is 40 mV in our measurements. The phase difference between V_1 and V_2 can be observed using the oscilloscope. This phase difference is due to the effect of the double layer capacitance Cs. The frequency of V_1 can be increased maintaining the same ratio V_2/V_1 by varying Rp. When the frequency is increased the phase difference tends to disappear. In this way the term $(1/\omega R_pCs)$ is negligible. The value of the solution resistance, Rs, can be read from the ohmmeter.

4.   Results

In Fig. 3 we show the results for our resistivity measurements as a function of $\tau = \omega/2\pi$, for several metals on the electrodes. The metals we considered on the electrodes are: Al, Cu, Fe, stainless steel, and bronze. These metals were cleaned but they were not polished. The electrolytic solution has a concentration of $1M$ for KCl. The reported value

TABLE I. Obtained adjusted values for ρ_0, ρ_H (in Ohm-cm) and the % difference for molar concentrations of KCl, shown in the graphs.

Electrode	[KCl] 1 M	
	ρ_o Ohm-cm	$\Delta\%$
Bronze	**11.4**	**27.5**
Al	**9.2**	**2.9**
Cu	**9.5**	**6.3**
Stainless steel	**9.99**	**11.7**
Fe	**9.6**	**7.4**
Handbook Values ρ_H [9]	**8.93**	

TABLE II. Obtained adjusted values for ρ_0, ρ_H (in Ohm-cm) and the % difference for all the molar concentrations of KCl we have considered.

[KCl] M	ρ_o (Ohm-cm)	ρ_H(Ohm-cm)[9]	$\Delta\%$
0.01	**707.3**	**709**	**0.2**
0.05	**155.8**	**161.8**	**3.7**
0.1	**86.9**	**84**	**3.4**
0.5	**19.2**	**18.6**	**2.9**
1.0	**9.1**	**8.9**	**1.9**

for the resistivity for this solution in handbooks [9] is ρ_H. We consider a series expansion.

$$\rho(0) = \rho_0 + \left[\frac{d\rho}{d\tau}\right]_0 \tau + \frac{1}{2}\left[\frac{d^2\rho}{d\tau^2}\right]_0 \tau^2 + ... \qquad (7)$$

where $\tau = 2\pi/\omega$; ρ_0 is the value of the resistivity at the origin. From Fig. 3 we can see that the closest value of ρ_0 to ρ_H occurs when we have Al on the electrodes. We considered several concentrations: 1, 0.5, 0.1, 0.05 and 0.01 M. We found for all these concentrations that the value of ρ_0 for Al is the closest one to ρ_H. In Table I we show the value for ρ_0 when we have Al on the electrodes for all the solution concentrations we have considered. We can see that the difference between the obtained ρ_0 and ρ_H is always less than 3.5% when we have Al on the electrodes. In one case this difference is 0.24%. For the rest of considered metals on the electrodes we have differences between ρ_0 and ρ_H larger than 10%.

5. Conclusions

We used a.c currents and high frequencies (>25 KHz) to measure the resistivity of an electrolytic solution. In our method we take the limit by extrapolation, when the frequency goes to infinity. We are not using IPE. We used 40 mV to facilitate the amplification of the signal. We have considered a saline solution. This was a KCl electrolytic solution. We studied the behaviour of several metals for the electrodes: Cu, Fe, Al, bronze, and stainless steel. In this way we were using polarizable electrodes. These electrodes tend to oxidize in contact with water. In steady state conditions the oxidation current is negligible. In these conditions the resistivity measurements can be performed. The electrodes oxidization has no effect on the resistivity measurements. We found that, of the set of metals we considered, Al is the best material for the electrodes with this method to obtain solution resistivity. In some cases the difference between the ρ_0 and ρ_H obtained when Al is used is less than 1%, as can be seen in Table I. With this method a direct measurement of the resistivity of saline electrolytic solutions is possible using Al.

Acknowledgements

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