The electric resistance in electrolytic solutions

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We present a new method to measure the electric resistance of electrolytic solutions contained in conductivity cells. The innovations are the use of a new type of conductivity cell, with variable longitude and to take into account the phenomenon of electric resonance in order to cancel the effects of the double layer capacity at electrode-solution interfaces. Analysis of error propagation on geometric parameters of the cell was performed and absolute measurements were done, without chemical patterns of calibration. The results obtained with this new method and new cell type suggest the possibility of covering a wider range of values for the conductivity of electrolytic solutions.

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

Se presenta un método nuevo para medir la resistencia eléctrica de soluciones electrolíticas, cuyas innovaciones son la utilización de un tipo de celda de conductividad de longitud variable, así como el aprovechamiento del fenómeno de resonancia eléctrica para cancelar los efectos de la capacidad de la doble capa en las interfases electrodo-solución. Con base en el análisis de la propagación de errores de los parámetros geométricos de la constante de la celda, se realizaron medidas absolutas omitiendo el uso de patrones químicos de calibración. Los resultados obtenidos abren la posibilidad de cubrir una gama más amplia de valores de conductividades de soluciones electrolíticas con este nuevo método y nuevo tipo de celda.

Descriptores: Física-Química; electroquímica; celda de conductividad.

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1. Introduction

A solution contained in a conductivity cell, with a given geometry, presents the conductivity $\boldsymbol{k}$ = (1 /R$_S$) ϑ, where R$_S$ is the electric resistance due to the solution bulk between the electrodes; and ϑ is known as the constant of the conductivity cell [1-3]. Traditionally the evaluation of $\boldsymbol{k}$ has been made measuring R$_S$ with alternating current bridges using very small voltages and currents ($\sim$ mV, mA), in conductivity cells of fixed volume and impolarizable electrodes, in order to neglect the undesirable effects in the measurements [4,5]. For the determination of the cell constant, ϑ, calibration solutions are usually employed in different concentrations whose conductivity values have been determined with high precision, in different types of cells under different temperatures [6-10]. In this way, with a solution pattern, the resistance is measured to know the constant ϑ which is used in any other solution evaluation, with the same cell. There is no doubt that chemical patterns are the most precise and repeatable way to calibrate conductivity cells.

The measurement of electrolytic resistance has many important applications in science [11,12]. In this work, we give a very precise technique to get an absolute measurement of the resistance of electrolytic solutions, without using chemical patterns to calibrate the conductivity cell. This is a very useful alternative when calibration solutions are not easily available.

2. Conductivity cell of variable longitude

Figure 1 shows our conductivity cell made in lucite. Its cylindrical geometry, with variable separation between electrodes (l) and fixed area (A), leads ϑ = l/A. This cell even though involves additional geometric errors in regard to one of fixed volume, offers versatility in covering a wider range of electrolytic solution conductivities, due to the advantage of adjusting l to get values of Rs within the range of measurements of a particular ohmmeter. It also allows a better understanding of phenomena involved in the measurement.

In regard to the geometric parameters, the relative uncertainty Y for the cell constant ϑ is

$$Y = \frac{dl}{l} + 2\frac{dD}{D}, \qquad (1)$$

where D and l are diameter and longitude of the cell, whose absolute uncertainties are dl = dD = Δl. Using the fac-

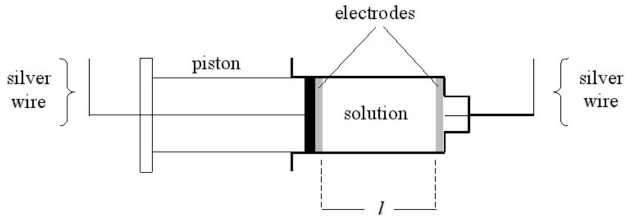

FIGURE 1. Conductivity cell developed.

tor X≡l/D for field uniformity [13]; and the longitude l in terms of a given volume V, the previous equation yields

$$Y = 2(\Delta l)\left(\frac{\pi}{4V}\right)^{\frac{1}{3}}\left[X^{\frac{1}{3}} + \frac{1}{2}X^{\frac{-2}{3}}\right]. \tag{2}$$

An analysis of Y in Eq. (2) using Δl = 0.0025 cm and V = 1 cm^3, is showed in Fig. 2, where is remarkable the linear behavior (correlation 0.999) in the propagation of uncertainties for values of X $\geq$ 1.

3. Resonant measurement system

It has been demonstrated [4,5] that a very good model of a conductivity cell for many electrolytic solutions, is the electrolyte resistance R$_S$ in series with the double layer capacitance C$_S$, corresponding to electrode-solution interfaces. This impedance allows the use of an external inductance L$_B$ (with internal resistance R$_B$) and an external reference resistance R$_P$, both variables, to form an RLC circuit which resonates for a previously selected frequency f$_o$. This allowed us to measure R$_S$ eliminating any significant contribution of C$_S$, because at the resonance frequency f$_o$, the inductive part of L$_B$ cancels the double layer capacitance ($C_S=(2\pi f_0)^{-2}L_B^{-1}$). In this way, the analysis of R$_S$ is simplified to a voltage divider circuit; then R$_S$ is expressed by Eq. (3), with *Vi* and *Vo* the corresponding input and output voltages to the RCL circuit [14]:

$$R_S = R_P\left(\frac{Vi}{Vo} - 1\right) - R_B. \tag{3}$$

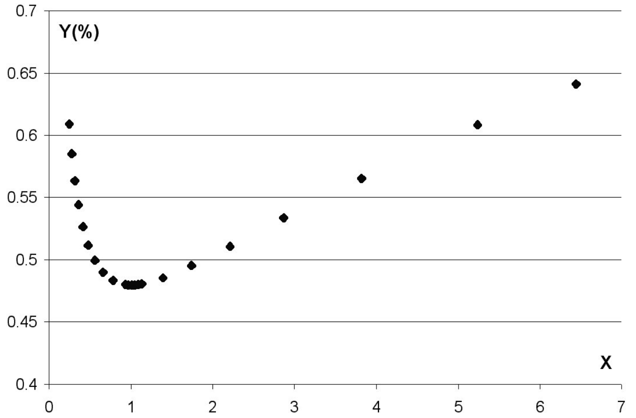

FIGURE 2. Relative uncertainty propagation in the constant of the cell.

For accuracy improvement in R$_S$ measurement following Eq. (3), instead of absolute measurements for *Vi* and *Vo*, a fixed value was established for *Vi*/*Vo* ratio, known with the smallest possible uncertainty (less than 0.1 %). We chose *Vi*/*Vo* ≡ 2; thus, Eq. (3) is simplified to R$_S$ = R$_P$ – R$_B$. This was made by amplification of signals *Vi* and *Vo* (exclusively for its comparation) using electronics with high coefficients of noise rejection [15-17]. Figure 3 shows our complete system for R$_S$ measurement, where switch 1 selects balance (B) of the resonant condition, or a measurement (M) state and switch 2 allows us to make an approximation to the resonant frequency (Δf$_o$ position) or its definition (f$_o$) with high precision. For more details, see Ref. 18.

4. Experimentation

A solution of potassium chloride, 0.1 M, with a temperature of 18.5 ± 0.1°C, was analyzed in a cell of 3 cm^3 as maximun volume (Fig. 1), with AgAgCl electrodes. We made use of the experimental system shown in the Fig. 3, with *Vi* = 40 mV peak and resonance frequency around 8 kHz. Initially, with maximum longitude l, the corresponding R$_S$ value was registered. Then, displacing the piston in steps of 0.5 mL, the value of R$_S$ was again measured. In Table I, the values obtained for Rs are shown, besides the solution conductivity ***k*** for each measurement, including the error propagation due to uncertainties on R$_S$ and the constant of the cell.

Each value obtained for the conductivity corresponds to the usually reported one, 113.36x10^{-4} S/cm [13], within the ranges of uncertainties; except for the corresponding to the minimum longitude, in which the border effects were important for the electric field. This minimum longitude corresponds to the ratio l/D = 0.99 (see Fig. 1).

These observations allow discarding the last value in Table I and they define the range of variation of the cell longitude: from their maximum value up to 33% of it; this means that we can analyze volumes between 3 and 1 mL. The average of the conductivity and the dispersion reported at the end of the Table I, correspond to values for this volume interval.

TABLE I. Experimental values obtained.

Volume (mL)	***l* (cm) ±0.0025 cm**	**Rs (Ω)**	***k* (10^{-4} S/cm)**
3	5.165	825 ± 0.32%	112.97 ± 0.96%
2.5	4.300	679 ±0.35%	114.27 ± 0.99%
2	3.410	544 ±0.38%	113.11 ± 1.02%
1.5	2.620	411 ±0.44%	115.03 ± 1.08%
1	1.745	279 ±0.56%	112.86 ± 1.20%
0.5	0.835	145 ±0.89%	103.91 ±1.53%
		Average *k* =	**113.65**
		Dispersion =	**0.84%**

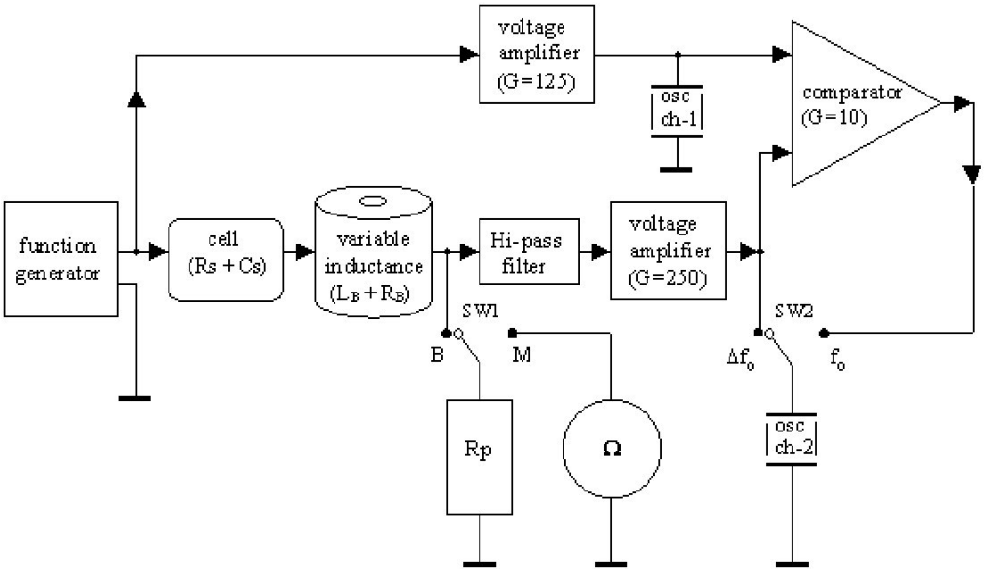

FIGURE 3. Measurement system for electrolytic solutions resistance.

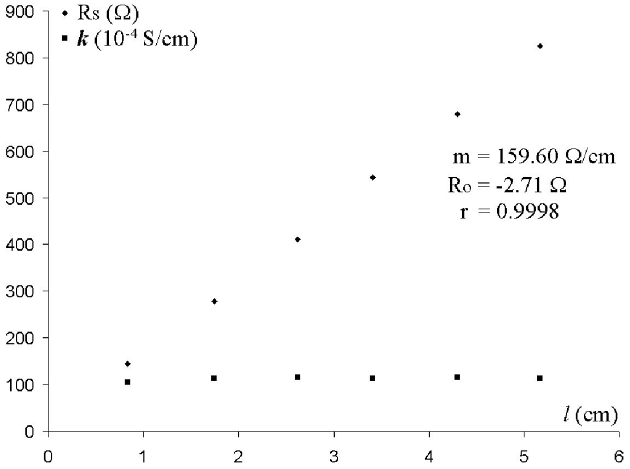

FIGURE 4. Resistance and conductivity of the solution vs longitude of the cell.

The resulting average for the conductivity differs from the expected value in 0.29 x 10^{-4} S/cm (*i.e.* 0.26 %). In Fig. 4 the results are also shown and the correlation coefficient 0.9998, guarantees the process linearity. Theoretically a null value was expected for the ordinate to the origin (R_o), the obtained one can be attributed to the prospective experimental uncertainties.

5. Conclusions

Without using chemical patterns for the calibration of the constant cell, good absolute values for the conductivity of the analyzed solution were obtained for different volumes. The analysis of the error propagation in the geometric part for the constant cell, demonstrates that there is a minimum value in the relationship of the parameters l and A attributable to the field uniformity factor, l /D. This assures a good range of validity for our cell of variable longitude, in order to cover a wider range of values for the conductivity of other electrolytic solutions.

The use of the electric resonance and the electronics developed for the comparison of the solution resistance R_S against the external and known resistance Rp, has an equivalent precision to the one of the a.c. bridge method. Besides, our new method has the advantage of eliminating all spurious impedances by using in an appropriate fashion the resonance phenomenon in a convenient RLC circuit; *i.e.*, the solution resistance R_S is practically isolated from undesirables effects during its measurement.

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