Optimal Frequency Range for the Measurement of A.C. Conductivity in Aqueous Solutions

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Abstract

The measurement of electrolytic conductivity is widely applied as a control parameter for different types of aqueous solutions. In order to obtain absolute methods this measurement has recently undergone a critical revision; several criteria have been established defining the experimental chain leading to conductivity values traceable to the SI units. In this work the attention is focussed, under a.c. regime, on the electrical behaviour versus frequency of the cell-solution system, which is represented through a lumped parameter model comprehending parasitic effects. Conductivity has been measured using an a.c.-bridge in the frequency range 12 Hz-200 kHz on solutions with very different ionic content: from ultrapure water to 0.1 m KCl. Results have been compared under the prospect of the reported electrical model. The model correctly represents the electrical behaviour versus frequency of the samples. It has been observed that stray effects at the electrode-solution interface and in the bulk solution differently affect the measurement when dilution is varied. A frequency range can be identified where parasitic effects are minimised and the measured electrical properties confidently can be attributed to the solution ionic content. This is valid for any measurement conditions even if when dilution level increases the valid range decreases in width and drifts towards low frequency values.

1. Introduction

The electrolytic conductivity χ of aqueous solutions, expressed in siemens per centimeter $(S\,cm^{-1}$ or $\Omega^{-1}cm^{-1})$, is an important control parameter whose usage and relevance are continuously increasing in industrial, pharmaceutical and environmental processes, for example. Consequently, the measurement of χ and its traceability to SI units are recently returned the subject of wide research activities, especially when extremely diluted, upward ultrapure, water solutions are considered. In fact, χ depends on the amount and on the charge transport ability of the ions dissolved in a solution and from electrolytic conductivity value it is possible to deduce a corresponding ionic content or to evaluate a purity level with regard to the ionic concentration.

We consider an electrolytic cell as a generator connected to two electrodes which are within a glass chamber containing the solution, then electrolytic conductivity can be calculated by equation 1:

$$? = \frac{k}{R_c} \tag{1}$$

R_c (Ω) is the electrical resistance of the solution and k (cm^{-1}) is a characteristic geometric cell constant. For a cylindrical cell and electrodes with parallel surfaces in front of each other, k can be approximated as:

$$k = \frac{l}{A} \tag{2}$$

where l (cm) is the distance between the cell electrodes and A (cm^2) is the electrode effective surface area. The experimental effort in the determination of the electrical conductivity of a solution does consist then in the accurate evaluation of the cell constant k and of the resistance R_c.

In the last years several primary standards have been introduced for the measurement of conductivity in electrolytic solutions [1]. Different criteria are proposed for the selection of the appropriate solvent-solute couple [2] and reliable electrical instrumentation [3], for temperature control [4-6], for sample preparation and preservation [2] and for the determination of cell constant [1]. The usual physical layout of the cell-solution system does not allow for electrical measurement in d.c., mainly because at the electrode-solution interface and in the bulk of the solution polarization effects arise. Unless non-polarized electrodes are used [7], conductance, i.e. resistance, measurements must be performed in a.c. regime. Under these conditions, we measure a complex impedance $Z(f)$ dependent on frequency f and represented as:

$$Z(f) = R(f) + j\,X(f) \tag{3}$$

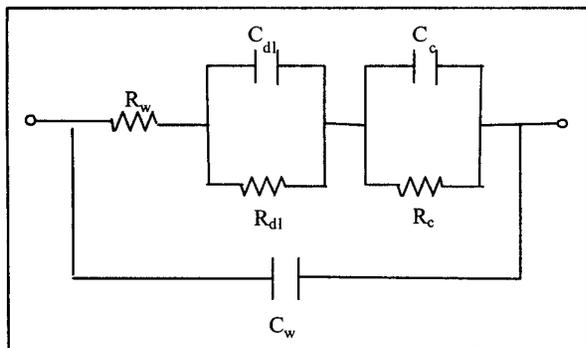sum of a the real resistive term, $R(f)$, and of the complex capacitive term, $X(f)$.

Fig.1: Cell-solution equivalent circuit as proposed by Thornton [3] representing the lumped electrical parameters corresponding respectively to: R_c, C_c = Resistance and Capacitance between the electrodes of the cell, R_{dl}, C_{dl} = double layer Resistance and Capacitance, R_w, C_w = connecting wires Resistance and Capacitance.

It must be stressed that R_c is not necessarily coincident with the real part of $Z(f)$ because of the several parasitic effects caused by the physical layout of the cell and by the connection lines to the measuring apparatus. Uncertainty is difficult to be reduced below ± 1 % if R_c is let to coincide with $R(f)$ and the error increases when extremely diluted solutions are analyzed, as will be seen later. The lack of accuracy in extrapolating R_c from the evaluated impedance was confirmed since when the first experimental works dedicated to this measurement technique appeared [10-11]. In particular, on the same sample a different behavior of R_c on frequency had already been observed, even if not clarified, when the geometric constant k was varied [12]. Some of the primary standards recently proposed for electrolytic conductivity are exactly based on designs of the cells with variable central sections and differential measurement [1], in this case it must be observed that the effects of stray parameters with the variation of the cell geometry has to be considered.

The importance of limitations to the excitation frequency applicable to infer conductivity directly from $R(f)$ is best appreciable when an electrical model of the cell with its solution is worked up. Parasitic parameters effects can be described with a reliable model and the dependence versus f of $R(f)$ can be provided according to the cell geometry and the ionic concentration of the solution.

The aim of this work, rather than to provide a standard for the accurate measurement of electrolytic conductivity, is to show that the effects of the parasitic parameters on conductivity measurement can be identified and minimized. This can be accomplished through an appropriate selection of the working frequency range, a careful cell design and the definition of a due lumped parameter model of the cell-solution electrochemical setup.

2. Experimental

Four different samples (A, B, C, D) have been prepared. Two of them consisted of KCl solutions with concentrations corresponding, approximately, A to 0.1 m KCl and B to 0,01 m KCl (expressed in molality units m corresponds to the number of moles of the solute, KCl, diluted in 1000 g of solvent, water). Respectively, 7.4365 g (A) and 0.7440 g (B) of dry KCl pure salt have been weighed with an analytical balance and added to 1.000 kg of ultrapure water weighed with a technical balance. Two other samples have been analyzed consisting, C of ultrapure water whose CO_2 content had been previously equilibrated with atmosphere [7] and D of ultrapure water continuously flowing from the refining supplier (Flow rate ~ 10 liter/hour). For D there was a direct piping between the ultra-pure water production apparatus and the measuring cell, in order to minimize CO_2 contamination of water.

Three cells with different k constants, depending on the conductivity values of the analyzed solutions (see eq.1), have been used in order to maintain the resistance value to be measured as close as possible to the optimal range of the electrical equipment (100 Ω – 10^5 Ω). For the KCl solutions the cells consisted in pyrex chambers containing two platinum electrodes disposed in parallel and separated by a cylindrical central section whose length was different for A and B. For the water samples C and D the same cell was used, consisting in a cylindrical pyrex chamber with parallel platinum electrodes separated by only 1 cm length l. The cell constant values k are reported in table I.

Electrical measurements have been carried out using a General Radio Digital RLC Bridge, mod. GR1693. The bridge has been connected to the cell electrodes with wires whose resistance R_w had been previously evaluated. A constant a.c. voltage of 0.5 V_{rms} has been applied. The result of each measurement corresponded to a total impedance $Z(f)$ separated in its series components $R(f)$ and $X(f)$. The behaviours of $R(f)$ and $X(f)$ has been analysed in the range from 12 Hz to 200 kHz. The temperature control was maintained in the range 21.5 ± 0.5 °C.

3. Electrical Model

Among others Thornton [3] proposed a lumped parameter model representing the main elements of the cell-solution electrochemical system comprehensive of the wiring circuitry. This model has been here adopted and is represented in figure 1. R_c and C_c represent, respectively, the resistance and the capacitance of the solution between the electrodes. R_c is exactly the resistance term to be extrapolated from measurements in order to calculate the electrolytic conductivity χ of the solution.

Tab. I: Cell-solution parameters used in the model of Fig.1 to fit the experimental results of electrolytic conductivity in the KCl solutions A and B and in the ultrapure (UP) water samples C and D. Reported values for C_c, C_{dl}, R_{dl}, C_w and R_w are compared with literature available data, in parenthesis [1-7].

[T = 21.5 ± 0.5 °C]	KCl 0.1 m A	KCl 0.01 m B	UP water CO_2 equilibrated C	UP flowing water D
Cell constant, k (cm^{-1})	15.05	15.43	0.102	0.102
Electrolytic conductivity, χ (μS/cm)	12236	1319	1.41	0.051
Cell resistance, R_c (Ω)	1.25 10^3	11.7 10^3	725 10^3	1.98 10^6
Electrodes resistance, R_{dl} (20 – 200 kΩ)	10 10^3	10 10^3	200 10^3	200 10^3
Electrodes capacitance, C_{dl} (10 μF – 2 mF)	5 10^{-5}	1.8 10^{-4}	2 10^{-4}	2 10^{-4}
Cell capacitance, C_c (10 – 100 p F)	1 10^{-12}	1.1 10^{-12}	145 10^{-12}	110 10^{-12}
Wire resistance, R_w (1 Ω)	0.1	0.1	0.1	0.1
Wire capacitance, C_w (10 – 100 pF)	1 10^{-12}	1 10^{-12}	8 10^{-11}	8 10^{-11}

The electrochemical behaviour of the electrode-solution interface is extremely complex and represents the major font of parasitic terms, including polarizing effects. We can helpfully describe it through the electrical double layer (dl) that represents the whole array of charged species and oriented dipoles existing nearby the electrodes. Its presence is interpreted in the model as an obstacle to the charge transfer in the vicinity of the electrodes, i.e. as an additional resistive term R_{dl}. At the same time the existence of charged layers in the solution, counteracting the electrode charge, can be interpreted as a capacitive effect, C_{dl} [13].   Finally

a contribute from the wiring circuitry is considered, consisting in a resistive additional term R_w and a shunt capacitance term C_w. The model has been used to calculate the total impedance $Z(f)$, which one has in a real measurement, as a function of frequency. The cell constants k are known from geometrical measurement. R_w is directly measured in d.c.. C_w is calculated through the measurement of the empty cell, when C_{dl}, R_{dl} are ineffective and C_c is negligible because the permittivity of air is vanishing if compared whit that of water solutions. At a first step C_c has been calculated too assuming that the dielectric constant
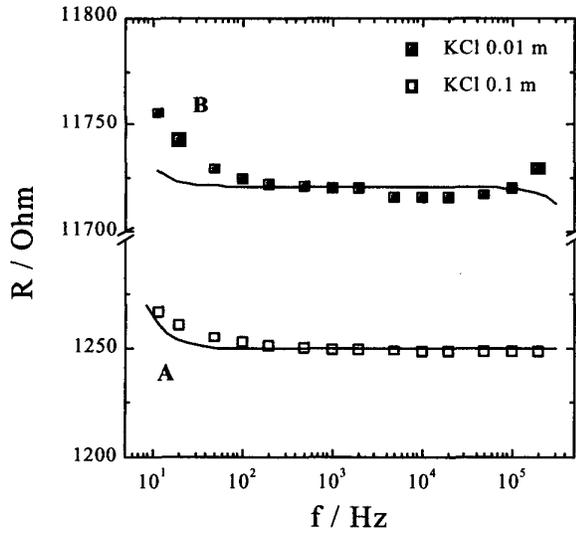

Fig.2: Resistance values versus frequency as measured on samples A, KCl solution 0.1 m (?), and B, KCl solution 0.01 m ( ).
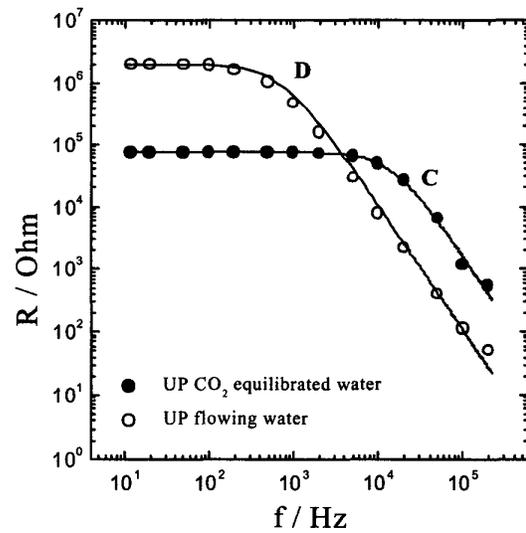

Fig.3: Resistance values versus frequency measured on samples D, ultrapure (UP) water continuously flowing in the cell (Flow rate ~10 L/min) (O), and C ultrapure water CO_2 equilibrated (?).
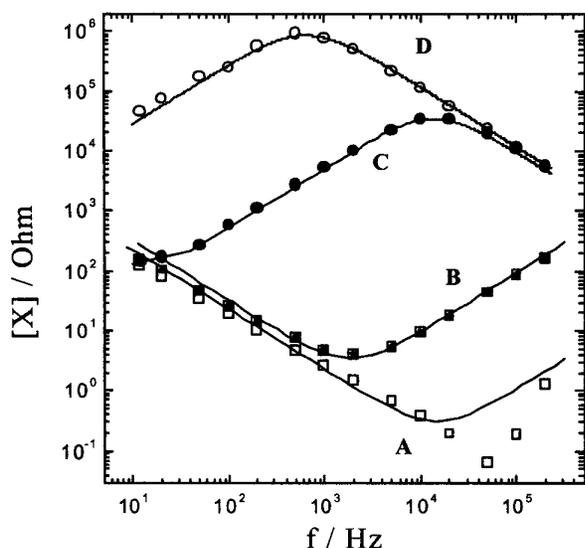
Fig.4: Absolute values of the reactance terms ¦ X¦ versus frequency for the samples here examinated: A KCl 0.1 m solution (?), B KCl 0.01 m solution (▪), C ultra-pure water CO_2 equilibrated (?) and D ultra-pure water continuously flowing (Flow rate ~10 L/min) (O).

of the solution is known [13]. C_{dl} and R_{dl} can not be easily calculated or measured but some data are at disposal in literature [1-9]. The values of these parasitic parameters are reported in table I. The conductivity of the solution has been obtained through the best fit of the model on the experimental points, choosing C_{dl} and R_{dl} to vary only within the range of the calculated or available data.

In this context inductive terms are considered negligible, as expected unless measurements are accomplished with coaxial electrodes and a high purity level in the solution is approached [3].

4. Results and Discussion

The fits of the model (lines) and the experimental data (points) are shown in figure 2, 3 and 4. In particular, in figure 2 experimental points are reported corresponding to $R(f)$ for the KCl samples A and B. In figure 3 experimental points are reported of $R(f)$ for the UP water samples C and D. In figure 4 experimental points corresponding to $X(f)$ are reported for all of the samples (A, B, C and D) as absolute values in a logarithmic scale.

We see that the model accurately fits qualitative and quantitative features of the experimental data. An interesting result considering the large variations of $R(f)$ and $X(f)$ observed among the samples and versus frequency. Most of the deviations of the fits from the experimental data could be not significant, as they appear at the edges of

the frequency range. In fact the variation with frequency in the accuracy of the measurement with the electrical apparatus is retained within an uncertainty equal to ± 0.02 % around 1000 Hz, but this value shows a steep decay when frequency values extreme in the range 12 Hz – 200 kHz are approached.

A very different behavior of the samples on frequency confirms that the effects of the parasitic elements are directly related with the sample dilution. From figure 2 one can observe a stable and reliable behavior over a large frequency range of the $R(f)$ values reported for the KCl solutions A and B. Polarization effects, increasing $R(f)$, are observable for f < 500 Hz, while parasitic effects show up only for f > 20 kHz. In figure 3, $R(f)$ is reported for UP water samples C and D. The measured conductivity is abruptly varied among the samples as well as its huge dependence versus frequency is modified due to the different CO_2 content.

In substance it is possible to affirm that, for electrolytic solutions, the behavior of the $R(f)$ versus f is strictly connected with the ionic content. The frequency range over which R_c and $R(f)$ are comparable is progressively reduced in width and is shifted toward lower frequency when sample dilution increases. In order to evaluate the conductivity, using the model, it is possible either to use the value of R_c as extrapolated from the best fit or to select the appropriate frequency range over which R_c can be confidently approximated to $R(f)$. This latter capability, to determine conductivity with a single point detection within the confidential frequency range, is of fundamental importance for technological applications. As a final remark, from a metrological point of view, it must be observed that, in the case of ultrapure water, measurement of conductivity are extremely difficult because of intrinsic limitations in the accuracy of the electrical equipment in the frequency range related with a stable electrical behaviour (f < 100 Hz). Additionally the resistance value to be measured must be maintained within the extent whose traceability is traditionally maintained for a.c. measurement ($R(f)$ = 100 kΩ) through an appropriate selection of the cell geometry. At the same time an accurate knowledge of the theoretical behaviour of water dissociation equilibrium is necessary because some of the circuit terms previously negligible can become more and more important.

5. Conclusions

When electrolytic conductivity is determined in a.c. regime the chemical-physical phenomena occurring at the electrodes and in the bulk of the solution modify with frequency their relative contribution to energy dissipation processes, thus affecting the measurement of the electrical properties of the solution. To study the effects of the parasitic phenomena when the resistance of the solution, R_c,

is assumed as the real part $R(f)$ of the total impedance $Z(f)$, in this work four samples with different ionic content have been prepared and the corresponding $R(f)$ measured in the range 12 Hz –200 kHz. A lumped parameter model of the cell-solution system has been adopted able either to rationalise the behaviour of $R(f)$ as well as to extrapolate R_c, taking into account the contributions of the main stray parameters identified. When the dilution of the ionic content increases, the frequency range over which R_c can be confidently identified with $R(f)$ is observed to reduce in width and to shift toward lower frequencies. This range falls into the low frequencies regions, where classical electrical equipment for a.c. measurements are hard to be accurately controlled, when extremely diluted solutions are considered and this negative item is added to difficulties in maintaining the measured resistance value within the traceable chain.

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