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HOW TO MEASURE ELECTROLYTIC CONDUCTIVITY SUCCESSFULLY

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Abstract – Measurement of electrical conductivity of liquids (electrolytic conductivity), despite of its apparent easiness, can cause serious problems – especially when is performed in conditions different from those defined by the manufacturer of the conductivity meter applied or when an instrument of own design is used. The purpose of this paper is to present the most substantial and most frequent problems that may occur in such measurements and how to master them. Effective remedial measures were indicated.

Keywords: electrical conductivity, cell constant, sources of measurement error, electrode polarization, four-electrode method

1. INTRODUCTION

Among the liquids conducting electric current a great majority are electrolyte solutions that are also the main component of all living organisms. Hence measurements of electrolytic conductivity (electrical conductivity of electrolyte solutions) are carried out commonly, in all areas of industry, economy and scientific research, as well in biology and medicine. Usually they do not cause problem if one is using a ready-made conductivity meter co-operating with a single, permanently connected to it conductivity cell or with a set of exchangeable cells recommended by the manufacturer. Under particular measurement conditions, uncertainty of the results obtained can be calculated following recommendations given by the manufacturer. Contemporary conductivity meters are usually equipped with a temperature sensor and can perform a temperature compensation of the conductivity values. Then the user obtains as the final result the conductivity value corrected to a reference temperature (at present 25^0C is recommended), with the cell constant included. When the temperature compensation is switched off, the conductivity value at the actual temperature of measurement is obtained.

Measurements become more complicated when conductivity meters are used with the cells coming from a different manufacturer. In this case it is recommended to study carefully (if necessary, also to check experimentally) metrological properties of the conductivity meter and each of the cells. Unfortunately, these properties are not provided uniformly. Some manufacturers state the total uncertainty (error) of the conductivity measurement carried out by the conductivity meter equipped with a particular cell; others give information on measurement uncertainty of the cell resistance (conductance). Information about the cells is usually limited to the cell constant value and limits of measured conductivity. Full characteristics of the cell, in various measurement conditions, are very rarely available in application notes. If doubt, it is recommended to check correctness of the conductivity meter indications using a calibration solution.

It may prove difficult to estimate temperature compensation error because the manufactures usually provide only the error of the solution temperature measurement. Particular attention should be paid when carrying out measurements in a wide range of temperature, with the temperature compensation switched on, as a large variety of temperature coefficients may occur (they may depend on the kind and concentration of the solution, and the temperature range). This problem does not occur if one has a specialized instrument, adapted to measuring particular liquids (eg. pure water, H_2SO_4, NaOH, etc.).

The worst situation occurs when conductivity meters and conductivity cells are used without proper metrological documentation, eg. self-made ones. In such a case, a more detailed and advanced knowledge in the range of conductometry is necessary to organize and perform the measurements properly. The most common and perhaps the most serious problem is variation (apparent variation) of the cell constant that can be observed when changing the measurement conditions. Therefore it will be discussed in detail further in this paper. Although a lot of useful and good quality technical brochures on the measurement of electrolytic conductivity and suitable instrumentation are available, e.g. [1][2], none of them can substitute this paper.

2. MAIN PROBLEMS

Electrolytic conductivity cannot be measured directly. It is necessary to use a proper conductivity cell (a sensor) that encloses a sample of solution and forces flow of electric current in it – by means of electrodes or by magnetic, or capacitive coupling. One measures resistance (or conductance) of the solution which fills the cell and calculates the solution conductivity κ by applying a cell constant K – conversion coefficient characterizing geometry of the cell:

$$\kappa = \frac{K}{R_e} = K \cdot G_e \approx \frac{K}{R_c} = K \cdot G_c \qquad (1)$$

where: R_e and G_e – resistance and conductance of the solution filling the cell, R_c and G_c – measured resistance and conductance of the cell (R_c and G_c should be very close to R_e and G_e, respectively).

In practice, the cell constant value is determined experimentally, usually by measuring a calibration solution. One assumes that the cell constant K has a certain, constant value. This assumption can be fulfilled with some approximation only – and this approximation is one of the main sources of error in conductometry. Discrepancies between the cell constant values assumed for the purposes of calculations and the real value result mostly from the differences between the measured resistance of the cell and real resistance of the solution filling the cell, under actual measurement conditions (that relates to the measurement as well as to calibration).

The second major source of error in conductometry is very large and strongly differentiated change of the solution conductivity in function of temperature. In this paper it is assumed, for simplification purposes, that the measurements are performed at one set temperature.

2.1. Influence of electrode impedance and residual effects

In practice, the majority of electrolytic conductivity measurements is performed by electrode methods (contact methods), usually two-electrode ones. The electrodes are necessary to provide transition from the ionic conduction in electrolyte solutions to electronic conduction in metal conductors. However, they can also be the source of serious problems. An electrode layer, having properties of electrical impedance which is capacitive in nature, is always formed at the interface boundary. The electrode impedance is commonly called "polarization impedance".

Electrode impedances, together with stray currents flowing outside the cell (if the cell has no closed vessel) and electrical residual parameters of the cell and its connections, are the main cause of variations of the cell constant value (or rather „apparent variations", as the cell geometry remains constant). An equivalent circuit of a real two-electrode cell is presented in Fig. 1.

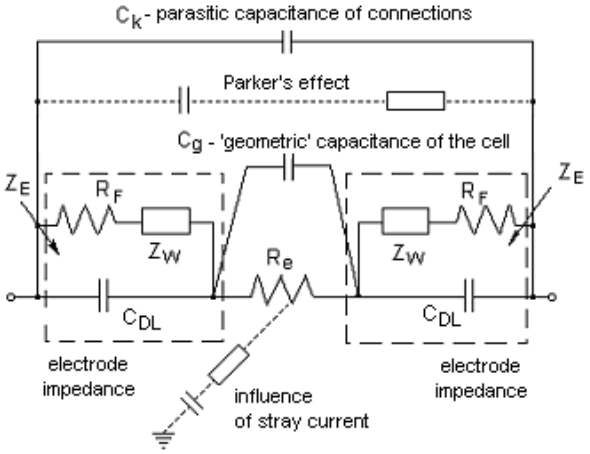

Fig. 1. Equivalent circuit of a two-electrode conductivity cell [3] (dash lines surround electrode impedances).

In Fig. 1 R_e represents the resistance of the bulk electrolyte solution (measurand), connected in series with two electrode impedances Z_E consisting of double layer capacitances C_{DL}, Warburg impedances (diffusion impedances) Z_W and Faraday resistances (chemical reactions resistances) R_F, where Z_W and R_F are frequency dependent – a suitable equivalent circuit is shown Fig. 2a (electrode impedances can be considered as linear ones only in the range of small electrical signals). By transforming this circuit to a serial form (Fig. 2b) one can show that the measured sensor resistance R_S is a sum of the solution resistance R_e and two frequency dependent polarization resistances R_p (generally, R_p should be considered as a sum of the polarization resistance and residual effects, like stray current, residual resistance and capacitance, etc.).

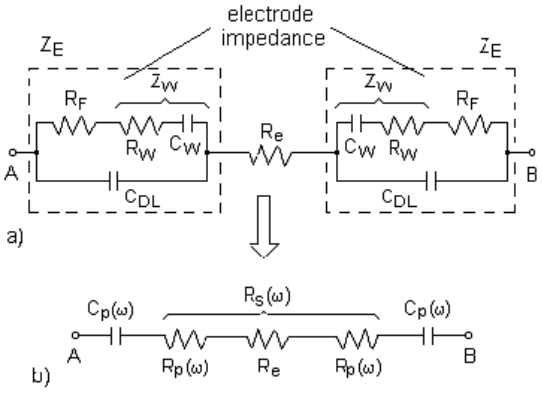

Fig. 2. Transformation of the serial-parallel circuit modelling a two-electrode conductivity cell (a) to an equivalent serial circuit (b) [4].

Parameters of the electrode impedance depend on many factors, mainly on the kind and concentration of the solution, material and roughness of the electrodes, temperature and also the measuring frequency. Electrode resistances can have very large values, especially for electrodes made of smooth metal – Fig. 3.

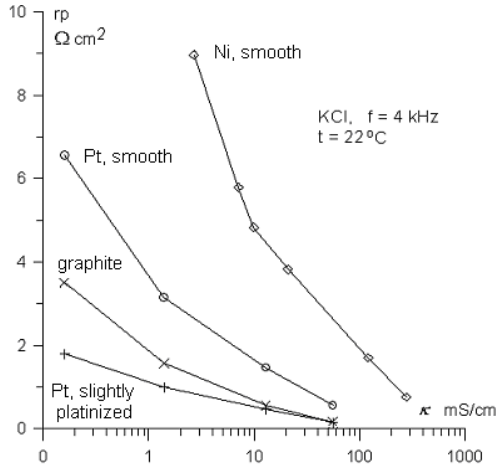

Fig. 3. Polarization resistance per unit for one electrode surface made up of different materials, as a function of conductivity [3].

The major challenge of the research is how to arrange the measurement to accurately extract the measurand R_e from the measured resistance R_s. It can be achieved by minimizing the contribution of the polarization resistances or applying the four-electrode method of measurement. Often both these approaches are necessary.

Figure 4. presents exemplary values of the measurement error of the electrolytic conductivity, carried out using a two-electrode cell, caused by the electrode impedances and residual parameters of the cell (mainly the capacitance of connections). In the range of low conductivities the error is determined by the parallel residual capacitances (positive error), and in the range of high conductivities – by electrode polarization (negative error).

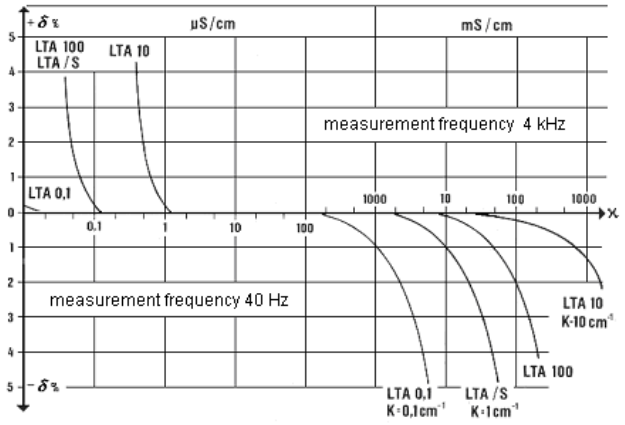

Fig. 4. Error of the conductivity measurement performed using two-electrode cells, as a function of conductivity, material of electrodes and cell constant: LTA 0.1 – Pt, bright, 0.1 cm^{-1}, LTA 100 – Pt, platinized, 1 cm^{-1}, LTA 10 – Pt, platinized, 10 cm^{-1}, LTA/S – Pt, platinized and sintered, 1 cm^{-1} (WTW cells [5]).

Fig. 4 contains directions how to properly choose favourable conditions for measurement of electrolytic conductivity:

- low conductivities should be measured using the cell with low cell constant and at low frequencies,
- high conductivities should be measured using the cell with high cell constant and at higher frequencies,
- in measurements of high conductivities it is advisable to apply electrodes of porous surface. However, its range of application may be limited (they are unsuitable in measurements of sticky and contaminating liquids, in medicine, etc.).

Contrary to some misconceptions on the subject, some of which may even be found in publications, it is impossible to eliminate influence of the polarization resistance by applying the phase-sensitive detection (see Fig. 2). In this way it is possible to elminate only the influence of capacitive component of the cell impedance and its connections. Also reduction of the influence of geometrical (interelectrode) capacitance of the cell is impossible without changing its cell constant, because both the conductance and the capacitance of the cell are determined by the same cell constant K. It is advisable to reduce, to a minimum, capacitance of the cell and its connections, and also the capacitance of parasitic couplings to the surroundings. It is also important to provide possibly uniform field distribution in the solution sample.

Miniaturization of two-electrode cells has a limited range because it reduces the ratio of the polarization resistance to the solution resistance, and thus increases the error of conductivity measurement [4]. The best reduction, a theoretically full elimination, of the polarization influence can be achieved by applying the four-electrode method of measurement.

2.2. Four-electrode measurements

In the four-electrode method of the electrolytic conductivity measurement two electrodes, the current ones, are used to generate current flow in the solution and two others, the potential ones, are applied for measuring the voltage drop across the solution. The resistance of the solution is determined as the ratio of the voltage drop to the current intensity. From earlier considerations it is evident that all four electrodes always have electrode layer with attributes of electrical impedance (Fig. 5). At least in theory, it is possible to avoid their disturbing influence if proper conditions of measurement are ensured:

1) measurement of the voltage drop is performed without drawing any current,
2) potential electrodes are negligibly small in comparison with the cell dimensions and do not disturb original (i.e. resulting from the geometry) electric field distribution in the cell.

Although voltmeters of very high input resistance are available at present, it may be difficult to reduce residual capacitances sufficiently, especially capacitances of the connections.

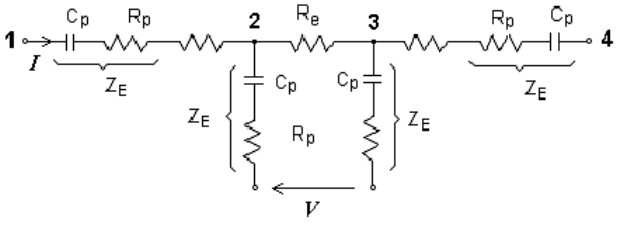

Fig. 5. Equivalent circuit of a four-electrode conductivity cell: 1 and 4 – current electrodes, 2 i 3 – potential electrodes [3].

It can be expected that also the four-electrode cells may demonstrate the effect of the cell constant variation resulting from the electrode impedances and residual capacitances. However, it should be significantly smaller than that observed in the two-electrode cells. Miniature four-electrode cells can demonstrate greater variations because of much smaller electrode surfaces and therefore much higher electrode impedances.

Variations of the cell constant observed in the four-electrode cell with relatively large electrodes made up of stainless steel, with smooth surface, are shown in Fig. 6, in function of measuring frequency and for two concentrations of aqueous solution of KCl. In such conditions the cell

constant variations do not exceed ±2% in the frequency range 500Hz – 4 kHz. It is few taking into account smooth surface of the electrodes and relatively high conductivity value. In turn, variations of the solution conductance measured using this cell are presented in Fig. 7 in function of the measuring frequency, in different areas of the current electrodes (whole electrodes clean or curtained in 50%). These variations do not exceed ±2% in the frequency range 200Hz – 12 kHz. That confirms significant effectiveness of the four-electrode method and its immunity to electrode contamination.

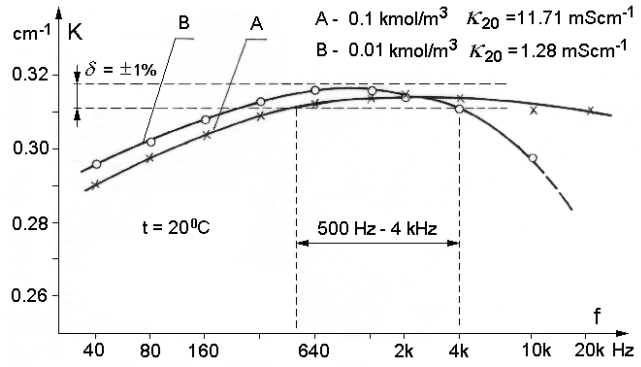

Fig. 6. Variations of the cell constant of a four-electrode conductance cell in function of frequency, for two concentrations of KCl solution [3].

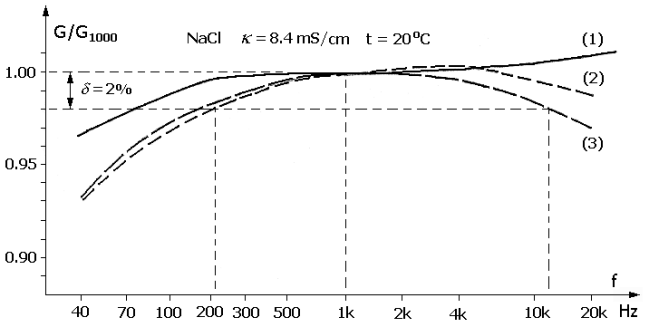

Fig. 7. Influence of variations of the current electrode area on the measured cell conductance, in function of frequency: (1) both current electrodes clean, (2) 50% of one electrode screened, (3) 50% of both electrodes screened; G_{1000} – the conductance at 1 kHz [3].

3. SUMMARY

A number of general directions enabling successful measurement of electrolytic conductivity result from the considerations presented in this paper:

- Measurement accuracy of electrolytic conductivity depends mostly on the conductivity cell and its properties. Usually it is easier to manufacture a good conductivity meter (meant as an impedance meter) than a good conductivity cell.
- Selection of the proper cell (two- or four-electrode) and its parameters (cell constant value, material and surface of electrodes) is of crucial importance. The same applies to the measuring frequency. Recommendations given by the manufacturer (if available) should always be followed.
- Generally, application of the four-electrode method is recommended in measurements performed in the high conductivity range and the two-electrode method in the low conductivity range.
- Application of the four-electrode method of measurement does not automatically mean that the problem of electrode impedance may be neglected. Also the cell constant of four-electrode cells can vary depending on the measured conductivity, measuring frequency and electrodes (surface state, contaminations). However, variations observed in such situations are usually many times smaller compared with two-electrode cells.
- Miniaturization of the two-electrode cells is applicable only in a limited range because it worsens the ratio of the polarization resistance to the solution resistance and thus increases the error of electrolytic conductivity measurement. Miniature conductivity cells intended for measurements of higher conductivity values should be applied in the four-electrode version.
- Negative consequences of miniaturization can be noticeable also in the case of four-electrode conductivity cells.
- Electrolytic conductivity measurements should be performed at constant, known temperature or suitable temperature correction of the conductivity value should be applied.

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