Modern Advances in Electrical Conductivity Measurements of Solutions[†]

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Abstract

The temperature and concentration dependence of the electrolyte conductance is one of the most appropriate methods for studying ion-ion, ion-solvent and solvent-solvent interactions in solutions and can be widely applied in diverse ionic systems. In this work an improved method for determining the precise temperature-dependent electric conductivity data in a more user-friendly way is described.

Key words: electrical conductivity measurements, electrolyte solution

1. Introduction

The temperature and concentration dependence of the electrolyte conductance has been proved as one of the most appropriate methods for studying ion-ion, ion-solvent and solvent-solvent interactions in solutions. Evaluating the conductivity within the framework of present electrolyte theories requires high accuracy in measurements which is difficult to achieve over a sufficiently large temperature range. In order to obtain the sufficiently accurate conductance data which could be used in conductance equations, it is necessary to have an equipment which allows reasonably quick and accurate measurement at different temperature values. Temperatures need to be accurate within 0.001-0.005 K to achieve the required reproducibility of data. There is a thermostat assembly which meets these requirements and has been described in detail in literature.[1]

The concentration dependence of conductance can be determined in different ways. Usually, solutions are prepared by mixing the solvent and electrolyte compounds by weight. A method, which allows stepwise concentration by successive additions of weight samples of the electrolyte compound (pure or in solution), starting from the pure solvent, has proved to be very useful.

Every method requires appropriate measuring cell, built according to the requirements of the electrolyte solution and the desired concentration range to be studied. At the University of Regensburg different conductance cells were developed which showed excellent characteristics needed for high accuracy measurements. They have been described in detail in literature[2] but are still not commercially available.

The conductivity measurement in the measuring cell has been accomplished by using an electrode assembly in the arm of an a.c. bridge, built on the classical lines of Jones[3] and Shedlovsky.[4] Using the precise conductance bridge, the electrolyte conductance at every temperature was obtained with accuracy better than 0.01%. More information on this measuring equipment, temperature control and measuring method is given elsewhere.[1] This equipment has been used by the Institute of Physical and Theoretical Chemistry, University of Regensburg, Germany for more than 30 years. The evidence of its excellence is reported in more than 100 papers on high precision conductance data of (mainly) non-aqueous electrolyte solutions. It is necessary to stress that the described equipment (conductivity cells, temperature bath, a.c. bridge) was entirely developed in the laboratories and workshops of the University of Regensburg and is therefore unavailable commercially. Nevertheless, this equipment is a master piece of work and means actually the borders of feasibility in conductivity measurements.

With the kind help of Professor Barthel and Dipl. Ing. Herbert Hilbinger from the Institute of Physical and Theoretical Chemistry, University of Regensburg, similar equipment has been built at the Chair of Physical Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia, allowing measurements between 5 and 45 °C. In our

case some parts of the equipment have been replaced by commercially available apparatus: Lauda WK1400 which serves as a cold bath and Lauda UB40 functioning as a precise measurement thermostat. The temperature of the measurement thermostat is controlled by precision platinum resistance thermometer Pt 100 (MPMI 1004/300 Merz) attached to a HP 3458A Multimeter. Resistance thermometer is calibrated regularly at the National laboratory, authorized for thermometer calibration.

Each temperature value of the chosen temperature program was attained within 15 minutes with an accuracy of better than 0.005 K. It was closely monitored that both short, as well as long-term temperature fluctuations were below 0.005 K, and no considerable temperature drift beyond this limit could be observed. However, this accuracy is still five times lower than the accuracy reported by the University Regensburg for its specially designed equipment. Nevertheless it turned out that this accuracy in the temperature setting and reproducibility still allows the accuracy in the measurement of data required for the evaluation within the framework of current electrolyte theory.

Using a three-electrode conductivity cell for dilute solutions and a set of nine capillary cells, which we obtained as a gift from Professor Alexander Apelbat (Ben Gurion University of the Negev, Beer-Sheva, Israel) and Professor Josef Barthel (University of Regensburg, Germany), the resistance of the electrolyte solutions in the cells was measured, using a highly precise conductance bridge (LEEDS & NORTHRUP). At 25 °C and relative humidity not exceeding 50%, the precision of the bridge at 0.02 % is decleared in its technical specification.

The measuring equipment described above has proved successful in some investigations carried out in aqueous[5-8] and also in non-aqueous electrolyte solutions.[9]

Despite the high precision which has been achieved for the temperature-dependent electric conductivity measurements the method is not widely used. Moreover, it has been labelled as an »old fashioned« procedure compared to other »modern« methods (spectroscopy, scattering techniques...). One reason for this opinion certainly may be that the precise temperature-dependent electric conductivity measurement is a very time consuming method. It demands a person to carefully monitor the temperature cycle and record the frequency-dependent electric resistance for each temperature of the program. For this reason this procedure is not particularly attractive for modern generations who are used to computer and quick solutions. This attitude can be observed with our students who see the conductivity bridge for the first time and look upon it as something out-of-date.

However, the advantages is that the precise temperature-dependent electric conductivity measurement can be widely applied in ionic systems (electrolyte and polyelectrolyte aqueous and nonaqueous solutions, ionic surfactants, microemulsions containing ionic surfactants…). We belive that a lot of challenging work still remains in the field of theoretical work, especially studying concentrated electrolyte solutions, non-symmetrical electrolytes and higher-charged electrolytes, which needs to be supported by reliable and precise experimental data.

To eliminate some of the deficiencies of the system we tried to make the temperature-dependent electric conductivity measurements more »user friendly« and attractive for contemporary students by using modern technology, and still not to lose precision requirements.

The weaknesses of the existing system in our laboratory can be summarised as the following:

i.   Manual measuring.

ii. Long measuring times giving small number of results.

iii. Very narrow impedance measurement range in limited frequency range, limiting measurement possibilities, consequently leading to larger number of measuring cells with adopted impedance.

iv. The system is not "user friendly". It demands permanent presence of a laboratory worker to record the resistance values and adjust the temperature at a desired value.

To avoid the above mentioned weaknesses it has been decided to replace and/or upgrade some system components. The scheme of the upgraded system is shown in Figure 1, followed by detailed explanation.

The control of the measuring instruments and process is entered with the computer, which gathers measurement results (Figure 2). The laboratory worker needs only to

i.   select a temperature range and define the allowed temperature deviation for the beginning of the temperature stabilization (A),

ii. choose the time of the temperature stabilization of the sample (B),

iii. enter the number of measured cells (C),

iv. specify the file, where the data are stored (D) and

v.   the desired range and frequency step (E).

All this data can also be written in the "setup file" (F) and confirmed by "load setup" (G). At this point the measurement is started (H). The cold bath and the measurement thermostat are set at the first temperature value of the program. After reaching the desired
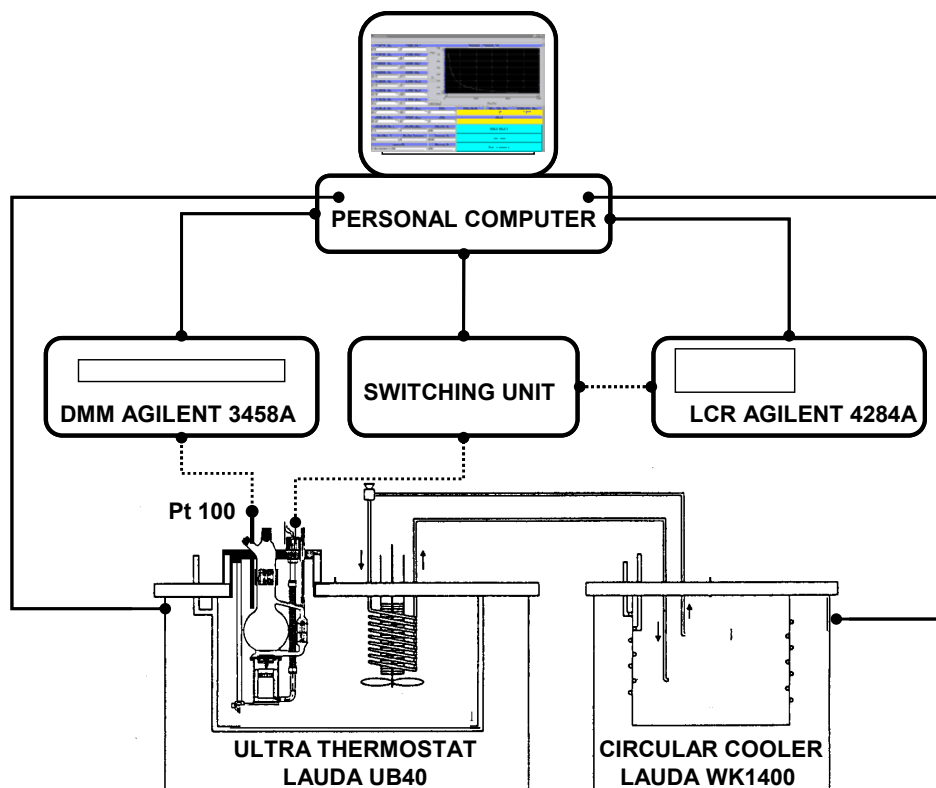
Figure 1. Thermostat assembly with a cold bath (Lauda WK1400), a measurement thermostat (Lauda UB40) with an immersed conductivity cell, attached to the new measuring equipment. The weaknesses in impedance measurements of the system were eliminated by purchasing an Agilent Technologies 4284A automatic electronic impedance analyzer of highest measuring accuracy. This instrument allows accurate measurements disregarding the resistance of the sample. The adaptation of the expected resistance with the cell constant, which enables the measurement by the resistance bridge, is not needed. In terms of automation of the system the general requirement was that all system components should have a suitable interface to connect to a computer. This required the replacement of some system components. Finally, by adapting the switching unit the system allows selection of a single cell or a set of cells (up to 9) for measurements.
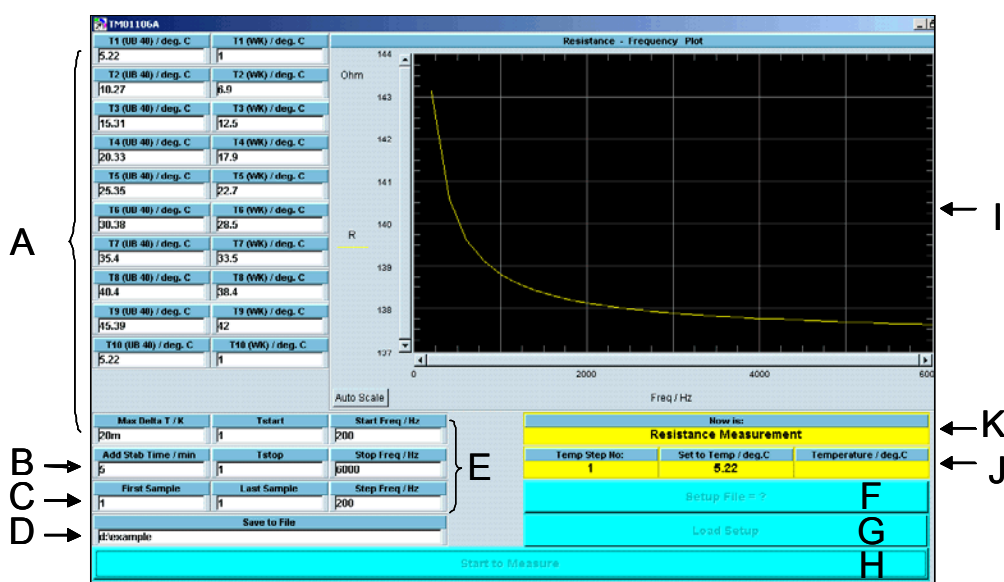

Figure 2. An example of the display with graphical user interface showing the measurement process. For explanation see the text.

temperature with defined precision, the program will procede with thermostating the sample (stabilization time) which is followed by measuring the resistance in the desired range of the frequencies (usually between 200 and 6000 Hz in steps of 200 Hz). The measured resistance values are shown on the display (I) in relation to the frequency. Finally, the temperature in the measurement thermostat is controlled (Pt 100, Agilent 3458A, Figure 1) and displayed (J). In case of a single cell measurement the system is switched to another temperature of the program and the procedure is repeated. If the set of cells is being measured, the program will measure the resistance of all samples at the set temperature, and only then the temperature is changed.

Thus the graphical user interface keeps the experimentator updated on the measurement process status (K) and displays measured results. The remote control of the entire measurement process is possible either through local area network or from the internet. The results (temperature and the frequency dependent resistance) are saved in a file (D) and available for further analysis.

Basic specifications of the improved measurement system are:

i. Temperature range 0-45 °C, stability ±0.005 K.

ii. Measurement uncertainty for resistance measurement: > 0.05 %.

iii. Measuring frequency range: 20 Hz - 1 MHz.

iv. Simultaneous measurement up to 9 conductivity cell with automatic switch between them.

However, the temperature range is still limited by the characteristics of the cooler and the thermostat in our equipment. In the future it needs be improved by their replacement. It should also be mentioned that the temperature of the cooler and thermostat should be set appropriately (see A in Figure 2) to obtain the desired temperature with sufficient accuracy. So far these values have been obtained by introducing of some additional measurements following the temperature oscillations in the measurement thermostat. Consequently, the actual temperature is also controlled separately by the help of the calibrated Pt 100 resistant thermometer (Figure 1).

In order to check the reliability of this upgraded equipment some paralel measurements were carried out using the same solutions. Firstly, the resistance was obtained by the help of LEEDS & NORTHRUP conductivity bridge, followed by measurement using LCR meter Agilent 4284 A. As usually, the resistance measurements were made at different frequencies from which the value R at infinite frequency was obtained by linear extrapolation.[1] Figure 3 shows the comparison

of measurements on aqueous solutions of saccharine (c = 7.317·10⁻⁴ mol dm⁻³) at 35 °C. The extrapolation values were 2638.7 Ω and 2640.3 Ω measured by LEEDS & NORTHRUP conductivity bridge and a precision LCR meter Agilent 4284 A respecitively. The obtained difference is still within the declared precision of the bridge and the LCR meter. For this reason the new upgraded equipment could be regarded as an excellent substitute for the old one.
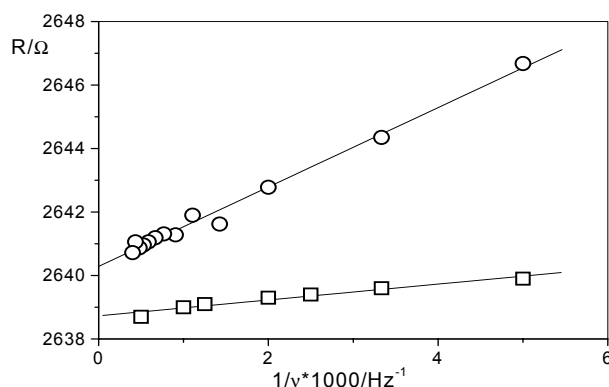

Figure 3. Frequency dependence of measured solution resistance at 35 °C (aqueous solutions of saccharine; c = 7.317·10⁻⁴ mol dm⁻³); (□) LEEDS & NORTHRUP conductivity bridge, (O) Agilent 4284A.

We may conclude that the improved method is a useful and reliable technique for determining the precise temperature-dependent electric conductivity data in a more user-friendly way which makes made this method more interesting and appealing for many laboratories and even companies.

We would like to emphasize that the conductivity cells play an important role but are not commercially available. Making a cell requires a highly skilled glassblower. Last but not least, it should be stressed that while modern technologies make measurements easier, the high precision, which has been achived by the apparatus developed by the Institute of Physical and Theoretical Chemistry at University of Regensburg[2] still remains inaccessible for general use.

2. Acknowledgment

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Povzetek

Temperaturna odvisnost električne prevodnosti raztopin je ena izmed najbolj primernih metod za študij interakcij v raztopinah različnih ionskih sistemov. V tem delu smo opisali posodobitev metode merjenja temperaturne odvisnosti električne prevodnosti.