6.2. Measurement of freezing point depression

I. Tasks: Determination of concentration of urea solution by measuring freezing point depression. Investigation of freezing point depression in case of total and partial dissociation.

Important concepts
Phase equilibrium, thermodynamic conditions of phase equilibrium, phase equilibrium in multicomponent systems, ideal solutions, Raoult`s law, chemical potential, chemical potential as the function of composition, colligative properties, freezing point depression, boiling point elevation, osmotic pressure, cryoscopic constant.

II. Freezing point depression - theory

Dissolving (non-volatile) solid material in pure solvent the freezing point of the solution is always lower than the freezing point of the solvent, if the solid phase is formed from the pure solvent only (the solute and the solvent do not mix in solid phase). The difference of the freezing points is called freezing point depression. The cause of the phenomenon is that the dissolved material decreases the chemical potential of the solvent. The freezing point depression of dilute solutions proportional to the concentration of the solute.

$$\Delta T = \Delta T_{\mathrm{m}} c_{\mathrm{R}}^{\mathrm{eff}} \qquad (1)$$

where ΔT_{m} is the molal freezing point depression (cryoscopic constant) of the solvent, $c_{\mathrm{R}}^{\mathrm{eff}}$ the Raoult concentration or molality of the present particles (number of moles of the solute / mass of the solvent in mol/kg unit).

The molal freezing point depression (ΔT_{m}) depends only on the physical constants of the solvent (enthalpy of melting, melting point), and does not depends on the properties if the solute. The freezing point depression (ΔT) depends on only the amount of the present dissolved particles, therefore it is called colligative quantity (similar as osmotic pressure, boiling point elevation, pressure of ideal gas).

$$\Delta T_{\mathrm{m}} = \frac{RT^{*2}}{\Delta_{\mathrm{fus}} H} M_A , \qquad (2)$$

where R is the molar gas constant, $\Delta_{\mathrm{fus}}H$ is the enthalpy of fusion of the solvent, T^* is the melting point of the pure solvent and M_{A} is the molar mass of the solvent.

Molal freezing point depression is high if the enthalpy of melting is small and the melting point is high.

Molal freezing point depressions of solvents

solvent	freezing point / °C	ΔT_{m} / (K kg mol^{-1})
water	0.0	1.86
benzene	5.5	5.12
naphthalene	80.2	6.9
camphor	178.4	37.7

From measuring the freezing point depression we can calculate the molar mass of the solute if we know its concentration OR knowing the molar mass we can calculate the concentration of the solution. If the solute dissociates the freezing point is lower than we expect based on the concentration calculated from molar mass. The freezing point depression depends on the number of moles of the species, so knowing the molar mass the calculations will give the „effective” molality (the total molality of the species present in the solution).

$$c_R^{\mathrm{eff}} = [1 + (\nu - 1)\alpha]c_R = ic_R \tag{3}$$

where ν is the number of the formed ions from the compound, *i* is the van't Hoff factor. From the effective molality (c_R^{eff}) and the calculated molality from molar mass (c_R) we can calculate the degree of dissociation (α).

During a freezing point experiment a liquid solution may be cooled down far below its equilibrium freezing temperature to a minimum supercooled temperature value, T_{sc} owing to certain stochastic features of the crystallization process. The degree of supercooling and the amount of pure solvent that freezes out are different from one experiment to the other. The actual freezing point of solution slightly depends on the amount of the phase frozen out (in diluted solutions it is the solvent), since the solution in equilibrium with the solid phase is more concentrated (a part of the solvent is frozen out) and we measure the freezing point of this solution. The mass of solid phase – here ice – can be estimated using the degree of supercooling ($\delta = T - T_{sc}$). The amount of ice is just enough to produce as much heat as it can increase the temperature of the supercooled system to the freezing point. We can draw the following simplified equation about this process:

$$m_i q_o = m_o\, c\delta$$

where m_i is the mass of ice, c is the specific heat capacity of water (4,186 J/(g K)), q_o is the specific heat of melting of ice (333,62 J/g), m_o is the mass of solution (30 g). The left side of the equation considers the heat produced during the freezing, the right side the heat need for the temperature increase. Note that we have assumed that the specific heat capacities of water and ice are equal and we have neglected the heat capacity of the other parts of the apparatus, the heat capacity of the thermometer and furthermore the heat loss is negligible due to the low heat conductivity.

Expressing the mass of ice:

$$m_i = \frac{m_o\, c\delta}{q_o} \tag{4}$$

The supercooling is advantageous from practical point of view, since this produces fine distributed solid phase and sharp, well reproducible freezing. The large surface contact of the solid and liquid phases is a practical condition of phase equilibrium.

III. Experimental procedure

The apparatus

We use the apparatus shown in Figure 1 for determination of the freezing point. Beside this we use another insulated container to freeze the liquids. For the measurement of temperature we use the electric resistance of a temperature sensor which is proportional to the temperature.

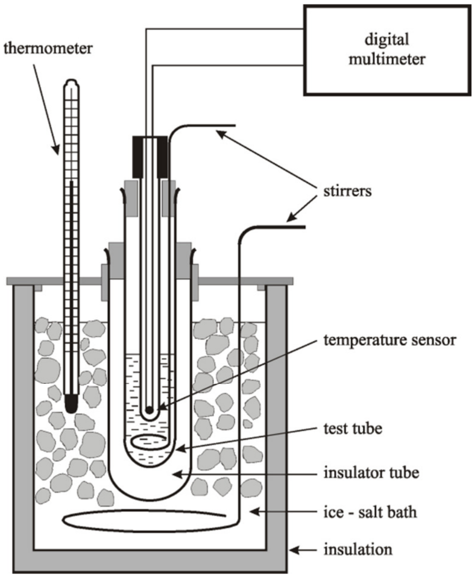


Figure 1 Cryoscope: an apparatus for the determination of the freezing point depression in diluted solution

Steps of the experiment

1. Preparation of the cooling mixtures

During the measurement we use a cooling mixture between –6 and –8 °C. The mixtures in the insulated containers are made of ground ice, clean water and salt. By adding salt and/or ice (and a little water) set the temperature of the mixture. Stir the ice-water-salt freezing mixture continuously, and check the temperature several times during the preparation. Use clean water provided in a plastic balloon for the preparation of the cooling mixture, and distilled water for the observation of the freezing point. Put the insulator tube in the cooling mixture.

2. Cooling the samples, detection of the freezing point

Fill 30 cm^3 of distilled water into a test tube. Place the stirrer and the temperature sensor in the solution. Immerse the test tube directly into the cooler freezing mixture and let it cool with constantly slow stirring.

Start the data collection using the provided computer program (see technical details in Appendix 2 SCOPEVIEW_program)! When the liquid starts to freeze the gradually dropping resistance suddenly jumps up to the resistance value of the equilibrium temperature. At this point take the test tube out of the cooling mixture, dry the outer wall of the test tube quickly, and place it into the insulator tube which is immersed in the freezing mixture. Keep stirring the solution slowly and continuously. Continue the data collection till the recorded data (seen on the screen) do not show any tendency (2–3 minutes). Melt the ice crystals completely by warming the test tube with your hand, and then repeat the experiment 2 more times. If ice crystals remain in the beginning of the experiment supercooling cannot be reached and the freezing point determination will be less accurate and takes much longer!

When you have finished the three experiments with distilled water dry the freezing tube and measure the freezing point of your unknown solution (given by the technician having exactly 30 cm^3 volume), the 0.5 mol/kg urea solution and finally the 0.5 mol/kg KCl solution. Repeat the freezing experiment 3 times with ALL liquids.
While measuring, always take care of the cleanness of the laboratory tools! While changing solutions, always pour the new solution into a clean, dry test tube.

The corresponding names of the datafiles and frozen liquids should appear in your lab report!

The files can be downloaded from the following link:
http://foundation01.chem.elte.hu/Adatsorok/Fagyaspontcsokkenes/

IV. Evaluation of the measured data

1. Take the average of the data in the equilibrium state. In case of water we can take the average of the freezing point at the different experiments (the frozen ice does not influence the freezing point of the pure solvent). In case of solution we take the averages separately (differently concentrated solutions have different freezing point). Calculate the mass of the outfrozen ice based on the equation 4.

Calculation of temperature difference using electronic thermometer

The resistance vs. temperature function of the temperature sensor has a slope $S = \frac{\Delta R}{\Delta T}$ Ω / °C. The slope value of the sensor provided in the lab must be used in the calculations.

Your data measured with the sensor:

Freezing point of distilled water:	R_0
Freezing point of solution:	R_s
Supercooling point of solution:	R_sc

The freezing point depression: $\Delta T = \frac{R_0 - R_s}{S}$

The degree of supercooling: $\delta = \frac{R_\mathrm{s} - R_\mathrm{sc}}{S}$

2.a We can calculate the initial mass percentage of the unknown solution:

$$w = \frac{(m_\mathrm{o} - m_\mathrm{i})}{m_\mathrm{o} \frac{\Delta T_\mathrm{m} \cdot 1000}{\Delta T \cdot M_\mathrm{b}} + 1} \qquad (4)$$

The derivation of this equation can be found in Appendix 1a in details.

We use urea as solute, therefore the molar mass of the solute is M = 60,06 g/mol. Since the solutions are dilute the masses of solutions are approximately 30 g in all cases.

2.b For the study of dissociation we calculate the van`t Hoff factor:

$$i = \left(\frac{m_\mathrm{o} - m_\mathrm{i}}{c_\mathrm{R}} - M_\mathrm{B} \cdot m_\mathrm{i} \right) \cdot \frac{\Delta T}{m_\mathrm{o} \cdot \Delta T_\mathrm{m}} \qquad (5)$$

The derivation of this equation can be found in Appendix 1b in details.

If we use urea as solute the molar mass of the solute is $M = 0.06006$ kg/mol. If we use potassium chloride as solute the molar mass of the solute is $M = 0.07455$ kg/mol. Since the solutions are dilute the masses of solutions are approximately 0.030 kg in all cases. Use the masses in kg, the molar mass in kg/mol.

Calculate the degree of dissociation (eq.(3)). Discuss the results!

V. Results (must be included in the lab report)

- the name of the files containing the measure data, the number of your unknown
- the resistances corresponding to the freezing point of distilled water and their average
- the resistances of the supercooling points and the freezing points for the unknown concentration urea solution (separately for each freezing experiment)
- the mass fraction of urea in the unknown solution with 95% confidence interval
- the resistances of the supercooling points and the freezing points for the known concentration KCl and urea solution (separately for each freezing experiment)
- the freezing point depressions for the known concentration KCl and urea solution and the consequences can be drawn
- the degree of dissociation for the KCl solution including the steps of calculation (assuming that the activity coefficients are units)

Appendix 1a Derivation of the equation used for the calculation of the composition

We would like to get the concentration of the solutions in mass fraction:

$$w = \frac{m_\mathrm{b}}{m_\mathrm{o}}$$

Let us express the mass of the solute (m_b) using the measured temperature difference (ΔT), the mass of the solution (m_o) and the ice frozen out (m_i)! Urea does not dissociate, therefore $c_\mathrm{R} = c_\mathrm{R}^\mathrm{eff}$.

From the measurement of the freezing point depression:

$$\Delta T = c_\mathrm{R} \cdot \Delta T_\mathrm{m}$$

The molality of the solution:

$$c_\mathrm{R} = \frac{n_\mathrm{b}}{m_\mathrm{water}} = \frac{m_\mathrm{b} / M_\mathrm{b}}{m_\mathrm{o} - m_\mathrm{b} - m_\mathrm{i}}$$

The mass of the solute can be expressed:

$$c_\mathrm{R}\left(m_\mathrm{o} - m_\mathrm{b} - m_\mathrm{i}\right) = m_\mathrm{b} / M_\mathrm{b}$$

$$c_\mathrm{R}\left(m_\mathrm{o} - m_\mathrm{i}\right) - c_\mathrm{R} m_\mathrm{b} = m_\mathrm{b} / M_\mathrm{b}$$

$$m_\mathrm{b} = \frac{c_\mathrm{R}\left(m_\mathrm{o} - m_\mathrm{i}\right)}{\frac{1}{M_\mathrm{b}} + c_\mathrm{R}}$$

We can write the molality calculated from the freezing point depression in the equation and rearrange it:

$$m_\mathrm{b} = \frac{\frac{\Delta T}{\Delta T_\mathrm{m}}\left(m_\mathrm{o} - m_\mathrm{i}\right)}{\frac{1}{M_\mathrm{b}} + \frac{\Delta T}{\Delta T_\mathrm{m}}} = \frac{\left(m_\mathrm{o} - m_\mathrm{i}\right)}{\frac{\Delta T_\mathrm{m}}{\Delta T}\left(\frac{1}{M_\mathrm{b}} + \frac{\Delta T}{\Delta T_\mathrm{m}}\right)} = \frac{\left(m_\mathrm{o} - m_\mathrm{i}\right)}{\frac{\Delta T_\mathrm{m}}{\Delta T \cdot M_\mathrm{b}} + 1}$$

Let us substitute back this to our first equation:

$$w = \frac{m_\mathrm{b}}{m_\mathrm{o}} = \frac{\left(m_\mathrm{o} - m_\mathrm{i}\right)}{m_\mathrm{o}\,\frac{\Delta T_\mathrm{m}}{\Delta T \cdot M_\mathrm{b}} + 1}$$

Since both the numerator and the denominator contains quantities with mass dimension their units are arbitrary, just the same should be used for both. The molar mass should be substituted in kg/mol. If we would like to use molar mass in g/mol the changing factor appears in the equation:

$$w = \frac{\left(m_\mathrm{o} - m_\mathrm{i}\right)}{m_\mathrm{o}\,\frac{\Delta T_\mathrm{m} \cdot 1000\,\mathrm{g/kg}}{\Delta T \cdot M_\mathrm{b}} + 1}$$

Appendix 1.b Calculation of the van`t Hoff factor from the freezing point depression taking into account the mass of the outfrozen ice

The effective molality in the original solution is:

$$c_{\mathrm{R}}^{\mathrm{eff}} = \frac{i \cdot n_{\mathrm{b}}}{m_{\mathrm{water}}} = \frac{i \cdot \dfrac{m_{\mathrm{b}}}{M_{\mathrm{b}}}}{m_{\mathrm{o}} - m_{\mathrm{b}}}$$

Taking into account the dissotiation (see theory equation (3) the molar mass from appendix 1.a can be written in the following form: $m_{\mathrm{b}} = \dfrac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{\dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + 1}$

By the help of the equation above the effective Raoult concentration can be written as:

$$c_{\mathrm{R}}^{\mathrm{eff}} = \frac{\dfrac{i \cdot \dfrac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{\dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + 1}}{M_{\mathrm{b}}}}{m_{\mathrm{o}} - \dfrac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{\dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + 1}} = \frac{i \cdot \dfrac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{M_{\mathrm{b}} \cdot \left(\dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + 1 \right)}}{\dfrac{m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + m_{\mathrm{o}} - m_{\mathrm{o}} + m_{\mathrm{i}}}{\dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + 1}} = \frac{i \cdot \dfrac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{M_{\mathrm{b}}}}{m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + m_{\mathrm{i}}}$$

$$c_{\mathrm{R}}^{\mathrm{eff}} = \frac{i \cdot (m_{\mathrm{o}} - m_{\mathrm{i}})}{M_{\mathrm{b}} \cdot \left(m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T \cdot M_{\mathrm{b}}} + m_{\mathrm{i}} \right)} = \frac{i \cdot (m_{\mathrm{o}} - m_{\mathrm{i}})}{m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} + M_{\mathrm{b}} \cdot m_{\mathrm{i}}}$$

Using $c_{\mathrm{R}}^{\mathrm{eff}} = i \cdot c_{\mathrm{R}}$:

$$i \cdot c_{\mathrm{R}} = \frac{i \cdot (m_{\mathrm{o}} - m_{\mathrm{i}})}{m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} + M_{\mathrm{b}} \cdot m_{\mathrm{i}}}$$

Dividing both sides by *i*:

$$c_{\mathrm{R}} = \frac{(m_{\mathrm{o}} - m_{\mathrm{i}})}{m_{\mathrm{o}} \cdot \dfrac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} + M_{\mathrm{b}} \cdot m_{\mathrm{i}}}$$

$$\left(m_{\mathrm{o}} \cdot \frac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} + M_{\mathrm{b}} \cdot m_{\mathrm{i}} \right) \cdot c_{\mathrm{R}} = m_{\mathrm{o}} - m_{\mathrm{i}}$$

$$m_{\mathrm{o}} \cdot \frac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} + M_{\mathrm{b}} \cdot m_{\mathrm{i}} = \frac{m_{\mathrm{o}} - m_{\mathrm{i}}}{c_{\mathrm{R}}}$$

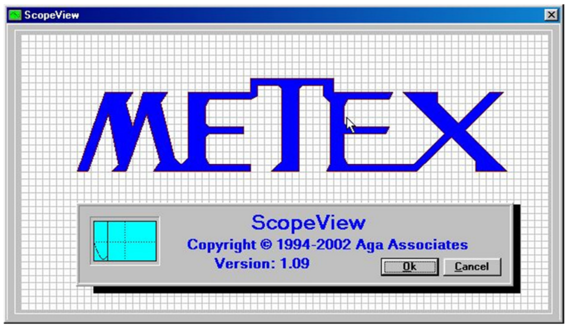
$$m_{\mathrm{o}} \cdot \frac{i \cdot \Delta T_{\mathrm{m}}}{\Delta T} = \frac{m_{\mathrm{o}} - m_{\mathrm{i}}}{c_{\mathrm{R}}} - M_{\mathrm{b}} \cdot m_{\mathrm{i}}$$

$$i = \left(\frac{m_{\mathrm{o}} - m_{\mathrm{i}}}{c_{\mathrm{R}}} - M_{\mathrm{b}} \cdot m_{\mathrm{i}} \right) \cdot \frac{\Delta T}{m_{\mathrm{o}} \cdot \Delta T_{\mathrm{m}}}$$

Use the masses in kg, the molar mass in kg/mol.

Appendix 2.

Usage of the METEX ScopeView program in the measurement of freezing point depression


ScopeView

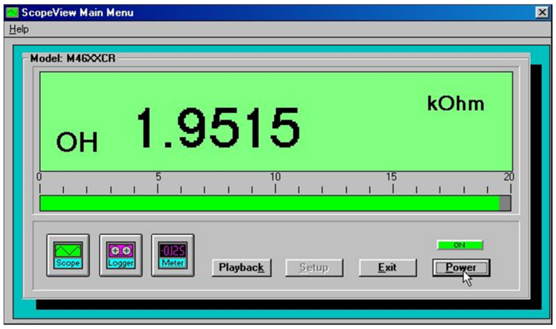
Copyright © 1994-2002 Aga Associates

Version: 1.09

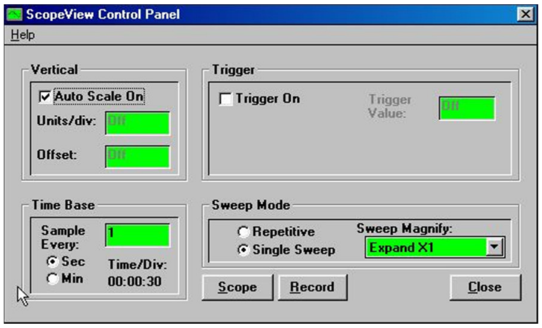
1. Be sure that the METEX multiméter is turned on and the function dial is on the 2 kOhm resistance measurement.

2. Start program ScopeView. For a short time a welcome screen appears and we get the Main Menu soon.

3. Connect the device to the program clicking on the Power button.



4. Clicking on the Scope icon we select the Scope mode. The setup screen of the mode appears:



Vertical
☑ Auto Scale On
Units/div: Off
Offset: Off

Trigger
☐ Trigger On
Trigger Value: Off

Time Base
Sample Every: 1
● Sec
○ Min
Time/Div: 00:00:30

Sweep Mode
○ Repetitive
● Single Sweep
Sweep Magnify: Expand X1

5. Set the following values:

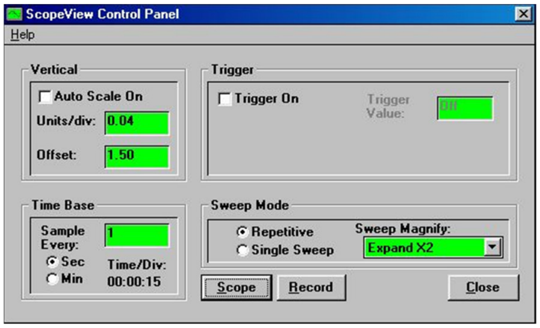
„Vertical" filed:
   - turn off the Auto Scale (deselect the checkbox before the Auto Scale, if needed)
   - Units/div: 0.04
   - Offset: 1.5

„Time Base" field:
   - Sample Every 1 Sec,

„Trigger" field:
   - turn off the Trigger (deselect the checkbox before the Trigger, if needed)

„Sweep Mode" field:
   - set it to Repetitive
   - set Expand X2 at Sweep Magnify

If we set up everything well the following screen can be seen:



Vertical
☐ Auto Scale On
Units/div: 0.04
Offset: 1.50

Trigger
☐ Trigger On
Trigger Value: Off

Time Base
Sample Every: 1
● Sec
○ Min
Time/Div: 00:00:15

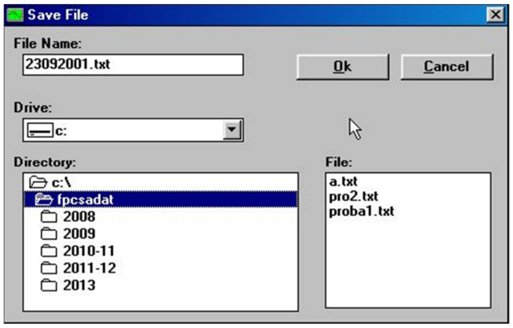
Sweep Mode
● Repetitive
○ Single Sweep
Sweep Magnify: Expand X2

6. Click on the "Record" button, and set the file name of the data collection in the "File Name" field according this scheme:

   (number of workplace 1-6)(last digit of year)(month 01-12)(day 01-31)(experiment number 01-99).txt

   Before the first experiment set the directory to „C:\FPCSADAT”.

   Clicking on „OK” we accept the settings and go back to the previous window.



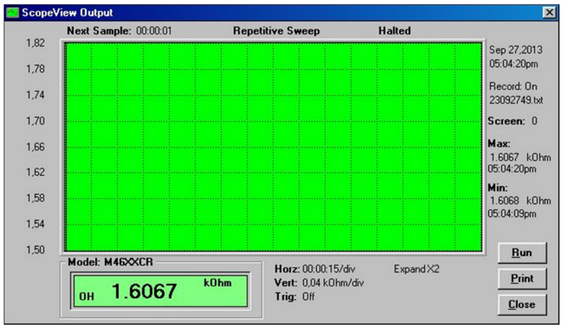
Save File

File Name: 23092001.txt

Drive: c:

Directory: c:\ fpcsadat

7. Clicking on the "Scope" button we get the ScopeView Output graphical screen. We will see the results of our measurement here. The resistance of the temperature sensor appears in the top left corner. We can start the collection of date clicking on „Run”. If the data collection is running we can stop it clicking on the „Stop” button appearing instead of the run button. At the end of the measurement push the „Close” button. This takes us not only back to the setting screen, but stores the measured data.



ScopeView Output

Next Sample: 00:00:01

Repetitive Sweep

Halted

Sep 27,2013 05:04:20pm

Record: On 23092749.txt

Screen: 0

Max: 1.6067 kOhm 05:04:20pm

Min: 1.6068 kOhm 05:04:09pm

Model: M46XXCR

OH 1.6067 kOhm

Horz: 00:00:15/div

Vert: 0,04 kOhm/div

Trig: Off

Expand X2

8. Repeat steps 6-7 for each freezing experiment.

How to process the ScopeView datafiles:

The files contain 20 lines header; this should be skipped when we import the files. The first column is the resistance of the sensor in kOhm. Time information is missing from the file; therefore we have to create a time column during the date processing (the collection of the datapoints was uniform in time; one point was measured in every 1 second).