1 The OSMOMAT 090 Membrane Osmometer

The OSMOMAT 090 is suitable for determining the osmotic pressure of higher molecular substances in aqueous or organic solvents. The substances must exhibit good solubility in the solvent in a concentration range of up to 20 g/100 ml depending on the molecular weight. To promote solubility, the OSMOMAT 090 can be used at cell temperatures of up to 125°C.

The osmotic pressure determined using the OSMOMAT 090 results from the number of particles (molecules) in the solution. The osmotic pressure is a direct measure of the molar concentration of the particular solution and makes it possible to calculate the molecular weight in connection with the specified concentration.

While the lower limit of the molecular weight to be determined is defined by the cut-off of the used semipermeable membrane, the upper limit is determined by the sensitivity of the pressure transducer. The number average of the molecular weight is calculated in the case of polydisperse polymers, and the molecular weight range can be approximately between 10,000 and 2,000,000 dalton.

1.1 The measurement method

The thermostatically controlled stainless steel measurement cell is divided by a semipermeable membrane into two cell halves. While the upper cell half is filled with a polymer solution, an underpressure corresponding to the osmolar concentration of the solution builds in the solvent-filled lower cell.

The osmotic underpressure is measured using a highly sensitive pressure transducer connected to the lower cell half.

The pressure measurement system is calibrated using a defined hydrostatic liquid column of the used solvent prior to measurement of the polymer solution. Glass, stainless steel, polytetrafluoroethylene (PTFE) and the membrane material must be resistant to the solvent. The polymer concentrations being used should be approximately between 0.2 and 20 g/100 ml.

The measurement cell is rinsed and filled with the various solutions via a inlet funnel, discharge valve, and suction bulbs.

1.2 Description of the system

1.2.1 The measurement system

The measurement system is comprised of the "OSMOMAT 090" cell unit and a control unit. The cell unit contains the osmotic measurement cell as well as all electronic components for thermostatic regulation and pressure measurement while the control unit is responsible for power supply, control, and measured value display and evaluation. The control unit SA has a monitor and a keyboard, uses software to guide the user through the measurement, displays the data graphically, calculates the molecular weight, and can print the measurement result with linear regression and the graphic via a

connected printer (not included in the delivery). There is a help file and separate operating instructions for the control unit SA. Reference is made to the relevant chapters in these user guide.

1.2.2 Design of the measurement cell

The cup-shaped lower measurement cell half (22) is built into a thermostat which ensures the set measurement temperature. The lower measurement cell half is connected to the pressure measurement cell outside the thermostat via a stainless steel tube.

The upper measurement cell half consists of a meander-shaped channel system which ensures that the semipermeable membrane has an optimal wetting surface for the solution. To introduce the sample solutions and rinse the cell, it is provided with a inlet funnel (15) and an outlet valve (14). The outlet valve has a spindle which functions like a water tap in that, when it is turned to the right, it presses a sealing cone against a Teflon universal seal and consequently closes the channel of the upper measurement cell half. The semipermeable membrane (23) is clamped between the lower cell half (22) and the upper cell half (21) via a plate (17) having a screw (16) in its center. The semipermeable membrane hermetically seals the lower cell half with respect to the outside. A large Teflon seal (19) seals a ring-shaped hollow space around the face side of the membrane. This hollow space protects the semipermeable membrane from drying out and can also be used to check the tightness of the osmotic cell.

Another small Teflon seal (20) is situated in the upper portion of the osmotic cell outside of the meander-shaped channel. This seal is provided for sealing the upper cell volume with respect to a stainless steel support sieve. The use of the support sieve for special solvents is explained under point **Using the supplied stainless steel support sieve 8.4**.

The measurement cell can be closed at the top by a heating head (13) which thermostatically controls the upper part of the measurement cell and in particular the inlet funnel and outlet valve to maintain the preselected cell temperature. The heating head is only necessary at working temperatures higher than 60°C or when using minimally permeable membranes. The heating head has a filling opening for filling the inlet funnel which can be closed by a cap (12). A valve extension (11) makes it possible to open and close the outlet valve (14) while the heating head is in place.

To suction the liquids through the upper cell half and to create suction in the inlet funnel in order to set a standardized fill level, the inlet funnel and outlet valve are connected via Teflon tubes to two suction bottles (2) and suction bulbs (1). Squeezing the suction bulbs creates a vacuum in the suction bottles which then sucks in the liquids. The pressure measurement system is comprised of the pressure measurement cell (10) including a built-in pressure transducer (9), a cover (7), and a plate (6) with a screw (4). A Teflon seal (8) between the cover and pressure measurement cell seals the pressure measurement system with respect to the outside. A plastic cover (5) protects the pressure measurement system from significant temperature fluctuations.

The solvent volume within the pressure measurement cell and the connection tube as well as beneath the semipermeable membrane is reduced significantly in order to stabilize the baseline. The solvent volume immediately beneath the semipermeable membrane is comprised of only one liquid film. As a

result, it is possible to quickly cleanse the lower cell half of permeated lower molecular polymer parts via back-permeation without having to prepare the measurement cell again.

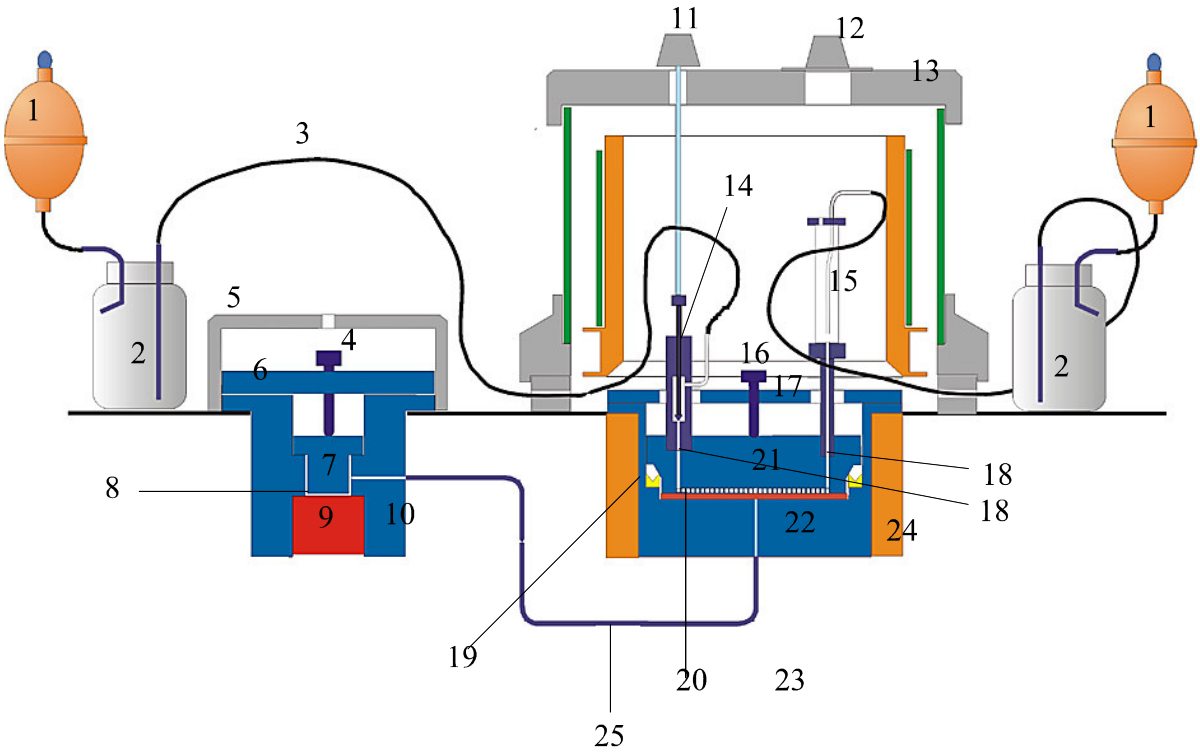

Figure 1-1

1. Suction bulb
2. Suction bottle
3. Teflon tube
4. Screw, pressure measurement cell (long)
5. Plastic cover
6. Plate, pressure measurement cell
7. Cover, pressure measurement cell
8. Teflon seal, pressure measurement cell
9. Pressure transducer
10. Pressure measurement cell
11. Extension for the valve spindle
12. Cover, heating head
13. Thermostat, heating head
14. Outlet valve
15. Inlet funnel
16. Screw, measurement cell (short)
17. Plate, measurement cell
18. Universal seal
19. Teflon seal, large
20. Teflon seal, small
21. Upper measurement cell half with meander-shaped channel system
22. Lower cell half
23. Semipermeable membrane
24. Cell thermostat
25. Connection tube

2 Starting up the measurement system with the control unit SA

The equipment has to be set up in a dry, shock-free and draft-free area. It has to be protected from direct sunlight and external heat sources such as lighting and heating equipment.
The measurement cell unit is connected to the relevant control unit via the supplied power cable and data cable.
When using the control unit SA, the data cable from the measurement cell is connected to the socket labeled "Cell-Unit". The power cable is used to connect the measurement cell and the control unit. A monitor, keyboard, mouse, and possibly a printer are also connected.
The power cable of the control unit is then connected to a power outlet. The line voltage of your power supply system has to comply with the voltage stated on the type lable of the equipment (110-115 or 220-230V).
Make sure that the equipment grounding is connected to the protective grounding of the power supply. The supplied power cable automatically provides grounding contact. If the connector of the standard power cable is replaced by another connector, you have to ensure that the grounding cable (green/yellow) is connected to the protective grounding.

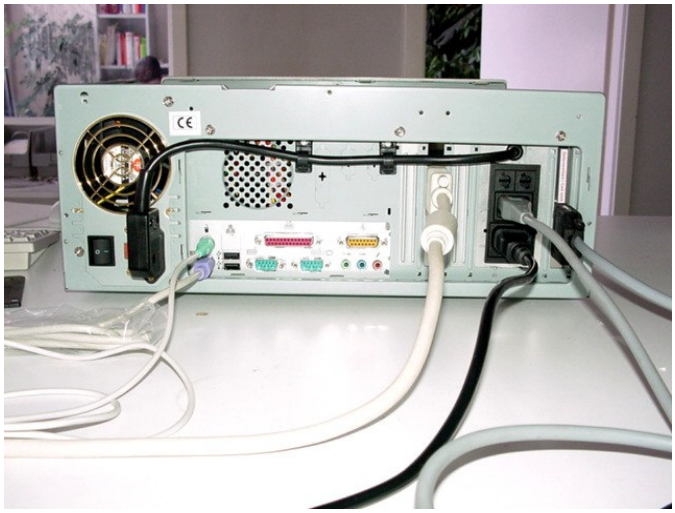

Figure 2-1

The grounding connection is absolutely necessary to prevent injury due to electric shock and interference with the functionality of the measurement system. To protect the highly sensitive pressure transducer from overpressure during cell preparation, the pressure ratios in the measurement cell and at the pressure transducer have to be continually monitored using the respective control unit. If the pressure reaches a critical point which could result in damage to the measurement system, an audible warning signal is generated.

3 Starting the program

The OSMOMAT program starts automatically after the control unit switches on and displays the following screen:

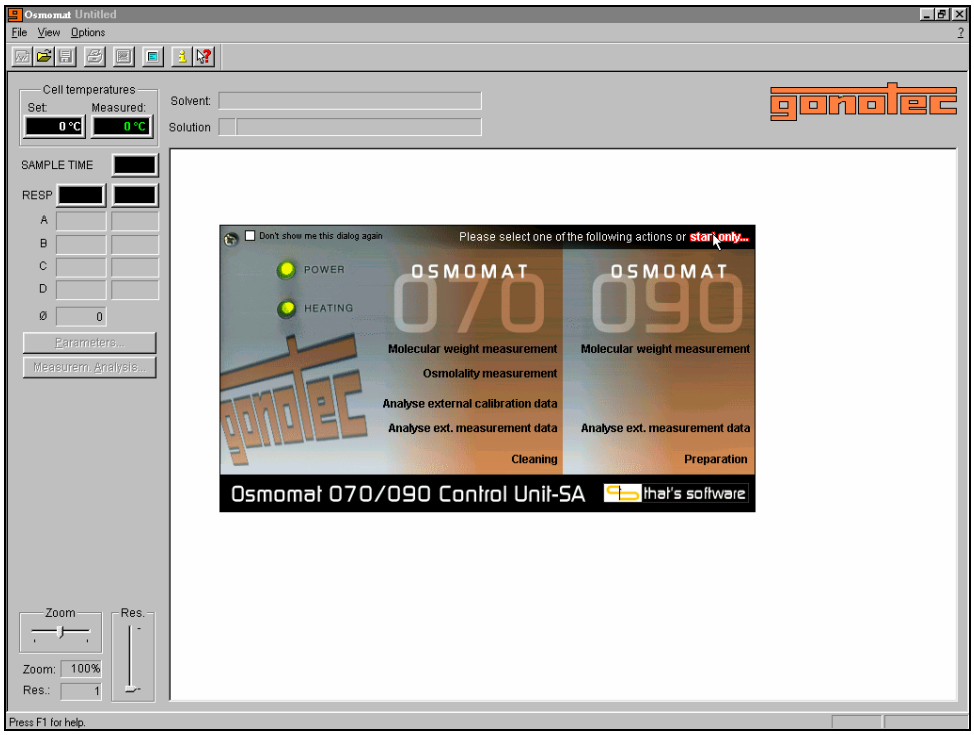

Figure 3-1 Welcome screen

The different program modes can be selected and started. The choice between membrane osmometer OSMOMAT 090 and vapor pressure osmometer OSMOMAT 070 directs you to the system-specific program portions. In the case of the membrane osmometer OSMOMAT 090, the selection of the measurement mode includes the possibility of analyzing already measured data and the *preparation* mode. The "*Start Only*" button (top right) launches a system-independent mode for viewing old measurements. This can be selected via the mouse, or the selection highlighted in white can be confirmed by pressing ENTER on the keyboard.

If you ended the program, the Windows user interface is displayed. You can restart the OSMOMAT program at any time by clicking on *Start, Programs, Gonotec, Osmomat*.

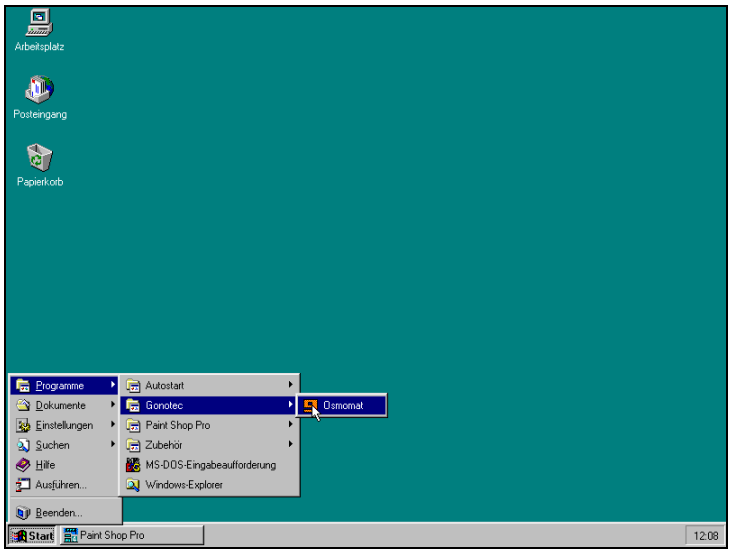

Figure 3-2: Restarting Osmomat

It should be mentioned again that the control unit is a personal computer that is equipped with additional hardware by Gonotec GmbH not limited to the installation of a special interface card. The OSMOMAT program designed specifically for this purpose ensures smooth and reliable functioning of the measurement system provided that no other programs are started. As a result, the Gonotec company cannot ensure smooth functioning of the measurement system if additional hardware or software is installed.

3.1 Main screen

All dialogs necessary for the measurement are displayed on the main screen. Appropriately modified versions guide you through the entire measurement.

The main screen displays the graphic measurement sequence and additional current information. The left side shows the defined and measured cell temperature, the current measured value (provided by the measurement cell), the history of the last four measured values for the particular sample solution including the average, and additional control elements and buttons.

The lower left portion of the screen shows the control elements for the graphical resolution. You can set the optimal resolution for your work here. The graphic can be optimized for subsequent printing so that only the important part is printed (only the part visible in the screen is printed).

3.1.1 Selecting the measurement parameters

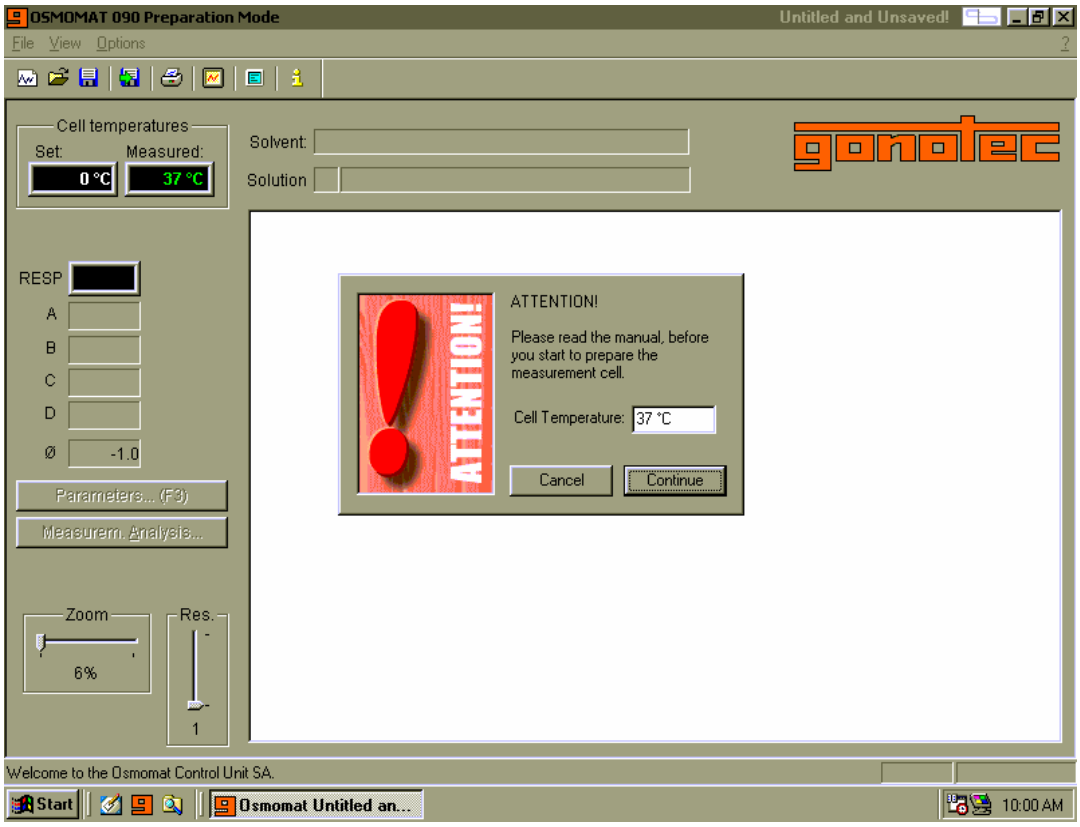

Figure 3-3

The measurement system should be connected to the control unit and switched on for all measurement cell work. After the control unit is switched on and the "preparation" mode is selected, you are requested to enter the desired cell temperature. For osmometric measurements to be performed within a temperature range of 5℃ above room temperature to 60℃, the cell temperature to be used later can be set directly. For measurements at high temperatures up to 130℃, however, the cell preparation should initially be performed at a maximum of 80℃. Following the preparation, the cell temperature is gradually increased to the high setting to avoid damaging the semipermeable membrane. After the temperature selection is confirmed, an x/t diagram showing the pressure ratios at the pressure transducer is visible on the monitor. At the same time the cell heater is activated, and the two-colored LED on the OSMOMAT 090 cell unit lights up red indicating "ready". The rate for heating the cell is approx. 2℃/minute. When the preselected cell temperature is reached, the two-colored LED turns green again. The baseline adjustment (BLA) button can be used to adjust the baseline to the smallest possible value, and at the same time the graph is set to zero. The two-colored graph of the pressure curve indicates whether the pressure ratios are in the positive or negative pressure range in relation to the last zero adjustment. A blue curve indicates a positive osmotic pressure corresponding to an underpressure (negative hydrostatic pressure) at the pressure transducer. In the case of an overpressure at the pressure transducer, a red curve is displayed.

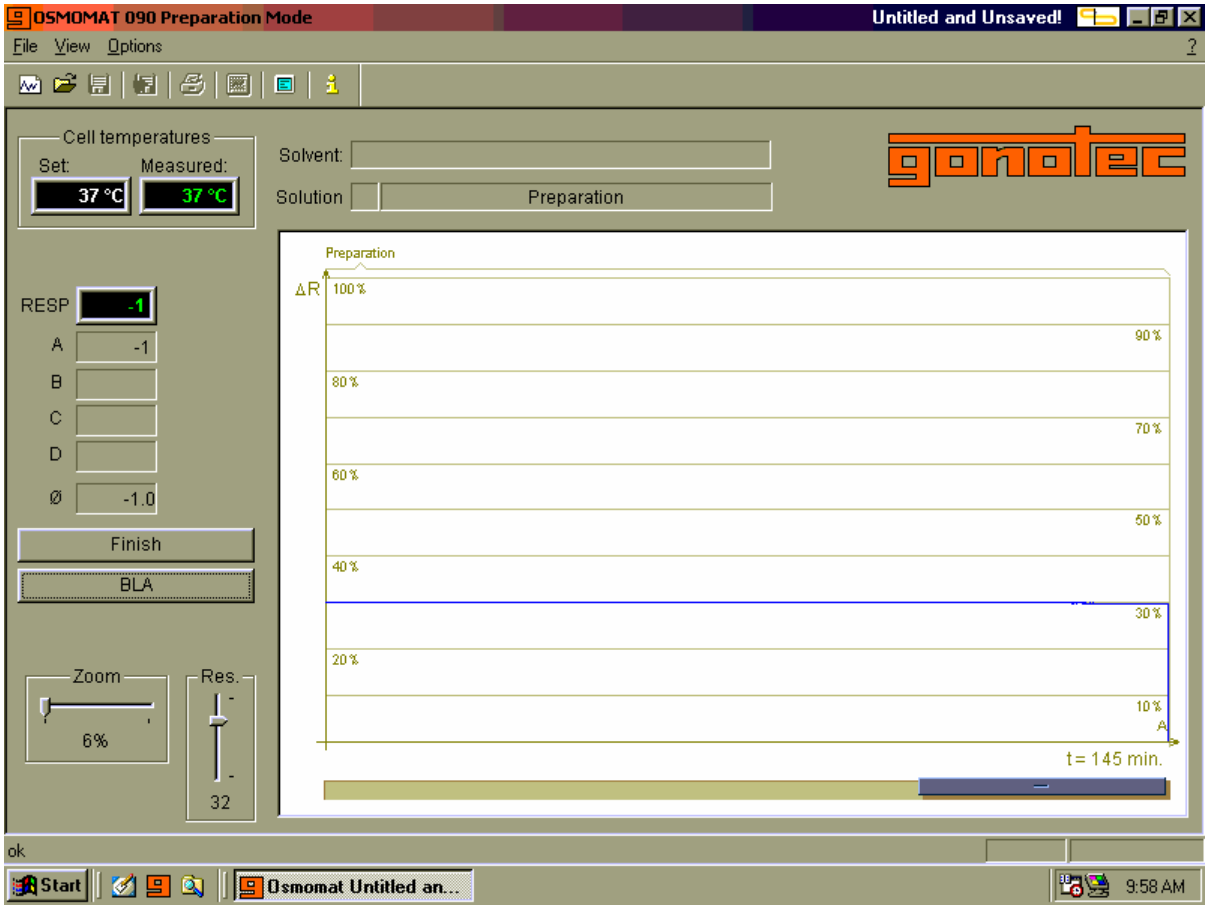

Figure 3-4

The temperature preselected in the "*preparation*" mode can only be changed by exiting this mode and calling it up again.

3.1.2 Preparing the measurement cell

Prior to using the measurement system for measuring osmotic pressures or molecular weights, the osmotic cell must be provided with a suitable solvent and semipermeable membrane. This operation requires great care. This ensures that the measurement system functions optimally and the highly sensitive pressure transducer is not damaged by an excessive over-/underpressure or by deformation of the ultrathin stainless steel pressure measurement membrane.

Information regarding the selection of a suitable solvent and semipermeable membrane as well as the conditioning of the membrane is described in the chapter **7**.

3.1.3 Preparing the measurement cell, preliminary work

The entire measurement system must be switched on and set to the "*preparation*" mode in order to be able to continually monitor the pressure ratios at the relevant control unit to protect the highly sensitive pressure transducer!

3.1.3.1 Initial situation of new deliveries:

The measurement cell and the pressure measurement cell must be opened. The heating head does not need to be connected for the preparation steps.
The plastic cover (5) is removed from the pressure measurement cell.
Using the Allen wrenches provided with the accessories, the screw (16) and the three Allen screws M3 in the plate (17) of the measurement cell and the screw (6) and the three Allen screws in the plate of the pressure measurement cell are loosened. The Allen screws M3 on the edge of the measurement cell and the pressure measurement cell are not to be loosened.
After removing both plates (6 + 17) by turning them slightly to the left, the support sieve and the two stainless steel template discs are removed from the measurement cell.

3.1.3.2 Initial situation of a measurement cell already prepared for measurement with the solvent and membrane (solvent and membrane change)

After removal of the heating head (13), the screw (16) is carefully loosened using the Allen wrench. **The pressure signal at the control unit must be monitored in this process!**

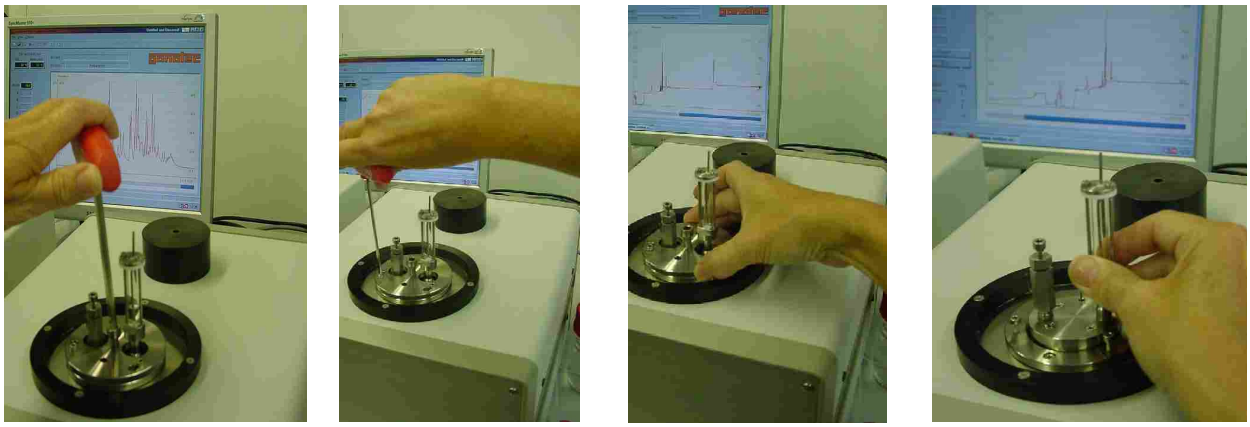

Figure 3-5

If the underpressure reaches a maximum value (approximately one third of the burst pressure), an audible warning signal is generated. The underpressure quickly dissipates as a function of the membrane pore size so that the unscrewing operation can be continued after a brief pause.
This operation may not be jerky or hurried.
After the screw (16) is loosened, the three Allen screws M3 are also loosened and the plate (17) is removed with a slight turn. The upper cell half (21) is removed.

After some solvent is added to the measurement cell, the semipermeable membrane is removed. **This membrane can no longer be used!** The protective cover (5) is removed, and once the screw and Allen screws M3 have been removed, the plate (6) is removed in the same manner. Using the pointed tweezers, the cover of the pressure measurement cell is carefully removed from the pressure measurement cell (7).

3.1.4 Adding liquids and cleaning the measurement cell:

The entire measurement system must be switched on according to chapter 4 and set to the "*preparation*" mode in order to be able to continually monitor the pressure ratios at the relevant control unit to protect the highly sensitive pressure transducer!

The large Teflon seal (19) is first removed from the measurement cell and then cleaned and dried if necessary.
Approximately 20 ml of the solvent to be used is then added to the lower cell half (22).
When using solvents with high surface tension, e.g. water or salt solutions, they must first be carefully degassed.
This can be achieved under a vacuum using a corresponding pump or the 30-ml medical plastic syringe in the standard accessories. The syringe is filled 2/3 with solvent and the syringe opening is closed by a tube with tube clamps without the use of a tube. A strong pull on the plunger creates a vacuum. The tube clamp is then opened. Air can escape. This operation is repeated three to four times. **Ultrasonic degassing is not sufficient!**

When using aqueous solvents, it is advisable to first fill and clean the cell system with alcohol or acetone in order to remove any grease from the metal walls and prevent subsequent adherence of miniscule air bubbles.
The organic alcohol or acetone which may be mixed with water is replaced by distilled water before the degassed aqueous solvent is added.

The measurement system is filled with liquids via the open lower measurement cell half (22). The solvent is rinsed from the measurement cell (22) into the connection tube via the glass syringe (1 ml) with a long tube contained in the standard accessories. The measurement system is completely filled in this way.

Never fill the pressure measurement cell (10) directly.

The Teflon tube is held manually in such a way that at least 10 cm of the free tube end is inserted into the pressure measurement cell. The intrinsic elasticity of the tube protects the sensitive pressure transducer membrane from damage when the tube end touches it provided that this operation is performed carefully (see **Figure 3-6**).
The measurement cell is rinsed several times and the excess solvent is sucked out via the Teflon tube.

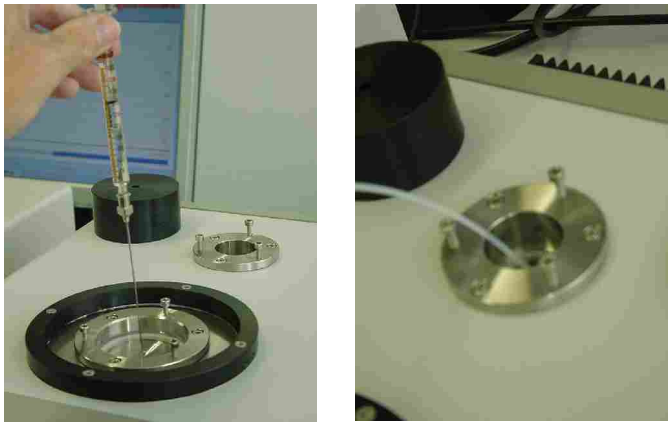

Figure 3-6

Warning!

When filling or emptying the measurement cell and in particular the pressure measurement cell, special care must be taken not to damage the highly sensitive pressure transducer!
Only the suction equipment comprised of the suction bulb (1) and the suction bottle (2B) and a long Teflon tube may be used to suction off the solvent.
The entire cross section of the base of the pressure measurement cell visible from above represents the highly sensitive stainless steel pressure transducer membrane! This pressure measurement membrane must **never** be touched by a hard, sharp-edged object.
Slight deformations of this membrane reduce the measurement sensitivity and result in an uncontrolled sudden shift in the baseline during the measurement.
Excessive over-/underpressure destroys the pressure transducer, and in an extreme case, the oil leaks out from the inside of the sensor and the sensor's electrical function is disrupted. A destroyed pressure transducer can no longer be adjusted to zero and the audible warning signal is emitted continuously.

Mechanical damage to the pressure transducer is excluded from the warranty service!

3.1.5 Removing air bubbles from the measurement cell

After the measurement system is cleaned and rinsed, the large Teflon seal (19) is inserted with the lips facing up into the measurement cell. The lips of the seal may not be notched since this would destroy the sealing effect!
The connection tube between the lower cell half (22) and the pressure measurement cell (10) is then carefully cleared of air bubbles via the glass syringe (1 ml) with a long thin tube by sucking in the solvent and then forcing it through (aqueous solvent must be degassed). The meniscus of the solvent should be at approximately the same level as the top edge of the large Teflon seal. Once the connection tube has been rinsed to clear it of air bubbles, it is subsequently cleared of any remaining air bubbles by again sucking in solvent.

3.1.6 Closing the pressure measurement cell

After the measurement system is carefully filled with the solvent without any air bubbles, the pressure measurement cell has to be closed.
The solvent is filled into the measurement cell without air bubbles to a liquid level above the large Teflon seal (19). The fill level in the pressure measurement cell should be set to be 1 to 2 mm above the Teflon lip seal (8) by sucking off the solvent so that the solvent does not subsequently overflow.

The cover (7) of the pressure measurement cell is first inserted into the pressure measurement cell using the pointed tweezers (standard accessories). A corresponding solvent amount is displaced thus resulting in an increase in the fill level.
The solvent is then over the cover if the correct fill level was previously set.

After insertion of the cover, it is carefully moved up and down via the tweezers so that this pumping motion removes any air bubbles from the system. This pumping motion should be performed below the liquid level so that new air bubbles are not introduced into the system.
When using aqueous solvents, the cover must first be completely cleansed of grease and salt remnants so that the surface is completely wetted by water.
The solvent above the cover can then be suctioned off. The pressure measurement cell is then closed with the plate (6) in that it is snapped into place by turning the three Allen screws to the right.
After moderately screwing on the plate via the three screws, the system is sealed by screwing in the screw (4).
This screw-tightening operation should entail a certain degree of force but not to the extent that the plate is deformed. When tightening the screw (4), it must be ensured that the resulting volume shift of the solvent does not form an excessive overpressure that could damage the sensitive pressure transducer!
The plastic cover (5) is then placed on the closed pressure measurement system to protect it from thermal effects.

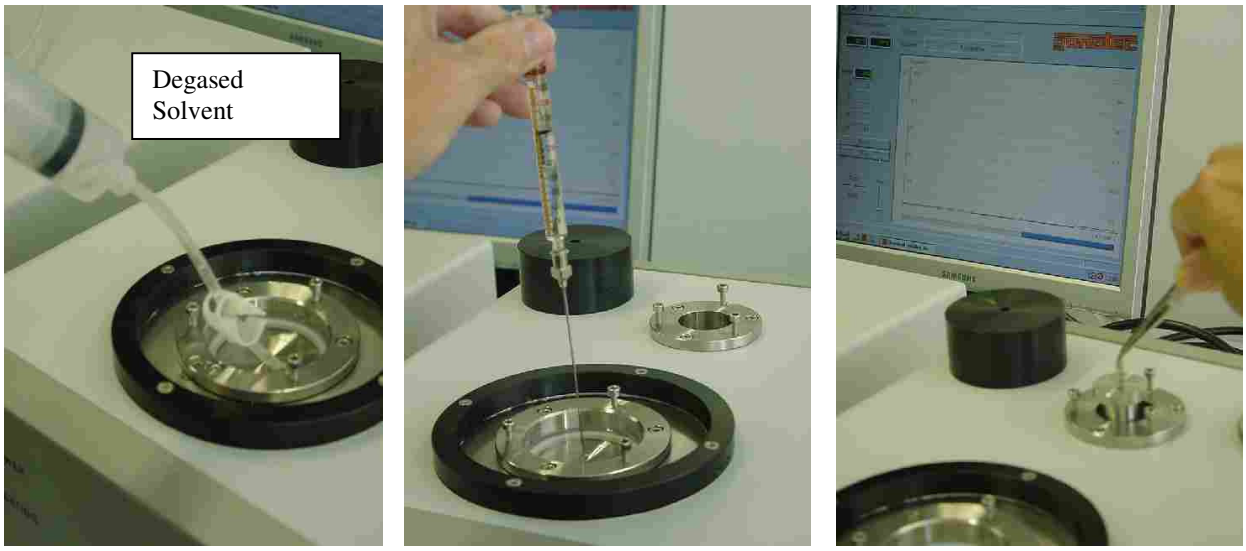

Figure 3-7

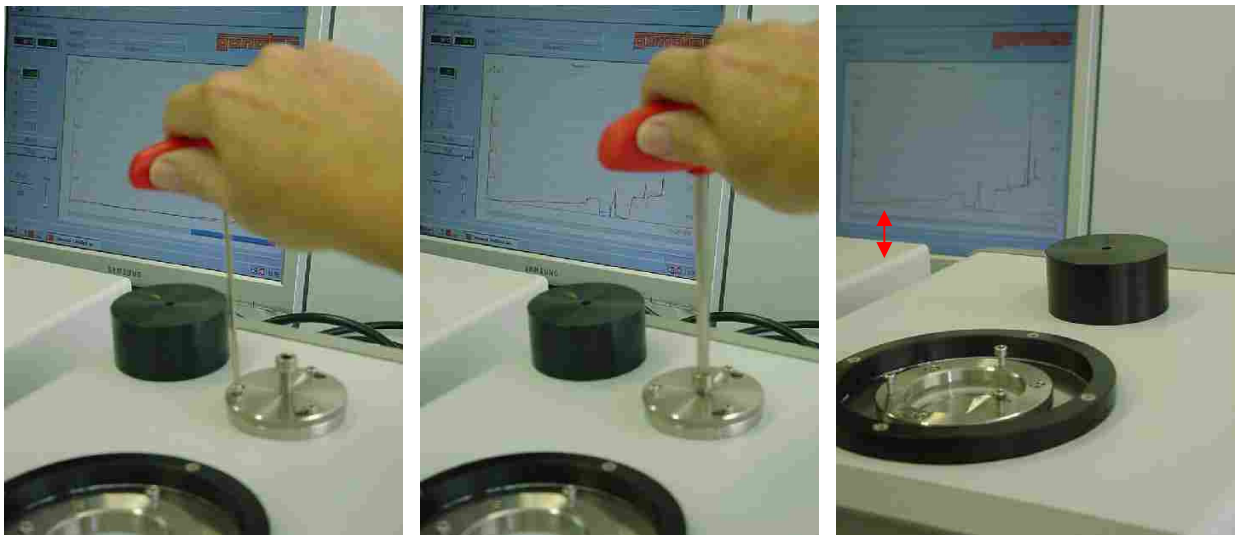

Figure 3-8

Note:

In the case of high temperature measurements, the measurement cell should first be prepared at approximately 60°C. When heating the prepared measurement cell to the working temperature, overpressure effects can occur if the permeation of the semipermeable membrane is insufficient so that the expansion volume of the solvent cannot escape through the membrane.

In this case, the measurement system can be slightly opened by loosening the screw (4) of the pressure measurement cell during the heating phase in order to protect the pressure transducer.

The solvent volume should have a fill level of 5-10 mm above the cover of the pressure measurement cell so that no air bubbles can enter the system. After reaching the working temperature, the pressure measurement cell is closed again.

3.1.7 Installing the semipermeable membrane

Initial situation:

The measurement cell and the pressure measurement cell are filled with solvent without air bubbles and the pressure measurement cell is closed.

The measurement cell (22) is filled with the solvent to the top edge of the Teflon lip seal (19).

The appropriately prepared and tailored membrane (see paragraph **7**) is inserted into the lower measurement cell. There may not be any air bubbles below the membrane. It must also be ensured when using asymmetrical membrane material that the active layer (glossy, hydrophobic side) is aligned with the defined pores facing up. After the membrane has been pressed lightly onto the base of the measurement cell, the upper measurement cell half (21) is inserted into the measurement cell.

The upper measurement cell half is already provided with the inlet funnel (15) and the outlet valve (14). The plate of the measurement cell (17) is locked in place by turning the three Allen screws slightly to the right.

The three Allen screws M3 are tightened with moderate force.

The upper cell half is then pressed via the screw (16) against the lower cell half.

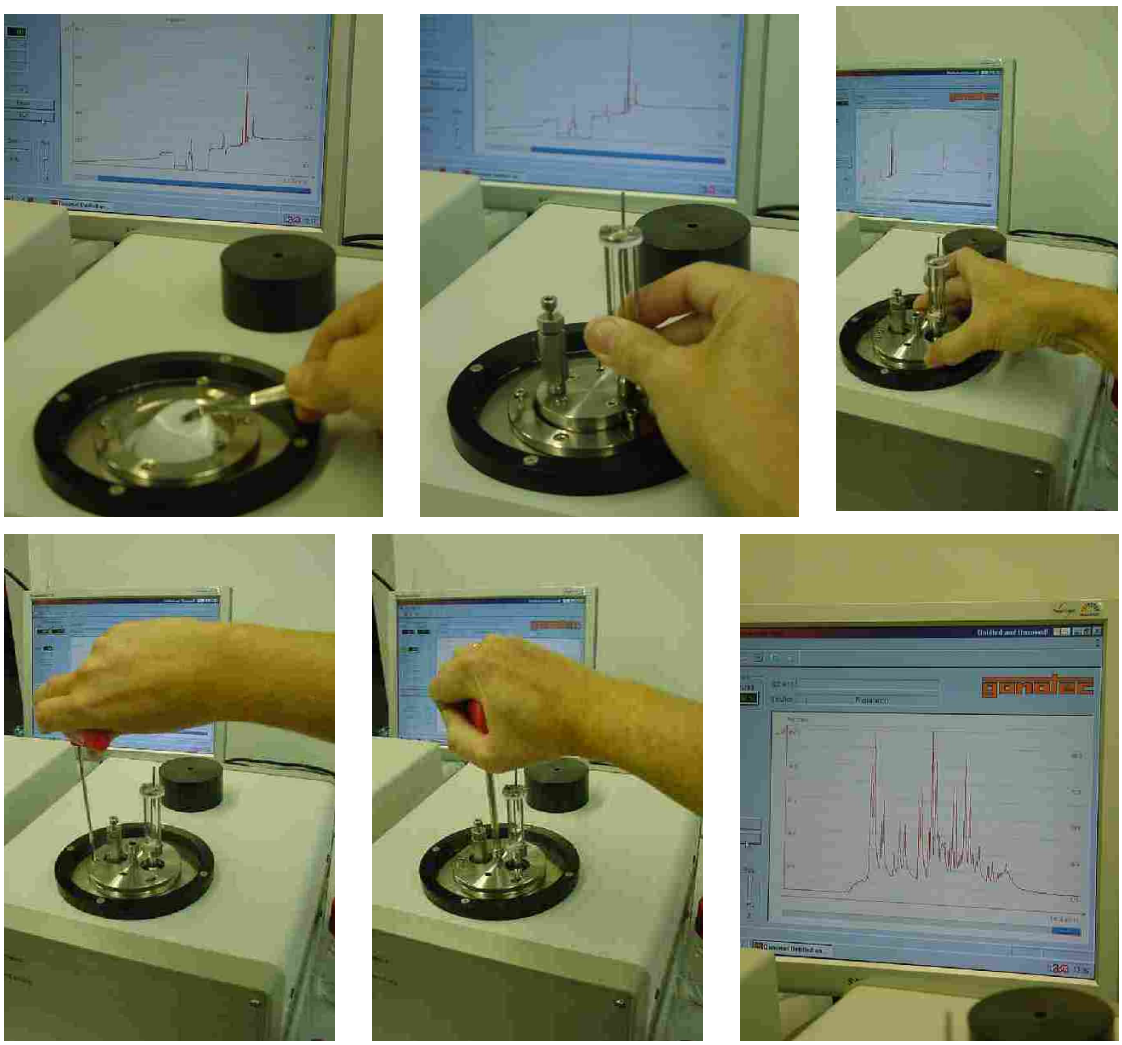

Figure 3-9

WARNING!

When screwing together the measurement cell, some of the solvent is displaced resulting in an increase in pressure in the osmotic cell as soon as it is sealed by the semipermeable membrane. To protect the highly sensitive pressure transducer, the pressure ratios must be monitored at the measurement cell. This is performed by the relevant control unit which emits an audible warning signal when a critical pressure is reached. An overpressure at the pressure transducer results in a red curve diagram. The acoustic signaling is automatically switched on at control unit SA when the system is operated in software mode “090”. The audible warning signal is generated when the pressure in the lower cell half is approx. 1/3 of the pressure that would destroy the pressure transducer. As soon as the membrane begins to seal the lower measurement cell when the measurement cell is being carefully screwed together, the overpressure increases and the warning signal is generated. The screwing together operation must then be stopped immediately. The overpressure typically decreases quickly via permeation of the solvent through the semipermeable membrane. The measurement cell shouldn't be further screwed together until the pressure signal has decreased to approximately half of the maximum pressure. The pressure ratios are monitored on the control unit SA monitor during this process.

The measurement cell is screwed together until the screw (15) can no longer be turned.

A certain degree of force is necessary since the inner lip of the large Teflon seal (19) is also compressed during this operation.

However, the pressure should never be such that the plate (17) curves upward.

After the measurement cell has been screwed together, the Teflon tubes are installed and connected to the appropriate suction bottles. The connection tubes between the suction bottles A/B (2) and the suction bulbs (1) should be approx. 25 cm long. The connection tubes between the suction bottles A/B (2) and the outlet valve (14) and the inlet funnel (15) should be approx. 45 cm long. The latter are guided through the bore holes in the plastic ring of the measurement cell.

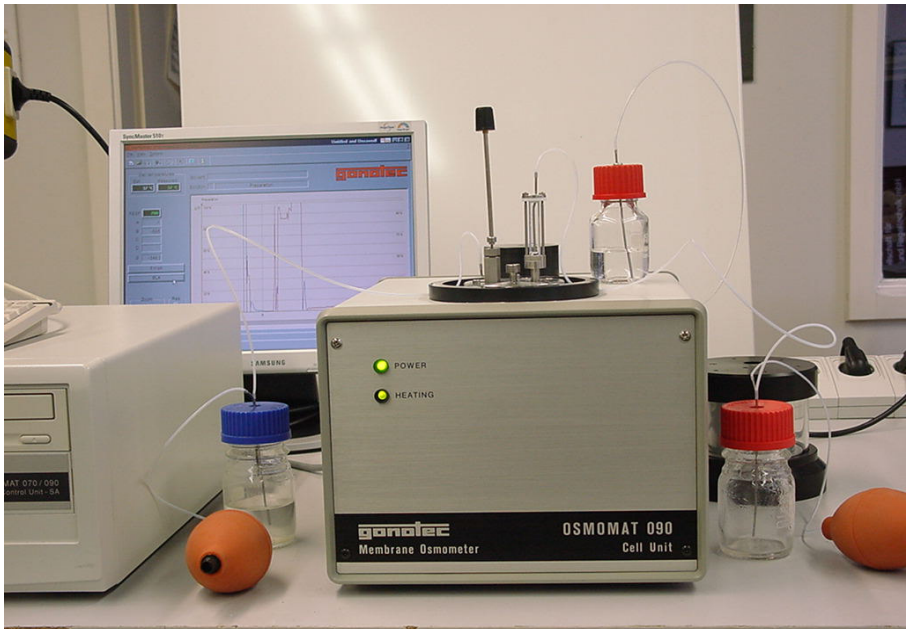

Figure 3-10

Prior to the Teflon tube ends being slid onto the stainless steel tubes, they are expanded via an expansion tool included in the accessories. A small strip of sandpaper also included with the accessories can be used to secure the Teflon tube ends during the expansion operation and when they are being slid onto the tubes.

The outlet valve (14) and the inlet funnel (15) should be screwed on again carefully.

The solvent is then filled into the inlet funnel via the glass syringe with the long tube and the outlet valve is opened. The outlet valve has a similar design to that of a water tap.

A turn of the valve spindle to the left opens the valve and a turn to the right closes it while a sealing cone of the valve is pressed against a Teflon “universal seal” (18).

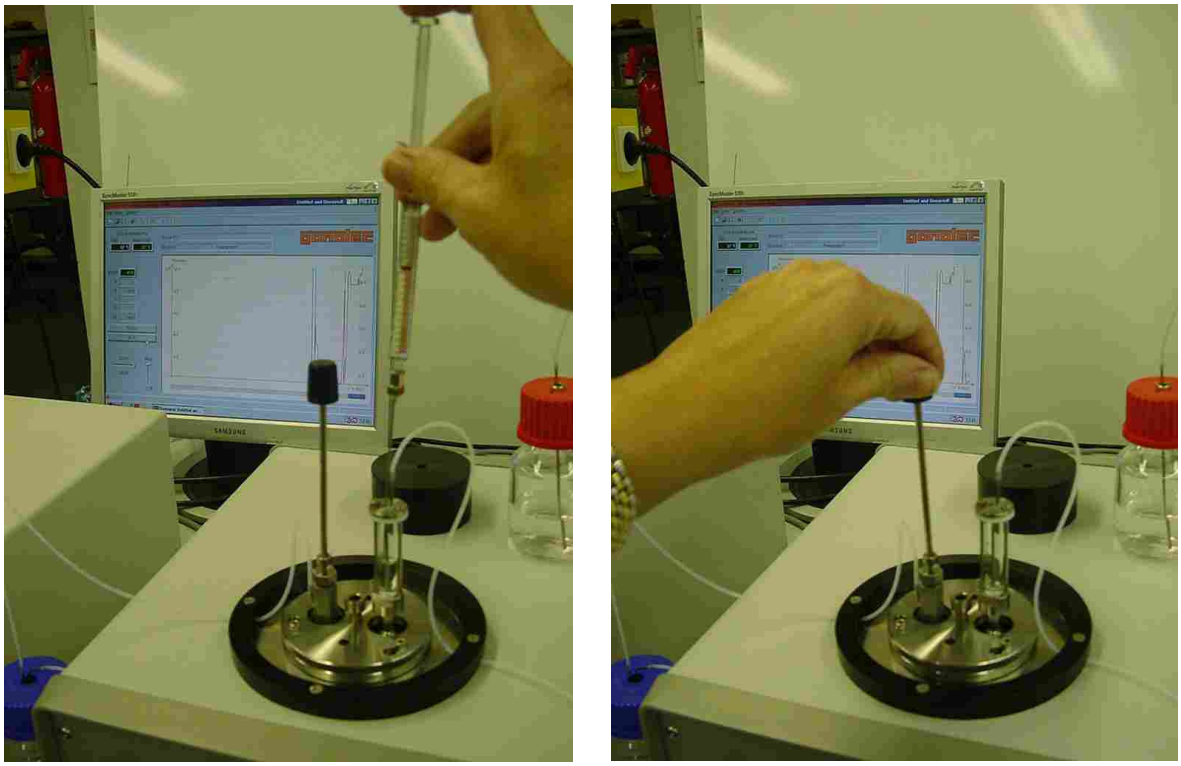

Figure 3-11

The suction bulb (1) of the suction bottle "A" is squeezed thus creating a vacuum which causes the solvent in the inlet funnel to be sucked through the meander-shaped channel system of the upper cell half into the suction bottle "A".

The outlet valve is closed when the meniscus of the solvent is approx. 2 mm above the end of the suction tube, which is located in the center of the inlet funnel. This procedure is repeated until no more air bubbles exit the outlet of the outlet valve.

By squeezing the suction bulb of the suction bottle "B", the remaining solvent is sucked out of the inlet funnel, and a reproducible fill level is set.

This exact fill level setting of the solvent and subsequently of the solutions can be reproduced by the suction equipment of the inlet funnel with a high degree of precision and must be performed after every rinse operation. Since the resolution of the pressure transducer is approx. 0.1 mm, a visual setting with the necessary precision is no longer possible. This fill level normalizes the hydrostatic liquid column which acts on the pressure transducer through the semipermeable membrane.

In the case of the solvent, this defined liquid column represents the base value for the pressure measurement.
After the measurement cell has been rinsed with solvent several times and the baseline is largely stabilized, a new zero adjustment can be performed. The baseline adjustment (BLA) button can be used to adjust the baseline to the best possible value, close to zero, and at the same time the graph is set to zero. This adjustment takes approx. 15 seconds. The set numeric value for the zero point is subsequently subtracted from the measured values.

After the baseline has stabilized, the measurement cell is prepared for the polymer solution measurements.
The "*preparation*" mode should be exited once the baseline has stabilized.
The measurement cell is now prepared for solution measurements and must be calibrated.

3.1.8 Measurements at high temperatures

If measurements are to be performed at high temperatures, the measurement cell must first be carefully gradually set to the appropriate temperature.
This is performed prior to a measurement by increasing the cell temperature setting in temperature increments of 10 to 20°C in the "*preparation*" dialog.
When changing the cell temperature, the different expansion coefficients of the measurement cell and the solvent can result in significant pressure effects in the osmotic cell if the permeability of the semipermeable membrane is too low.
This can damage the highly sensitive pressure transducer.
If possible, only semipermeable membranes with sufficient permeability should be used.
Once the working temperature has been reached, the "*preparation*" dialog is exited and the heater is automatically switched off.
The basic settings for the measurement including the cell temperature must then be immediately entered and saved in the "*parameter*" dialog.
Additional heating of the measurement cell is only activated when the screen is exited by pressing the "start" button.

Note:
In the case of high temperature measurements, the measurement cell should first be prepared at approximately 60°C.
When heating the prepared measurement cell to the working temperature, overpressure effects can occur if the permeation of the semipermeable membrane is insufficient so that the expansion volume of the solvent cannot escape through the membrane.
In this case, the pressure measurement cell can be slightly opened by loosening the screw (4) of the pressure measurement cell during the heating phase in order to protect the pressure transducer.

However, a solvent volume should be at a fill level of 5-10 mm above the cover of the pressure measurement cell so that no air bubbles can enter the system.
Once the working temperature is reached, the pressure measurement cell is carefully closed again.

3.1.9 Heating head

In the case of cell temperatures higher than 60°C, the heating head (13) should be set on the measurement cell during the measurement and connected to the heating head socket at the back of the measurement cell.
The heating head then automatically heats the inlet funnel and the outlet valve to the selected cell temperature and protects the measurement cell from significant temperature errors.
When using semipermeable membranes with a relatively low permeability, the use of the heating head (13) is recommended even for low cell temperatures to minimize significant baseline noise caused by room temperature fluctuations.
The use of the heating head is also suitable when polymer solutions in which the polymer is only soluble at high temperatures are to be measured (>100 °C)

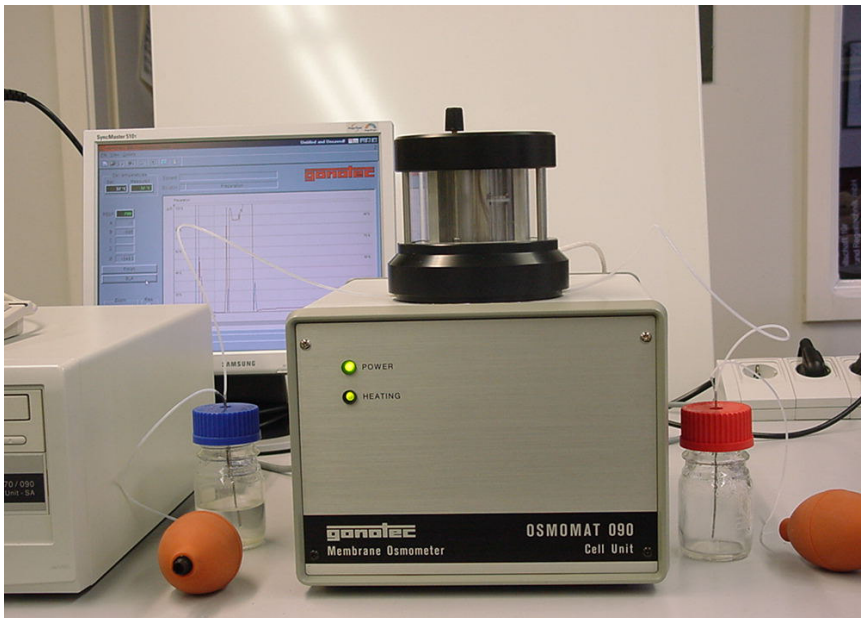

Figure 3-12
The measurement cell is prepared for measurement and must be calibrated.

4 Calibrating the pressure transducer

The membrane osmometer OSMOMAT 090 uses a direct measurement method and is calibrated with the solvent used in the osmotic cell via a hydrostatic liquid column.

Initial situation:

The measurement cell is prepared for measurement according to the paragraph **3.1.7**, the cell temperature is stabilized at the desired temperature value, and the baseline has achieved the necessary stability.

4.1 Preparing the measurement cell for calibration

For calibration, the inlet funnel (15) is replaced by the stopper with a tube (see Fig. 4-1) and the suction bottle B (2) is replaced by the calibration bottle. The calibration bottle (25) is filled at least halfway with the solvent.

Once the calibration bottle has been set on the top edge of the measurement cell housing, the suction bulb (1) of the suction bottle B (2) is squeezed and the outlet valve (14) is opened. The vacuum sucks the solvent from the calibration bottle through the measurement cell into the suction bottle.

The outlet valve is closed when no more air bubbles exit the measurement cell and all tubes are filled with the solvent without air bubbles.

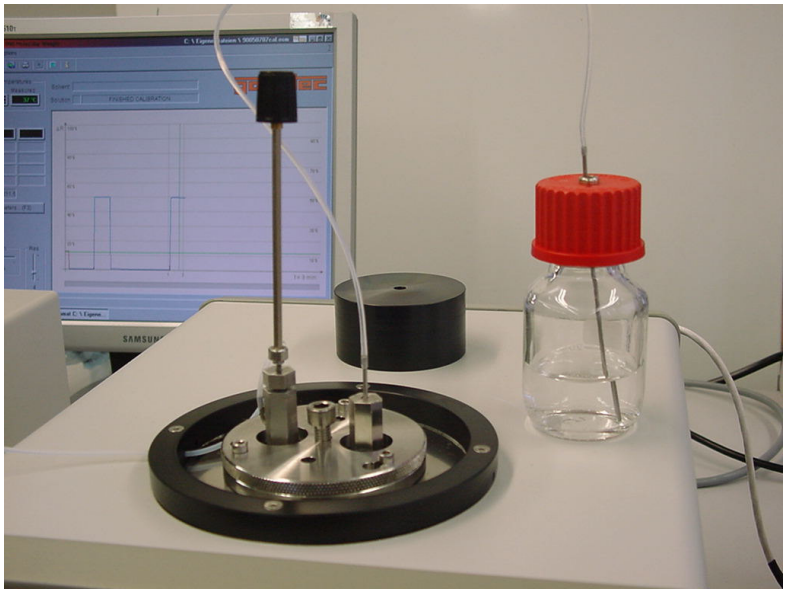

Figure 4-1

4.2 Calibration

To calibrate the system, the "*Preparation*" mode must be exited via *Finish*.

The *090 Molecular Weight Measurement* is then started via *File - New Measurement*. You will be requested in the parameter dialog to select a solvent or to create a new one.

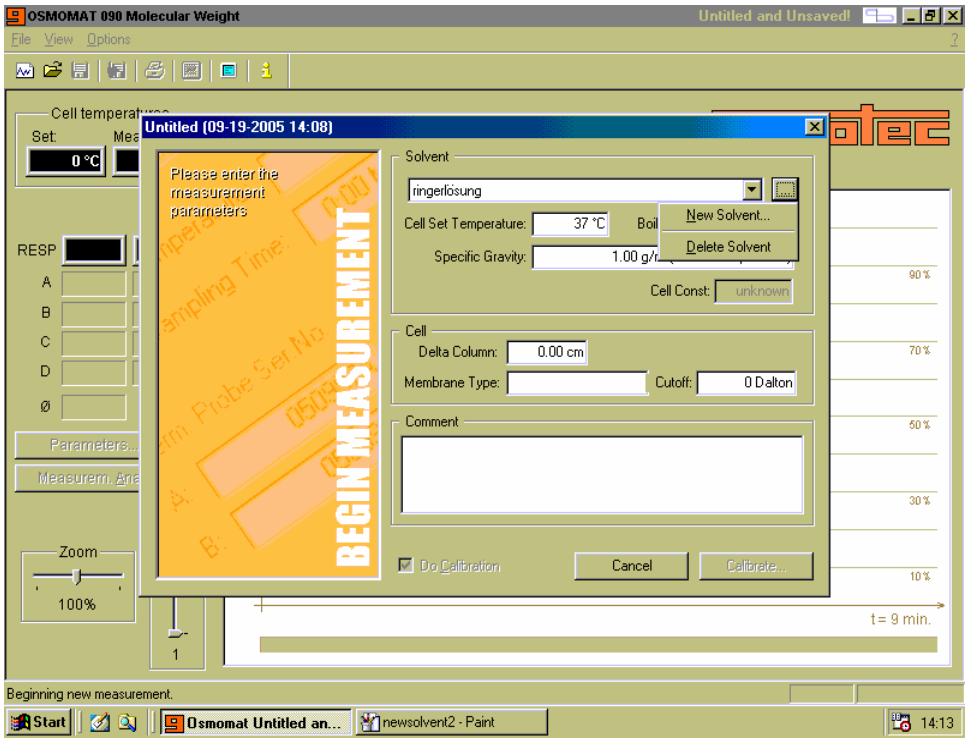

Figure 4-2

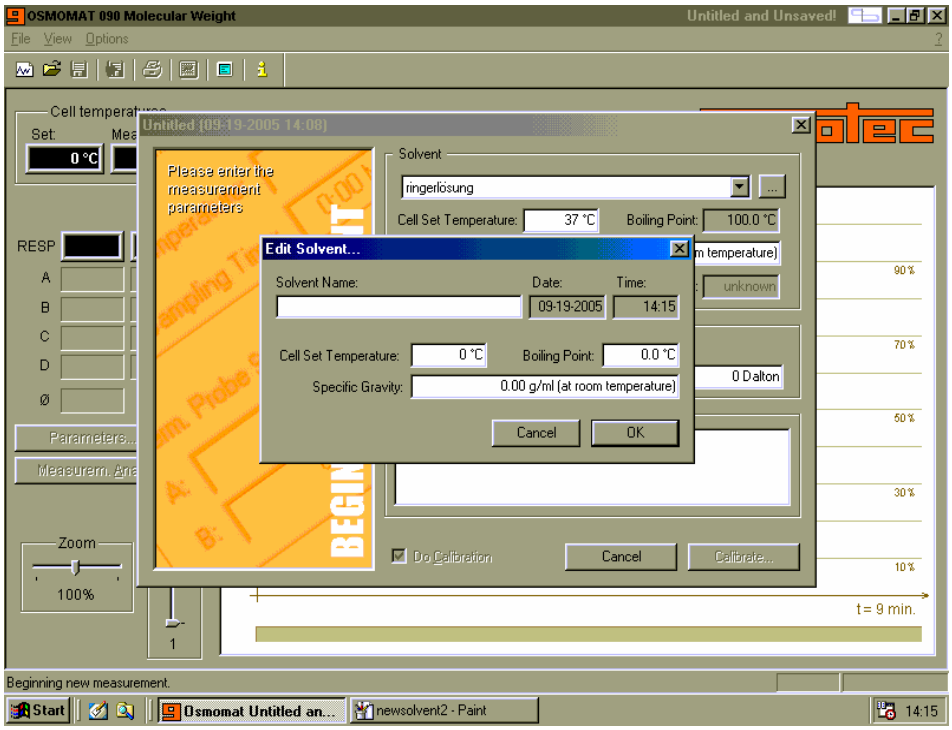

Figure 4-3

Enter the required parameters. The *Delta Column* is the housing height. It is provided on the right side of the cell unit. The membrane type and the cut-off are only comment fields and are not included in the calculation.

After entering all necessary parameters, begin the calibration by clicking on the *Calibrate* button. If you create a new solvent or enter another parameter, the *Do Calibration* box is automatically activated. Make a selection from the list of already available solvents, activate the *Do Calibration* box, and then click on *Calibrate*.

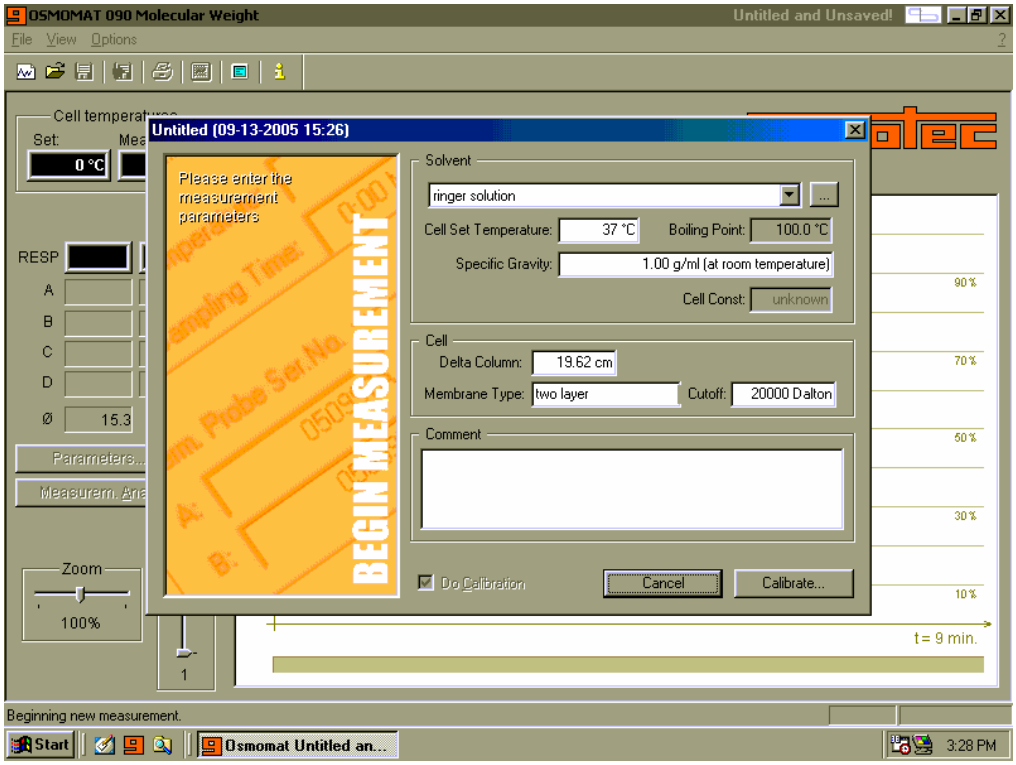

Figure 4-4

The program guides you through the calibration. Wait until a stable value is set and click on *OK*.

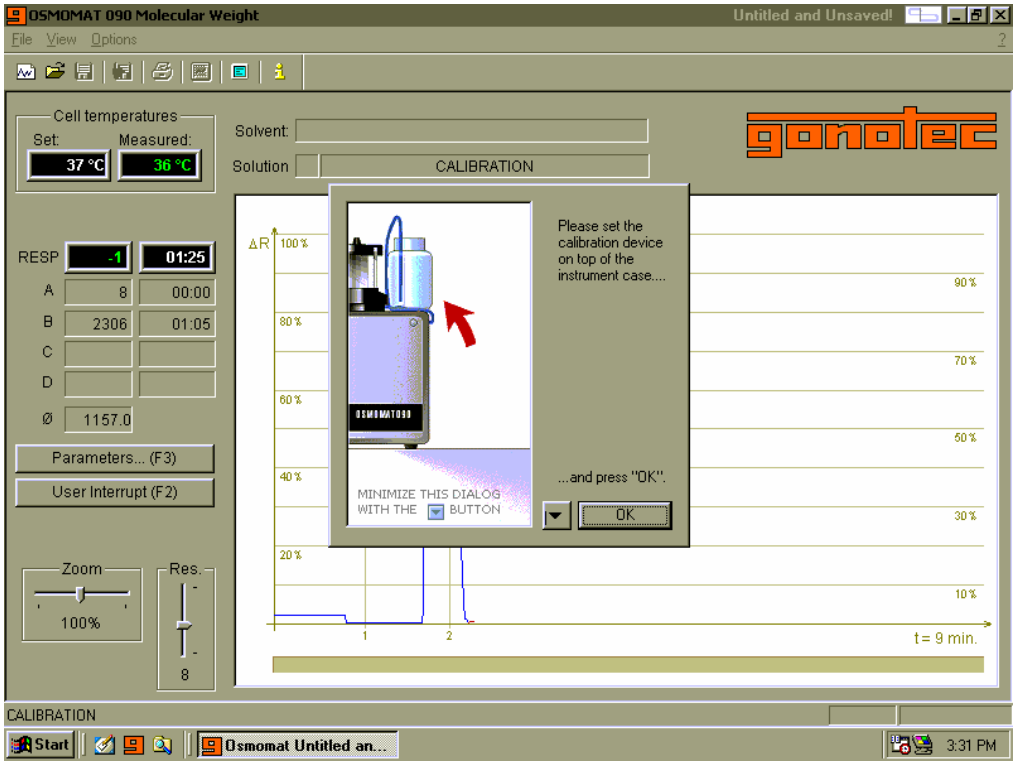

Figure 4-5

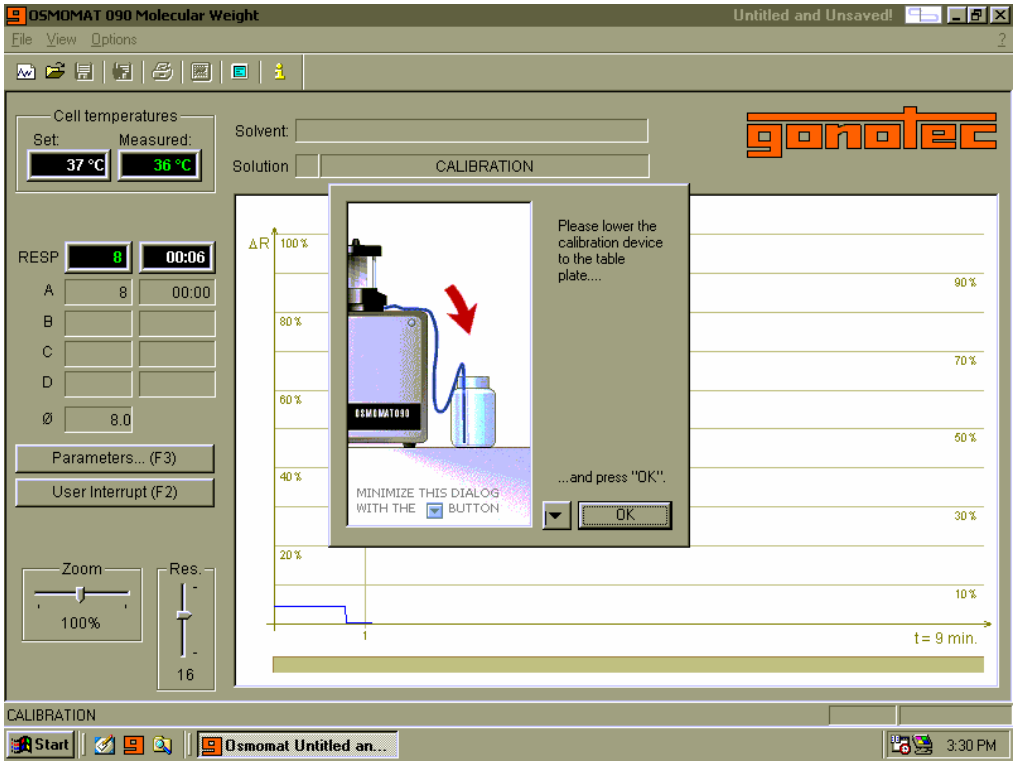

Figure 4-6

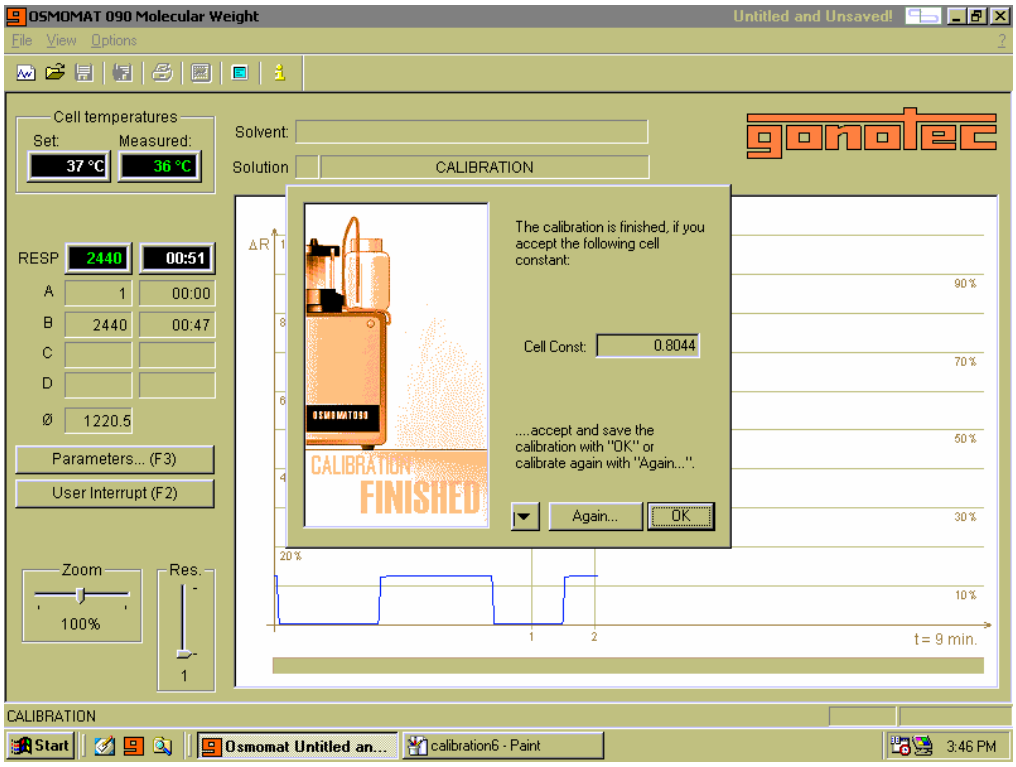

Figure 4-7

The calibration should be repeated several times in the same way to ensure baseline stability and the reproducibility of the calibration value. The cell constant value is 0.8 in aqueous solutions, for example.

This cell constant is calculated by the software, saved for the solvent with the set parameters, and used for the following measurements for determining the molecular weight. The membrane osmometer measures the osmotic pressure directly. During calibration, the displayed digits are assigned to a specific pressure signal via the hydrostatic pressure difference so that the molecular weight can be subsequently determined during the measurement using the cell constant from the measured osmotic pressures of the solutions.

5 Determining molecular weights

5.1 Making of sample solutions

A complete molecular weight determination requires a minimum of three solutions of the same polymer sample with stepped concentration (typically, four solutions are used).

The concentration range used for the sample solutions depends directly upon the molecular weight of the polymer to be measured.

The following table shows the measurement effect to be expected in relation to the weight concentration and the molecular weight.

Molecular weight	Concentration [1 g / 100 ml] equivalent to a molality of	Measurement effect Osmotic pressure in [cm] water column
2 x 10 E4	0.5 mMol / kg	12.6
4 x 10 E4	0.25 mMol / kg	6.3
6 x 10 E4	0.165 mMol / kg	4.2
1 x 10 E5	0.1 mMol / kg	2.53
2 x 10 E5	0.5 mMol / kg	1.27
1 x 10 E6	0.1 mMol / kg	0.243

Figure 5-1

The OSMOMAT 090 has a measuring resolution of approx. 0.1 mm liquid column per digit.

To ensure maximum measurement accuracy, the lowest polymer concentration should result in a measurement value of 50 to 100 digits equivalent to an osmotic pressure of 0.5 to 1.0 cm at the osmometer.

This results in the following concentration series:

Molecular weight	Concentration [g / 100 ml] lowest concentration	 highest concentration
2 x 10 E4	0.04 to 0.08	0.16 to 0.32
4 x 10 E4	0.08 to 0.16	0.32 to 0.64
6 x 10 E4	0.12 to 0.24	0.48 to 0.96
1 x 10 E5	0.2 to 0.4	0.8 to 1.6
2 x 10 E5	0.4 to 0.8	1.6 to 2.3
1 x 10 E6	2.1 to 4.2	8.4 to 16.8

Figure 5-2

Four solutions with stepped concentrations between the lowest and highest concentration are prepared.

Example: 0.04 - 0.08 - 0.12 - 0.16 g/100 ml

However, these figures are only reference values and can be adjusted to the actual solubility behavior of the polymer and amount of polymer available.

The measurement of a solution requires approx. 2 to 3 ml of the sample solution.

However, for increased accuracy, larger sample volumes are recommended particularly in the lower molecular weight range to account for the accuracy of the weighted sample.
The solvent should be weighed out as well and calculated based on the density of the solvent volume.
Diluted series made from a mother solution are not recommended for reasons of accuracy.
For polymer samples with unknown molar mass, a survey measurement with an average concentration has to be conducted before making a concentration series.

5.2 Performing the measurement

The measurement cell has been prepared for the measurement using a suitable solvent and membrane and calibrated according to chapter 4.
In addition, the inlet funnel (15) and outlet valve (14) have been attached to the measurement cell as shown in figure 1.1.
To start a new measurement, select the *File, New Measurement* menu item and then *090 Molecular Weight Measurement* or click the *New* button (on the left side of the toolbar).
If the unit has been calibrated for the solvent used for the measurement, you can click the *Start* button to enter the measurement mode.
The following dialog requests you to enter the concentration of the sample solutions. You can also enter a *Sample ID* and a *Sample No.* for easier identification on measurement printouts. After entering a minimum of one or a maximum of eight concentrations, you can exit the dialog by selecting *Start.*

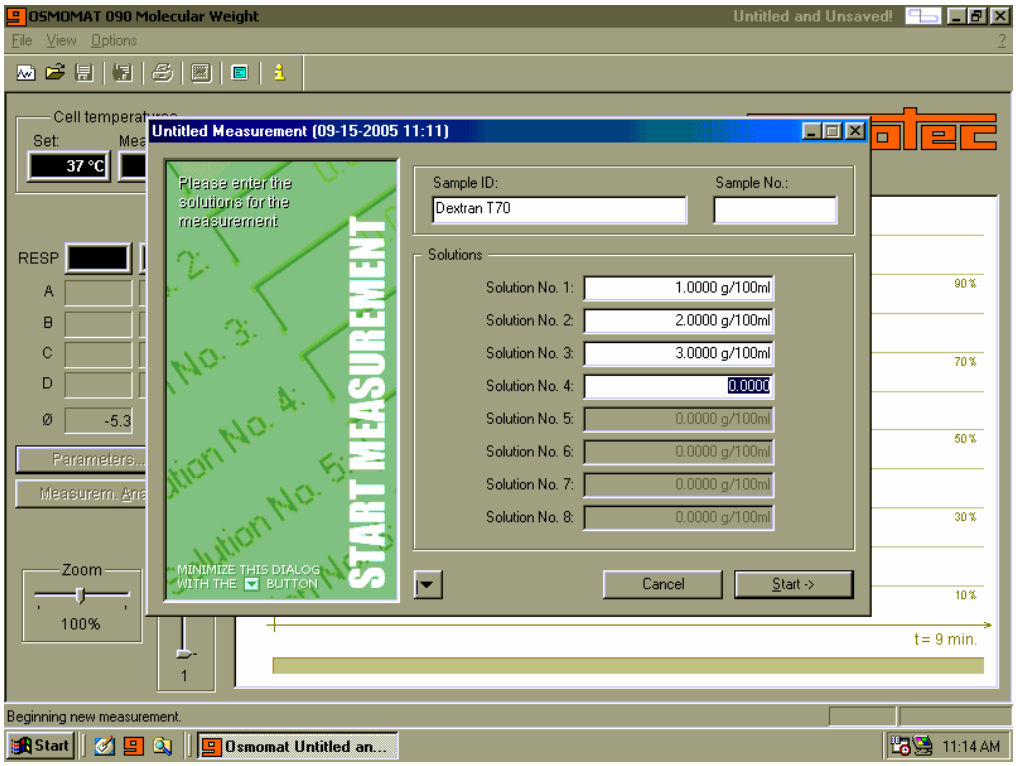

Figure 5-3

If the temperature of the measurement cell does not match the required temperature parameter, a message informs you that the system is waiting for the correct temperature.

A selection dialog will guide you through the following measurement procedures. The measurement starts with a baseline adjustment, with an additional zero (hardware) adjustment during the initial adjustment.

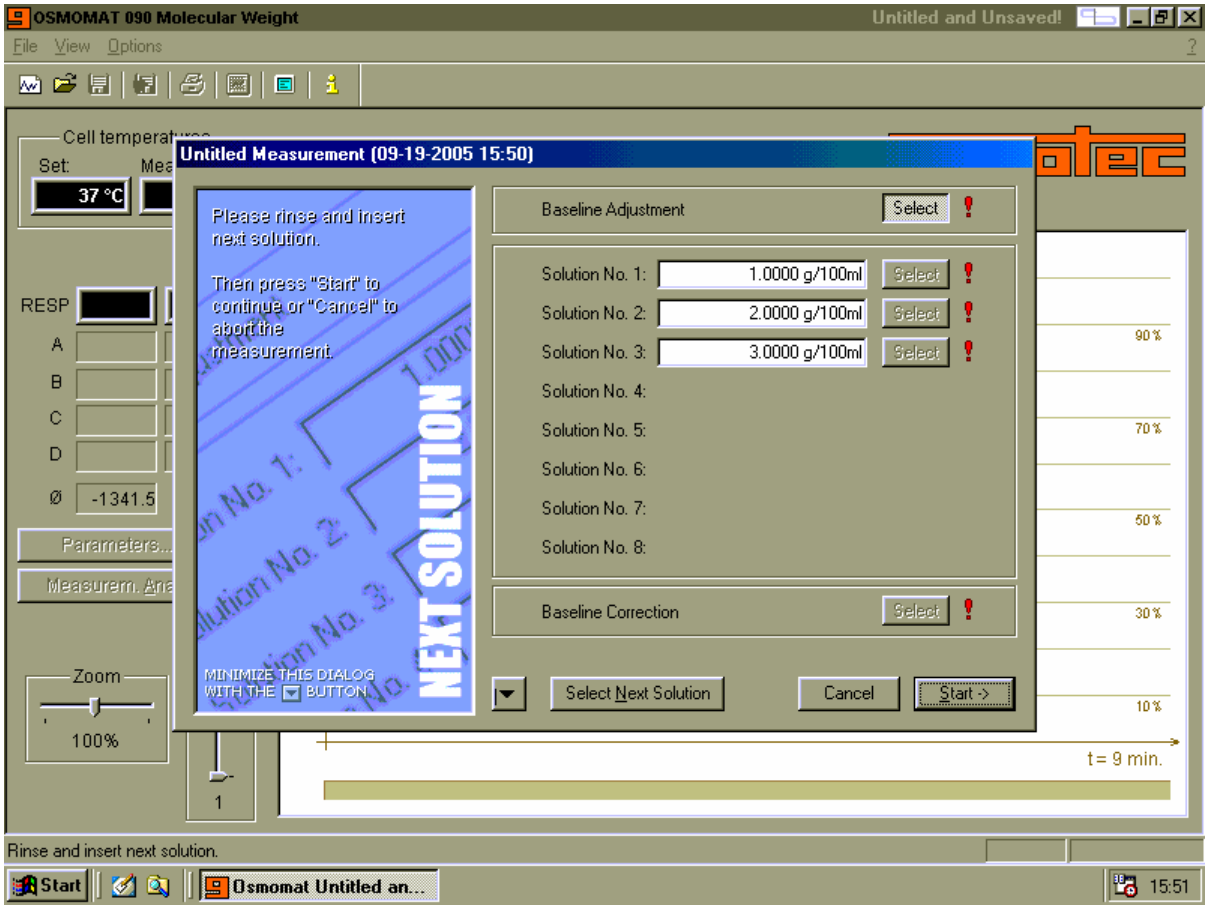

Figure 5-4

After the cell temperature has stabilized (indicated by the baseline stability on the y/t graph - use the right arrow to set the sensitivity of the graphic to 128), approx. 0.6 ml of solvent are filled into the inlet funnel using the glass syringe (1 ml) and long tube.

The calibration bottle (25) can be used to hold additional solvent.

Next, the solvent is sucked into the measurement cell as follows.

Before opening the outlet valve (14), the suction bulb (1) of the suction bottle A" is squeezed. This creates a vacuum which causes the solvent in the inlet funnel to be sucked into the suction bottle A" through the meander-shaped channel system in the upper cell half.

The outlet valve is closed when the meniscus of the solvent is approx. 2 mm above the end of the suction tube, which is located in the center of the inlet funnel.

By squeezing the suction bulb of the suction bottle B", the remaining solvent is sucked out of the inlet funnel. The remaining solvent sets at a reproducible fill level.

After the currently adjusting baseline has stabilized, an electronic zero adjustment of the amplifier is performed.

During this procedure, the measurement system is gradually zero-adjusted to a smallest possible value.

The reproducibility of the baseline can be verified by rinsing the measurement cell with solvent again. Each time, the baseline value is re-determined. After rinsing the measurement cell with solvent, click *Start.* The selection screen disappears until a measurement value has been applied. The measurement value is applied automatically after remaining constant for at least 10 seconds or if you interrupt the measurement by selecting *User Interrupt.* The selection dialog re-appears. Click the arrow icon in the lower left corner of the dialog to minimize it for a better view of the measurement graph. Click the *Continue* button to re-display the selection dialog.

Repeat the baseline measurement cycle until the baseline appears to be constant.

After obtaining a stable and reproducible baseline, you can start the measurement of the prepared polymer solutions. Please note that the measurement cell has to be rinsed at least three or four times using the same concentration to saturate the upper half of the measurement cell with the respective solution. Solutions with a higher viscosity tend to require more rinses.

You can measure your sample solutions one by one. Starting with the lowest concentration, one solution after another is introduced into the measurement cell as described for the solvent. The measurement cell has to be rinsed repeatedly with the same solution until a stable and reproducible measurement value is obtained. It is recommended to rinse the measurement cell more often using smaller volumes (0.3 ml). After each rinse, the measurement value is applied as described for adjusting the baseline. You cannot start with the next solution until a reproducible end value for the respective solution is obtained.

The measurement value is applied automatically after the value has been constant for 10s or if you select *User Interrupt* after the measurement value enters a constant drift.

While you can perform any number of measurements with a sample solution, only the last four measurements per sample solution are recorded and identified in the graphic as A, B, C, and D. These last four values per sample solution are also used for the subsequent evaluation. The sample solutions are selected by clicking the respective *Select* button or choosing *Select Next Solution.* The procedure is identical to the baseline adjustment. The equilibration graph for a polymer solution depends mostly on the saturation behavior of the upper cell half with the respective solution and the permeability of the semipermeable membrane.

While the saturation behavior can be manipulated by frequently rinsing the cell with the same solution, the permeability of the semipermeable membrane depends on the size and number of pores.

However, the equilibration speed can also be reduced by small air bubbles which may be contained in the lower half of the measurement cell.

After measuring all prepared solutions, the measurement cell is again rinsed with solvent and the baseline adjustment is checked.

This again requires multiple rinses to remove the solution from the upper half of the measurement cell and to obtain a reproducible baseline value.

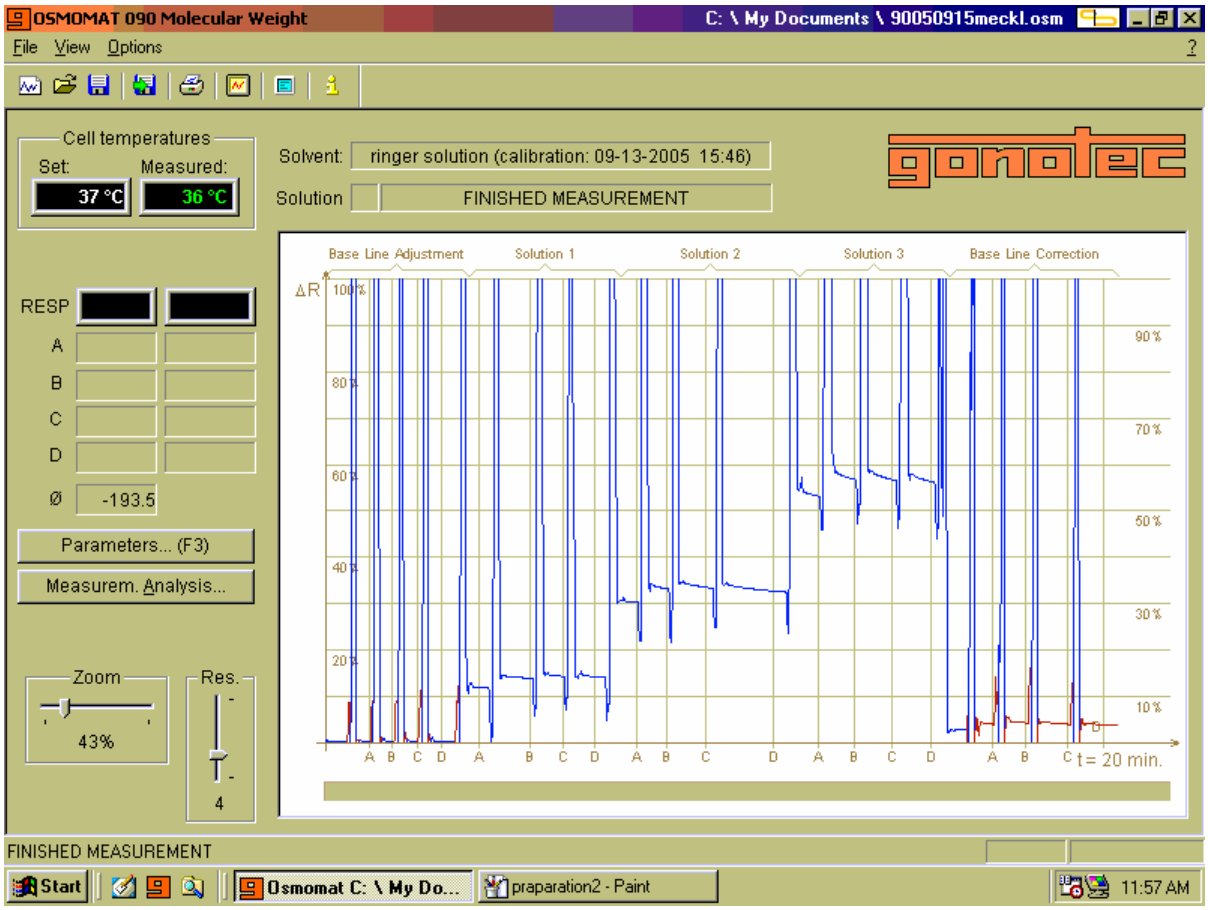

Figure 5-5

It is possible that the baseline sets at a negative value.

This can occur if the polymer to be measured has a broader molecular weight distribution with the lower molecular weight part below the "CUT OFF" of the membrane used.

The lower molecular polymer parts, that permeated into the lower cell half during the measurement, will permeate back relatively fast after the rinsing with the solvent, reproducing the original baseline after a short time.

However, during the subsequent calculation, the baseline shift into the negative cannot be considered to be a baseline drift, nor can the temporary loss of the permeated polymer part be taken into account because its weight is unknown.

In this case, the measurement result is faulty, indicating a higher molecular weight.

After the measurement is completed, click the *Measurem. Analysis* button.

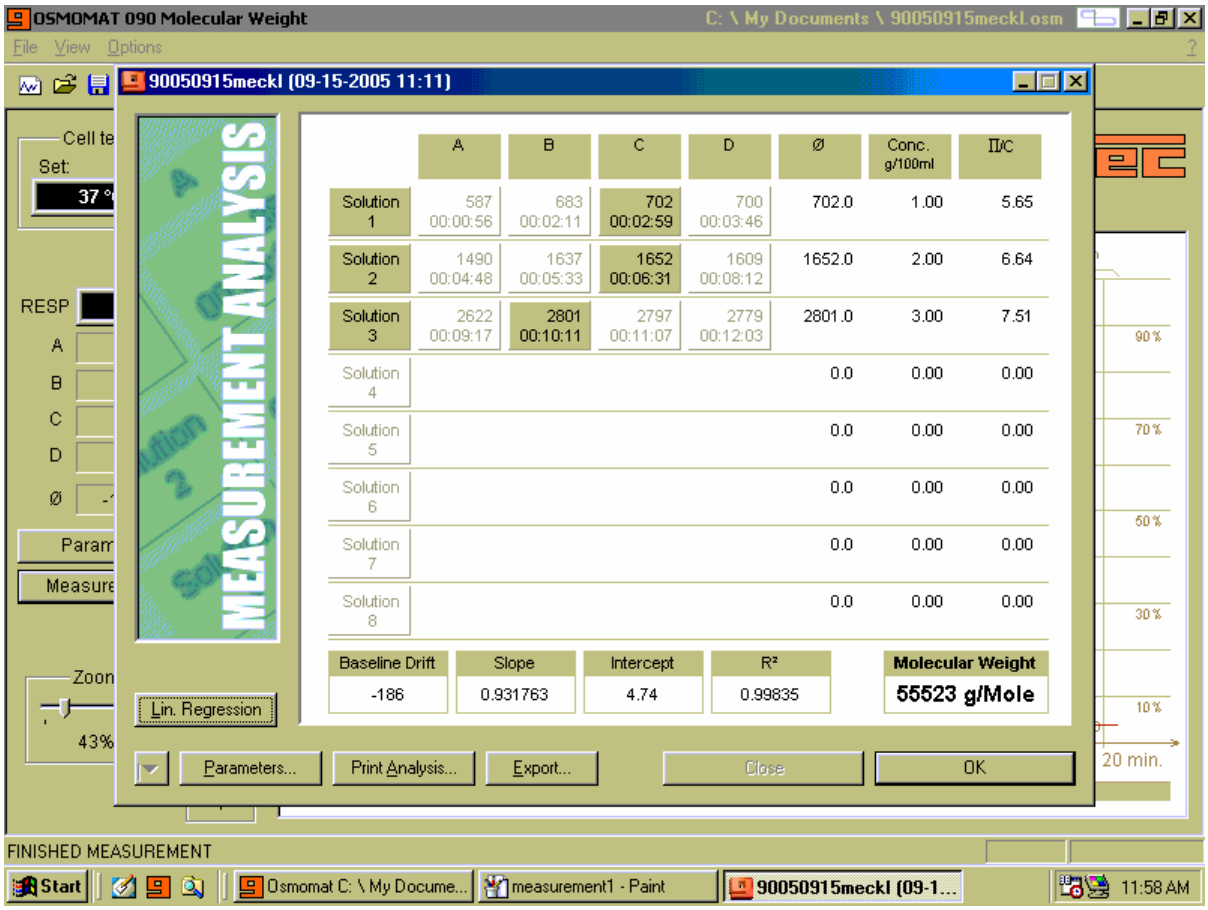

Figure 5-6

The evaluation dialog shows the measurement values including the respective concentrations of the sample solutions. By default, only the last measurement value of each sample solution is considered for the subsequent calculation. However, you can click the individual measurement values to activate and include them in the evaluation. Activated values are displayed in bold letters, while deactivated values (excluded from the evaluation) are displayed in plain letters. First, the values are used to establish the ¶/C quotient for each sample solution. A linear regression is applied to these values. The resulting value is displayed and used to calculate the molecular weight, which is displayed as well. The linear regression analysis results in the Intercept (extrapolation value toward the zero concentration) and Slope (of the regression curve) values.

The linear regression can be graphed by clicking the *Lin. Regression* button.

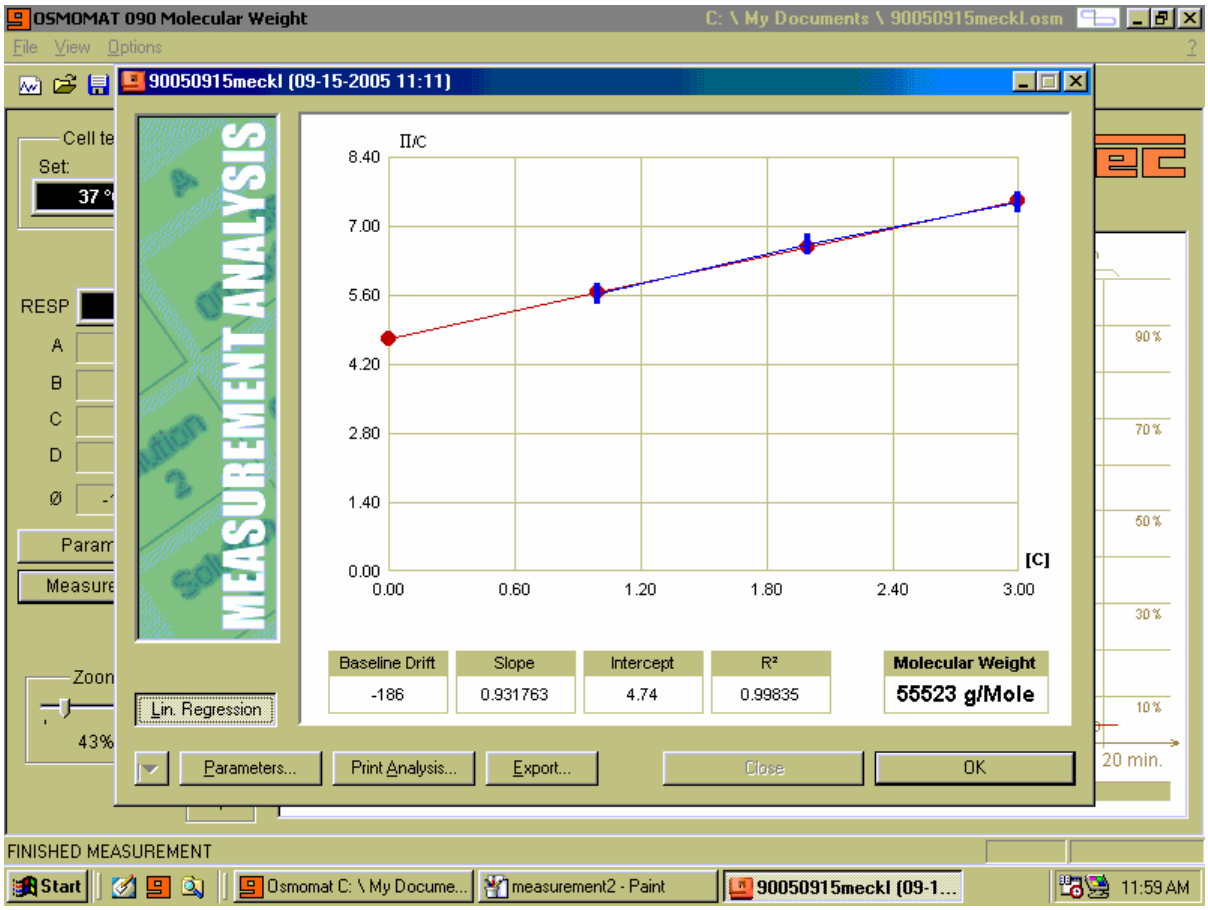

Figure 5-7

If you are not satisfied with the results of a sample solution, you can return to the measurement by clicking the *Back to Measurement* button. You can now repeat the measurement of the respective sample solution. You must note, however, that all sample solutions following this sample solution and the baseline drifts have to be re-measured. For example, if you repeat the measurement of sample solution 4 (Solution 4), you have to re-measure the following sample solutions (if applicable) and the baseline drift as well.

If you are satisfied with your measurement results, complete the measurement by clicking the *Stop&Save As* button. The save dialog requests you to enter a name for your measurement. This name is used to save the complete measurement sequence including graphic and evaluation, which can be accessed at any time. The evaluation dialog disappears after saving, but can be re-displayed by clicking the *Measurem. Analysis* button. If you make further changes (such as activation of measurement values), you are requested to save your changes. The *Close* button changes to a *Save* button, which takes you back to the save dialog where the existing measurement name is displayed. You can overwrite the previous measurement or enter a new name to create a new file.

5.3 Evaluating external data

To evaluate existing measurement values which e.g. were acquired using the control unit B or are available in handwritten form only, you can use the *external Data* mode. This mode can be accessed via the start dialog or the *File, New external Data* and *090 Molecular Weight Measurement* menu item. This opens the evaluation dialog where you can enter your data.
To calculate the molecular weight, the measurement data have to be complemented by the respective concentrations of the solutions and the parameter dialog has to be completed. To open the parameter dialog, click the *Parameters* button. However, only the *Cell Const.* parameter is necessary to calculate the molecular weight. All other parameters are optional and can be entered for completeness.
Individual measurement values can be activated or deactivated, similarly to evaluating a "real" measurement (see **5.2**). However, the entry field is divided by a horizontal line. Click the area above the line to enter a new value and use the area below the line to activate or deactivate the value.
The results can be printed and saved to a file.

5.4 Printing

To print from the main screen, select *Print* from the *File* menu or click the printer icon in the toolbar. When printing from the main screen, only the contents of the graphic window and some additional information is printed.
The evaluation can be printed using the *Print Analysis* button in the evaluation dialog. This prints all the parameters, concentrations, evaluation results, as well as the linear regression.
A print menu lets you select a printer. The printer set up under Windows 95 is selected by default.

5.5 Printer installation

This software can print to all Windows 95 printers using a **parallel interface**. If your connected printer is not listed in the list of available printers, you have to install it. Set it as the default printer to avoid having to select the printer from the print menu each time you print.
Exit the OSMOMAT program before installing or setting a printer as default.
To set a printer as default, select *Start, Settings, Printers* to display the list of installed printers. Click the printer to select it and then select *File, Set as Default Printer.* Select *File, Close* to close the list of printers.
To install a printer, access the list of printers as described above and double-click the *New Printer* icon. You are guided through a set of dialogs to select a printer from a list of manufacturers and to set it as *Default* (select *Yes* when prompted). Typically, the default settings can be accepted with *Next* because the printer interface requires no further configuration. Print a test page for verification.

6 Starting up the measurement system with the control unit B

6.1 Electrical installation with the control unit B

The equipment has to be set up in a dry, shock-free and draft-free area. It has to be kept from direct sunlight as well as external heat sources such as lighting and heating equipment.
When using the control unit SA, the data cable from the measurement cell is connected to the socket labeled "Cell-Unit". The power cable is used to connect the measurement cell and the control unit. The power cable of the control unit is then connected to a power outlet. The line voltage of your power supply system has to comply with the voltage stated on the type lable of the equipment (110-115 or 220-230V).

Make sure that the equipment grounding is connected to the protective grounding of the power supply. The supplied power cable automatically provides grounding contact. If the connector of the standard power cable is replaced by another connector, you have to ensure that the grounding cable (green/yellow) is connected to the protective grounding.
The grounding connection is absolutely necessary to prevent injury due to electric shock and interference with the functionality of the measurement system.

To protect the highly sensitive pressure transducer from overpressure during cell preparation, the pressure ratios in the measurement cell and at the pressure transducer have to be continually monitored using the respective control unit. If the pressure reaches a critical point which could result in damage to the measurement system, an audible warning signal is generated. If the back panel of the control unit B has a switch, it must be pressed to enable the warning signal for over-/underpressure. In newer models of the control unit B without a switch, the signal is enabled internally.

6.2 Preparing the measurement cell with the control unit B

For osmometric measurements to be performed within a temperature range of 5°C above room temperature to 60°C, the cell temperature to be used later can be set directly. For measurements at high temperatures up to 130°C, however, the cell preparation should initially be performed at a maximum of 80°C. Following the preparation, the cell temperature is gradually increased to the high setting to avoid damaging the semipermeable membrane. The temperature is set using the "Cell-Temp" digital switch on the left side. The "sampling time" is set to zero.

The "Cal" potentiometer is turned all the way to the right for maximum sensitivity. The current temperature in the measurement system can be displayed by pressing the "TEMP" button. Pressing the "RESET" button reverts to the measurement value.
The procedures performed on the measurement cell are identical to those described under point 3. The pressure transducer is controlled using the digital display. In addition, a recorder can be connected to the recorder socket on the control unit B using the recorder cable from the standard accessories kit. For baseline control, the recorder is set to 1V maximum deflection. The zero line of the recorder should be configured with 10 scale divisions to allow monitoring of the baseline progression even for negative drift. During calibration, a measurement value of >3000 digits is generated so that the recorder may have to be set to 2-5V for maximum deflection. The paper feed can be set to 12-30cm/h.
The measurement system is adjusted by pressing the "ZERO" button. The adjustment takes approx. 15s. A base value is reached. Using the "ZERO" potentiometer, this value is set to 0.000 on the digital display and locked.
The rinsing of the baseline is repeated until a constant value is reached.
(See chapter 3.)

6.3 Calibrating the measurement cell with the control unit B

The measurement cell is prepared for calibration as described under chapter 4.1, the bottle for calibration is filled with solvent (figure 4-1) and placed on the housing of the measurement cell. First, another zero adjustment is performed by pressing the "ZERO" button. Next, the digital display is set to 0.00 using the "ZERO" potentiometer. The stability of the baseline has to be checked using the display or recorder. After the baseline has stabilized, the value has to be read off the digital display (VALUE 1). Afterwards, the bottle is moved from the housing onto the tabletop, which results in a negative hydrostatic pressure difference on the pressure transducer shown as a positive value on the digital display (VALUE 2). This numeric value corresponds to the hydrostatic pressure of the liquid column resulting from the height of the case of the measurement instrument.
The calibration should be repeated several times to check the baseline stability and calibration value.
The cell constant, indicating the relation between the directly measured hydrostatic pressure and the displayed digits, is calculated as follows:

$$\text{CELL CONSTANT} = \frac{h \times 100}{\text{VALUE 2 - VALUE 1}}$$

where **h** is the height of the housing in cm (indicated on the sticker on the right side of the housing). For aqueous solutions, the second measurement value is approx. 2400 digits if the first value approximates zero. The cell constant in aqueous solutions is then approx. 0.8.

6.4 Measurement using the control unit B

The measurement sequence is identical to the one described under chapter **5.2**. First, the baseline is rinsed until the value has stabilized. Next, the digital display is set to 0.000 using the "ZERO" potentiometer. After pressing the "TIMER START" button, the measurement value is stored and displayed on the digital display as fixed value. A line mark is set on the strip chart recorder. The display is cleared by pressing the "RESET" button.

After the baseline has stabilized, the measurement of the polymer solution is started. Each time, the measurement value is applied using the "TIMER-START" button. The resulting measurement values are noted.

The following formulas can be used to calculate the molecular weight (automatically calculated for measurements using the control unit SA):

Formula 1 ¶ = (cell constant x digit (measurement result)) / 100 = osmotic pressure

¶ = osmotic pressure in [cm solvent column]

cell constant = solvent column in [mm x 10 E-1] / digit

Formula 2

$$\overline{Mn} = \frac{848 \times (\text{CELL SET PT } [\,^{\circ}K\,])}{\left(\frac{\P}{C}\right)_{(C\to 0)} \times \text{density of solvent}} = [\text{g / Mol}]$$

Mn = number average of the molecular weight

848 = constant

CELL SET PT = selected cell temperature in degrees Kelvin

C = concentrations of solvents in [g / 100 ml]

¶ / C (C->0) = extrapolated value of ¶ / C of all solutions toward the zero concentration

density = density of the used solvent at room temperature

For the evaluation, the osmotic pressure ¶ is calculated from the highest value of the different solutions. Then, the quotient of the osmotic pressure and the respective concentration is calculated for each solution. These results are entered into a coordinate system (¶/c over c), and the ¶/c quotient for the zero concentration is established through graphic extrapolation toward the zero concentration.

The result is used in formula 2 to determine the average molecular weight.

The extrapolation can be performed much more accurately using the linear regression analysis, available with the control unit SA.

7 Semipermeable membrane

The semipermeable membrane is a main component of the osmotic cell. The defined pore size allows only the lower molecular solvent to permeate, while the higher polymeric substances of the measurement solution are retained. In addition, the membrane material seals the osmotic cell.

The pore size or pore size range is the typical factor for the retention and called "cut off". The membranes used for membrane osmometry usually have a cut off between 5,000 and 30,000 dalton. The pore sizes specified by the membrane manufacturers are reference values only. They do not indicate the actual pore size or an existing pore size distribution.
Organic solvents affect the pore size. The flow characteristic (permeability) depends on the number of pass-through pores and their diameter.
A membrane with a cut off of 5,000 requires a sufficient number of pores to ensure adequate permeability. This is evident from the pressurization during the preparation of the measurement cell and the time it takes for the osmotic pressure to build up during the measurement.
Only membranes with very thin layers containing a supporting material for mechanical reasons (so-called two-layer membranes) can provide adequate permeability. Depending on the manufacturer, both layers are made of the same or different materials. Aqueous solutions place hardly any restrictions on the membrane material used. However, when using organic solvents, the resistance to solvent has to be considered. Regenerated cellulose is a membrane material for universal use.
Cellulose acetate or nitrate, on the other hand, can be used only for a limited number of organic solvents.
Two-layer membranes with a supporting layer of polypropylene cannot be used in the membrane osmometer because the texture hardens in organic solvents and the cell is not sealed as required.
When selecting a new membrane type, ensure that the membrane material (active layer and supporting layer) is resistant to the organic solvent used.
The diameter of the membrane changes in organic solvent. Therefore, it should be approx. 45 to 48 mm in a dry state to ensure a trimmed diameter of 40 mm after conditioning the membrane to the solvent.

7.1 Preparation of the semipermeable membrane using cellulose triacetate as an example

The cellulose triacetate two-layer membrane is available with pore sizes of 5,000, 10,000, and 20,000 dalton. The membrane is delivered in a dry state with the pores filled with glycerin.

7.1.1 Preparation for aqueous solvents

When using aqueous solvents, the membrane can be trimmed in a dry state to a cell size of 40 mm using the template discs provided with the standard accessories kit.

The membrane is placed between the stainless steel template discs and trimmed using scissors. To prevent small cracks on the cutting edge, the scissors should be applied only in a tangential fashion. The active membrane layer is the shiny one, the hydrophobic side in the wet state.
The trimmed membrane is placed with the shiny side onto the surface of distilled water while keeping the supporting layer (dull side) dry.
The water penetrates the pores from below and displaces the glycerin. After a short time, small water droplets are visible on the supporting side, and the membrane shows a slight discoloration.
The membrane remains on the water surface until is it evenly discolored. Depending on the pore diameter, this can take from a few seconds to an hour.
Next, the membrane is completely submerged into the water and ready for installation into the membrane osmometer for measurement of aqueous solvents. It is important to install the membrane in the measurement cell with the active layer facing up.

If necessary, you can verify which of the two sides is the active layer.
Carefully remove the membrane from the water using stamp tweezers. The active side of the membrane has hydrophobic properties, while the supporting layer is hydrophilic.

It is important that the membrane not dry out because this would affect the pore size.

7.1.2 Preparation of the membrane for organic solvents

First, the membrane material is pretreated in distilled water as described in the previous chapter. However, the membrane is **not** trimmed to a cell size of 40 mm in the dry state because the membrane diameter changes during preparation for the organic solvent through shrinking or expansion.
The conditioning of the membrane material has to be performed with great care in several steps using different solvent mixtures to avoid damage to the pore structure. During the entire procedure, the membrane must never dry out or its edges protrude from the solvent.

The solvents used in sequence have to be mixable, and the conditioning has to be performed in steps using three to four intermediate concentrations.
The membranes have to remain in the respective solvent mixtures for at least two hours and must never dry. We recommend weighing bottles with glass cover, a diameter of approx. 60 mm and a capacity of approx. 45 ml as containers for the solvent mixtures.
You should prepare several membranes at once because this preparation procedure can extend over two days.
After being placed in distilled water for several hours, the membranes are restacked into the next solvent mixture one by one using stamp tweezers.
You have to ensure that the membrane surfaces do not dry and that the membrane position (active/supporting layer) is not changed.

A subsequent identification of the respective layer is impossible because the membranes lose their typical surface characteristic in organic solvents.

During restacking, a sufficiently large filter paper is placed between each membrane as a spacer to prevent them from warping and sticking together (Round filter, diameter 55 mm).
The filter paper spacers are restacked into the new solvent mixture together with the membranes.

Example for membrane conditioning from water to toluene in steps of 25%:

Ethanol can be used as intermediate solvent. The mixtures have to be thoroughly blended before introducing the membranes.

25% ethanol	+	75% water	Wait time: 2 hours
50% ethanol	+	50% water	Wait time: 2 hours
75% ethanol	+	25% water	Wait time: 2 hours
100% ethanol			Wait time: 8 hours

25% toluene	+	75% ethanol	Wait time: 2 hours
50% toluene	+	50% ethanol	Wait time: 2 hours
75% toluene	+	25% ethanol	Wait time: 2 hours
100% toluene	+		Wait time: 8 hours

Following these steps, the membranes are ready to be installed in the membrane osmometer.
Depending on the type of solvent or membrane material, the membranes may exhibit a certain degree of expansion or shrinkage following the conditioning. In addition, their consistency may change and they may become transparent which makes them barely visible in the solvent.
In any case, use only solvent mixtures of solvents that are mixable. When using isopropanol as intermediate solvent, the wait time should be increased to 4 hours in each instance. Ensure that the membrane material is resistant to the solvent used.
Under time constraints, conditioning in steps of 33% may be sufficient. Following conditioning, the membrane is trimmed to 40 mm using the template discs. To prevent the membranes from drying, each membrane is placed between two filter paper spacers with a light solvent coating. They are then trimmed in a tangential fashion between the template discs using scissors. The appendix of this user manual provides a list of solvents declared as usable with the cellulose triacetate two-layer membrane by the membrane manufacturer.

8 Important notes

These special notes concern the basic function of membrane osmometry and have to be observed!

8.1 Reproducibility

One requirement for reproducible measurements is that the system is leak-proof in the area of the valve sealing and the inlet funnel with the universal sealings.
These PTFE sealings have to be replaced after extended use when a leak-proof fit is no longer guaranteed or when cold flow has reduced the bore holes in the sealings to a point where the cell can no longer be rinsed.
To replace a universal sealing, simply press into the soft sealing from above using a large screwdriver (6 mm blade width).
The sealing can be removed from the threading like a screw by turning counter-clockwise. The cell does not have to be opened for this procedure.
Furthermore, the valve spindle has to be leak-proof when solvent is sucked from the calibration bottle through the measurement cell during calibration to fill the upper measurement cell system with solvent while avoiding air bubbles.
The system is typically filled without air bubbles when no more air bubbles escape through the outlet valve during the suction.
If the valve spindle leaks, this is no longer guaranteed.
To fix the leakage, turn the screw at the upper part of the outlet valve clockwise to further compress the PTFE sealing built into the valve. However, the sealing should be compressed only to the point where the valve spindle can still be turned comfortably. If a leak-proof fit can no longer be guaranteed after several refittings, the entire outlet valve has to be replaced.

8.2 Leak-proof fit of the self-sealing semipermeable membrane

The semipermeable membrane built into the measurement cell is surrounded by a circular channel terminated by a large lip seal toward the outside.
The circular channel is filled with solvent automatically during the cell preparation and has only one opening to the outside via a stainless steel tube.
This channel protects the face side of the installed semipermeable membrane from drying out, which would result in baseline drift and later leakage of the measurement cell. The tube with attached short teflon tube protruding from the upper part of the osmotic cell should always be filled with solvent. Solvent can easily be added using the syringe.
This tube can also be used to test the assembled measurement cell for leakage by attaching a syringe filled with solvent and equipped with a 1/8in tube to the end of the teflon tube.
Pressing down on the syringe creates overpressure in the circular channel which would affect the pressure transducer in case of membrane leakage.
If the membrane has a leak-proof fit, only a slight overpressure can be observed.

In case the membrane leaks as described or solvent escapes at the side of the measurement cell, the cell may have to be further compressed.
If only solvent escapes from the measurement cell while the pressure transducer does not show significant pressure fluctuations, only the large lip seal has to be replaced.
An inadequately sealed osmotic measurement cell can result in baseline drift and a non-reproducible pressure measurement or prevent the buildup of osmotic pressure.

8.3 Permeation of lower molecular parts

Ideal measurement conditions

When measuring a monodisperse polymer in the membrane osmometer with a molar mass significantly higher than the cut off of the semipermeable membrane, the osmotic pressure that builds up after the saturation of the upper half of the measurement cell remains stable for a long time.
The baseline after the measurement shows the same value as before the measurement.

Measurement conditions with a broad molecular weight distribution

When measuring a polydisperse polymer with the lower molecular parts below the cut off of the semipermeable membrane, polymer parts will permeate into the lower half of the measurement cell during the measurement. The resulting measurement graph initially shows the increasing osmotic pressure with each rinsing through saturation of the upper half of the measurement cell.
However, this saturation effect is immediately offset by a more or less significant permeation effect which counteracts the buildup of osmotic pressure.
After cell saturation, the osmotic pressure reaches a peak value followed by a steady decline in osmotic pressure.
The osmotic pressure would stabilize (and be representative of the non-permeated polymer parts) only after reaching a concentration equilibrium of the permeated polymer parts in the upper and lower half of the measurement cell.
After re-rinsing the baseline with solvent, a baseline shift can be observed, resulting in a negative value depending on the amount of the permeated part.
However, because the quantitative part of the permeated polymers is unknown, these measurements cannot be corrected.

These measurement conditions result in higher molar masses than expected.
Therefore, a reliable measurement result can be obtained only if the permeation effects are non-existent or negligible. A very good indicator for this is the baseline value following the overall measurement.
Due to the very small cell volume in the lower cell half, representing only a liquid coating below the semipermeable membrane, saturation with lower molecular parts is achieved relatively quickly.

Rinsing with the solvent results in back-permeation. After repeatedly replacing the solvent in the upper cell half, the baseline quickly returns to the initial value.
Therefore, the construction of the measurement cell does not require re-preparation of the lower measurement cell in case of permeation.

8.4 Using the supplied stainless steel support sieve

A quick and error-free measurement with the membrane osmometer requires a precise fixation of the semipermeable membrane in the osmotic cell (No balloon effect!).
Due to the special construction of the measurement cell of the OSMOMAT 090, the semipermeable membrane is pressed against the cell floor with the cell volume of the lower cell half constituting only a liquid coating below the membrane.
When the osmotic pressure builds up in the lower cell half, the semipermeable membrane, which would normally give due to this underpressure, has nowhere to go because it is pressed against the cell floor. This ensures a quick buildup of the osmotic pressure.
However, this requires a sufficient mechanical stability of the semipermeable membrane in the solvent used.
If the membrane material in the solvent used expands, the pressure on the pressure points of the installed membrane causes the membrane material to partially give to the pressure and enter into the channel area.
The membrane bulges, which creates cavities below.
When the underpressure builds up in the lower cell half, the bulged membrane will give to the underpressure, causing a balloon effect and solvent to permeate in the direction of the solution.
The osmotic equilibrium takes longer to adjust, and the sample solution is diluted, resulting in lower measurement results.
To prevent the falsification of the measurement value described above, a support sieve can be placed onto the membrane for better fixation.
While this will not shorten the adjustment time because part of the active membrane surface is covered by the support sieve and thus no longer available for permeation, the balloon effect falsifying the measurement result can be largely avoided.
When using the support sieve, the upper cell half bears directly on the metal surface of the sieve instead of the membrane. A small lip seal in the upper cell half seals it against the metal surface of the support sieve.

The support sieve should only be used if an extended buildup time of the osmotic pressure due to air bubbles in the lower cell half can be ruled out or if the membrane material already exhibits significant expansion following the conditioning.
Experience shows that the use of the support sieve can be recommended for measurements with pure water as well.

Appendix:

Resistance table for cellulose triacetate

(Information based on resistance table by Sartorius Göttingen)

- Benzene
- n-butanol
- n-butyl acetate
- Cyclohexane
- Diethyl ether
- Ethanol
- Ethylene glycol
- Glycerin
- n-heptane
- n-hexane
- Isobutanol
- Isopropanol
- Isopropyl acetate
- Methanol
- Methyl isobutyl ketone
- Monochlorobenzene
- n-pentane
- Perchloroethylene
- Carbon tetrachloride
- Toluene
- Trichloroethane
- Trichloroethylene
- Xylene