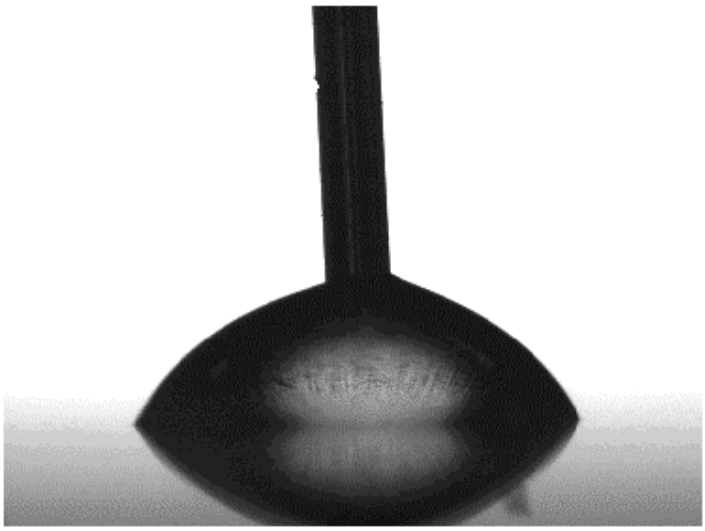
DSA1 v 1.9
Drop Shape Analysis
for DSA100



User manual
V1.9-03

Contents

1 Introduction

With the DSA1 software for drop shape analysis you have acquired a powerful tool for the computer-supported generation of liquid drops, for recording their video images and then evaluating these images. Together with the contact angle measuring system DSA100 the program provides you with the following possibilities:

- Measurement of contact angles with the DSA1 component **SW3201**
- Calculation of the surface energy of solids with the DSA1 component **SW3202**
- Measurement of the surface tension of liquids with the DSA1 component **SW3203**

In detail the DSA1 program provides you with the following possibilities:

- Computer-supporting generation of drops of liquid
- Sequential recording and evaluation of drop images at predefined intervals
- Determination of the contact angle in any system consisting of liquid, gas and solid
- Calculation of the surface free energy of solids from contact angle data
- Determination of the interfacial tension of any liquids in gaseous or liquid surroundings
- Recording and evaluation of drop videos
- Generation of measurement protocols and graphics.

About this manual

This manual provides you with all the necessary information for successful work with the DSA1 program. The theoretical background of the evaluation methods is also covered in detail.

We recommend that, before you start to use the system, you study this manual carefully in order to ensure the proper installation of the system, to accelerate familiarization with its operation and to eliminate operator errors that could cause injury or damage the measuring system.

Apart from this introduction, this manual is arranged in 15 further sections. It is extended by a glossary, in which the most important terms are explained, and an index. A brief description of the individual sections is given below:

Section 2 **Quick start**. This section offers a rapid introduction to the measuring procedure with the DSA100. A prerequirement is that the setup and installation have already been carried out.

Section 3 **Installation**. This section guides you through the installation of the DSA1 software in detail.

Section 4 **Introduction to the DSA1 program**. This introduction to the DSA1 program covers the structure of the menus and windows in the DSA1 program; information about its operation is also provided.

The sections 5 to 7 cover the PC-controlled components of the DSA100.

Section 5 **Control of the movable axes**.
Section 6 **Deposition and syringe control**.
Section 7 **Controlling the optics**

If your system does not have the corresponding components, you can skip these sections.

Section 8 **Obtaining an optimum drop image**. This section describes in detail the procedure for recording a drop image.

Section 9 **Evaluation of the drop image**. This section contains all the information you require for determining the contact angle from the image of a sessile drop and for calculating the surface tension from the image of a pendant drop.

Section 10 **Presentation of the measurement results**. The subject of this section is the tabular and graphical presentation of the recorded measured values.

Section 11 **Determination of the surface energy**. The possibilities and procedures for determining surface energies are described in this section.

Section 12 **Databases**. This section covers the handling of the databases that are incorporated in the DSA1 program.

Section 13 **Working with the TrackerMan**. This section explains the procedure for the program-controlled recording of a series of drop images and their automatic evaluation with the aid of the TrackerMan.

Section 14 **Recording and evaluating video sequences.** A description of the recording and evaluation of drop videos is given in this section. The settings that have to be made for this are also described in detail.

Section 15 **General settings**. The versatility of the system and the possibility of working with different instruments and cameras means that the basic settings must be matched to the particular application. The necessary settings for the frame-grabber card, the instrument, for selecting the measuring method and for fitting are described in detail in this section.

Section 16 **Theory**. The theoretical background of the evaluation methods included in the program for determining the interfacial tension by drop shape analysis and determining the contact angle are described in this section. In addition, the determination of surface energies by the methods contained in the DSA1 program are also described.

Conventions

In this manual the names of particular keys on your keyboard are written in small caps (ENTER KEY, BACKSPACE, TAB KEY, etc.). These names may be abbreviated on your keys, e.g. the ARROW KEYS are normally marked with arrow symbols and not with the name ARROW KEY UP.

A plus sign (+) between two key names means that both these keys must be pressed at the same time in order to carry out the corresponding function. For example, ALT+X, means that the ALT KEY must be pressed and held down and then the X KEY pressed at the same time.

The DSA1 program is chiefly controlled by **menus**, submenus and dialog windows. From the menu bar at the upper margin of the screen the path to the required program function is chosen by selecting the menu or window entries in sequence; the individual entries are shown separated by arrows.

Example: "Option"→"Drop Info"→"Parameters"

The main menu item "Option" is first selected in the menu bar. In the pull-down menu which opens select "Drop Info" followed by the file card "Parameters" in the dialog window which then appears.

When the right-hand mouse key is pressed down when the mouse arrow is positioned on an opened window a so-called **"Context menu"** opens. This menu contains the relevant menu entries for the active window. In the text in this manual the corresponding context menu is called by the window name.

Quotations from the software which appear in dialog windows and menus are shown in quotation marks.

The DSA program can normally be operated with either the mouse or via the keyboard. In general operation with a mouse is described. If an alternative operation mode is possible then this is mentioned clearly in the text.

2 Quick start

This section is intended to help you to familiarize yourself with the DSA100 before you concern yourself with all the details of drop shape analysis. We initially assume that the instrument has been set up by a KRÜSS technician. If you intend to carry out setup and installation yourself then you must follow the instructions given in the separate Installation Manual for the DSA100 and in Section 3 of this manual.

2.1 Quick start: contact angle

Contact angle 1: Preparations
Switch on the DSA100 and then your computer. Start the DSA1 software with the shortcut symbol  .
Click on the button  to set image transmission to the live mode. Move your hand through the light path to check transmission.
Turn the angle of inclination of the prism (Tilt) to 2°. 
In the menu “Options” select in sequence the options “Drop Type” and “Sub Type”. For “Drop Type” select the option “Sessile Drop” and for “Subtype” the option “Normal Sessile Drop”.    
Prepare the deposition system: 1-place deposition system: fill the syringe with water and insert it. Multi-deposition systems: fill the storage bottle for Syringe 1 with water. However, if a different syringe has already been used for water then select this syringe for the quick start.

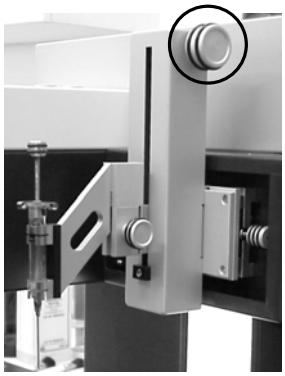
<table>
<tr><th colspan="2">Contact angle 2: Positioning the sample</th></tr>
<tr><th>Manual</th><th>PC-controlled</th></tr>
<tr><td colspan="2">Place a clean CD blank on the sample table support and fix it in position with the two clips.</td></tr>
<tr><td>Rotate the x-axis and the y-axis to a central position using the knobs.</td><td>Click on the FG window (video image) with the mouse
Move the x-axis and y-axis to a central position
Control (keyboard):
<x+↑> and <x+↓> for x-axis
- <y+↑> and <y+↓> for y-axis .</td></tr>
<tr><td>Turn the z-axis downward so that the sample is located below the camera illumination plane.</td><td>Turn the z-axis downward so that the sample is located below the camera illumination plane.
Control (keyboard):
<z+↑> and <z+↓></td></tr>
<tr><td colspan="2">Regulate the illumination to obtain a medium brightness. The change in brightness should be visible on the monitor.
Control:
Illumination brighter: key <PGUP↑>
Illumination darker: key <PGDN↓></td></tr>
<tr><td colspan="2">Move the sample table upward again until the sample appears in the camera image and fills the lower section of the image to no more than half.
 
During subsequent optical settings height and illumination can be further adjusted.</td></tr>
</table>

Contact angle 3: Positioning the needle

Manual

Move the needle downward until it is just above the sample.

This is done by rotating the top right knob on the stand.



PC-controlled

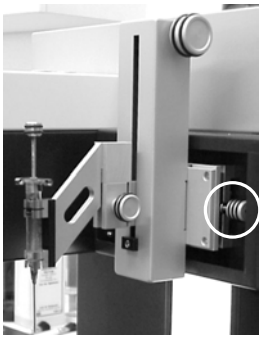
Move the needle downward until it is just above the sample.

Control (numerical key block):

- quickly downward: key <2>
- step by step downward: key <Ctrl+2>
- quickly upward: key <8>
- step by step upward: key <Ctrl+8>

Avoid contact between needle and sample. Check the distance between needle and sample not only via the monitor, but also directly.

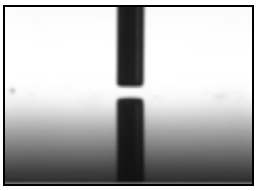
If necessary, move the needle to the center of the image. This is done by rotating the knob on the dosing system fastening (the example shown in the illustration is a manual dosing unit):



Contact angle 4: Optical settings

Manual

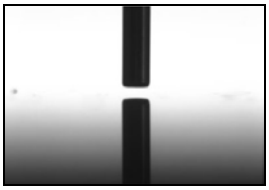
Regulate the lens zoom so that the image of the needle occupies max. 10% of the frame.



This is done by rotating the "Zoom" knob at the top left of the DSA100 housing.

As the section shown could change it may be necessary to adjust the height of the needle and sample table.

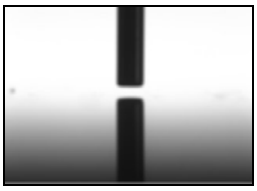
Adjust the focus so that the edges of the needle are as sharp as possible.



This is done by rotating the "Focus" knob at the top left of the DSA100 housing.

PC-controlled

Regulate the lens zoom so that the image of the needle occupies max. 10% of the frame.

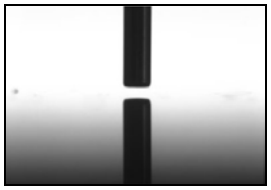


Control:

- magnify: key <Ins>
- diminish: key <Del>

As the section shown could change it may be necessary to adjust the height of the needle and sample table.

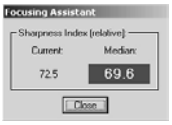
Adjust the focus so that the edges of the needle are as sharp as possible.



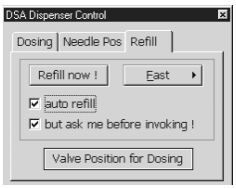
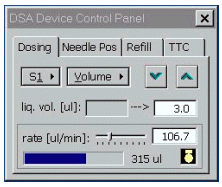
Control:

- increasing focal length: key <Home>
- decreasing focal length: key <End>

After clicking on the icon  in the symbol bar the focus wizard opens; this helps you with setting the sharpness of the image.



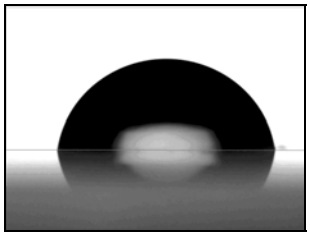
The field "Median" should appear in green and the numerical value shown should be as large as possible.

Contact angle 5: Drop dosing	
Manual	**PC-controlled**
	In “Device Control Panel” select the tab sheet “Refill”.  Click on the button “Refill Now”. The syringe will be filled from the storage container for water.
Turn the micrometer screw on the syringe clockwise to generate a drop.  Stop deposition before the drop reaches the edge of the frame.	In “Device Control Panel” select the tab sheet “Dosing”.  Click on the right-hand arrow key to start deposition.  Stop deposition before the drop reaches the edge of the frame by clicking on the same arrow key again.
Move the needle upward so that it is no longer inside the drop.	Move the needle upward so that it is no longer inside the drop. Control: key <8> of the numerical block

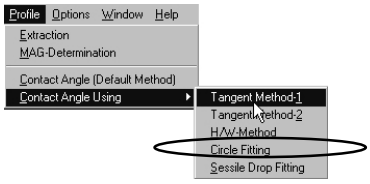
Contact angle 6: Contact angle measurement

Click on the symbol  in the symbol bar in order to determine the baseline automatically. The baseline is the line of contact between the sample surface and the drop.

The baseline can then be seen in the drop image as a colored line.

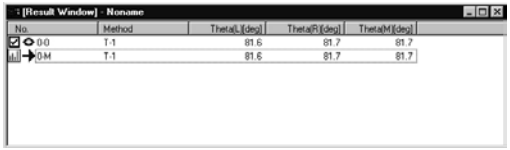


Open the menu "Profile" and from the drop-down menu select "Contact Angle Using" the method "Circle Fitting".



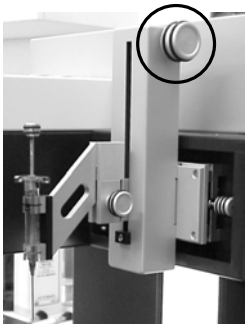
The drop image is fitted to a circular function; the resulting contour is shown around the drop image.

The result can be seen first at the bottom left in the status line. By clicking on the symbol  in the symbol bar the Result Window opens in which all the results of contact angle measurements are collected automatically.

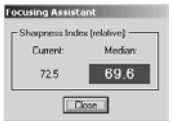
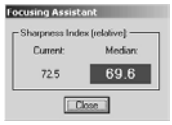


2.2 Quick start: Surface tension (pendant drop)

Surface tension 1: Preparations
Switch on the DSA100 and then your computer. Start the DSA1 software with the shortcut symbol  . Remove the protective cap from the prism.
Click on the button  to set image transmission to the live mode. Move your hand through the light path to check transmission.
Turn the angle of inclination of the prism (Tilt) to 0°. 
In the menu "Options" select in sequence the options "Drop Type" and "Sub Type". For "Drop Type" select the option "Pendant Drop" and for "Subtype" the option "Top→Bottom".    
For pendant drop measurements a special deposition needle with a broader diameter is used. If a disposable needle is used then the diameter must be determined exactly. If a reusable needle is used for the pendant drop then its diameter has already been measured by KRÜSS and its value is given. Fill the syringe to be used with water and insert it in the manual deposition system or in the manual position of the multi-deposition system.
Open The menu "Options"→"Drop Info" and select the card "Parameters". Under "Needle Diameter" enter the exact diameter of the needle in mm to two decimal places.
Click on the symbol  in the symbol bar. This opens the focus wizard, which helps you in setting the sharpness of the image.
Set the illumination to a medium brightness. The window with the video image (FG window) must be active. Control: Illumination brighter: key <PGUP↑> Illumination darker: key <PGDN↓>

Surface tension 2: Positioning the needle	
Manual	**PC-controlled**
	Select the tab sheet "Dosing" in the Device Control window. Select the syringe indicated by "M" (manual) from the drop-down menu at the top left. 
Move the needle downward until it appears in the image.  This is done by turning the knob at the top right of the stand. 	Move the needle downward until it appears in the image.  Control (numerical block keys): - quickly downward: key<2> - step by step downward: key<Ctrl+2> - quickly upward: key<8> - step by step upward: key<Ctrl+8>
Move the needle to the center of the video image.  This is done by turning the knob at the right of the stand attachment.	Move the needle to the center of the video image.  Control (numerical block keys): - quickly to the left: key<4> - step by step to the left: key<Ctrl+4> - quickly to the right: key<6> step by step to the right: key<Ctrl+6>

Surface tension 3: Optical settings

Manual	PC-controlled
Regulate the lens zoom so that the image of the needle occupies about 20% of the frame.  This is done by rotating the "Zoom" knob at the top left of the DSA100 housing.	Regulate the lens zoom so that the image of the needle occupies about 20% of the frame.  Control: - magnify: key<Ins> - diminish: key<Del>
If the zoom alteration causes the image to become darker then readjust the brightness.	
Adjust the image sharpness: The field "Median" should appear in green and the numerical value shown should be as large as possible.  This is done by rotating the "Focus" knob at the top left of the DSA100 housing.	Adjust the image sharpness: The field "Median" should appear in green and the numerical value shown should be as large as possible.  Control: - increase focal length: key<Home> - decrease focal length: key<End>

Surface tension 4: Drop dosing

Generate as large a drop as possible hanging from the needle.

This is done by turning the syringe plunger screw clockwise.

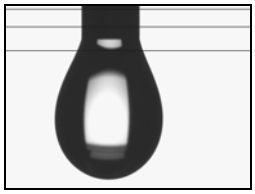
Adjust the zoom and needle height so that the drop occupies as much as possible of the whole frame height and that part of the needle can be seen.

Surface tension 5: Measurement

The image contains three colored lines (some of which may be invisible at the top margin of the frame). These three lines are used to define the part of the drop image that is to be evaluated. They can be moved by keeping the mouse key pressed down.

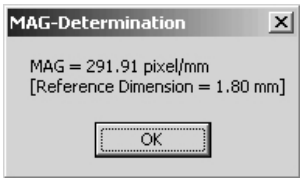
Measuring the needle width: the two top lines are placed across the needle one above the other. The width of the needle image is measured between these two lines.

Exclusion of the image sector immediately beneath the needle: the lower line is placed slightly below the point of transition between the needle and the drop. Only the drop image below this line will be evaluated.



Click on the symbol  in the symbol bar.

The scale of the image is calculated from the entered needle diameter and the measured width of the needle image and displayed.



Click on the symbol  in the symbol bar. DSA1 determines the drop shape; a contour appears surrounding the drop.

Click on the symbol  in the symbol bar. The surface tension of the liquid is calculated using a Young-Laplace fit. The measured value appears in the status line.

Click on the symbol  in the symbol bar.

The measured and calculated data is shown in the Results Window.

3 Installation of the DSA1 software

If you bought the computer together with the measuring device from KRÜSS then all necessary installations and the proper adjustment of the DSA1 Software have already been done. In this case, reading the chapters 3.1 and 3.2 is not necessary. In case you by further equipment or you have to install the software on your own, please read the following remarks carefully to avoid possible damage or operator errors.

3.1 Computer system requirements

Install the computer and any peripherals according to the manufacturer's instructions. Make all the necessary connections. Further details can be found in the relevant operating instructions.
The DSA program requires a computer which is 100% IBM-AT compatible. The following list contains the minimum requirements; of course there is no upper limit for the computer performance.

- IBM-AT or compatible computer with Pentium processor
- 16 megabyte working memory (RAM); 32 megabyte recommended
- Windows 98, 2000, XP (professional or home edition) or Windows NT with Service Pack 6
- CD-ROM disk drive
- hard disk with at least 40 megabyte free memory
- Free PCI master slot (full length) for Falcon frame grabber board
- a parallel or serial connection for operating a printer
- a serial connection for operating a mouse
- a graphics card compatible to VGA, 800 X 600 pixel (recommended resolution 1024 X 768 pixel)
- a color monitor

3.2 Installation procedure

For the installation you require:

- the CD-ROM with the DSA1 program
- the CD with the license key

A frame-grabber card must be installed before you install the software.

1. Set the monitor resolution to 1024*768. The procedure is described in the documentation for your Windows version.

2. Place the DSA1-CD in the CD-ROM drive.

3. Select the CD-ROM drive in Explorer.

4. Start the program “SETUP” in the directory “Disk1”. A welcome and information window appears. Continue with “Next”.

5. A further information window informs you that a frame-grabber card must be installed before the installation of the software. Continue with “Next”.

6. The license conditions for DSA1 appear. You must accept them with “Yes” in order to continue with the installation.

7. Now enter a user name and the name of your company. Confirm with “Next”. A further window appears for checking your entry. Confirm with “Next” to continue with the installation.

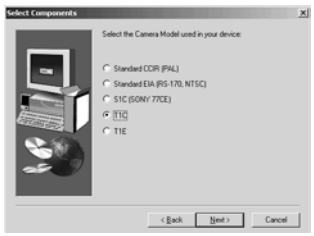
8. The folder for the DSA1 files to be copied is given. Click on “Next” to select the default folder, or select one yourself via “Browse”. In each case you should note the path, as you require it later for copying the license key.

9. The instrument type is requested. Select “DSA100” and confirm it with “Next”.

10. Select the installed frame-grabber card and continue with “Next”.

A Falcon card is normally used.

11. Select the built-in camera.



The usual model is “T1C”.

12. The following dialog window provides information about the extent of the installation. We recommend selecting “Typical” for the complete installation of the necessary components. Continue with “Next”.

13. A folder in the start menu is selected in which the program symbols are to be stored. Confirm the default folder with “Next” or enter your own folder name.

14. All the data of the installation inquiry are again listed together. Check the installation and, if necessary, return with “Back” to make any alterations that may be necessary. “Next” confirms all the entries and starts the installation procedure.

15. After successful installation a question appears to ask whether the necessary restart of Windows is to take place immediately. **Do not carry out the restart yet**.

16. Place the CD with the license key in the CD-ROM drive.

17. The CD contains the file “**dsasp.dat**”. Copy this file into the program folder in which the DSA1 program has been installed.

Now restart the computer. The installation of the DSA1 software is finished.

3.3 Computer port for DSA100

The computer port to which the DSA100 is connected must be selected in the menu "Options"→"Device Control Options...".

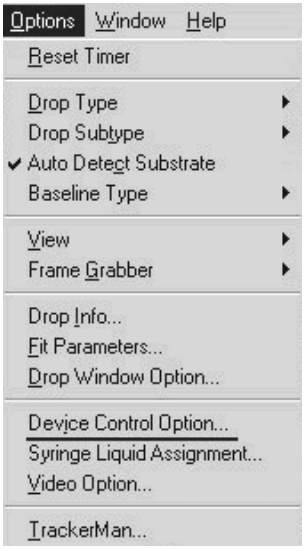


Fig. 3.1: Selection of the menu item "Device Control Options..." from the "Options" menu

The following menu opens:

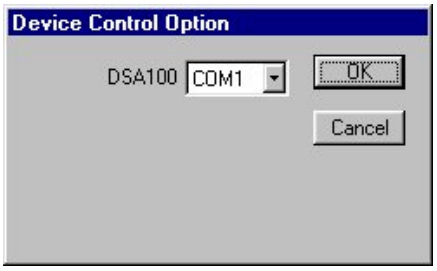


Fig. 3.2: Selection of the computer ports for the peripherals

Select the computer port used for the DSA100 and confirm with „OK“.

4 Introduction to the DSA program

4.1 Starting the DSA program

It is assumed that the software has already been properly installed on the hard disk of your computer as described above.

The program is started by double clicking the program symbol on the Windows desktop:

4.2 Screen arrangement

The illustration shows the different types of windows contained in DSA1. Several windows can be open at the same time. During the operation of the program a series of further windows appear to display information, instructions or as dialog windows in which you can make entries.

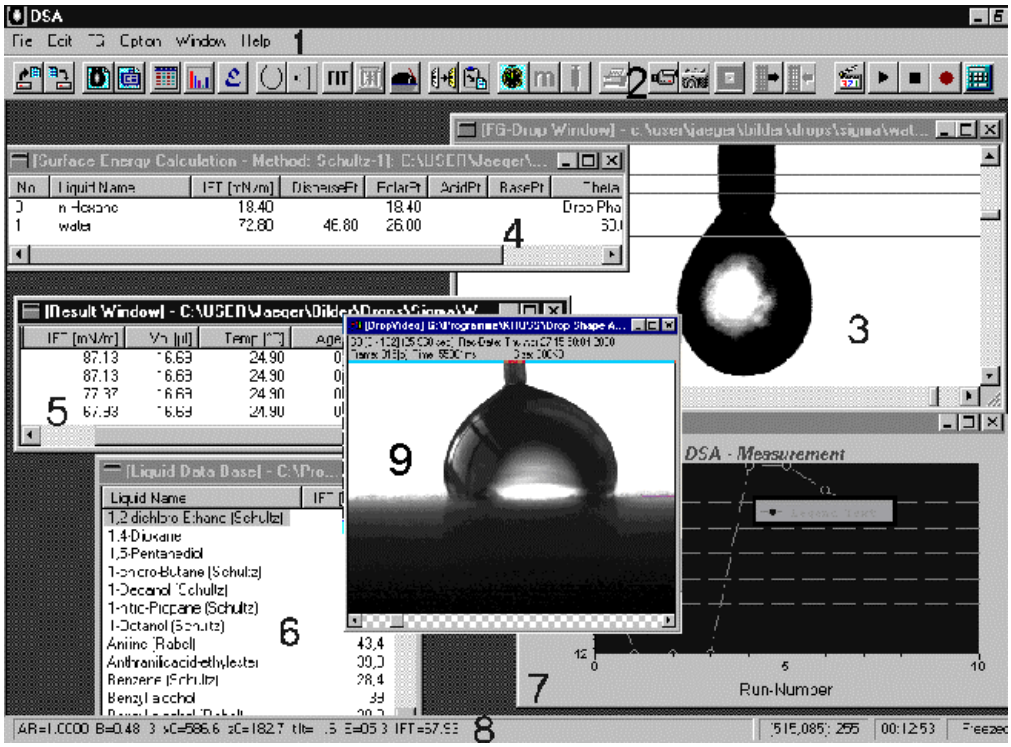


Fig. 4.1: User interface of the DSA program

The operating elements in Fig. 4.1 are:

- **Menu bar (1)**: The menu bar contains various main menu items; depending on the active window different pull-down menus with the relevant program items can be opened. In principle the whole program run can be controlled from the menu bar.
- **Command icons (2)**: In this bar you will find a series of icons (symbol areas), with which you can control certain program functions directly. The icons function like switches or keys; you can click them to carry them out.
- **Frame grabber window (3)**: This window is used to show the drop image on the computer screen. Either the live image or a still image is displayed in this window. To switch between these two modes click on the icon

   .

  When the live mode is active, the icon is shown as pressed.

  
- **Surface Energy Calculation (4)**: In this window the necessary data for SFE calculation is collected and shown in tabular form. Different calculation methods for determining the surface energy can be selected from the corresponding context menu or via the menu bar.
- **Result window (5)**: In the result window the results of the measurement of a series of measurements are shown in tabular form.
- **Liquid Data Base (SFT)**: The data base window shows the data base containing information about the surface tension of liquids and is used for the calculation of the surface energy. This data base can also be used as a reference book for sample data (densities, viscosities, surface tensions, etc.). The data base (IFT) window has a similar arrangement with values for the interfacial tension of different pairs of liquids.
- **Plot window (7)**: The contents of the result window are shown as a graph in the plot window.
- **Result line and comment line (8)**: In this program line the result is shown immediately after the measurement and calculation have finished. If the calculation is interrupted a comment is also made here.
- **Video-Window (9)**: Loaded videos are played back and evaluated in the video window
- **Drop Window (not shown)** : The drop windows contains loaded images which were previously stored. Evaluation of the image is carried out in the same way as in the FG Window.

4.3 Window arrangement

If a number of windows are open then these should be clearly arranged. The windows may partially overlap or all can be fully visible. The principle window arrangement is determined in the main menu item "Window".

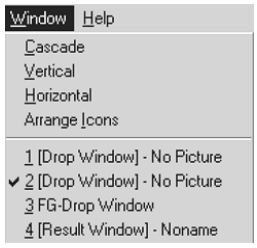


Fig. 4.2: Main menu item "Window"

A uniform and partially overlapping cascade arrangement is produced by "Window | Cascade". The windows can be shown completely visible above each other either vertically by "Window | Vertical" or horizontally by "Window | Horizontal". In the lower part of the pull-down menu the open windows are listed. The currently active window is indicated by a tick. A window can be activated by moving the mouse cursor to the required window or to the corresponding entry. The tick appears in the corresponding place.

Individual windows can be moved by holding down the left-hand mouse key on the upper window margin and moving the mouse cursor.

4.4 Command icons and function keys

Some functions of the DSA program can be carried out directly by pressing particular keys or clicking certain command icons.

4.4.1 Command icons

Icon	Function
	Opens a file of the active window type.
	Stores the contents of the active window.
	Opens a drop window. As many drop windows can be opened as are required.
	Opens the FG-window. Only one FG-window is possible.
	Opens the result window. Only one result window is possible.
	Opens the plot window.Only one plot window is possible.
	Opens the surface-energy calculation window. Only one SEC-window is possible .

Icon	Function
	Baseline determination
	Extraction of the drop profile . (Determining the drop contour lines)
	Determining the magnification factor (MAG).
	Starts fitting the Young-Laplace equation to the drop contour.
	Starts contact angle determination by the default method.
	Copies window contents to buffer memory ("copy“).
	Inserts the contents of the buffer memory ("paste“).
	Resets timer to "0“ ("reset timer“).
	Opens the “Device Control Panel” for PC control of the instrument.
	Assigns the following measurements to a new measurement series.
	Prints out window contents, e.g. results ("print“).
	Transfers the live drop image from the camera to the 2nd monitor ("Acquire“).
	Snapshot of drop ("Snap“), shown in FG-window. Data are read out from the camera into the FG and displayed in the FG-window.
	Activates digital focusing aid ("focusing aid“).
	The last "snapshot“ image is transferred to the drop window.
	Drop window contents taken over by FG-window.
	Opens a video window. Only one video window is possible.
	Plays back the current video sequence.
	Stops the playback/recording of a video sequence.
	Records a video.
	Starts calculating a video sequence.

4.4.2 Function keys in the FG Window

The following keys and combinations are used **only when the FG Window is active**.

Key	Function
F1	General Help
F3	Start/Stop video recording
F5	Set FG Window to live
F6	Freeze FG Window
F7	Snap FG Window
F8	Start Focussing Assistant
F9	Perform Default Calculation on current image
F11	Decrease drop volume
F12	Increase drop volume
↑	Baseline: Move up
↓	Baseline: Move down
←	Baseline: Rotate left
→	Baseline: Rotate right
Insert	Increase Zoom
Delete	Decrease Zoom
Pos1	Increase Focus
End	Decrease Focus (only GH100)
Page up	Increase Illumination intensity
Page down	Decrease Illumination intensity
8 or ↑	Move needle up (use CTRL for single step)
2 or ↓	Move needle down (use CTRL for single step)
4 or ←	Move needle to the left (use CTRL for single step)
6 or →	Move needle to the right (use CTRL for single step)
x, y, z + ↑	movement of the x-, y- or z-axis to the right, rearwards resp. upwards
x, y, z + ↓	movement of the x-, y- or z-axis to the left, to the front resp. downwards

5 Controlling the movable axes

This section describes the control of the motor-driven axes by the DSA1 program. If your system is only equipped with manual axes then you can skip this section.

When starting up the movable sample table and, depending on the settings, after starting or terminating the DSA1 software, the movable sample table automatically moves to the zero position. If you handle the instrument during the movement you run the risk of injuring yourself. Please ensure that no persons or objects are within the range of movement.

For the tilting table: please ensure that any objects on the sample table are fastened in position and cannot fall off during movement.

Before using the sample table you should set the speed at which the axes are to move (see Section 5.2). Otherwise unexpectedly violent movements could occur.

The axes are controlled via the „Device Control Panel". Open this panel with the icon

 .

The PC-controlled axes for the x-direction (left-right), y-direction (front-back) and z-direction (up-down) as well as the tilting table are controlled via the tab sheet "ST" (Sample Table) of the Device Control window.

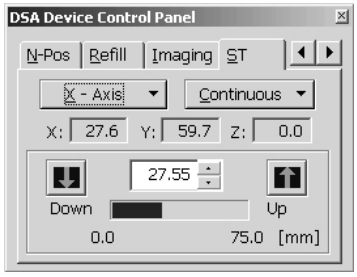


Figure 5.: The tab sheet "ST" for controlling the movable axes

The up and down arrows do not show the direction of movement directly, but indicate the increase or decrease in the value that gives the absolute position of the corresponding axis. A click on one of the arrows moves only the axis that is currently selected.

Clicking on the button at the top left opens a drop-down menu for selecting the current axis:

If not all the axes that are actually present are shown, check the y-axis is, as intended, connected to Port 2 on the rear panel of the DSA100.

The option “Set as...” can be used to store three positions:

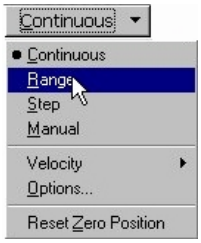
- A “Standby Position” for the resting position of the sample table
- A “Parking Position” for the position of the table between individual deposition procedures
- A “Dosing Position” that directly defines the position of the table during drop deposition

The current position is always saved simultaneously for all existing axes under “Set as”, not just for the currently selected axis.

These positions are used whenever an automatic deposition procedure is used. However, they can also be moved to directly with the option “Go to”.

5.1 Movement modes (Continuous, Step, Range)

If the mouse cursor is moved to the arrow of the upper right button then a pull-down menu opens.



You can switch between the three movement modes by selecting the menu items. The currently selected movement mode appears as the label on the button. The “Step” and “Manual” modes are not available yet for DSA100. Also, no “option” can be set yet despite the existence of a corresponding menu item.

5.1.1 Continuous movement

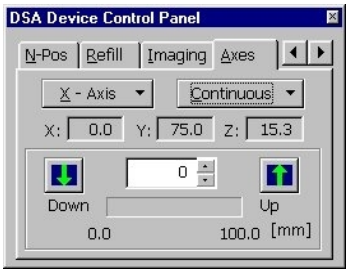


Fig. 5.1: “Continuous” movement mode

In the continuous mode the sample table moves in the corresponding direction when one of the two arrow keys is clicked on. The movement only stops when the front or rear end of the field of movement has been reached, or when the same arrow key is activated again. In the display the distance of the sample table from the zero position is shown in mm.

By using the two small arrow keys  you can also enter a target value for the sample table movement. After pressing the ENTER key on the computer keyboard the sample table will move directly to the entered value.

5.1.2 Step-by-step movement

In the "Step" movement mode the two arrow keys can be used to move the sample table step by step in the required direction. This function is particularly suitable for positioning drops on a sample at regular intervals.
The display field shows the current position of the sample table; programming the step length takes place separately for each axis under the menu item "Options" (see Section 5.3).

As in the continuous mode, you can use the two small arrow keys to enter a particular target value directly and trigger the movement by activating the ENTER key.

5.1.3 Programming a range of movement

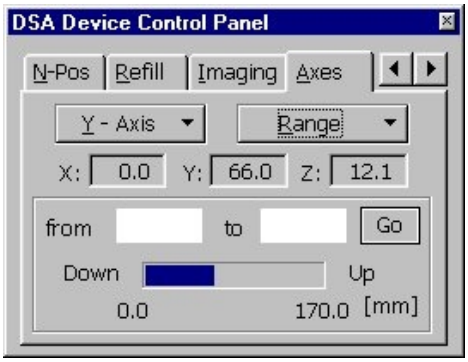


Fig. 5.2: Range of movement ("Range")

In the "Range" mode the sample table moves in a range whose limits can be defined in the two input fields "from" and "to" (distances from the zero position in mm). When the "Go" button is clicked on the sample table will move to the position defined under "from" and then move to the position defined under "to". The value of the first position can also be larger than that of the second one; the sample table will then move accordingly from the front to the back.

5.2 Speed of movement

Fig. 5.3: Selecting the speed of movement

When the mouse cursor is moved to the arrow behind the menu command "Velocity" a pull-down menu opens in which you can choose between the three speed steps slow, normal and fast ("Slow", "Normal", "High"). The "Fast" step corresponds to the maximum speed, under "Normal" the speed is reduced by 50% and under "Slow" to 25% of the maximum speed.

5.3 Options (Options...)

When the menu command "Options" is selected the page "General Parameters" opens for setting the sample table parameters for the currently selected axis. A further tab sheet ("Extra Parameters") is only available for the tilting table.

5.3.1 General options ("General")

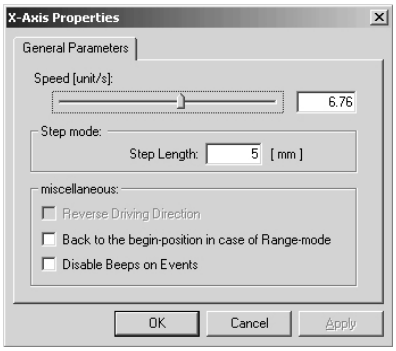


Figure 5.Fehler! Unbekanntes Schalterargument.: General options for the axes

Speed: you can use the slide controller to set the maximum speed for the current axis. The speed steps "Slow", "Normal" and "Fast" selected under "velocity" depend on this speed. For the start of your work with the DSA100 you should set the speed to about half of the highest value.

Step length: this is where you enter the step length for the step mode in mm. This entry must also be made individually for each axis.

Back to...: this option is only required for the range mode. If it is switched on then the axis will return to its starting position when the target position has been reached.

Disable Beeps...: you can use this option to switch off the beep signals that are produced when particular events take place, e.g. when an axis reaches its end position.

5.3.2 Special options for the tilting table (“Extra Parameters”)

The tab sheet “Extra Parameters” is only available when the tilting table has been selected as the current axis.

Figure 5.: Special options for the tilting table

With these options you can automatically film the drops after the start of the table movement. If the first option “Invoke video-recording...” is selected then filming starts immediately after the table starts to move. If the second option is selected then filming will stop automatically as soon as the sample table stops moving.

5.4 Reset Zero Position

From time to time, especially after manual conversions of the DSA100, the zero position must be reset for the DSA1 software to find the lower and upper limit of the axes.

6 Dosing and syringe control

The section deals with the operation of the PC-controlled dosing system for the DSA100. If you are only equipped with a manual dosing system you can skip this section.

The DSA100 dosing system is controlled via the „Device Control Panel“. Open this panel with the icon

 .

6.1 Syringe liquid assignment

Depending on its version, your instrument can be equipped with up to 8 syringes. In the DSA1 program you can assign a test liquid to each individual syringe. When selecting the syringe for dosing the drop the DSA1 program automatically used the data of the assigned test liquid. However, you must take care that the assignment of the liquids in the DSA1 program coincides with the actual filling.

To assign the test liquids select the menu "Options"→"Syringe Liquid Assignment" in the FG Window main menu or context menu.

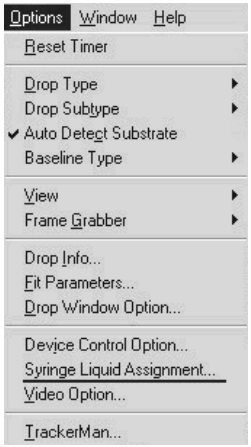


Fig. 6.1: Selection of the test liquid assignment in the FG Window main menu

The following menu opens:

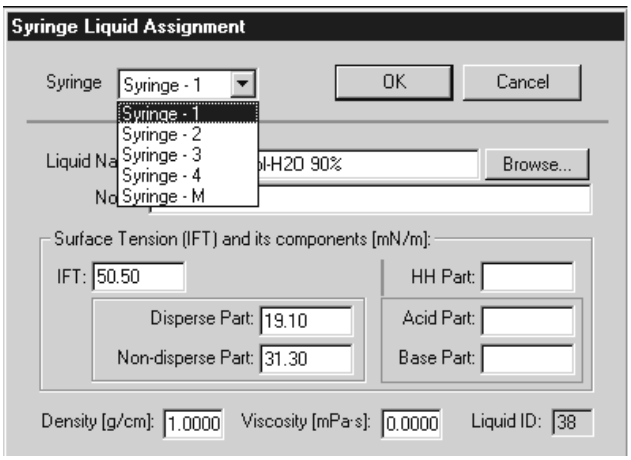


Fig. 6.2: Menu for assigning the test liquids to the syringes

Under "Syringe" you can use the arrow key to select the syringe to which you wish to assign a liquid. All available information about the required test liquid can be made in the input lines. If you wish to use a liquid for which there is an entry in the liquids database then you can make things easier for yourself by selecting the liquid directly from the database. This is done by using the Browse... button. After clicking on the button the liquids database opens with a list of liquids which can be selected. The required liquid is selected by double-clicking on the corresponding line and then closing the liquids database window. After this process the liquid data can be seen in the input lines of the menu.

If there are several entries for a particular liquid in the database then you should select the database entry which corresponds to the evaluation method to be used. If, for example, a measurement is to be carried out using benzyl alcohol and evaluated by the Rabel method then you should select the database entry "Benzyl alcohol (Rabel)". Details about the physical quantities in the input lines are given under "Drop Info..."→"Liquid Information" (Section 0).

6.2 Dosing

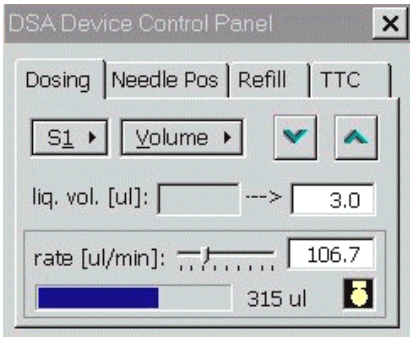


Fig. 6.3: Drop dosing settings

All commands which concern with the dosing procedure either directly or indirectly are carried out via the "Dosing" tab-sheet. Among these are:

- Syringe selection (depending on the setup there may be up to four automatic syringes and an additional manual syringe) and assignment of syringe parameters (filling level, filling volume, needle diameter); sect. 6.2.1 and 6.2.2,
- starting and stopping the dosing process; sect. 6.2.3,
- selection of the type of dosing (static, dynamic) and the dosing volume; sect. 6.2.4,
- needle control; sect. 6.2.5,
- definition of standard positions (default, parking position, dosing position; (sect. 6.2.6.1) and automatic recognition of the optimal starting position (sect. 6.2.6.2),
- programming movement procedures during dosing (sect. 6.2.6.3) with automatic detection of the sample surface (sect. 6.2.6.4),
- programming automatically triggered actions (single measurements, series measurements or video recordings) at different times during a run; sect. 6.2.6.5.

The syringes are operated completely independently from one another, i.e. all syringe properties, dosing parameters, positions and procedures are assigned individually to each

syringe. The assignment is always made to the syringe which is currently selected and whose number is shown on the arrow key 

.

6.2.1 Syringe selection

When the arrow key

Is activated the following pull-down menu appears:

Fig. 6.4: Pull-down menu for syringe selection

You can choose the current syringe by clicking on one of positions S1-S4 (or S6; as well as "SM" for the manual syringe); all subsequent entries and commands will apply to this syringe. As soon as a new current syringe is selected the needle changer will rotate to the corresponding position.

You can also ensure that, after a change, the needle will move directly to the default position assigned to it. A pull-down menu for this is hidden behind "More":

Fig. 6.5: Menu item "More"

If you have set a tick at "Auto go to Def. Pos." then the assigned default position will be moved to automatically as soon as the corresponding syringe is selected. By clicking on the command "Go to Def. Pos. Now!" the current syringe will move immediately to the default position. The choice of the last option "Go to Def. Pos. by Dosing" ensures that the default position will only be moved to when dosing starts. However, if a procedure in which the needle is to be moved to the parking or deposition position is linked to the dosing (see Sect. 6.2.6), then the procedure command has priority over the command in this menu. More details about the definition of the standard positions "Default", "Parking" and "Deposition" can be found in section 6.2.6.1.

If the current sample is thicker than that used for defining the default position, or if the sample table has been lifted the needle or the sample can be damaged when the default position is driven to automatically. In such a case, the sample table should be lowered before changing the needle.

When the needles change they move quickly. Hands and face must be held out of the movement region to prevent injuries. Make sure that there is no drop left pending from the needle before the needle changer rotates, especially when working with poisonous of corrosive liquids. Moving the needle sideways can throw off any drops which may be adhering to it. It may be necessary to ensure that any drops hanging from the needle are drawn into it automatically (see sect. 6.2.2).

6.2.2 Syringe parameters filling volume, length and diameter

Under "Options" you can access the two tab-sheets "Syringe Parameters" and "Miscellaneous" for the assignment of syringe parameters. Alternatively you can access the tab-sheets directly with a double-click on the syringe filling level display

.

The settings on these tab-sheets also apply only to the syringe which is currently selected.

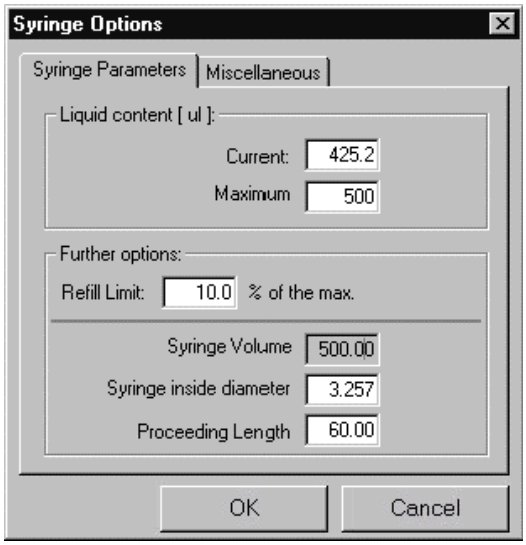


Fig. 6.6: Entering syringe parameters

Under "Current" the actual syringe filling level can be read off or, if you notice any variation, altered by making an entry. You can also define the maximum filling volume of the syringe ("Maximum"); when the syringe is refilled it will only be filled up to the volume entered here.

Under "Refill Limit" you can define the lower volume limit at which the liquid present in the syringe ("Current") will be topped up automatically (see "Refill" sect. 6.4).

The lower three fields contain the dimensions of the syringes supplied by KRÜSS. As alterations to these fields have a direct influence on the dosing volumes you should only alter these entries when other syringes have to be used. The inner diameter of the syringe is given under "Syringe inside diameter", the length of the syringe from the 0 µl mark to the filling level for

the maximum volume under “Proceeding length”. The volume (“Syringe Volume”) is calculated from the diameter and the length and therefore cannot be entered separately.

On the tab-sheet “Miscellaneous” you will find a further option which has been included for your safety. If you select the command “Draw back liquid into current syringe” then, when the needle is changed, any liquid drops which may remain on the needle will be drawn back into the needle. This prevents the drops from being flung off from the needle during the rotation. In the input line you can define the volume which is to be drawn back into the needle.

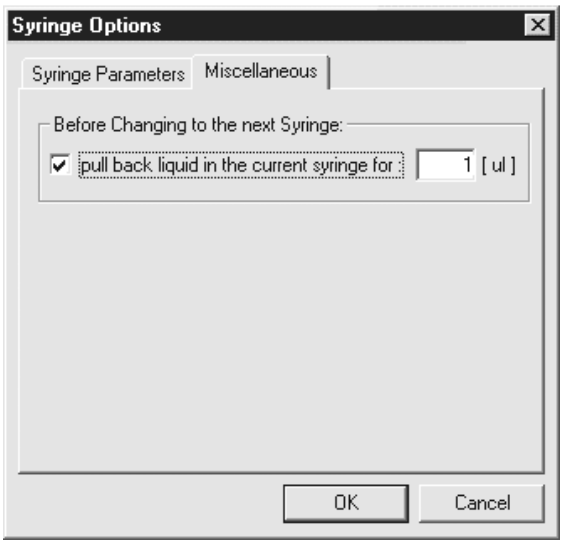


Fig. 6.7: Drawing back the drop after changing a needle

6.2.3 Start/Stop/Speed of the dosing

The two buttons

are used to start dosing. The direction of the arrows corresponds to the movement of the syringe plunger: **increase** the dosed volume with the **right-hand** key, **reduce** the volume with the **left-hand** key. If one of the dosing modes "Volume" or "Continuous" is selected then the stop symbol

will appear after the start of the dosing instead of the clicked-on button. Clicking on this symbol stops the dosing process.
Dosing can also be **stopped automatically** at the end of a video recording (see Section 14.2).

The **dosing speed** can be entered by using the input field or the sliding controller

The minimum and maximum speeds are given by the possible movements of the stepper motor; for the normally used 500µl syringes these values are 6.32 and 394.7 µl/min. However, higher speeds are not suitable for drop production but only for emptying or filling the syringe. Speeds above 10µl/min are only suitable for measuring a drop on rare occasions.

6.2.4 Selecting the dosing mode

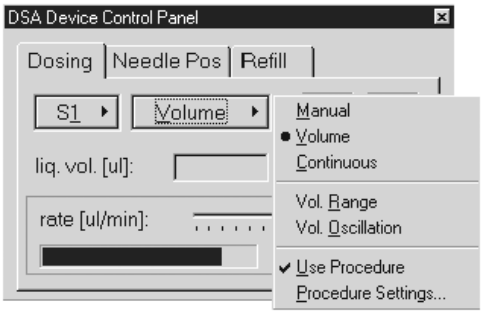


Fig. 6.8: Selection of the dosing mode in the "Device Control Panel"

"**Manual**": If "Manual" is selected then dosing will start when one of the two dosing buttons is operated with the left-hand mouse key pressed down. Dosing will stop as soon as the mouse key is released. As in this mode the dosing of a single drop can take place in several stages, the added volume for each individual step can be seen in the left-hand volume display field ("liquid vol." - grey background) while in the right-hand field (white background) the total added volume is displayed. If a value for the volume is already shown in the right-hand field before dosing starts then the value 0 can be entered. This is done by either a double-click on the right-hand volume display field or by entering 0 with the aid of the keyboard. The option can be used for static, advancing or retreating drops.

"**Volume**": If "Volume" is selected then the required final volume of the drop is entered in the right-hand display field. When the right-hand dosing button (volume increase) is operated dosing will start and continue automatically until the entered volume has been reached. In the left-hand volume display field the actual dosed-in volume is shown. When dosing starts the stop symbol appears; operating this symbol will stop the dosing process prematurely. The "Volume" option is only suitable for static or advancing drops; it is not suitable for retreating drops.

"**Continuous**": In the third option "Continuous" dosing starts when one of the dosing buttons is operated and only stops when you click on the stop symbol. As in "Manual" mode, dosing can be carried out in several steps. The volume produced up to "Stop" is again shown at the left; at the right-hand side the volumes of the individual steps are added together. If a value for the volume is already shown in the right-hand field before dosing starts then it can again be reset by either a double-click on the field or by entering 0 with the aid of the keyboard. The value entered in the left-hand field is automatically set to 0 when dosing starts. Like "Manual", this option is also suitable for static, advancing or retreating drops.

"Vol. Range"

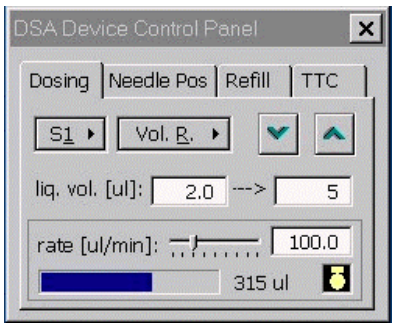


Fig. 6.9: Setting a volume range ("Vol. Range")

By using the "Vol. Range" function you have the possibility of defining an initial drop volume and, based on this volume, of enlarging or diminishing the drop at a selectable flow rate. This is done by first entering the required initial volume under "liq. vol" in the left input line and the required final volume in the input line at the right.

Under "rate" two different speeds can be entered and displayed in this mode; one for the generation of the initial drop and one for enlarging or diminishing this drop. To set the drop generation speed you should first click on the input line at the left. You then have about 20 seconds to set the speed at which the initial drop will be generated. The program then switches automatically to displaying the speed at which the drop will be enlarged or diminished, which you can now alter accordingly.

"Vol. Oscillation"

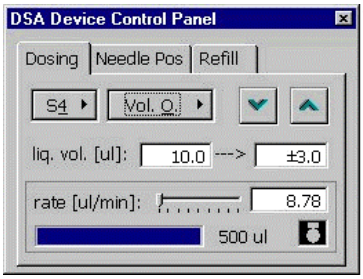


Fig. 6.10: Oscillating drop dosing

Here you have the possibility of enlarging or diminishing the drop by oscillation. By using this measuring option you can check the advancing and retreating angle as a function of time. The initial volume of the drop is entered under "liq. Vol"; in the input line to the right the volume by which the drop is to be enlarged and diminished during oscillation is entered. For example, if the initial volume is 10µl and the "Amplitude" is ±3µl, then a drop with a volume of 9µl will be generated and then alternately enlarged to 13µl and diminished to 7µl until the dosing process is terminated. The drop generation speed and the oscillation speed, as in other types of dosing, depend upon the speed entered in the lower input line.

Retreating drops: Retreating drops can be generated by using the "Manual" or "Vol. Range" dosing types. For the manual generation of a retreating drop a drop of the required size is first produced. The generated drop can then be diminished by using the left-hand dosing button .
With the "Vol. Range" function you can generate retreating drops by selecting the volume of the initial drop (left-hand input line) to be larger than the final volume.

6.2.5 Controlling the needle

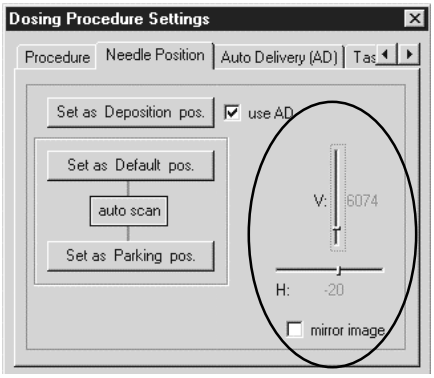


Fig. 6.11: Controlling the needle

Vertical and horizontal control of the needle is carried out with the two sliding controllers or via the keyboard in the card "Needle Position" in the submenu "Procedure Settings..".. The values for the current needle position are shown in the two fields H (horizontal) and V (vertical) in motor steps. In order to be able to determine the correct position for drop production the needle must be observed in the live image of the frame grabber window. The following tables list the keyboard occupancy for the controlling the needle.

Vertical position

key	movement
Cursor up	step by step upwards
Cursor down	step by step downwards
Page up	quickly upwards
Page down	quickly downwards
Pos 1	upper needle position
End	lower needle position

Horizontal position

key	movement
Cursor left	step by step to the left
Cursor right	step by step to the right
Pos 1	fully to the left
End	fully to the right

6.2.6 Automatic drop dosing and measuring (“Procedure”)

The two menu items “Use Procedure” and “Procedure Settings...” allow the definition of standard needle positions (default, parking and dosing positions), programming the needle movements before and after drop production as well as the automatic detection and movement towards the solid surface with automatic drop dosing. Moreover, certain steps of the procedure can be linked to automatically triggered actions as single calculation, a row measurement with the TrackerMan or a video recording.

A procedure is programmed by defining **three positions** of the needle, which are moved to in succession during dosing. The procedure always applies to the syringe that is currently selected and is programmed separately from the other syringes, so that the dosing procedure for all the syringes which are required can be defined before the start of the measurement.

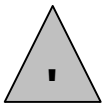
With “Use Procedure” you can switch the use of the procedure on and off. If “Use Procedure” is switched on then the procedure will start automatically as soon as you operate one of the drop dosing buttons. If “Use Procedure” is switched off then the needle movements must be controlled manually.

To start a procedure click on dosing switch  . To stop it, just hit the <Esc>-Key of your computer.

6.2.6.1 Programming standard needle positions

The definition of the positions for a procedure is carried out on the “Needle Position” card of the “Procedure Settings” window (see Figure 2.3). The programming of a procedure only makes sense when the height of the sample carrier or sample no longer changes before the measurement.

If the height of the sample carrier or sample has changed then, before changing the needle, you should move the sample carrier to its lowest position and update the programmed positions before starting a dosing process. Otherwise, owing to the automatic movement of the needle to the programmed positions, it is possible that the needle could become bent or damage the sample.



The positions described below are defined by moving the needle to the required position and then defining this position in the corresponding field as “default”, “deposition” or “parking position” with a mouse click. The positions are stored and are retained, both when the needle is changed and even after the program has been terminated.

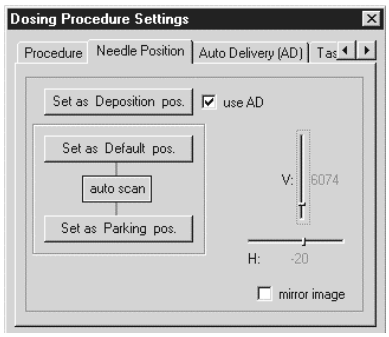


Fig. 6.12: Definition of the needle positions for a procedure

"Default position": With "default position" you define the initial position of the needle before the start of dosing. You can define this position either here or on the "Needle Position" card of the "Device control" window (see Section 6.3). The position is moved to automatically as soon as the needle for which the position has been defined is selected.

"Deposition position": The "Deposition position" is the position at which the drop is **placed** on the sample. The **generation** of the drop does not have to be carried out at this position; the drop can also be generated above the sample and then deposited upon it. The option "use AD" ("Auto Delivery") is required if you do not want to determine the dosing position yourself, but want to search for it automatically. The corresponding process is described in Section 6.2.6.4; here we assume that the dosing position is to be defined manually.

"Parking position" The "Parking Position" is the position that the needle takes up before and after depositing the drop. For measurements on static drops the needle should not remain in the drop; this is why if necessary the needle can automatically be moved to the "Parking position" after dosing.

By using these three positions you can define the whole series of movements for the needle during the dosing process. The procedure is described in the following section.

6.2.6.2 Auto scan for the optimal needle parking position

If the "Auto Scan" function is activated then the needle will be moved automatically to a position in the upper center of the screen which is particularly suitable as a needle parking position before dosing is carried out.

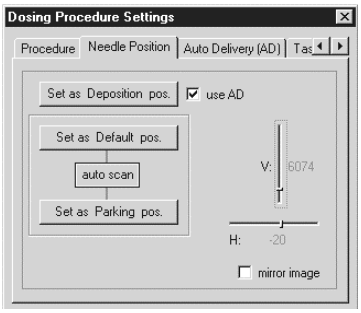


Fig. 6.13: Selection of the menu item "procedure settings"

Before you trigger the Auto-Scan function zoom and focus must be set to a medium range so that the needle image appears sufficiently sharp and not too large. The solid surface should still be outside the image area as otherwise, with unfavourable zoom and focus settings, the needle could come into contact with the sample.

Immediately after triggering the "auto scan" function the needle will move downward step by step and to the right and left at every step. As soon as the needle is detected in the video image the optimal parking position in the upper central part of the screen will be moved to. This found position is then defined automatically as the "Default Position" and "Parking Position". However, you can prevent the automatic definition of this position by holding down the shift key and clicking on "auto scan" at the same time. The connection lines above and below the "auto scan" key vanish accordingly:

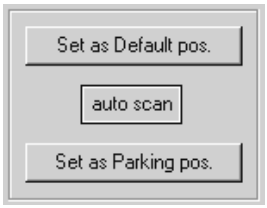


Fig. 6.14: "Auto scan" without automatic definition as the default and parking position

6.2.6.3 Movements during a procedure

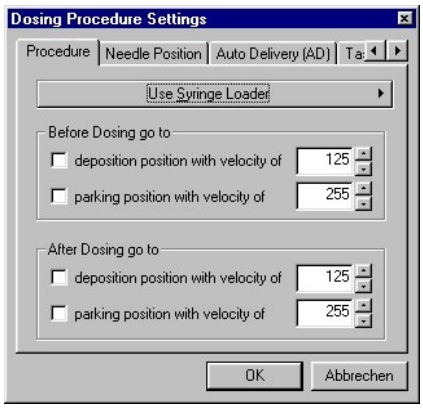


Fig. 6.15: Programming the series of movements in a procedure

The sequence of movements in dosing a drop is divided into the phases "Before Dosing" (before drop generation) and "After Dosing" (after drop generation).

"Before Dosing": Here you can decide whether the drop is to be generated at the dosing height (directly above the sample) or at the parking position (at a greater distance from the sample). If you select "Go to deposition position..." then the needle will move to that height position directly above the sample which you have defined under "Needle Position". The drop will then be generated there. On the other hand, if you select "Go to parking position" then the needle will move to that height further above the sample which has been defined as the parking position. The drop will be generated there and will initially remain suspended from the needle. When one of these possibilities has been selected the other will be inactive. If you do not select one of these options then you will have to move to the position at which the drop is to be generated manually.

"After Dosing": The movement of the needle after drop generation is defined here. After the drop has been generated it can first be deposited on the sample ("Go to deposition position..."). The needle can then be removed from the drop and brought to the parking position ("Go to parking position...". The two options are not self-exclusive. If neither of the options is selected then the needle will remain in the position it assumed during drop generation.

A click on the upper button opens a context menu where you can decide if either the needle places the drop onto the sample („Use Syringe Loader“) or if the sample moves upward to the drop to pick it up. For the second option, the corresponding positions have to be set for the axes (see section 5)

“Velocity”: You can define a speed for each automatic movement of the needle. This should be adapted to the particular purpose and the liquid system used (e.g. low speeds for small surface tensions or high viscosities).

The flexible control of the dosing process and the syringe movements provide you with a great variation in the possible measuring sequences. On the following page we give three examples of how you can use procedure programming to achieve the dosing sequence which you require.

6.2.6.4 Automatic surface search (“Auto Delivery”)

The “Auto Delivery” function allows the fully automatic recognition and movement toward the solid surface with subsequent dosing according to the dosing parameters set under “Dosing” (dosing type, dosing speed, dosing volume). For DSA100, it can only be used for multi-dosing systems and does not work together with a single-dosing system DS3210.

The “Auto Delivery” function is switched on under “Procedure Settings...” in the “Needle Position” card (set a tick in the in “use AD” box).

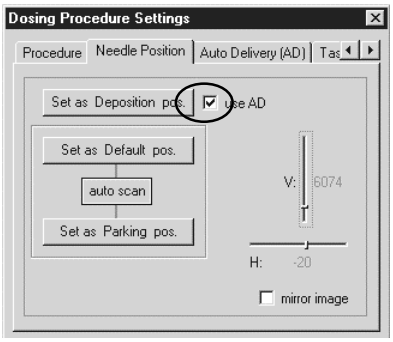


Fig. 6.16: Switching on the "auto delivery" function

If the “Auto Delivery” function is switched on then both the stored “Deposition” position and its associated approach speed will be ignored. Nevertheless, a suitable procedure must be selected which leads to an automatic movement to the deposition position before dosing:

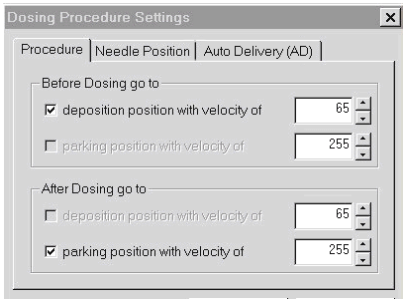


Fig. 6.17: Procedure suitable for the “Auto-Delivery“

Also, the option "Use procedure must be switched on:

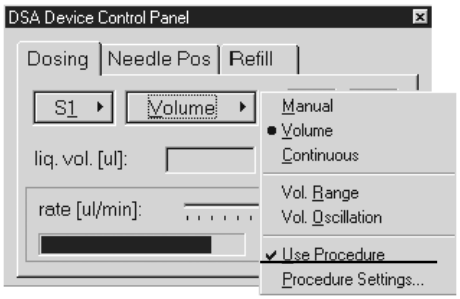


Fig. 6.18: "Use Procedure" must be switched on before using "Auto Delivery"

Finally the illumination, focus and zoom should be set correctly; the sample surface in the video image should be situated so that it does not occupy more than one third of the screen (and less if possible).

The parameters for the automatic surface search are entered on the "Auto Delivery (AD)" card.

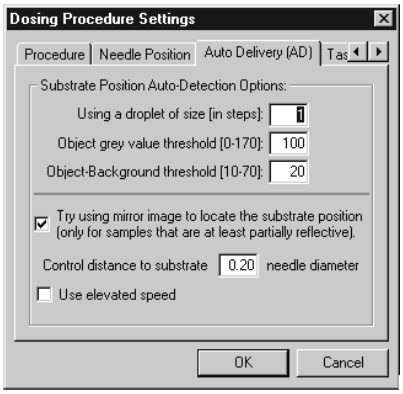


Fig. 6.19:"Auto delivery" parameters

The meaning of the parameters is explained below:

Using a droplet of size: The surface search routine in the DSA1 Software works more reliably when not only the image of the needle tip is available for the calculation, but when a small liquid drop is also suspended from the needle. This is why, when a value >0 is entered before the needle movement, a drop is produced which then also moves downward when the search with the needle is taking place. The volume of this "auxiliary" drop does not depend on the subsequent dosing volume; it is normally much smaller. Numerical values between 0 and 5 can be entered; however, this is not a set volume but a relative drop size. In most cases values of 1 to 3 are very suitable. The value 0, i.e. a surface search without an auxiliary drop, should only be selected when the surface provides a very clear mirror image and the image is optimally illuminated and has a high degree of contrast. If the value 0 is selected then the option "Try using mirror image..." further down the card must always be switched off.

Object grey value threshold: The value entered here gives the difference in the grey level value above which an object in the image will be recognized (drops, the needle, their mirror images). The optimal value depends on the condition of the sample, the image contrast and the illumination; in most cases values between 90 and 130 produce good results. Lower values (about 90) should be used for clear, high-contrast images; high values (115-130) for low-contrast images.

Object background threshold: This value indicates the degree to which the recognized object is to stand out against the background or, in other words, the extent to which the grey level transitions around the edge of the object are to be regarded as belonging to the object. The recommended values also depend on the image contrast; however, in this case the higher the contrast, the higher the value that should be entered here. The default value of 20 set by KRÜSS ought to produce good results in most cases.

Try using mirror image... Selection of this option results in the DSA1 program using the mirror image of the needle (and, if applicable, the auxiliary drop hanging from the needle) when searching for the solid surface. The use of the mirror image results in improved accuracy in recognizing the surface; however, this option should only be switched on when the sample also provides a clear mirror image.

Control distance to substrate to: This option is only active when "Try using mirror image" has been switched on. You should enter the distance between the needle (or the lower edge of the auxiliary drop) and the detected sample surface. This distance is obtained from the needle thickness in the video image multiplied by the value in the input line.

Values <0.3 should only be used when an auxiliary drop is being used in the search for the surface. Values between 0.5 and 1 are usually recommended.

Use elevated speed: When searching for the sample surface the DSA1 software uses a standard speed. If the option "Use elevated speed" is switched on then the searching speed will be considerably increased. Although this method accelerates the search and therefore the measuring procedure, it also increases the risk of the needle contacting the sample surface and possibly reduces the reliability of the surface detection

6.2.6.5 Automatic tasks during the procedure

In the tab-sheet "Task to be invoked" you have the possibility that, when specific events occur during the procedure, these can be combined with certain actions. The actions listed under "Task" consist of:

- Carrying out a single measurement ("Evaluation") with the selected drop shape method (see sect. 9.2.3).
- Carrying out a series of measurements with the TrackerMan (see sect. 13)
- Starting a video recording ("Video Recording"; see sect. 14).

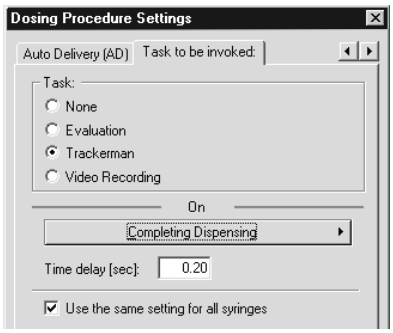


Fig. 6.20: Tab-sheet for options for automatically triggering an action

If “None” is selected then no automatic action will be carried out.

In the “Time delay” line you have the additional possibility of carrying out the action after a defined time has elapsed after the corresponding event; the delay time is entered in the input field in seconds. By setting a tick in the field “Use the same settings for all syringes” you can ensure that the entries made on this sheet will be automatically adopted for all the syringes.

By using the arrow key below “On” you can select the step in the procedure at which the selected action is to be carried out. If you click on the key then the following pull-down menu opens:

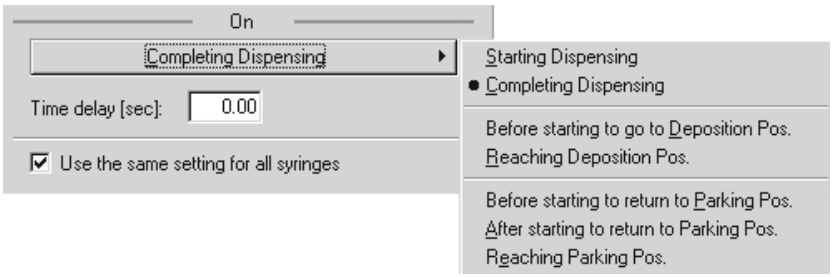
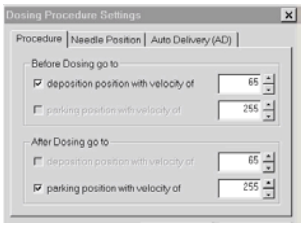
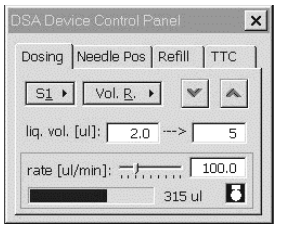
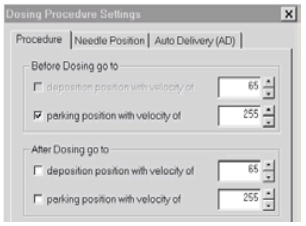
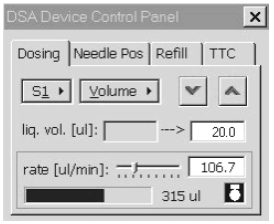
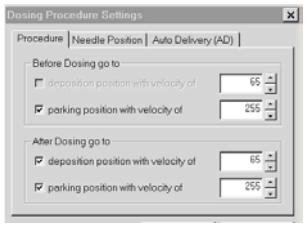
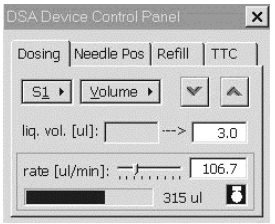
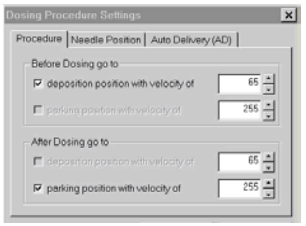
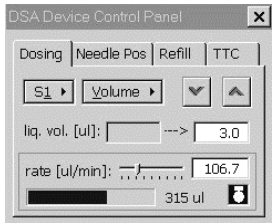


Fig. 6.21: Events with which the start of an action can be combined

The following table explains the individual positions of the menu. The examples shown and the procedures which are suitable for them are only suggestions; for your own individual procedures you can, of course, select other settings and combinations.

Condition for task start	Explanation	Example	Suitable procedure
"Starting Dispensing"	The task is started as soon as drop production begins.	Dynamic contact angle measurement (advancing or retreating angle)	 
"Completing Dispensing"	The task is started when the end volume set for dosing has been reached.	Static surface tension measurement on pendant drop	 
"Before starting to go to Deposition Pos."	The task is started immediately before the needle movement to the deposition position.	Static contact angle with drop to be deposited; the moment of surface contact when the drop is being deposited is to be recorded	 
"Reaching Deposition Pos."	The task is started as soon as the deposition position has been reached.	Static contact angle on deposited drops immediately after the drop has been deposited	as above

Condition for task start	Explanation	Example	Suitable procedure
"Before starting to return to Parking Pos."	The task is carried out immediately before the needle movement to the parking position.	Static contact angle; the whole of the needle movement in the drop and on exiting the drop is to be recorded	As above, or  
"After starting to return to Parking Pos."	The task is carried out immediately after the start of the needle movement to the parking position.	Static contact angle; the exit of the needle from the drop is to be recorded	As above
"Reaching Parking Pos."	The task is carried out as soon as the parking Position has been reached.	Static contact angle; recording is only to take place when the needle is outside the drop	As above

6.3 Needle positioning without a procedure ("Needle Pos.")

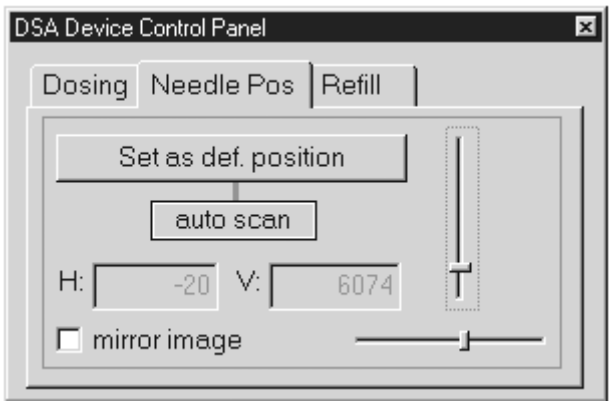


Fig. 6.22: Setting the needle position

Under “Dosing” we have already described how the needle is controlled in programming a procedure and how standard positions are defined for the needle. If you do not want to use these procedures and instead want to move the needle manually to the required position then this possibility is offered on the “Needle Position” card. The control of the needle is carried out exactly as described in 6.2.5 with the exception that no “Park” and “Deposition” positions cannot be defined on this card.

When you have set a suitable height and horizontal position of the needle for the sample you now have the possibility of defining the current needle position as the starting position (“default position”). This is done with a simple click on the “Set as default position” field. The default position is individually defined for each syringe; when the needle is changed the set default position for the corresponding needle will be moved to automatically.

To define the default position you can also use the ”auto scan“ function (see section 6.2.6.2).

The default position set here corresponds with the default position for the “Procedure Settings” on the “Dosing” card (see sec. 6.2.5); i.e. an alteration to the default position under “Dosing” will be automatically transferred to the “Needle Position” card (and vice versa). The default positions are stored for each needle, so that they are still present the next time that the program is started.

6.4 Filling and rinsing the syringes ("Refill")

Fig. 6.23: Options for filling the syringes

This card is intended for refilling the syringes of GH100 and DSA100 with a computer-controlled dosing system. With G2 the filling process must be carried out with the aid of the keyboard supplied.

For DSDA100, the “auto refill” function only works together with a multi-dosing system. If you are equipped with a single-dosing system DS3210, the syringe must be refilled between measurements using the “Refill now” button.

6.4.1 Triggering the refilling function ("Refill now")

As soon as the "Refill now" field is clicked on the valve switches automatically from the dosing position to the refilling position. The liquid is then aspirated from the storage bottle into the syringe. The refilling process continues until the set maximum volume of the syringe has been reached. If the process is terminated prematurely then the field can simply be clicked on a second time. The button to the right of the refill field can be used to select the speeds "Fast", "Normal" and "Slow". Filling can usually be carried out at a high speed, but the speed should be reduced for high-viscosity test liquids.

6.4.2 Automatic refilling ("Auto refill")

You also have the possibility of allowing the syringes to be refilled automatically so that their volumes do not have to be checked continually. With auto-refill switched on the refilling process is started as soon as there is only 10% of the total syringe volume present. The auto-refill process can be interrupted by clicking on the "Refill now" button.

In order to **prevent the auto-refill process from interrupting a measurement** an additional safety inquiry can be switched on. This is done by clicking on the field "But ask me before invoking". If this option is selected then the following window appears if the 10% mark is reached during drop dosing:

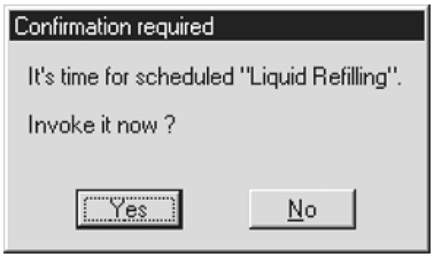


Fig. 6.24: Dialog for the automatic refilling process

Dosing continues in the background. If "No" is clicked on then no refilling takes place and dosing continues to the end. Clicking on "Yes" interrupts the dosing and the refilling process starts immediately.

6.4.3 Valve switching ("Valve position...")

The valve is normally always in the dosing position, i.e. the path from the syringe to the needle is open and the path to the sample bottle closed. If a refilling process is started then the valve switches automatically to open the path to the bottle; when the refilling process is finished it switches back automatically. In exceptional circumstances (e.g. rinsing the tubing to the storage bottle; emptying the syringe contents into the bottle) it may be necessary to open the path to the storage bottle. This is done by clicking on the field "Valve position for..."; "Refill" then appears in the field instead of "dosing". If a switch is then made to the "Dosing" tab sheet, then a safety inquiry is first made as to whether the valve setting "Refill" is to be retained for dosing. If one of the two dosing buttons is then operated this inquiry appears again. If you confirm that the refill position is to be retained then the syringe plunger immediately starts to move and the liquid is transferred from the syringe to the storage bottle or vice versa.

6.4.4 Rinsing a syringe („Squeeze"-modus)

With the squeeze function a syringe with needle and tubings can be rinsed. In the squeeze modus the selected syringe will be emptied completely and the refilled with the liquid in the connected storage tank. To clean a syringe an to change the liquid the squeezing process should be performed several times.

Fill the bottle with the rinsing liquid (e.g. Acetone) and lead the tubing belonging to the syringe to the bottle. Take care that the syringe empties into a waste tank. The rinsing liquid must be miscible with the liquid the syringe was filled with before. Also, substances dissolved in the syringe liquid (salts, surfactants) should be soluble in the rinsing liquid. Do not forget to put a collecting bottle under the syringe.

To switch on the squeeze modus, change select the tab sheet „Refill" of the „Device Control Panel". Press the <Shift> and <Ctrl> keys simultaneously, hold them pressed and click on the button „Refill now!". The rinsing process starts. The rinsing speed corresponds with the speed of the refill process (see sect. 6.4.1).

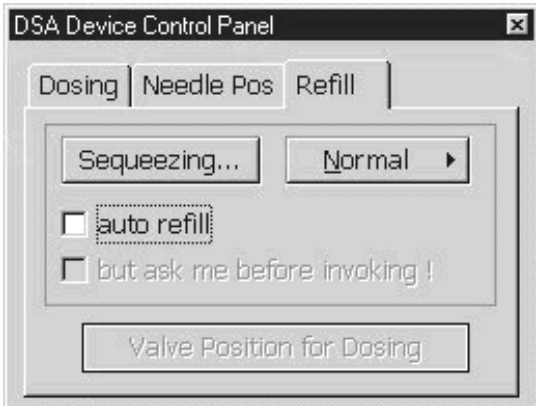


Fig. 6.25: Squeeze modus

7 Controlling the optics

This section covers the control of PC-controlled optics (focus, zoom, illumination). Illumination is always PC-controlled, depending on the equipment level focus and zoom can either be controlled by a PC or manually.

The optics are controlled via the „Device Control Panel“. Open this panel with the icon

 .

If the FG-Window is active then the optical elements can be controlled using the keyboard:

PGUP↑	Increases brightness
PGDN↓	Reduces brightness
Ins	Increases the magnification (zoom)
Del	Reduces the magnification (zoom)
Home	Increases the focal length (focus)
End	Reduces the focal length (focus)

The current setting is shown on the tab sheet “Imaging” of the Device Control window:

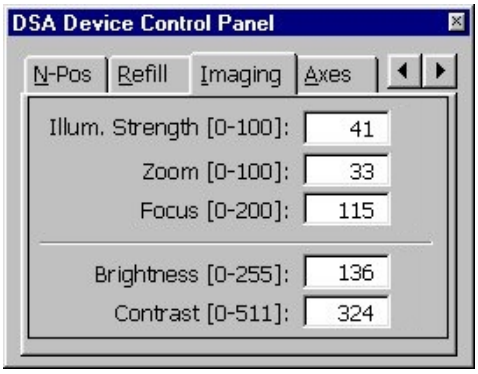


Figure 7.: Tab sheet “Imaging” for controlling the optics

By entering the required numerical values you can also make the optical settings directly on this tab sheet. The upper three options control the settings of the optical elements themselves, the two lower options are used for controlling the frame-grabber.

If possible, the image brightness should be controlled by using the light source (“Illum. Strength”), and not via the brightness setting of the frame-grabber (“Brightness”).

8 Producing an optimal drop image

The contact angle is measured by analysis and evaluation of the digitized drop image. The accuracy of the measurement requires that as good a video image of the drop as possible is recorded. This section describes how a suitable drop image is obtained. The three settings image size, brightness and image sharpness should be carried out in this sequence; however, setting one of these parameters usually requires slight adjustment of the two others.

8.1 Image sharpness

The image sharpness (focus) is a further important criterion for the accuracy of the measurement; the drop margin should not be blurred, but should be recorded as accurately as possible in the grey level analysis of the pixels. The optimal image sharpness can be estimated visually, but it is certainly better to use the focussing assistant. To open it click on the icon  :

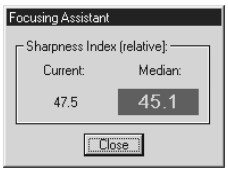


Fig. 8.1: The focussing assistant

The assistant calculates a sharpness index and indicates the current value and a running mean value over the recent values. This mean value should be as high as possible. If the sharpness is sufficient, the value is displayed on a green background.

8.2 Image size

The larger the image size appears, the more pixels are available for the evaluation of the drop edge area. The camera zoom should be used to obtain as large an image as possible on the screen. The drop should normally occupy at least 50% of the image width, for polynomial fitting (see Section 9.2.2) at least 75%.

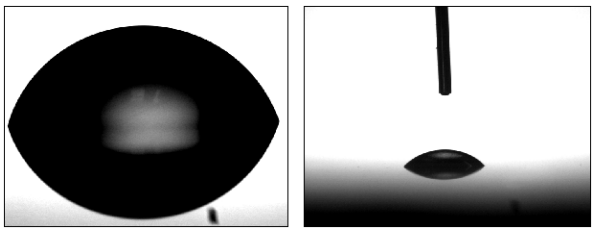


Fig. 8.2: Properly sized and too small drop image

For pendant drops the drop itself (not only the image) should be as big as possible. A part of the needle must also be visible at the top of the image for measuring the magnification (MAG).

Abbildung 8.3: Image of a pendant drop

8.3 Illumination

The image brightness should also be optimal for image analysis. It is best to start with the lowest intensity and gradually increase the brightness. Normally a weak separating line can be seen between an upper brighter area and a lower darker area. As the intensity increases the brighter area becomes larger and the separating line moves downwards. Optimal brightness is usually achieved when the dark area is just below the baseline. In the right-hand illustration the intensity is too bright so that the separating line is located too far down the screen.

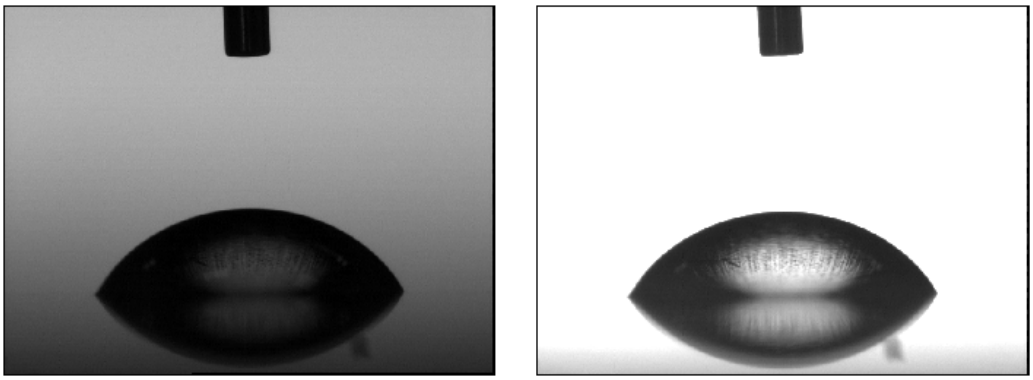


Fig. 8.4: Too dark and too bright drop images

8.4 Reflections

Reflections from the outside of a drop (as shown in Fig. 8.5), for example caused by incident light, should be avoided at all cost. In extreme cases this could cause a program crash if the reflections imitate a drop form which cannot be processed by the evaluation algorithm. A slightly increased brightness inside the drop is caused by the lens effect and has no influence on the measurement.

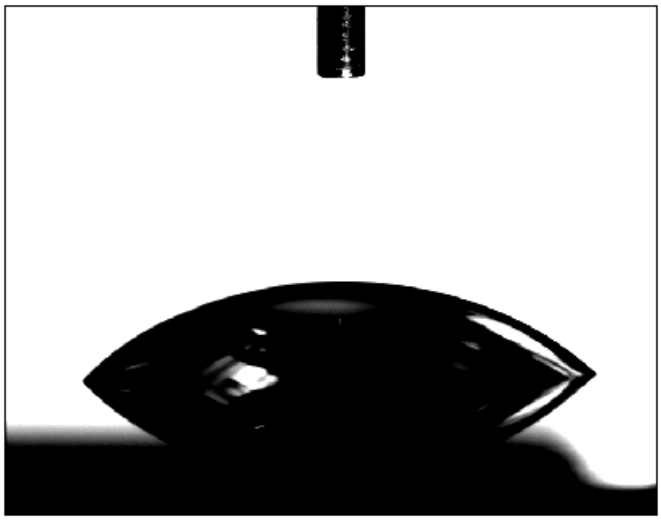


Fig. 8.5: Light reflections in a drop

8.5 Optimal image

Another drop image which is optimal for making a measurement is shown here (Fig. 8.6). The width of the drop is about 2/3 of the video image. The drop edge appears sharp and free from interfering reflections. The illumination is set so that there is a uniformly brighter grey level region above the baseline without the drop edge being flared. The mirror image of the drop is clear so that the software will have no difficulty in calculating a baseline.

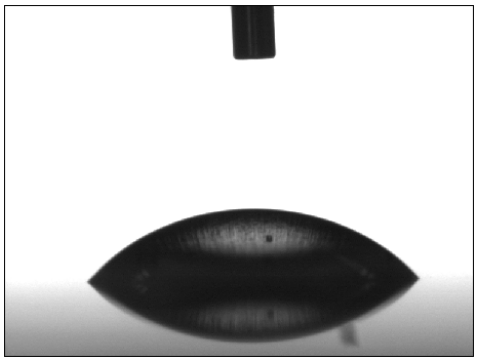


Fig. 8.6: Good drop image

8.6 Needle in drop

If static drops are to be measured then the needle must be removed from the drop after it has been produced and before it is measured. When dynamic drops are measured (advancing or retreating) then the needle must remain in the drop image. Care must be taken that the needle is located as much as possible in the upper region of the drop so that the needle does not affect the shape of the drop very much (see Fig. 8.7, left). Only those measurement methods can be used in which the whole drop outline is not needed for the calculation but only the region surrounding the three-phase point is evaluated; in most cases the polynomial method is recommended (also known as "Tangent method 2"; see Section 9.2.2).

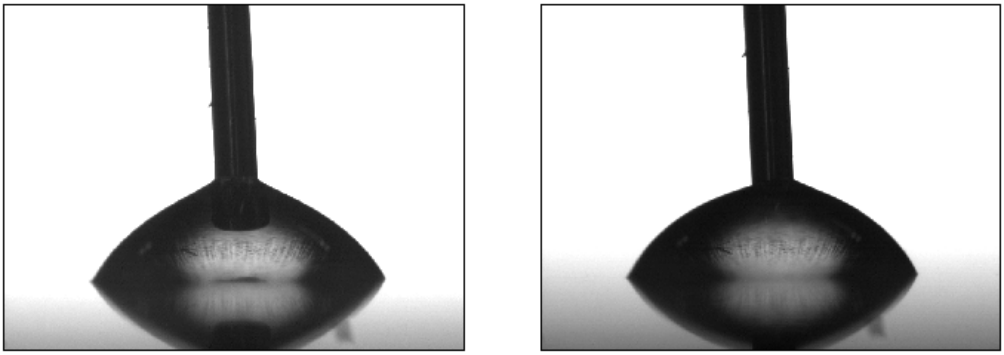


Fig. 8.7: Drop image with needle in drop; in the left-hand illustration the needle is located too deeply in the drop and greatly deforms it.

8.7 Very small contact angle

With very small contact angles the limiting angle for total reflection can be reached and the rays of light coming from the upper part of the light source can be reflected from the top of the drop. This falsifies the size of the drop image, as can be seen in Fig. 8.8b.

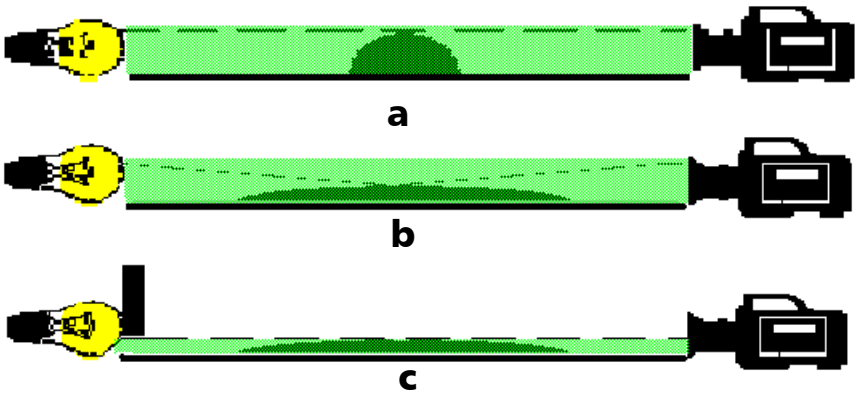


Fig. 8.8a-c: Avoidance of drop image distortion at small contact angles

As shown Fig. 8.8c, this effect can be avoided with the use of the aperture of the DSA100:

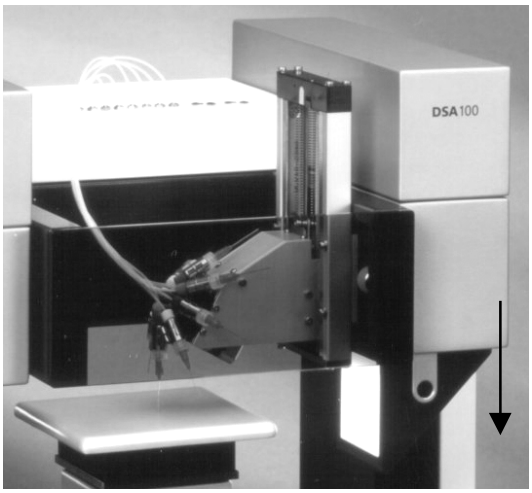


Fig. 8.9: Using the aperture

Pull the lever of the aperture downward to make the light slit smaller.

8.8 No mirror image of drop

The DSA1 program determines the baseline with the aid of the mirror image of the drop produced by reflection at the sample surface. You should ensure that this mirror image is as clear as possible. With sample surfaces which do not reflect very well it is normally possible to improve the mirror image by altering the sample stage inclination (Tilt). If it is still not possible to obtain a mirror image then the program will not be able to find the baseline automatically. In this case the baseline must be set manually.

There is also the problem that the lack of reflection means that the drop image is quite dark and poor in contrast so that it is even difficult to determine the baseline visually. You should therefore try to increase the contrast by adjusting the frame grabber settings (Section 15.2).

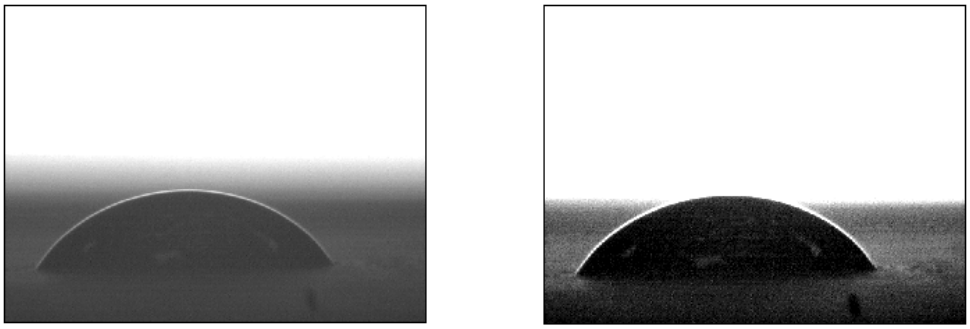


Fig. 8.10: Drop without mirror image, on the right with improved contrast

8.9 Uneven sample surface

Rough and uneven sample surfaces naturally provide either a poor mirror image or even none at all. All the possibilities mentioned in the previous section for optimizing the drop image can first be used. There is the additional problem that the contact angle cannot be measured at the three-phase point because of the unevenness. In such cases meaningful values can only be obtained with the height-width method (see Section 9.2.2).

9 Evaluating a drop image

This section contains all information concerning the evaluation of an image. Sessile drop and pendant drop measurement is dealt with in corresponding subsections:

- Section 9.1: Information concerning both measuring methods
- Section 9.2: Information concerning sessile drop measurement
- Section 9.3: Information concerning pendant drop measurement

9.1 Both measuring methods (sessile and pendant drops)

9.1.1 Live mode, snap mode and image storage

For observing the live image on the monitor, click on the icon or press the key <F6>.

By switching into the snap mode you obtain a photographic image of the drop. Click on the icon or press the key <F7>. The snap image can be saved with the menu order „save“ in the context menu of the frame grabber window.

Stored images can always be recalled. Select the menu order „File“→„New Drop Window“. A drop window opens where previously stored images can be evaluated. Select the menu order „File“→„Open...“ and select a drop image to be loaded into the drop window.

9.1.2 Determination of the Region of interest "ROI"

To avoid long calculation times for the drop profile, you have the option to define an area of the drop image which is relevant to the calculation, the so called "Region of interest, **ROI**". Only picture elements which lie inside of this area will be included in the calculation.

In both the FG-Window and the Drop Window the **ROI** is displaced as a rectangle framing the determined area. After opening of one these windows the **ROI** contains the entire image area and is therefore not visible. When you move the mouse cursor to the image's edge holding down the <Shift> key, the mouse cursor turns into a double arrow symbol. You can now change the size of the rectangle by simultaneously pressing the left mouse key and the <Shift> key.

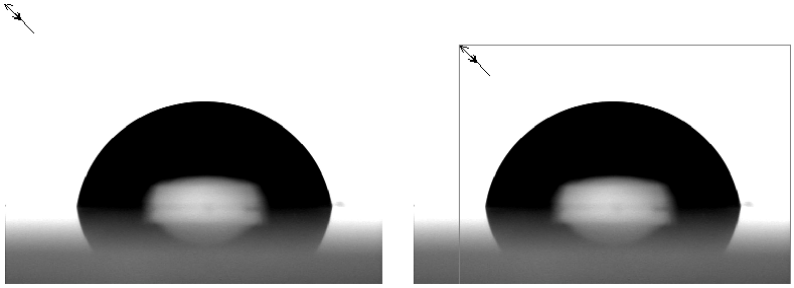


Fig. 9.1: Determination of the “Region of interest (ROI)“

Double-clicking the left mouse key while holding down the <Shift> key deletes the ROI-window and equates the Region of interest with the entire picture.

Alternatively to this procedure you can feed the image element data for the four rectangle points. This is to be carried out in the card "Options"→"Drop Window Option..."→"FG-Window specific".

9.1.3 Setting the drop type (pendant/sessile))

In the submenu “Drop Type” of the context menu in the “FG-Window” you must choose between “Pendant Drop”) and “Sessile Drop”).

The options in the submenu “Subtype” depend on the drop type that has been selected:

- Sessile Drop: you should usually select the option “Normal Sessile Drop”. The option “Captive Bubble” is only used for measurements on air bubbles located in a liquid below a solid surface.
- Pendant Drop: “Right → Left” describes a drop image in which the capillary is located horizontally on the right-hand side of the frame and the apex of the drop points toward the left-hand frame margin. A vertically hanging drop shown from top to bottom on the screen corresponds to the entry “Top → Bottom”.

9.1.4 Drop and measuring system properties ("Drop Info")

Before a measurement can be started or evaluated the physical properties of the drop must be entered. This is carried out in the "Drop Info..." menu of the FG Window. When a drop image which has already been stored is loaded then some of the data entered before storage is also loaded. The information to be stored together with the drop image can be defined under "Options"→"Drop Window Option..."→"Drop Info"; any data not stored must be entered here before the evaluation. Some of the data to be entered is only relevant for pendant drops (Section 9.3), some only for sessile drops (Section 9.2), so that you must first study the corresponding Sections in order to see which data you require before you laboriously put it together. The drop data is entered in four cards ("Sample Description", "Parameters", "Liquid Information" and "Other Information"); these are described in succession below.

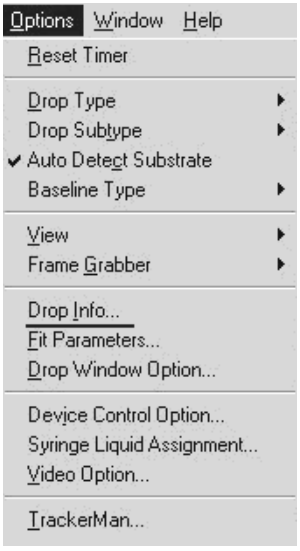


Fig. 9.2: Selection of the "Drop Info" menu for entering drop information

Sample description ("Sample Description")

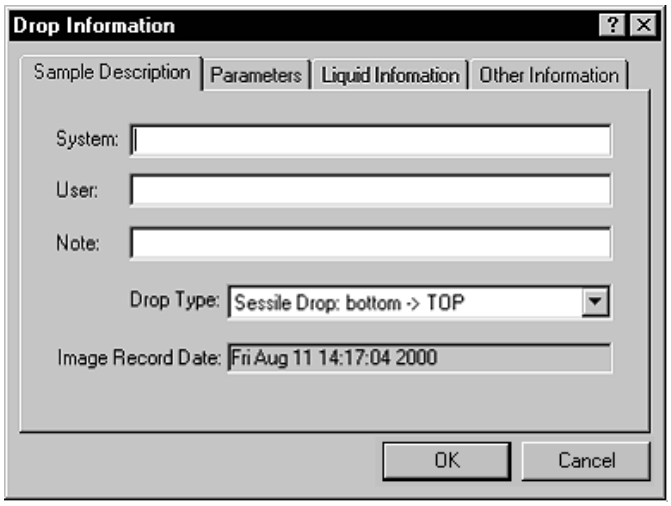


Fig. 9.3: Entering the sample description ("Sample Description")

In this card you can enter general information about the sample and the measurement. Under "System" the entry of a sample description can be made; the name of the operator should be entered under "User". Under "Note" you can make additional entries about the sample or the measuring conditions.

Under "Drop Type" you should enter the type of measurement to be carried out, i.e. pendant drop, sessile drop or captive bubble. The "Drop Type" corresponds to the entries made under "Options→Drop Type" and "Options→Subtype". If the entry of the drop type has already been made in one of these menus then the choice will also be shown here under "Drop Information...Drop Type"; the same applies in reverse.

In the "Image Record Date" line you cannot make any entries; the date is entered here automatically.

Drop and drop image parameters ("Parameters")

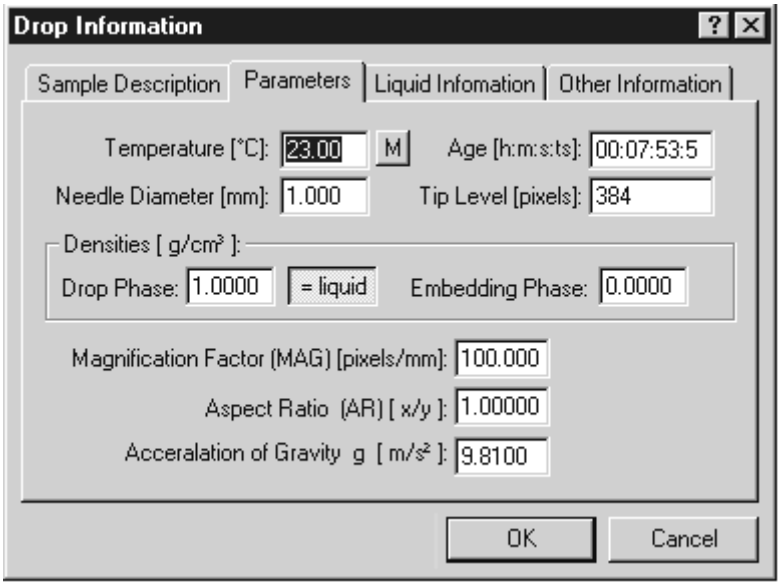


Fig. 9.4: Entry of physical drop parameters and drop image properties

The **measuring temperature** ("Temperature"), **drop age** ("Age"), **diameter of the needle used** ("Needle Diameter") and the **height of the evaluation line** ("Tip Level") are shown in the upper section.

The temperature can either be measured automatically or entered manually. If the measured temperature is to be accepted then operate the "M" button (measured"); editing in the input field is then no longer possible. Clicking on the button again switches back to the manual mode.

The needle diameter is required for determining the measuring scale in the FG Window; the "Tip-Level" is given automatically by the height of the evaluation limit line you have set in the FG Window. Do not make any entry here for the "Tip-Level"

Under "Densities" the **densities** of the **drop phase** ("Drop Phase") and the **surrounding phase** ("Embedding Phase", gaseous or liquid) are entered. The density of the surrounding phase is entered manually; for the density of the drop phase you have the choice of entering it manually or transferring it from the "Liquid Information" window. Automatic transfer is carried out via the = liquid button If this button is shown as light grey then the entry in the "Drop Phase" field corresponds to the density given in the "Liquid Information" card, so that an alteration in one of these two cards will be automatically transferred to the other one. Clicking on the light grey field switches it to dark grey = liquid; automatic transfer is switched off.

Entries have only to be made in the three input lines below on rare occasions. The **magnification factor** is required for calculating the absolute drop dimensions. It is automatically provided from the scale determination in the FG Window and should not be altered manually here. The "Aspect Ratio" is a camera constant which describes the **length/width ratio of the pixel**. During the installation and selection of the correct type of camera the value is entered automatically. Manual alterations should not be made. During a **new installation** of the DSA1 program the correct aspect ratio will only be entered automatically if camera installation is carried out properly; this is why you must strictly adhere to the corresponding installation instructions (see Section 3).
The **acceleration due to gravity** ("gravitational acceleration") is set to 9.81 m/s^2 during the first installation; if the local value is different then the correct value must be entered here.

Drop liquid data ("Liquid Information")

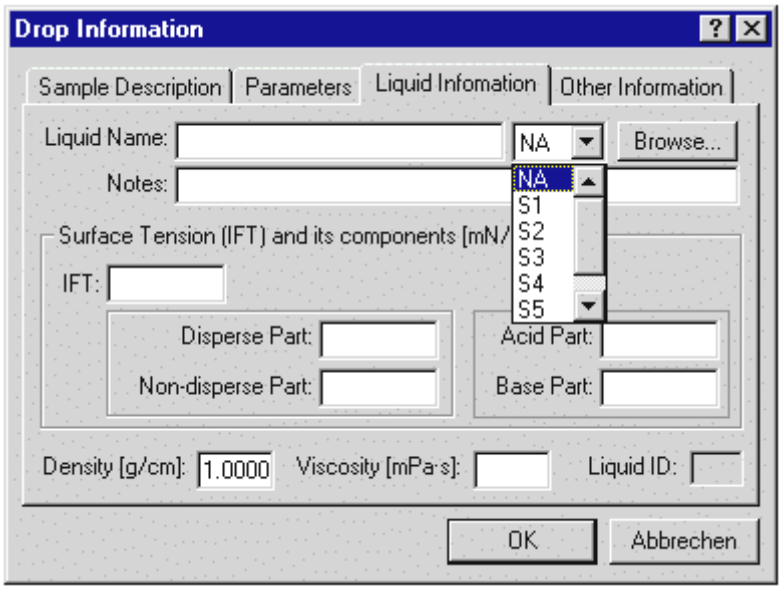


Fig. 9.5: Entering the drop liquid data

Physical data about the drop liquid used are entered in the third card "Liquid Information" of the "Drop Information" menu.

First the arrow key at the top right must be used to decide whether the information about the liquids assigned to the syringes is to be accepted (S1-S5), or whether a different liquid is to be used ("NA" for "not assigned"). In the first case the data for the liquid of the selected syringe is automatically entered in the menu.

The selection of a non-assigned liquid ("NA") can be carried out manually, or a liquid can be selected from the liquids database; its data will then be transferred automatically. This is done by clicking on the Browse... button. The liquids database then opens with a list of liquids which can be selected. The required liquid is selected by double-clicking on the corresponding line and then closing the liquids database window.

The name of the liquid is displayed or entered in the upper section. In the "Notes" line below you can enter additional information about the liquid.

In the "Surface Tension and its components" field all information about the surface or interfacial tension is entered. The "IFT" field initially contains the value for the surface or interfacial tension. Various theoretical considerations can be used to divide this value into several components: e.g. into a disperse part and a non-disperse part, or into an acid part and a base part. The liquids database does not contain information about all these quantities, so that these input lines accordingly remain empty. However, the entry of a surface or interfacial tension is always required.

The density and viscosity of the drop liquid are displayed or entered in the lower section of the card. If the "=liquid" button is depressed (button appears light grey) in the "Parameters" card (Section 0), then the value entered in the "Liquid Information" card will be transferred.

Further image information ("Other Information")

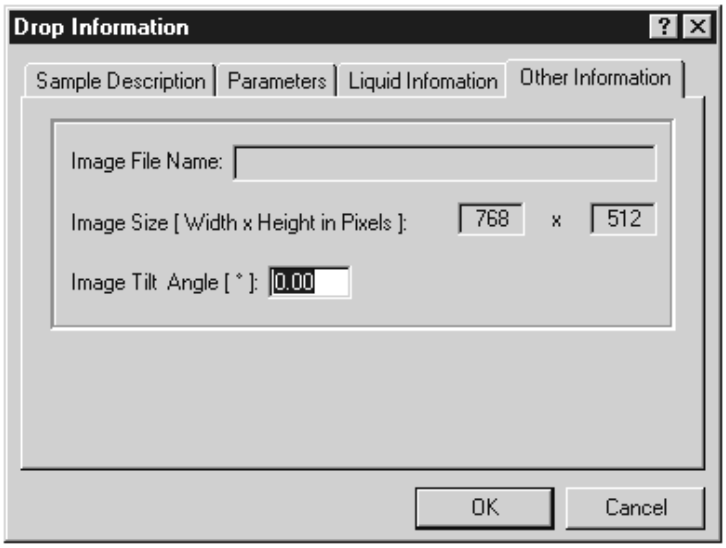


Fig. 9.6: Additional information about the drop image

When a stored drop image is called up or a current image is stored then a file name (with pathway) appears in the upper line ("Image File Name"). In the "Image Size" line beneath the width and height of the image are shown in pixels.

In the "Image Tilt Angle" line you do not need to make any entries. The value indicates the angle between the vertical camera table axis and the vertical camera axis itself; it is automatically determined by the DSA1 program and entered in this field.

9.2 Contact angle of a sessile drop / bubble

In this chapter the procedure for the determination of the contact angle is explained. The DSA program offers the possibility of measuring the contact angle of a drop lying on a solid surface (sessile drop) or a bubble caught beneath a solid surface (captive bubble). Recording the sessile drop or captive bubble is carried out in an analogous manner to that described for the pendant drop in the preceding chapter.

9.2.1 Determining the baseline ("substrate detection")

The baseline of a drop image is the boundary between the solid surface and the drop.

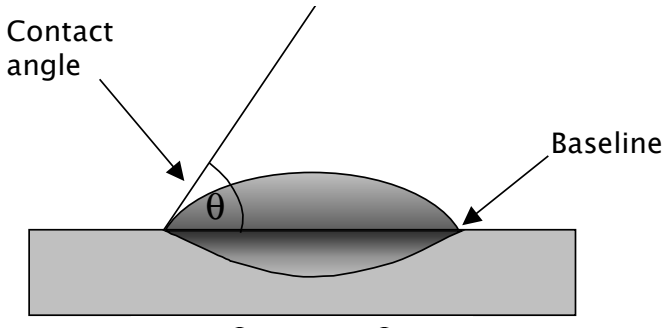


Fig. 9.7: Drop diagram with baseline

As the absolute height of the surface is unknown, the baseline must be determined mathematically in the evaluation of the drop image. For the exact calculation of the baseline this means that a high-quality drop image must first be available (see Section 7). In this section you will be informed about how to

- determine the baseline automatically,
- calculate the baseline for contact angles >90°,
- define the baseline manually,
- determine the baseline at a curved surface.

The individual options for determining the baseline can be accessed in an active FG-window or Drop window (in each case with a drop image present) by clicking with the right-hand mouse key on the

button in the symbol bar. The following pull-down menu opens:

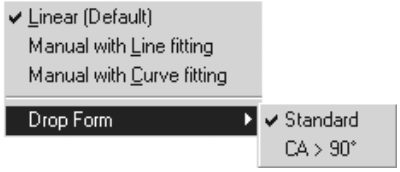


Fig. 9.8: Context menu of the baseline button

Alternatively you can access the menu via "Options"→"Baseline Type" in the FG-window.

Automatic baseline determination: In order to determine the baseline automatic you must set a tick at "Auto Detect Substrate". The requirement for obtaining an accurate calculation of the baseline is a sharp, high-contrast drop image and a clearly visible reflection of the drop.

The calculation algorithms for contact angles below 90° differ from those for angles above 90°; an automatic recognition is extremely difficult to achieve. For this reason the DSA1 software must be "told" whether the expected contact angle is below ("Standard") or above 90°. This is done by setting the corresponding marking under "Drop Form".

The menu command "Auto Detect Substrate" in the "Options" menu corresponds to the context menu command "Auto Detection".

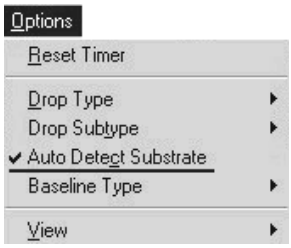


Fig. 9.9: Automatic baseline determination in the "Options" menu

If the automatic baseline determination is switched on or off here then the same also happens automatically in the context menu of the baseline button and vice versa.

Manual definition of a straight baseline: If automatic determination of the baseline is not possible for one of the reasons given above then a manual baseline can be defined. This is done by going to "Options" and switching off the option "Substrate detection". If the sample is plane you can select the setting "Linear (Default)" for the baseline type. You can move the shown line upwards and downwards by using the mouse or with the two arrow keys < ↑ >, < ↓ >.

Using the arrow keys < ← > and < → > tilts the baseline in order to adapt it to uneven sample surfaces. A double click on the base line while keeping the <Shift>-Key pressed alignes the baseline horizontally.

"Manual with line fitting": With this option, a line with two line points indicated by crosses appears. The line can be altered by moving these points, and you can also move the whole line horizontally and vertically. Setting further points changes the line into a linear regression line considering all points.
If the mouse cursor is not positioned directly on the line it will initially appear as cross hairs


,

whose crossing point indicates the **exact mouse position**.

As soon as the mouse cursor is located on the curve its appearance changes

and indicates that you can now **move the line**. This is done by pressing down the left-hand mouse key and moving the curve to the required position.

You can move a line point by touching it directly with the mouse cursor (mouse cursor turns into an arrow symbol) and move the mouse while keeping the left mouse button pressed.

Further points for the line fitting can be defined by pressing down the <Ctrl> key on the computer keyboard and simultaneously clicking the mouse on the required position of the point of curvature. Deleting a point of curvature is done by clicking on it with the <Alt> key held down; however, at least three points of curvature must always be present, so that these cannot be deleted at will.

Manual with curved fitting: By using the option "Manual with curve fitting" it is possible to define a baseline even for curved surfaces. However, this function should only be used when no plane sample surface is available or can be obtained. The accuracy of the baseline and the contact angle naturally becomes worse; in addition, uneven samples frequently provide poor drop images.

For a curved baseline there are only two calculation methods which can be used: "Tangent method 1" and "Circle fitting". Therefore the other calculation methods are inactive with curved fitting.

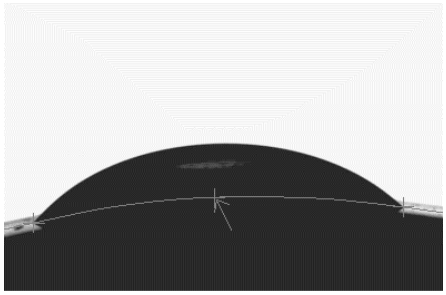


Fig. 9.10: Baseline for a curved surface

As soon as you select "manual with curve fitting" a curved line appears with 3 points of curvature indicated by crosses (see Figure 2.8). The mouse is used to set the shape of the curve and determine its horizontal and vertical position.

If the mouse cursor is not positioned directly on the curve it will initially appear as cross hairs  ,

whose crossing point indicates the **exact mouse position**.

As soon as the mouse cursor is located on the curve its appearance changes 

and indicates that you can now **move the curve**. This is done by pressing down the left-hand mouse key and moving the curve to the required position.

The **curvature of the curve** is defined by moving the mouse cursor directly to one of the points of curvature on the curve. The mouse cursor now appears as an **arrow** (see Figure 2.8). The curvature can be altered by moving the points of curvature with the left-hand mouse key pressed down.

Further points of curvature can be defined by pressing down the <Ctrl> key on the computer keyboard and simultaneously clicking the mouse on the required position of the point of curvature. **Deleting** a point of curvature is done by clicking on it with the <Alt> key held down; however, at least three points of curvature must always be present, so that these cannot be deleted at will.

9.2.2 Evaluation methods

Tangent method 1 The complete profile of a sessile drop is fitted to a general conic section equation. The derivative of the equation at the baseline gives the slope at the three-phase contact point and thus the contact angle.

Tangent method 2 The profile of a sessile drop in the region of the baseline is fitted to the rational function ($y=a+bx+cx^{0,5}+d/lnx+e/x^2$). From the fitted parameters the slope of the three-phase contact point at the baseline is first determined and used to determine the contact angle. This function has been selected from numerous theoretical simulations.

Height/width method (H/W-Method) This is a standard method in which it is assumed that the contact angle for small drops is not influenced by the absolute drop size. From the ratio of the maximum height and width of a sessile drop conclusions can be drawn about the contact angle.

If the needle diameter is known the absolute values for height, width and volume of the sessile drop can be determined. This is carried out by entering the needle diameter under "Drop Info | Parameters" in the context menu of the FG-window. The MAG is determined by pressing the icon  and is retained until the next alteration.

Young-Laplace method (Sessile Drop Fitting) The drop contour can be mathematically described by adapting the Young-Laplace equation for curved boundary areas. The contact angle is determined as the slope of the contour line at the three-phase contact point.

In addition, if the needle diameter and the density of the drop are known then the interfacial tension can be determined. To do this the needle diameter and the density of the drop must be entered under "Drop Info | Parameters" in the context menu of the FG-window. The MAG is determined by pressing the icon  and retained until the next alteration. Reliable values for the interfacial tension are obtained for contact angles which are well above 30°.

Circular segment method (Circle Fitting) This method is primarily suitable for small contact angles (<30°). The drop outline is adapted mathematically to a circular segment shape. In this way the whole drop outline can be evaluated and not just the area of intersection with the baseline.

9.2.3 Determination of the contact angle

The evaluation method to be used is selected from those described above in the pull-down menu "Profile" in the menu bar.

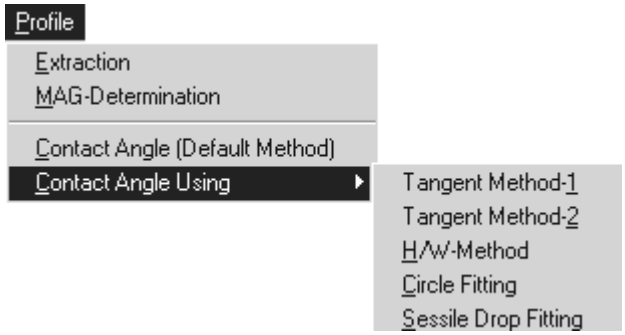


Fig. 9.11: Pull-down menu "Profile": selection of evaluation method.

By selection of "Profile | Contact Angle (Default Method)" the method designated as default method is selected and the contact angle determination started. Alternatively the icon can be pressed.

The default method must first be selected under "Option | Drop Window Option | Contact Angle Measurement". Under "Profile | Contact Angle Using..." the method will be used for a single calculation. The selection of one of the methods given here simultaneously starts the determination of the contact angle. By pressing the icons FIT or by selection of "Profile | Fit" the fitting of the Young-Laplace equation to the drop contour (Sessile Drop Fitting) will automatically be used as the method for determining the contact angle. In this method the interfacial tension is also determined at the same time if the MAG-factor has been determined correctly.

Clicking the required method starts the evaluation and determination of the contact angle. In all methods the drop contour is first digitized and the drop profile obtained in this way is shown. The result of the contact angle calculation appears in the lower result bar at the bottom margin of the program window. The values obtained for the left-hand side and the right-hand side of the drop can be seen together with their mean value. If the H/W-method is used only the contact angle together with the maximum drop height and width will be shown in mm. The drop height and width will be given correctly if part of the needle was available and the MAG-factor was determined correctly.

All measurement results are collected in the result window which can be opened with the icon .

9.3 Surface tension of a pendant drop

In this chapter important program functions for determining the surface and interfacial tension will be dealt with by working through the detailed measurement procedures.

9.3.1 Setting the "Limit Lines“

In the "FG-Window“ the region for determining the magnification factor using the needle and the height of the drop up to which the fit should be carried out must also be laid down. For this purpose the FG-Window contains three lines which run through the image in a way determined by their "Subtype": horizontally ("Top → Bottom“, "Bottom → Top“) or vertically ("Right → Left", "Left → Right"). If the mouse cursor is located near one of these lines, the particular line can be moved by holding down the left-hand mouse key; their sequence is pre-set. From the image side of the needle the first two lines (blue color) define the region of the needle which is used for the determination of the magnification factor (MAG). The third line (pink color) gives the level of the drop from which the drop contour to the drop apex is to be used for determining the interfacial tension. One of the lines could be initially located at the edge of the screen and therefore might not be visible. They can nevertheless be drawn from the edge into the screen.

9.3.2 Setting the test parameters

By selection of "Sample Description" in dialog window "Drop Info“ additional entries in the corresponding text fields can be made for the measurement protocol. The selection of the drop direction can also be made here (e.g. "Pendant Drop, Top → Bottom“). Under "Other Information" the path and name of the image document and its size in numbers of pixels should be entered. A correction of the tilt angle of the camera during recording can also be carried out here.

If we are dealing with the surface tension of a liquid under atmospheric pressure or under vacuum then only a knowledge of the liquid density at the measuring temperature is required. For the measurement of the interfacial tension between two liquids or a liquid and a compressed gas the densities of both phases involved must be known. By selection of "File | Open Liquid Data Base (SFT)" the "Liquid Data Base-Window" opens, in which a range of liquids together with some of their properties are listed. Among other properties their densities are given. These apply for 20°C, if nothing else is mentioned.

9.3.3 Determining the magnification factor

By selection of the function "MAG-Determination" in the context menu of FG-window or by "Profile“ →"MAG-Determination"

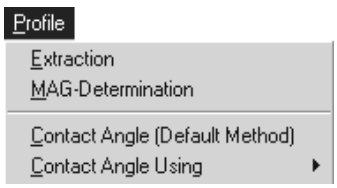


Fig. 9.12: Pull-down menu "Profile"

or by clicking the icon the magnification factor is calculated as the quotient of the real capillary diameter entered in the dialog window "Drop Info" and the number of pixels in the

capillary diameter shown as determined by the program. The result appears in a window on the screen.

If an error message appears then the setting of the image region lines must be checked and the process repeated. A manual setting of the "MAG" can be made in the dialog window "Drop Info". If in the menu table "Profile Extraction" of the dialog window "Option | Drop Window Option..." the function "Check MAG-Factor automatically" is active then this step can be left out as it will be carried out automatically. This simplifies the measurement.

The "MAG" is retained until the next alteration, e.g. by selection of a different needle diameter and subsequent operation of the icon  .

9.3.4 Determination of the profile line

The profile line is determined and shown on the screen by selection of "Profile | Extraction" or by clicking "Extract Profile" in the context menu of the "FG-Window". Alternatively the icon  can be selected. This step is contained in the determination of the surface tension by selection of "Profile | Fit" or the icon  and does not need to be carried out separately.

In this way the representation of the digitized contour line in a single step for making a special check of the correct recognition of the drop profile by the program is possible. This step can be helpful in the case of doubtful results obtained from poor-quality images or if an automatic determination has been broken off for unknown reasons.

9.3.5 Fitting

Fitting the Young-Laplace equation to the digitized drop profile obtained by profile extraction is the central step in the determination of the interfacial tension. This fitting can be activated by

- Selection of the "Fit Profile" function in the context menu of the FG-window
- Selection of "Profile | Fit"
- Pressing the icon 

After calculation the value obtained for the interfacial tension is shown in the display bar at the lower margin of the DSA program window together with several settings and geometric data. Additionally the Laplace contour line fitted to the drop profile will be shown overlaying the drop image. In this manner deviations of the calculated drop contour from the actual drop contour can be optically recognized.

The results are collected in the Result Window which can be opened with the icon 

10 Presentation of results ("Result Window")

The software allows the results to be shown both graphically and in tabular form.

10.1 Tabular presentation of the measurements

The results of the current series of measurements are shown in tabular form in the Result window. The "Result window" is opened by selecting "File"→"Open Result Window" or by operating the icon . At the start of the DSA1 program a new result window with the working heading "Noname" is automatically generated. New measurements are always shown in the current Result window.

10.1.1 Arrangement of the "Result window"

No.	Vol [µl]	IFT [mN/m]	Method
0-76	7.01	23.10	L-Y
0-77	6.88	23.18	L-Y
0-78	6.99	23.17	L-Y
0-79	6.98	23.13	L-Y
0-80	6.95	23.12	L-Y
0-81	6.94	23.22	L-Y
α 0-M	7.91	23.83 ± 0.63	L-Y
1-0	10.07	24.42	L-Y
1-1	9.84	24.70	L-Y
1-2	9.69	24.67	L-Y
1-3	9.59	24.63	L-Y
1-4	9.55	24.56	L-Y
1-5	9.53	24.56	L-Y

Fig. 10.1: Example of a table in the Result window

Fig. 10.1 shows the tabular presentation of measurements in a Result window. The quantities to be shown can be freely selected (see Section 10.2.8.1), this is why the table on your screen will probably have a slightly different appearance.

10.1.1.1 Measuring series and measuring points

The measurements are arranged one under the other and collected in a series of measurements. At the end of a series of measurements the mean value of the data is shown; the mean value line is indicated by the symbol . As many series of measurements as required can be generated in one Result window, and as many individual measurements as required can be included in a series of measurements.

A **new series of measurements** is generated by operating the m button in the symbol bar. Alternatively in the context menu of the Result windows (right-hand mouse key) a new series of measurements can be generated via the menu command "New"→"New Measurement Series".

New data is automatically assigned to the particular series of measurements which is selected as being the current series of measurements. If you generate a new series of measurements then this is automatically selected as being the current series of measurements. If a different

series of measurements from the current one is to be selected then this is carried out by clicking on the required series of measurements with the right-hand mouse key (the context menu opens) and then selecting the menu command "Set as actual Series". In the table the current series of measurements is indicated by the symbol → instead of the mean value symbol $\overline{\alpha}$.

The drop symbol shown in each measurement line indicates the type of drop for the measurement: the symbol stands for measurements on sessile drops, the symbol for measurements on pendant drops.

The consecutive number of the measuring point (see Fig. 10.1, left-hand column) should always be shown for reasons of clarity. The number in front of the hyphen shows the number of the series of measurements to which the measuring point belongs; the number behind the hyphen stands for the consecutive number of the measuring point in the series of measurements.

10.1.1.2 Display of drop information

By double-clicking on a measurement line you can call up 6 cards containing all the measuring data and drop information belonging to this measuring point.

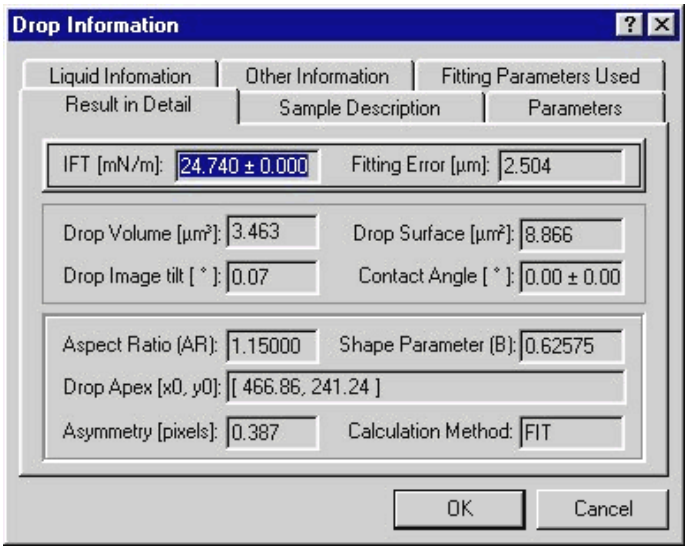


Fig. 10.2: Display of all measuring data and drop information for a measuring point

10.1.1.3 Obtaining a mean value

By removing/setting the tick in the table you can deselect/select those measuring points to be shown in a graph.

At the same time you can use the ticks to decide which measuring points are to be included for obtaining the mean value. However, the option "Actualize Summary automatically by selection/deselection" must be switched on in the card "Result-Window"→"Options"→"Result Window Option..."→"Other" (see Section 0). If this option is switched off then the measuring points not marked with a tick will also be included for calculating the mean value.

If you have added new measuring points to a series of measurements which already exists then you can update the mean value calculation by activating the corresponding mean value line in the context menu (right-hand mouse key) and executing the command "Update Mean Value".

However, then mean value will be automatically updated in any case when on the card “Result window”→”Options”→”Result Window Option...”→”Other” (see Section 0) you have selected the option “Actualize Summary automatically by adding members”.

10.2 Options of the Result window in the context menu

If you operate the right-hand mouse key in the Result window a context menu opens from which you can access all the options for working in the Result window.

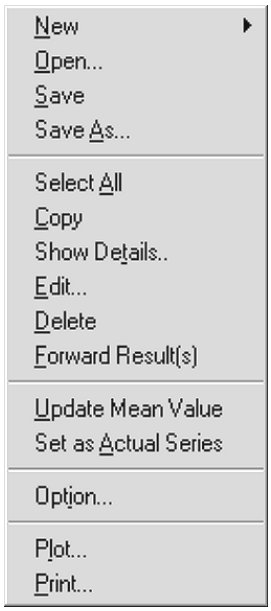


Fig. 10.3: Context menu in the “Result window”

The menu items are explained below in sequence.

10.2.1 Open a result window (“New...” and “Open...”)

If a new result table is to be generated for the following measurement then “New” is selected. You are given the possibility of saving the previous measurements, as these would otherwise be rejected.

By clicking on “Open...” a result table which has already been generated and stored can be called up and displayed.

10.2.2 Storage ("Save" / "Save As...")

A results table can be stored by clicking "Save" or "Save As...", if a new file name is to be allocated. Tables are stored in the DSA program with the extension "*.DPR".

Note: if the program is exited without the result window having been stored, then this is saved automatically under ”~lastrun.dpr” .

10.2.3 Display of measurement details ("Show Details")

If "Show Details" is clicked then various details of the measurement are shown. In this case when the menu is opened in the result window the measurement must be selected by clicking the relevant line in the extreme left-hand column.

10.2.4 Editing entries ("Edit...")

The measurement selected by clicking the relevant line in the extreme left-hand column can be called up by clicking "Edit..." so that alterations to the entries can be made.

10.2.5 Deleting a line ("Delete")

The measurement selected by clicking the relevant line in the extreme left-hand column can be deleted by clicking "Delete"" or pressing the DELETE KEY. Several lines can be marked and deleted at the same time by clicking the individual lines while keeping the CONTROL KEY held down. To delete a whole measuring series its first and last lines are selected and then the SHIFT KEY + left-hand mouse key are pressed.

10.2.6 Data transmission (”Forward Results“)

By means of this function the contact angle of the marked measurement is transmitted to the SE-window for the determination of surface energy and appears there in the last line. If several contact angles are selected (with SWITCH KEY + left-hand mouse key or CONTROL + left-hand mouse key), then the mean value is calculated and than transmitted to the SE-window together with the liquid parameters. The entry is made in the last line of the SE-window.

10.2.7 Updating the mean value (”Update mean value“)

Under ”Option“ (Kap. 10.2.8) an automatic adaptation of the mean value to changes in the measurement value list can be switched on.

If this option is switched off, the actualization can take place manually by selecting ”Update...“. In order to open the required context menu put the mouse pointer on the **average** value line to be actualized; a click on a measurement value line will not activate this function.

10.2.8 Test parameters to be shown/mean value options ("Option")

Under "Option..." various test parameters and characteristics can be selected for presentation in the result window.

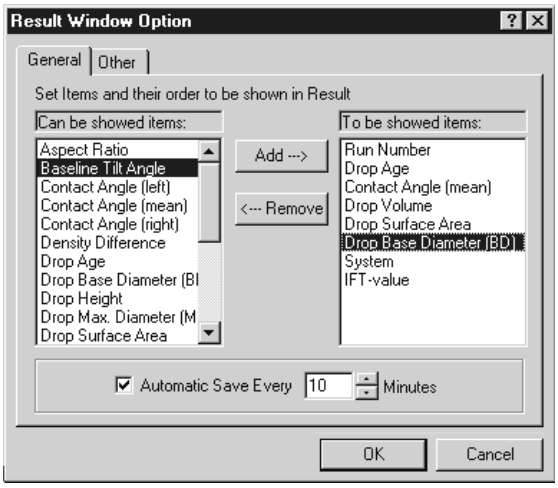


Fig. 10.4: Selection of the values to be shown in the Result-Window

10.2.8.1 Values to be shown (“general“)

In the left-hand column all the possible parameters are listed which can be selected by clicking with the left-hand mouse key and then, by clicking "Add" patch panel, selected for display in the result window. The selected parameters appear in the right-hand column of the dialog window: in a similar way parameters in the left-hand column which are not to appear in the result window can be removed by marking them and clicking the "Remove" patch panel.

The selection only changes the view options in the result window, the data storage for a measurement is independent from the selected items.

Note: the determination of the surface tension and of absolute drop dimensions is only possible with the evaluation methods "Fit" and "Tangent 1".

Note: A contact angle is also calculated for pendant drops, but surface energy values can only be obtained with sessile drop measurements!

The intervals at which the results table is to be stored automatically can be entered in this dialog window.

10.2.8.2 Type of mean value formation/Outliers (“Statistics”)

You can choose between the arithmetic mean value and the median for calculating the mean value.

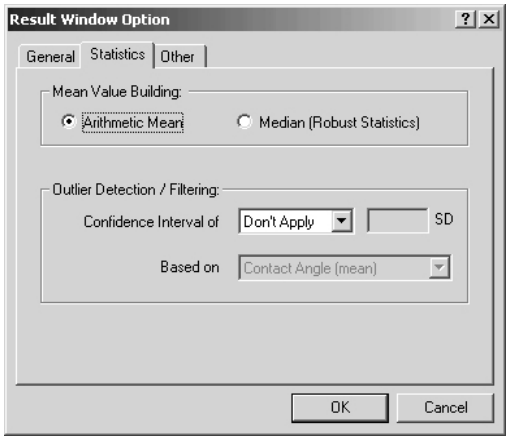


Fig. 10.5: Tab sheet “Statistics” for choosing the mean value formation

For a normal distribution of the measured values the arithmetic mean provides the most reliable mean value. If outliers are suspected, or if distribution is asymmetric, the median should be chosen instead.

In the “Outlier Detection / Filtering” field you can conceal measured values that lie outside a tolerance range that can be defined.

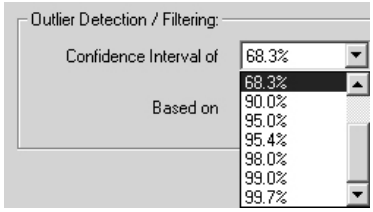


Fig. 10.6: Filtering out outliers

Under “Based on” you can define to which of the quantities the given tolerance range is to apply.

Mean value options (“Other“)

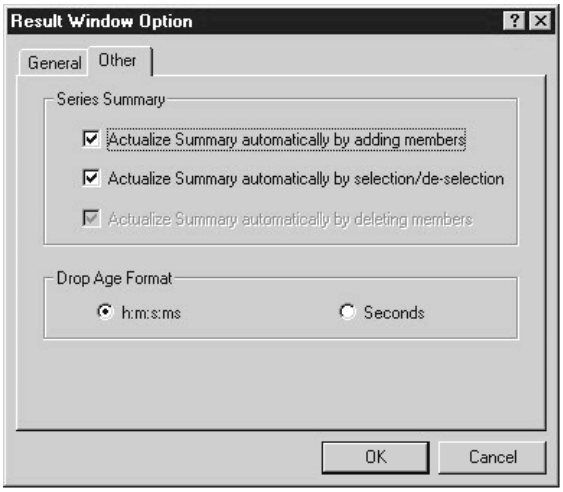


Fig. 10.7: Options for average value calculations in the result window

In this panel you can decide if changes in the measurement value table will lead to an automatic update of the mean value. A tick in the upper line (”Actualize... by adding members“) means that the mean values will be actualized automatically when new data is added to a measurement series. ”Actualize... by selection/de-selection“ will lead to an automatic recalculation of the mean value if measurement lines in the Result Window table are selected/deselected. The option ”Actualize Summary automatically by deleting members“ is always selected and is therefore inactive in this state of the DSA1-Software.

In the lower part a decision between two drop age indication formats can be made: ”h:m:s:ms“ (hours:minutes:seconds:milliseconds) or just ”Seconds“.

10.2.9 Graphical presentation ("Plot")

By calling up "Plot" a plot window is called up automatically. All data of the last measurement series are shown graphically in the plot window. The further processing and other possibilities of using this window are described below.

10.2.10 "Print“

Printout of the results in tabular form is carried out by the command "Print".

10.3 Graphical presentation

The results of the running series of measurements can be shown in graphical form in the plot window. The plot window is opened by "File | Open Plot Window" or by pressing the icon  . The measuring data from the result window are shown graphically in the opened window. For the presentation of a stored series of measurements from a previous test these must first be loaded into the opened result window (see previous section, "Open..."). When the plot window is opened the accompanying graph appears.

The plot window is continuously updated, i.e. it always shows the current data from the result window.

By operating the right-hand mouse key in the diagram window the context menu of the plot window appears with several possibilities of adjusting the settings ().

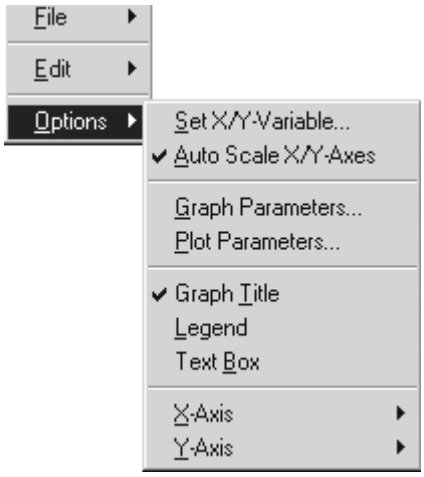


Fig. 10.8: Context menu in plot window

10.3.1 File options ("File")

Under "File" the graph can be stored as "enhanced Metafile". In this way the diagram created is accessible to word processing programs (from MS Word 97) for further processing. In addition there is the possibility of printing out the graph by "File | Print". The appropriate printer settings are selected by "File | Printer Setup" and "File | Printer Options".

10.3.2 Editing a graph ("Edit")

The graph can be copied into the buffer memory with "Edit". This submenu contains two submenus for selection, "Copy Graph" and "Copy Page"; "Copy Graph" is used for preference.

10.3.3 Settings ("Option")

For producing the required graph a range of settings can be carried out in the submenu "Option". Depending on the menu entry either a submenu or a dialog window is opened or the particular option activated/deactivated (indicated by a tick).

Function	Description
Set X/Y-Variable	Selection of the test parameters to be shown as X and Y values
Auto Scale X/Y	Option for automatic axis scaling (activation indicated by tick at the left-hand side).
Graph Para-meters	Dialog window for moving and scaling the graph and settings the colors.
Plot Parameters	Dialog window for setting the measurement graphs and presentation of the measuring points.
Graph Title	Option for entering a title (activation indicated by tick at the left-hand side).
Legend	Option for entering legends for the measuring points shown (activation indicated by tick at the left-hand side).
Text Box	Option for showing a text box (activation indicated by tick at the left-hand side).
X-Axis	Option for showing the title (Title) and scale numbers (Labels) of the X-axis.
Y-Axis	Option for showing the title (Title) and scale numbers (Labels) of the Y-axis.

Table 10.1: Settings for the graphical presentation of the measurements under "Option"

The dialog windows listed in Table 10.1 are explained below.

"Set X/Y-Variables..."

From the list shown in the dialog window (Fig. 10.9) the required parameters for the X and Y variables of the graph are selected by clicking and then pressing the patch panels "As X" or "As Y". (e.g. X: Run number, Y: IFT-value)

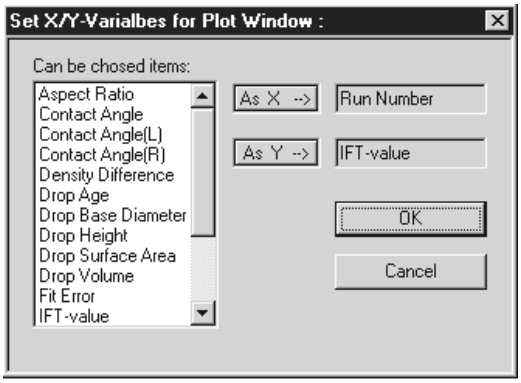


Fig. 10.9: Dialog window "Set X/Y-Variables..."

"Graph Parameters..."

If "Graph Parameters..." is selected the following dialog window opens:

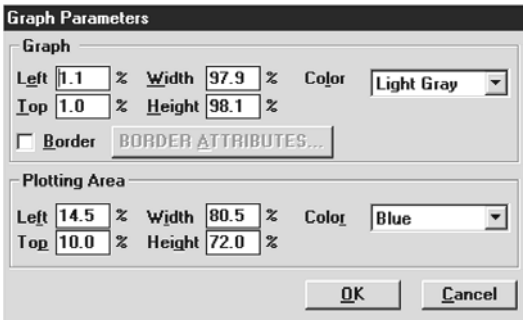


Fig. 10.10: Dialog window "Plot Parameters"

In the upper block of the dialog window "Graph Parameters..." the position and size of the graph including all markings within the plot window is set by entering the position of the left upper corner of the graph ("Left" and "Top") and its width and height ("Width" and "Height"). In addition, by clicking the switch "Border" a frame for the graph can be produced, whose properties (line thickness and color) can be selected under "BORDER ATTRIBUTES...". The background color of the plot window is selected under "Color".

In the lower block the position and size of the plotting range is set in the plot window analogous to "Graph". The color of the graph and the background for the graph can also be selected here.

"Plot Parameters..."

If "Plot Parameters..." is selected the following dialog window opens:

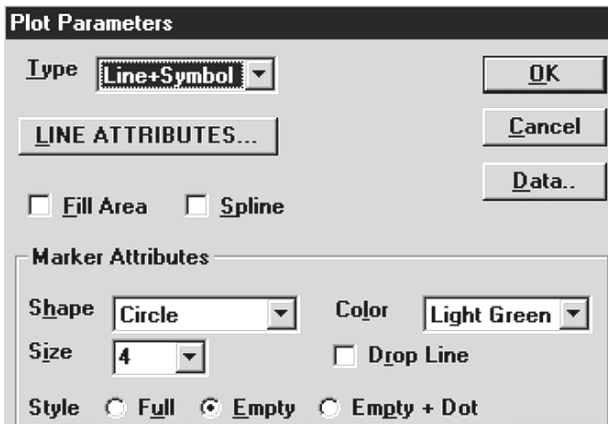


Fig. 10.11: Dialog window "Plot Parameters"

In this dialog window entries about the type of graph can be made. This can be shown by individual symbols, additional lines connecting the measuring points or by horizontal or vertical bars. The settings are accepted in the "Type" field.

Under "**LINE ATTRIBUTES...**" the dialog window "Line Parameters" (Fig. 10.13) is opened, in which settings for the color, type and thickness of the connecting lines between the measuring points can be made.

If "**Spline**" is activated (shown by a tick), then a curve passing through the middle of the measuring points will be produced. Bars can be filled by activating "Fill Area".

In the lower half of the dialog window the **type, color and size** of the symbols can be set.

Under "**Data**" a table opens in which those X/Y-values are listed which are shown graphically in the plot window. These pairs of values can be exported for further processing in other programs by pressing "Copy" in this window. If the DSA program is installed on a computer which works with decimal points, (e.g. 3.124) then exporting works perfectly.

In those cases in which a comma is used is a decimal separator (e.g. in Germany), the comma (",") must be converted into a full stop (".") before processing can be carried out, e.g. with Excel. This is important as spreadsheet programs can then recognize the data in the buffer memory as numbers and not as text. This is checked under Windows at "Start | Settings | Control panel | Regional settings" on the file card "Currency" where the decimal separator can be found and, if necessary, altered. This alteration only becomes active when Windows is rebooted.

10.3.4 Alterations to the graph

For altering the axis markings and scaling, the legends, the title and the graphical presentation the particular position in the current graph is selected by a double-click with the left-hand mouse key and altered in the dialog window which appears.

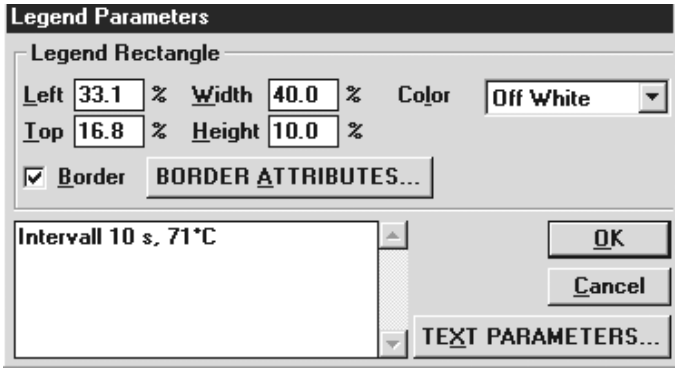


Fig. 10.12: Dialog window for setting the legend parameters

In lower left-hand corner of the dialog window "Legend Parameters" the text should be entered which is to appear in the legend beside the measuring point symbol. The fields beside the entries "Left" and "Top" determine the position of the legend within the graph. This can be moved by clicking the legend in the plot window with the left-hand mouse key and holding the mouse key down. The fields beside the entries "Width" and "Height" give the dimensions of the legend field. The values to be entered are the shares of the whole diagram in per cent.

If the legend is to be surrounded by a frame then the box beside the entry "Border" should be selected until a tick appears. In this case if "BORDER ATTRIBUTES..." is selected the dialog window "Line Parameters" opens in which the color, style and width of the legend border can be selected (see Fig. 10.13).

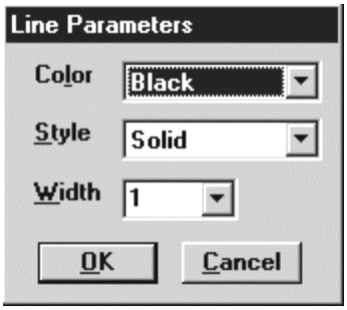


Fig. 10.13: Dialog window "Line Parameters"

The color of the legend background can be selected in the field beside the entry "Color". If "TEXT PARAMETERS..." is selected the dialog window "Text Parameters" opens, in which font, style and size can be altered (see Fig. 10.14).

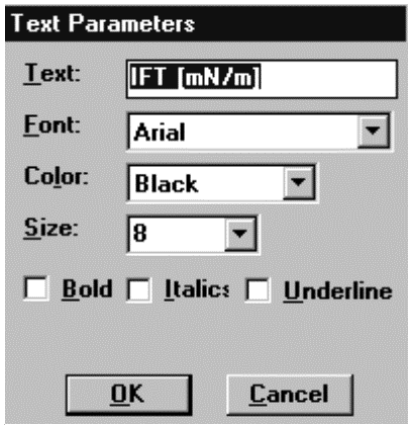


Fig. 10.14:Dialog window "Text Parameters"

The dialog window "Text Parameters" also appears if the title or the axis markings of the graph are double-clicked. The font, style and size can also be altered here.

If the vertical axis is selected by double-click with the left-hand mouse key then the dialog window "Vertical Axis" opens, in which the axis scale, the divisions in ticks, their positioning as well as the introduction of grid lines can be carried out. In this dialog window logarithmic scaling can also be selected.

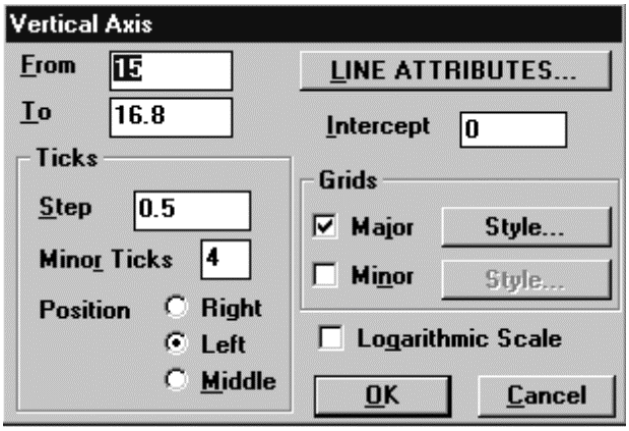


Fig. 10.15: Dialog window "Vertical Axis"

The selection of "LINE ATTRIBUTES.." opens the dialog window "Line Parameters" (see Fig. 10.13), in which color, style and width of the vertical axis can be set. The selection of "Style..." opens the same menu for setting the major and minor grid lines, depending on which grid lines have been activated (indicated by a tick).

In the field "Intercept" the intercept with the X-axis should be entered. If this falls outside the selected area of the Y-axis then the X-axis will vanish from the plot window.

The parameter settings for the (horizontal) X-axis are carried out in the same manner.

11 Calculation of the surface free energy

Eight calculation methods are available in the DSA program for calculating the surface energy. In all these methods the surface energy of a solid is determined from a series of contact angles. In addition to the contact angle the surface tension of the liquid used and its polar and dispersive components must be known. This measuring system can be used for determining the surface tension according to the pendant drop method. In a data base available in the DSA program the polar, dispersive, acidic, basic and hydrogen bondage components of the surface tension of a range of liquids are listed.
A calculations of surface free energies are not only possible for current measurements, but also for stored measurements. With the help of the menu items "Add" and "Edit" (see chapter 11.2.5) you can even calculate surface free energies from literature contact angle data of liquid drops on solids.

Surface energies can only be calculated from contact angle data of sessile drops. Pendant drops provide contact angle data which are not useful for surface energy calculations. A data transfer from the Result Window to the Surface Energy Calculation (SEC) Window is not possible for this reason.

11.1 Calculation methods

In the following table the methods used together with their characteristics and requirements are listed.

Method	Description	Requirements
Acid-Base	Surface energy of a solid divided into a dispersive, a positive and a negative polar component	3 pairs of values SFT-Theta polar component = 0 (e.g. diiodomethane) Acidic = basic component (e.g. water) Acidic ≠ basic component and ≠ 0 (e.g. formamide)
Equation of state	Surface energy of a solid	2 pairs of values SFT-Theta
Fowkes	Surface energy of a solid divided into dispersive and polar (non-dispersive) components.	- 2 pairs of values SFT-Theta (σ^p,σ^d known) - 1 SFT consists only of a dispersive component (σ^{nd} = 0)

Method	Description	Requirements
Fowkes (Extended)	Surface energy of a solid divided into disperse and polar (non-disperse) fractions. In the polar fraction the fraction of the surface energy resulting from hydrogen bondings is also given separately.	3 pairs of values SFT-Theta (σp,σd known) 1 SFT consists only of a disperse fraction ($\sigma^{nd} = 0$) 2 SFT with polar fraction, at least one of which with known hydrogen bonding fraction
Owen-Wendt-Rabel-Kaelble	Surface energy of a solid divided into dispersive and polar components.	- 2 pairs of values SFT-Theta (σ^p,σ^d known)
Schultz-1 / 2	- Determination for high-energy surfaces. - Division into dispersive and polar components	3 pairs of values IFT – Theta (σp,σd known) Normally: water/n-alkane
Wu	Surface energy of a solid divided into dispersive and polar components.	- 2 pairs of values SFT-Theta (σ^p,σ^d known) - SFT contains polar component ($\sigma^p \neq 0$)
Zisman	Critical surface tension of a solid.	- 2 pairs of values SFT-Theta (SFT known)

Table 11.1: Methods of calculating the surface energy

A detailed explanation of the various calculation methods is given at the end of this manual. As a procedure for determining the surface energy the following program items should be gone through in sequence and carried out if necessary.

11.2 Procedure for surface energy calculation

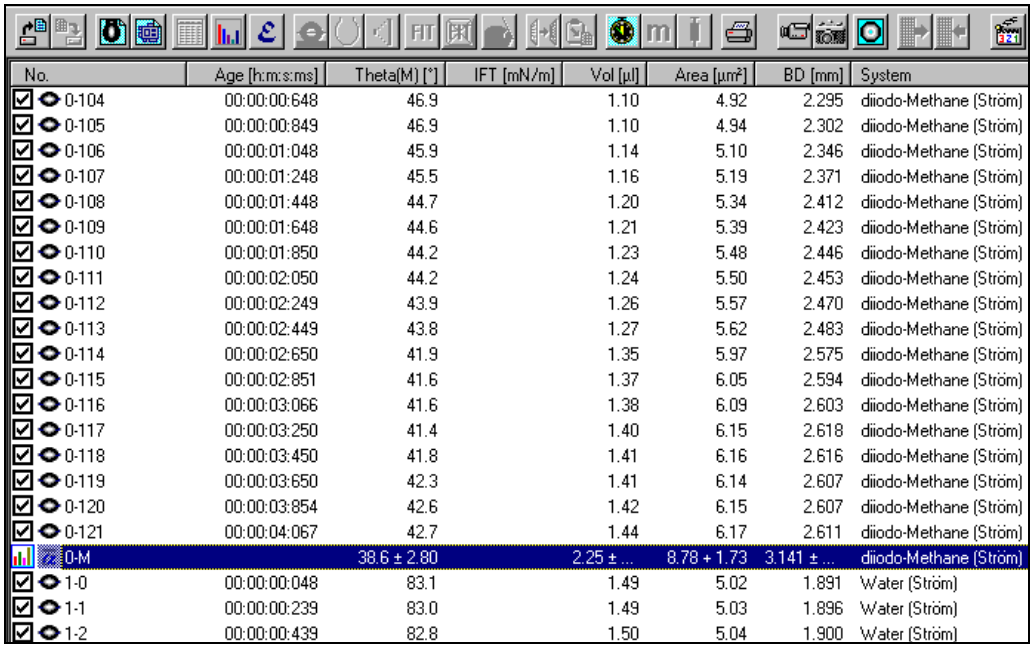
The calculation of the surface energy is carried out in the surface energy calculation (SE-) window, which is opened by selecting "File | Surface Energy Calculation.." or by pressing the icon  .

11.2.1 Assembling the measuring data for the SE calculation

When the "Surface Energy Calculation" is opened an empty sheet appears first on the screen; The "SE window" contains no measuring data. This must be assembled from the opened Result window, i.e. either from measuring data that has just been determined or from previously stored and called-up results. Contact angle data from several measurements can also be assembled by calling up several Results windows one after the other, but this only makes sense when all the measurements have been carried out on one and the same sample.

Transferring the measuring data from the Result window is carried out as follows:

First open the Result window in which the measuring data for the surface energy calculation is contained.



No.	Age [h:m:s:ms]	Theta(M) [°]	IFT [mN/m]	Vol [µl]	Area [µm²]	BD [mm]	System
0-104	00:00:00:648	46.9		1.10	4.92	2.295	diiodo-Methane (Ström)
0-105	00:00:00:849	46.9		1.10	4.94	2.302	diiodo-Methane (Ström)
0-106	00:00:01:048	45.9		1.14	5.10	2.346	diiodo-Methane (Ström)
0-107	00:00:01:248	45.5		1.16	5.19	2.371	diiodo-Methane (Ström)
0-108	00:00:01:448	44.7		1.20	5.34	2.412	diiodo-Methane (Ström)
0-109	00:00:01:648	44.6		1.21	5.39	2.423	diiodo-Methane (Ström)
0-110	00:00:01:850	44.2		1.23	5.48	2.446	diiodo-Methane (Ström)
0-111	00:00:02:050	44.2		1.24	5.50	2.453	diiodo-Methane (Ström)
0-112	00:00:02:249	43.9		1.26	5.57	2.470	diiodo-Methane (Ström)
0-113	00:00:02:449	43.8		1.27	5.62	2.483	diiodo-Methane (Ström)
0-114	00:00:02:650	41.9		1.35	5.97	2.575	diiodo-Methane (Ström)
0-115	00:00:02:851	41.6		1.37	6.05	2.594	diiodo-Methane (Ström)
0-116	00:00:03:066	41.6		1.38	6.09	2.603	diiodo-Methane (Ström)
0-117	00:00:03:250	41.4		1.40	6.15	2.618	diiodo-Methane (Ström)
0-118	00:00:03:450	41.8		1.41	6.16	2.616	diiodo-Methane (Ström)
0-119	00:00:03:650	42.3		1.41	6.14	2.607	diiodo-Methane (Ström)
0-120	00:00:03:854	42.6		1.42	6.15	2.607	diiodo-Methane (Ström)
0-121	00:00:04:067	42.7		1.44	6.17	2.611	diiodo-Methane (Ström)
0-M		38.6 ± 2.80		2.25 ± ...	8.78 + 1.73	3.141 ± ...	diiodo-Methane (Ström)
1-0	00:00:00:048	83.1		1.49	5.02	1.891	Water (Ström)
1-1	00:00:00:239	83.0		1.49	5.03	1.896	Water (Ström)
1-2	00:00:00:439	82.8		1.50	5.04	1.900	Water (Ström)

Fig. 11.1: Opened Result window

No individual data from a measuring series can be transferred, but only the mean data that appear in the Result window at the end of each series of measurements (see marked measured value line in Fig. 11.1. Use the right-hand mouse key to click on the line containing the mean values that you require. The following context menu appears:

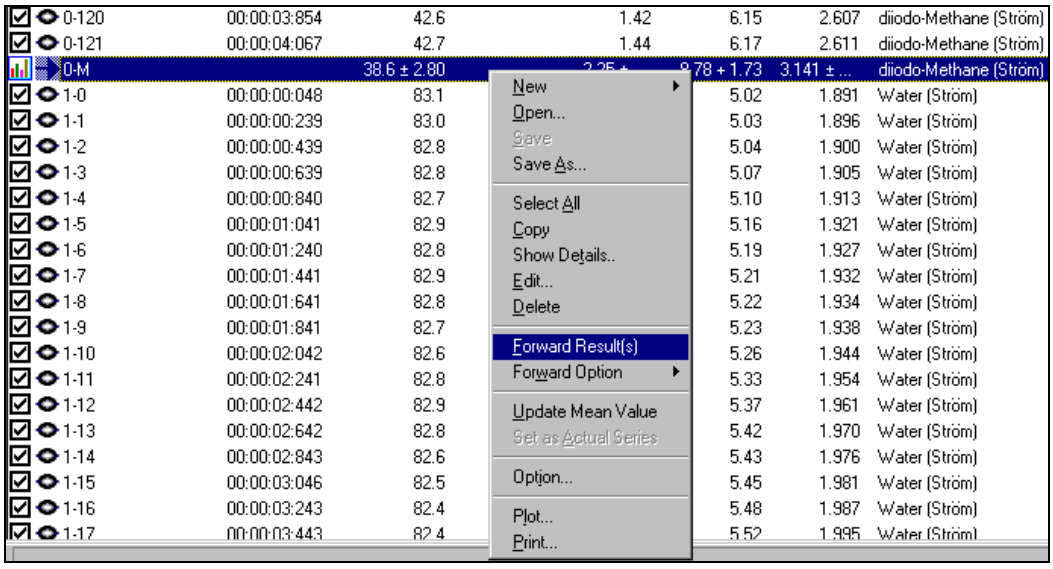


Fig. 11.2: Context menu of a mean value line in the "Result window"

For the transfer to the SE window you require the two menu commands "Forward Result(s)" and "Forward Option". If the command "Forward Result(s)" is selected then the selected mean value line will be transferred to the SE window. If the "Forward Option" menu command is selected then the following submenu appears:

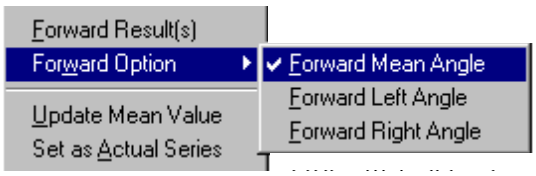


Fig. 11.3: Submenu "Forward Option"

Here you can choose whether the contact angle measured on the left-hand side ("Left Angle") or on the right-hand side ("Right Angle") of the drop is to be transferred or the mean value of both of them ("Mean Angle").

You can transfer as many contact angle values as you like from the current Result window or from successive Result windows to the "SE window". However, only a single measured value can be used for each particular drop liquid. If you try to transfer a measured value for a particular drop liquid for which data is already present in the "SE window" then a query will appear asking whether the old contact angle data for the liquid is to be retained or overwritten.

11.2.2 Selection of the calculation method (“Method”)

The selection of the calculation method to be used can be made under “Method” in the main menu of the SE window. A selection can be made from the list of methods with a mouse-click.

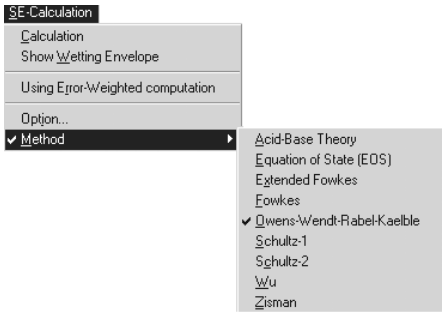


Fig. 11.4: Selection of the calculation method

The currently selected method for calculating the surface energy appears automatically in the title line when the SE window is opened, even if no results are present. If the calculation method is changed while the SE window is opened then this alteration will be automatically updated in the title line.

11.2.3 Carrying out the surface energy calculation (“Calculation”)

If the information contained in the table is sufficient for carrying out the calculation according to the selected method then the “Calculation” function is active.

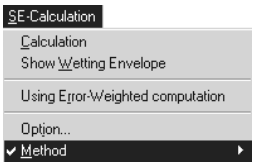


Fig. 11.5: Menu "SE calculation"

The calculation of the surface energy according to the previously defined method (“Method”) is started by clicking on the menu command “Calculation”. The result of the calculation appears in a separate window:

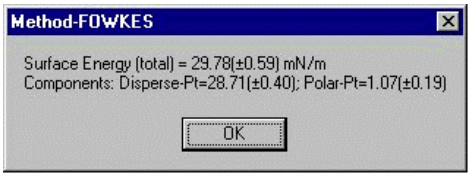


Fig. 11.6: Result of a surface energy calculation (according to Fowkes as an example)

With most calculation methods the result is shown as a graph which also appears automatically on the screen when the “Calculation” command is triggered. The calculated result does not appear on the screen in the data list in the SE window but is included when the current SE window is printed out.

The quantities shown depend on the method chosen for the calculation of the surface energy. In each case the calculated value for the surface tension (“Surface Energy (total)”) will be outputted; an estimation of the error resulting from the inaccuracy of the contact angle

measurements is also included. If the selected calculation method is based on splitting the surface tension into several components then their calculated values will also be shown.

Prediction of the wettability (“Show wetting envelope”)

Predictions about the wettability of a solid with various liquids can be made from the contact angle data of a measurement. The wettability can be read off from a special type of presentation of the calculation result, the so-called “Wetting Envelope”. The “Wetting Envelope” is always calculated according to the method that has been used for the surface energy calculation. The graph showing the “Wetting Envelope” will be displayed as soon as the corresponding menu command is carried out (see Fig. 11.5).

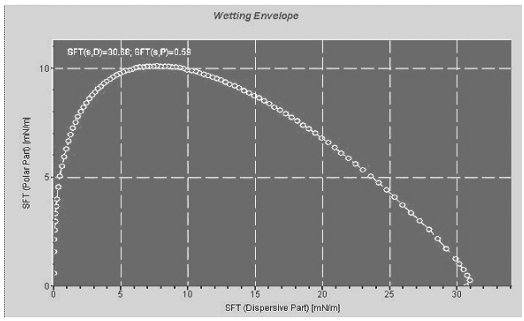


Fig. 11.7: “Wetting Envelope” for a surface energy calculation (here: according to Fowkes)

The “Wetting Envelope” shows a plot of the disperse fraction of the surface tension against the polar fraction. The wettability of the solid can be read off from the area limited by the curve and the X-axis. All liquids, whose polar and disperse fraction of the surface energy lie within this area, will completely wet this solid.

11.2.4 File management for SE-Calculations

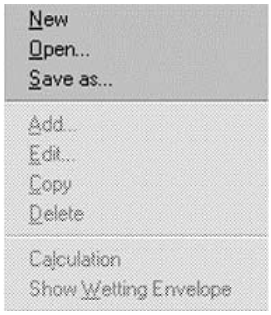


Fig. 11.8: Part of the context menu in the SE-Window

Renewing the SE-windows ("New")

Renewing the SE-window is carried out by selecting "New“. The SE-window is then available for new entries and a new calculation. All previously existing entries are deleted. The operator is first asked whether the data are to be stored.

Opening an SE-file ("Open...")

By clicking "Open..." an SE-file which has already been stored can be opened and processed in the SE-window. Files for calculating the surface energy in the DSA program have the extension "*.SED“ .

Storing SE-files ("Save...")

The files created are stored by selecting "Save..." and then entering the required file name and path. Files for calculating the surface energy in the DSA program normally have the extension "*.SED“. Other data formats can be selected in the field beside "Data type“. A click on the patch panel beside this field opens a window with the available data formats, which can be selected by mouse click.

11.2.5 Editing the SE-Window (”Add...“, ”Edit...“, ”Copy“, ”Delete“)

Fig. 11.9: Part of the context menu in the SE-Window

Adding measurements ("Add...")

Various possibilities exist for adding data required for the calculation. An adequate number of measurement data sets must be entered. By clicking "Add..." substance data and measured values can be added manually. They appear as additional lines beneath the last existing line. The values are entered in the dialog window shown in Fig. 11.10.

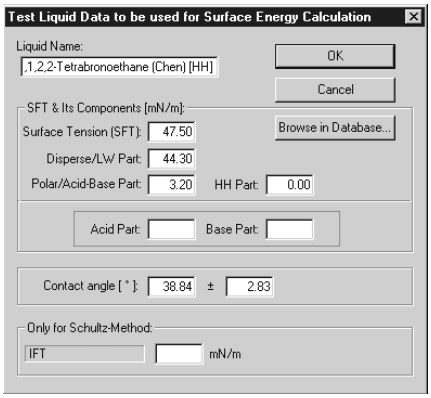


Fig. 11.10: Dialog window for altering the liquid data in the SE-window

Within the dialog window the data base belonging to the DSA program can be called up ("Look up in Data Base") . A double-click with the mouse key on a line in the data base window

transfers the values automatically to the SE-window. It may also be necessary to enter values from the literature here.

If the contact angle for a substance to be entered is not known then initially all the known values for that substance can be entered. The measurement of the missing contact angle is carried out and the value obtained is automatically transferred to the last line of the SE-window. In the same way a selection can be made in the result window and the transfer to the SE-window carried out by means of "Forward Results". If several data are to be transferred from the result window then the mean value is formed and appears as the last line in the SE-window.

Editing a measurement line ("Edit")

For processing and altering data which have been entered the left-hand column of the line to be altered must first be clicked to mark it. By operating the right-hand mouse key a menu appears with the program item "Edit" which can be activated. By clicking "Edit" the menu shown in Fig. 11.10 opens with the values which have already been entered. By appropriate selection with the left-hand mouse key the required alteration or new entry can be carried out here.

Deleting a measurement line ("Delete")

To remove a measurement line the left-hand field in the line is clicked to mark it. It is also possible to mark several lines by keeping the CONTROL KEY pressed when the individual lines are clicked. For deleting a complete series of measurements the first and last measurements are selected and then the SHIFT KEY + left-hand mouse key are pressed. By operating the right-hand mouse key a menu appears in which the function "Delete" can be activated. Selecting "Delete" removes the lines. The DELETE KEY can also be pressed.

11.2.6 Measurement options ("Option...")

Fig. 11.11: Part of the context menu in the SE-Window

In the table additional information or parameters, which e.g. are only required for the particular calculation method can be shown. In the same way data which are not required can be removed from the whole table. Under "Option..." the following menu opens:

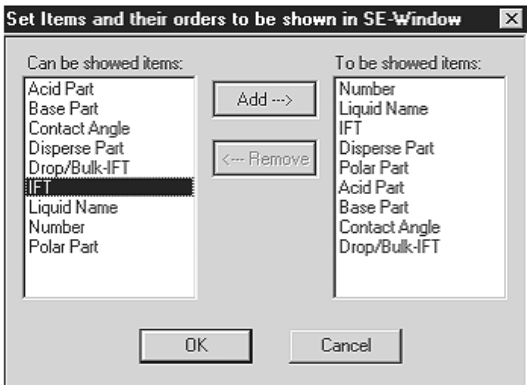


Fig. 11.12: Menu for selection of parameters to be shown in the SE-window.

In the following table the individual parameters and their names are explained. The term used in the SE-window is given in brackets.

Name	Parameter	Explanation
Acid Part (AcidPt)	Acidic component	Acidic component of the polar surface tension
Base Part (BasePt)	Basic component	Basic component of the polar surface tension
Contact Angle (Theta)	Contact angle	Contact angle of the drop liquid in the three-phase point
Disperse Part (DispersePt)	Disperse component	Dispersive component of the surface tension
Drop/Bulk-IFT	Interfacial tension	Liquid-liquid interfacial tension between drop phase and surrounding phase (Schultz method)
IFT	Surface tension	Surface tension Sum of σ^p and σ^d
Liquid Name	Name of liquid	Name of the substance to be investigated
Number	Line number	Line number in SE-window
Polar Part (PolarPt)	Polar component	Polar component of the surface tension

Table 11.2: Parameters used for calculating the surface energy

11.2.7 Select of calculation method ("Method")

The selection of the calculation method to be used is carried out under "Method". A selection can be made from the methods listed in Table 10.1 (at the start of this chapter) by mouse click.

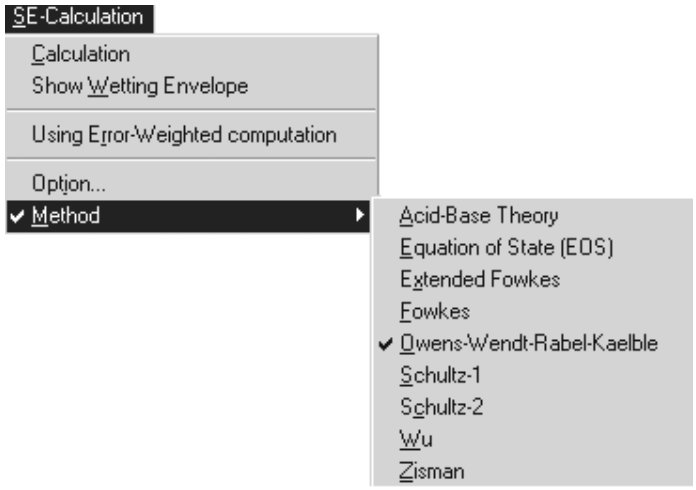


Fig. 11.13: Selection of the calculation method

11.2.8 "Print..."

Printout on the connected printer is started with "Print".

12 Data bases

In the DSA program two data bases are available, which contain specific substance values relating to interfacial tension for a range of substance systems. The entries are listed in tabular form and can be extended or altered by the operator as required. The substance data contained in the data bases are used for the calculation of surface energy, but can also be used as a reference book, e.g. for providing density values in the measurement of the interfacial tension. The data bases are opened in the pull-down menu "File". To open the data base containing values of the surface tension of liquids the entry "Open Liquid Data Base (SFT)" is selected. If the entry "Open Liquid Data Base (IFT)" is selected a data base is opened which contains values for the interfacial tension between two liquids.

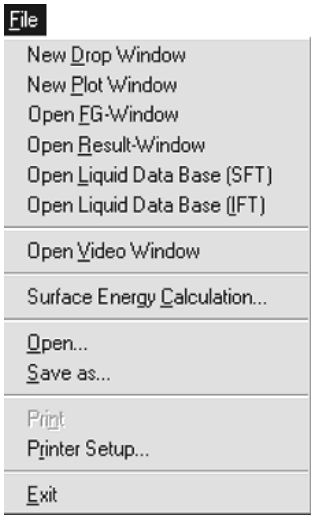
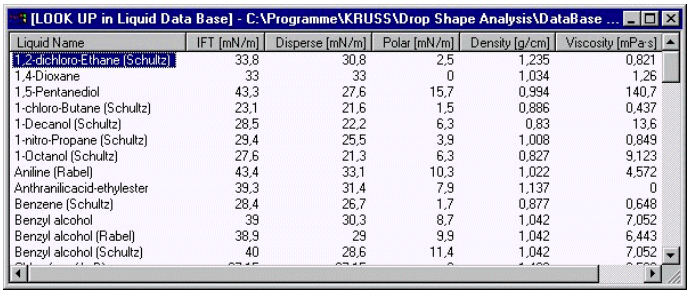


Fig. 12.1: Pull-down menu "File“ for opening the data bases

12.1 Data base for surface tension

The data base "Data Base (SFT)" contains data which are mainly concerned with the surface tension of liquids against air and has the basic arrangement shown in the following illustration.



Liquid Name	IFT [mN/m]	Disperse [mN/m]	Polar [mN/m]	Density [g/cm]	Viscosity [mPa·s]
1,2-dichloro-Ethane (Schultz)	33,8	30,8	2,5	1,235	0,821
1,4-Dioxane	33	33	0	1,034	1,26
1,5-Pentanediol	43,3	27,6	15,7	0,994	140,7
1-chloro-Butane (Schultz)	23,1	21,6	1,5	0,886	0,437
1-Decanol (Schultz)	28,5	22,2	6,3	0,83	13,6
1-nitro-Propane (Schultz)	29,4	25,5	3,9	1,008	0,849
1-Octanol (Schultz)	27,6	21,3	6,3	0,827	9,123
Aniline (Rabel)	43,4	33,1	10,3	1,022	4,572
Anthranilicacid-ethylester	39,3	31,4	7,9	1,137	0
Benzene (Schultz)	28,4	26,7	1,7	0,877	0,648
Benzyl alcohol	39	30,3	8,7	1,042	7,052
Benzyl alcohol (Rabel)	38,9	29	9,9	1,042	6,443
Benzyl alcohol (Schultz)	40	28,6	11,4	1,042	7,052

Fig. 12.2: Basic arrangement of "Data Base(SFT)“

By operating the right-hand mouse key in "Data Base Window" a context menu opens, in which the data base processing can be carried out.

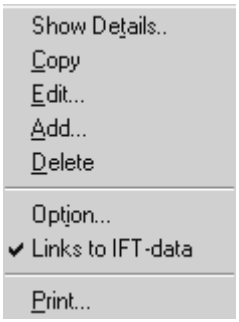


Fig. 12.3: Menu in data base window

"Show Details..." This menu item can only be activated if the context menu has been opened by operating the right-hand mouse key **after** a data line of the data base has been selected by operating the left-hand mouse key in the left-hand field of the required line.

By selecting "Show Details..." a dialog window is opened whose basic arrangement can be seen in Fig. 12.4, in which, however, the entries for the particular substance system cannot be altered. In order to alter entries the menu item "Edit.."‘ must be selected; this is described below. "Show Details..." can also be called up by a double-click on the first column of the required line.

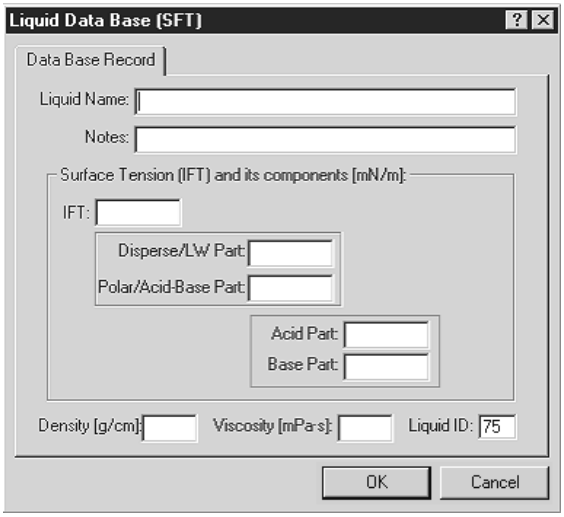


Fig. 12.4: Dialog window for displaying and entering substance data in the data base

Processing a data base entry ("Edit...") For processing and altering data contained in the data base the line to be altered must again first be selected by operating the left-hand mouse key at the left-hand margin of the line to mark it. Operating the right-hand mouse key shows the context menu (Fig. 12.3) with the program item "Edit..." which can be activated. By clicking "Edit..." the menu shown in Fig. 12.4 appears with the values which have already been entered. By appropriate selection with the left-hand mouse key the required alteration or new entry can be carried out here.

Adding substance systems ("Add...") By clicking "Add..." in the context menu the data of a further substance system can be entered into the data base. These data are entered in the opened dialog window (Fig. 12.4). The menu item "Add..." can always be activated in the data base menu (Fig. 12.3).

Deleting a data base entry ("Delete") To remove a measurement line the left-hand field in the line is selected with the left-hand mouse key to mark it. By operating the right-hand mouse key the context menu appears (Fig. 12.3) in which the "Delete" function can be activated. By selection of "Delete" the line to be removed will be deleted after a safety query. Pressing the DELETE KEY when a line has already been marked also deletes that particular entry.

It is also possible to delete several lines at the same time. This is done by clicking the individual lines while keeping the CONTROL KEY pressed down. For deleting a complete series of measurements the first and last measurements are selected and then the SHIFT KEY + left-hand mouse key are pressed.

Measurement options ("Option...") In the data base window various information or parameters can be shown. Data which are not required can also be removed from the display. Under "Option..." in the context menu the following dialog window opens in which this can be carried out:

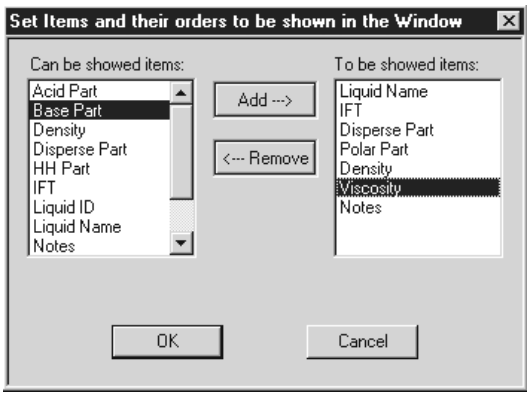


Fig. 12.4: Dialog window for selection of parameters to be shown

The removal of individual data from the display does not mean that these data are deleted, i.e. these data can be redisplayed in the data base display when required. In the following table the individual parameters and their names are explained. The terms used in the data base window are given in brackets.

Parameter	Name	Explanation
Acid component	Acid Part (AcidPt)	Acidic component of the surface tension
Basic component	Base Part (BasePt)	Basic component of the surface tension
Liquid density	Density	At 20°C, if not otherwise mentioned
Disperse component	Disperse Part (DispersePt)	Disperse component of the surface tension
Surface tension	IFT	Surface tension against air
Substance name	Liquid Name	Name of the substance to be investigated
Remarks	Notes	e.g. different temperature / text field
Polar component	Polar Part (PolarPt)	Polar component of the surface tension
Viscosity	Viscosity	At 25°C, if not otherwise mentioned

Table 12.1: Parameters available in the data base

"Links to IFT-data" By selecting this program item the connection to the interfacial tension data base for exchange and access of data between the data bases will be made; this is indicated by a tick to the left of the entry. In each case the first liquid (liquid 1) of the substance pair entered in the IFT data base will receive the identification number (ID) under which this substance can be found in the SFT data base.

Data base printout ("Print...") The data base can be printed out if a printer is connected via the menu entry "Print..." A Windows dialog window appears for the selection of the printer or printer options.

12.2 Data base for interfacial tension

The data base "Data Base (IFT)" contains data which are mainly concerned with the interfacial tension between two liquids and has the basic arrangement as shown in Fig. 12.4.

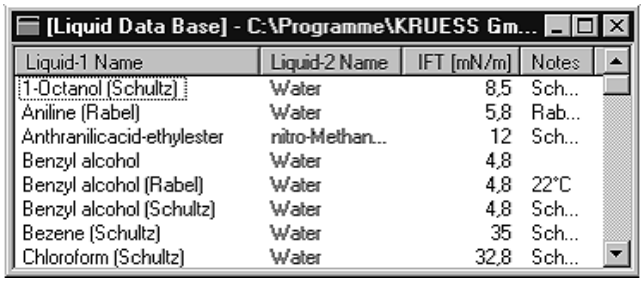


Fig. 12.5: Basic arrangement of "Data Base (IFT)"

By operating the right-hand mouse key in the data base window the context menu opens in which the data base processing can be carried out.

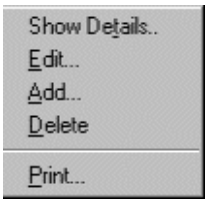


Fig. 12.6: Context menu in data base window (IFT)

Display of details ("Show Details...")

This menu item can only be activated if the context menu has been opened by operating the right-hand mouse key **after** a data line of the data base has been selected by operating the left-hand mouse key in the left-hand field of the required line.

By selecting "Show Details..." a dialog window is opened whose basic arrangement can be seen in Fig. 12.7, in which, however, the entries for the particular liquid system cannot be altered. In order to alter entries the menu item "Edit..." must be selected; this is described below. The identification number of Liquid 1 in the SFT data base appears beside the entry "Liquid-1 ID".

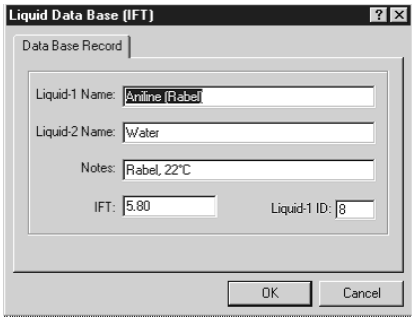


Fig. 12.7: Dialog window for display and entry of substance data in the data base

"Show Details..." can also be called up by a double-click on the first column of the required line.

Processing a measurement line ("Edit...") For processing and altering data which have already been entered the line to be altered must again first be selected by operating the

left-hand mouse key at the left-hand margin of the line to mark it. Operating the right-hand mouse key shows the context menu (Fig. 12.6) with the program item "Edit..." which can be activated. By clicking "Edit.." the menu shown in Fig. 12.7 appears with the values which have already been entered. By appropriate selection with the left-hand mouse key the required alteration or new entry can be carried out here.

Adding substance systems ("Add...") By clicking "Add..." in the context menu the data of a further substance system can be entered into the data base. These data are entered in the opened dialog window (Fig. 12.7). The menu item "Add..." can always be activated in the data base menu (Fig. 12.6).

Deleting a measurement line ("Delete") To remove a measurement line the left-hand field in the line is selected with the left-hand mouse key to mark it. By operating the right-hand mouse key the context menu appears (Fig. 12.6) in which the "Delete" function can be activated. By selection of "Delete" the line to be removed will be deleted after a safety query. Pressing the DELETE KEY when a line has already been marked also deletes that particular entry.

It is also possible to delete several lines at the same time. This is done by clicking the individual lines while keeping the CONTROL KEY pressed down. For deleting a complete series of measurements the first and last measurements are selected and then the SHIFT KEY + left-hand mouse key are pressed.

Data base printout ("Print...") The data base can be printed out if a printer is connected via the menu entry "Print...". A Windows dialog window appears for the selection of the printer or printer options.

Adding new measurements

From the IFT or contact angle measurements shown in the result window the values for interfacial tension or contact angle can be transferred to the SE-window by selecting "Forward Results" in the context menu of the result window (right-hand mouse click). If several measurements have been marked then the mean value is formed and this is transferred. The transferred value is inserted in the last line of the SE-window.

13 Automatic measurement with the TrackerMan

The DSA program allows the automatic recording and evaluation of a sequence of drop images at previously defined time intervals. In order to use this program function the FG-window must first be opened ("File | Open FG-Window"). In the pull-down menu "Option" the entry "TrackerMan" appears.

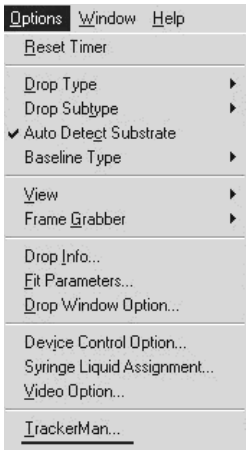


Fig. 13.1: Pull-down menu "Option"

Select "Option | TrackerMan...". The "TrackerMan" menu appears.

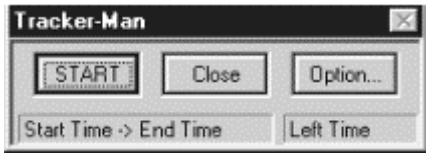


Fig. 13.2: Tracker manager

By selecting "Option.." in this menu the option menu shown in Fig. 13.1 is opened, in which various entries concerning the recording sequence can be made.

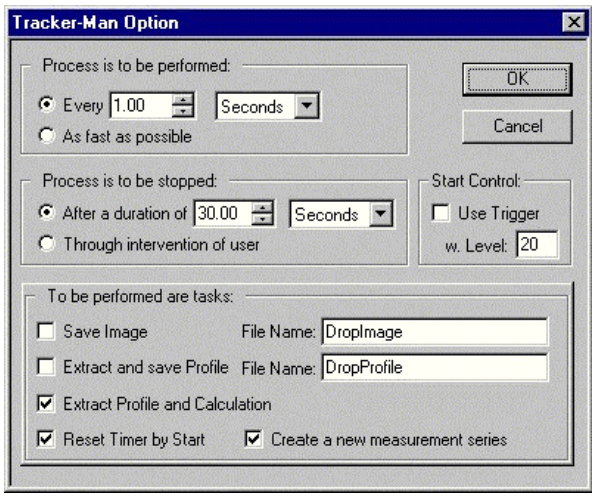


Fig. 13.3: Option menu of the Tracker manager

Before a new TrackerMan test run the settings in this menu should always be checked. Frames divide the option menu into three blocks: these are explained below.

13.1 "Process is to be performed"

In this block the time intervals between the measurements are defined. This is done by entering the time interval between two recordings beside the entry "Every" as a whole number with the appropriate units of time (seconds, minutes). By selecting "As fast as possible" the next measurement will be started as soon as the previous one has finished.

13.2 "Process to be stopped"

In this block the conditions for ending the series of measurements are defined. The length of time for the automatic measurement must be entered as a whole number with the appropriate units of time (seconds, minutes) beside the entry "After a duration of".

By selection of "Through intervention of user" manual termination can be defined.

13.3 "Start control"

With the function "Start Control" the TrackerMan can be started automatically when the drop is being dispensed. For this purpose a trigger function is used which can be activated by setting a tick at "Use Trigger". When this function is active, the TrackerMan "waits" for relevant changes in the video image before the measurement gets started.

Under "Level" the sensitiveness of the trigger function is set. A value of 20 is recommended for most cases; it should be decreased if the image contrast gets poor. The trigger level in this card does not correspond with that used for video recordings.

13.4 "To be performed are tasks"

Not only the intervals and length of a series of measurements can be defined but also tasks to be carried out for each measurement can be defined. This is done by selecting the processes to be carried out after a drop has been recorded in the lower block. The selection or deselection of the individual processes is carried out with the left-hand mouse key in patch panel beside the particular entry. A process will only be carried out if a tick is visible in the corresponding patch panel.

In Table 13.1the processes which are possible and their explanations are summarised.

Process	Explanation
"Save Image"	Stores the particular drop image.
"Extract and save profile"	Extracts and stores the digitized drop profile under a name to be entered.
"Extract Profile and Calculation"	For automatic evaluation and determination of interfacial tension or contact angle.
"Reset Timer by Start"	Real-time counter to start the measuring series at "0".

Table 13.1: Possible processes for automatic measurement with the TrackerMan

Confirm the entries in the option menu by clicking "OK". The measurement will start when "Start" in the "TrackerMan" menu is clicked. During the measurement the starting and finished times appear in the lower line together with the remaining test time.

14 Recording and evaluating video sequences

The TrackerMan described in Section 13 is used for the automatic creation and evaluation of single images and is suitable for observing drop alterations over a longer period of time. For the microanalysis of the changes occurring during rapid drop formation you also have the possibility of recording a video as the drop is produced and then evaluating it. The necessary **settings** (Section 14.1) for recording a video are made in the menu "Options"→"Video Option...". **Recording** a video (Section 14.2) is always carried out from the active FG window (in the live mode!). For the **evaluation** (Section 14.3) the recorded video must first be stored; the video window is then opened and the video file which has been created is then loaded.

14.1 Settings for recording and evaluating a video

Several settings must be made before you can start recording a drop video. The necessary entries are made under the menu item "Options"→"Video Option...". The entries are made on four cards. The "Recording parameters" card (Section 14.1.1) is used for setting the recording duration and the image frequency; you can also define whether the video is to be loaded into the working memory or stored directly onto the hard disk. Under "Recording start" (Section 14.1.2) the conditions for starting a recording are entered. On the third card "Play and Calculation" (Section 14.1.3) the portion of the video to be evaluated is entered. In the fourth car "REC-Adv. Timing" there are three further parameters available for programming the recording of a video sequence in several steps.

14.1.1 Recording parameters

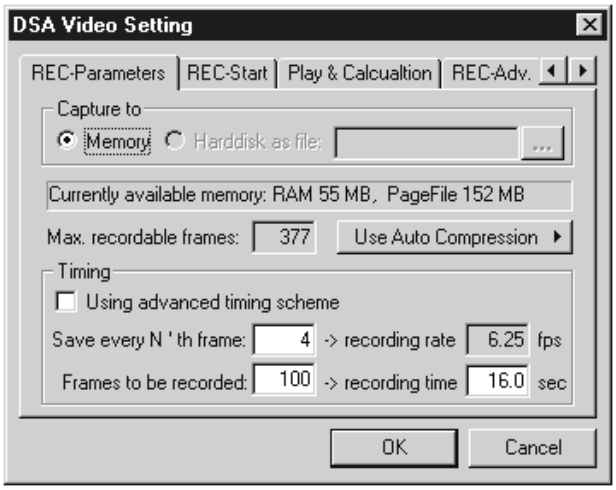


Fig. 14.1: Parameters for recording a video

"Capture to Memory/Hard disk as file": This option has not yet been implemented. It is intended that a decision can be made here as to whether the video sequence to be recorded is to be stored completely in the working memory before it is saved ("Memory") or whether the hard disk is to be used as the storage medium during data recording.

"Currently available memory": If "Memory" is selected then this line will contain working memory which is currently available.

"Max. recordable frames": The program calculates the maximum number of single images (frames) which can be recorded in the video from the available memory space and the memory required per frame.

"Compression": The button 

presents you with three choices: leave the video uncompressed (Use no compression); compress it (Use compression); or to allow the computer to decide automatically whether compression should be used or not (Use auto compression). When an image is compressed areas of the image with the same grey level are collected together so that each individual image pixel must not be stored separately. Compressed images therefore require less memory space and, if **"Use compression"** is selected, a larger number of storable images will appear under "Max. recordable frames". The disadvantage is that on-line compression requires a rapid computer; if the computer speed is not quick enough errors may occur in recording the video. If **"Use auto compression"** is selected then the software checks whether the capacity of computer is sufficient for compression; compression is only carried out if the computer speed is quick enough.

"Using advanced timing scheme": The settings in the "Timing" field of this card described below only apply to the programming of a video sequence in one recording step. In the fourth "Recording Parameters" card (Section 14.1.4) you can instead program the video sequence in several steps with different single frame frequencies and recording times. If you wish to use this option you must click on the option "Using advanced timing scheme". The input lines for the timing are then deactivated in this card.

"Save every N'th frame": Normally a frame is transferred from the camera to the computer every 40ms. If not every transferred image is to be recorded and stored then you can enter here the frequency with which the transferred images are to be recorded. If 1 is entered then each frame will be recorded, with 10 every tenth frame, etc. The recording speed (**"recording rate"**), i.e. the number of images recorded per second is given by the selected entry.

"Frames to be recorded" / "recording time!" In these two fields the total number of frames to be recorded for the video is entered as well as the total recording time. This two fields are linked with each other, i.e. when the required number of frames is entered in the left-hand field the calculated recording time appears in the right-hand field; if the required time is entered in the right-hand field then the calculated number of frames will appear in the left-hand field. Please note that the number of frames must not exceed the "Max. recordable frames".

14.1.2 Starting conditions ("Recording start")

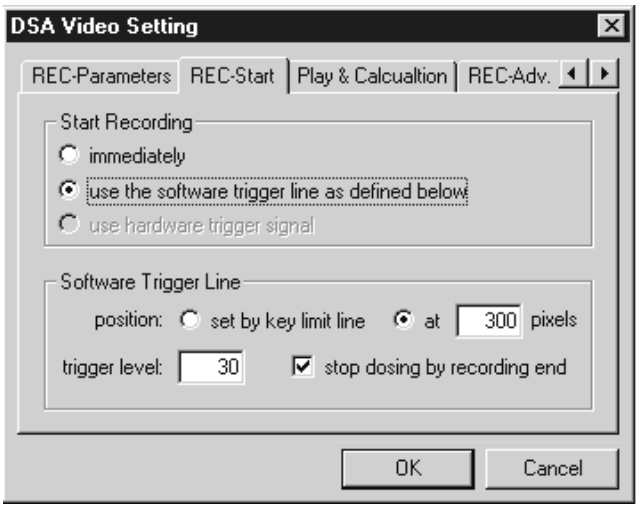


Fig. 14.2: Entering the starting conditions for video recording

The way in which the recording is to be triggered is defined on this card. On the one hand you can start recording directly by operating the recording start button (see Section 14.2.1). You can also define a starting condition ("Trigger"). Recording does not start immediately after the recording symbol button is operated, but only when an alteration to the grey level occurs in a previously determined section of the image marked by a line ("Trigger line") (see Section 14.2.2).

"Start recording": A decision can be made here as to whether the recording is to start immediately after the recording symbol is operated ("immediately") or whether the start should be determined by a set trigger line ("software trigger line"). The possibility of triggering the start by an external signal ("hardware trigger signal") has not yet been implemented.

"Position" The height of the trigger line is defined here. If **"Set by key limit line"** is selected then the recording will be started when an alteration occurs at the lowest of the three lines in the FG window (see Section 14.2.3). If you choose **"at...pixels"** then the start line depends on the entered pixel level; the displayed trigger line will be ignored. The value to be entered represents the Y-co-ordinate of the Windows standard co-ordinate system; increasing the number corresponds to a downwards movement. If the mouse is moved in the FG window the X and Y-co-ordinates are shown in the status line so that it is easy to estimate the necessary pixel value.

"Trigger level" The minimum alteration to the grey level value in the trigger region which will start the recording is defined here. The value of 30 shown in Fig. 14.2 does not normally need to be altered.

"Stop dosing by recording end" If the further drop formation process is not of interest after the video recording is finished then drop dosing can be stopped automatically at the end of the video. Dosing will then be stopped no matter which dosing mode has been selected.

14.1.3 Playback and evaluation options ("Play and Calculation")

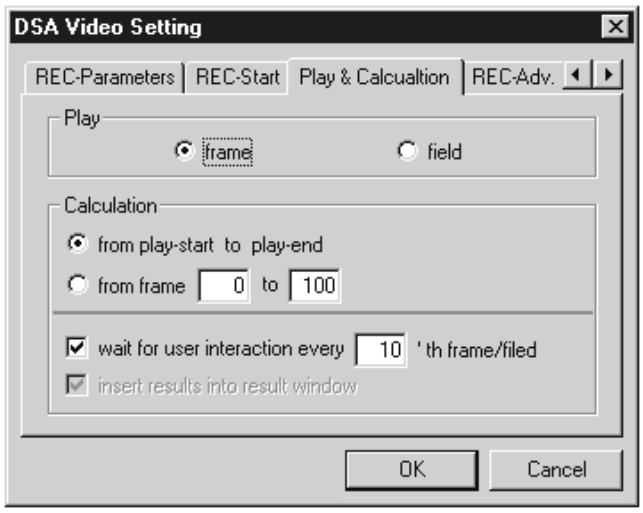


Fig. 14.3: Options for playing back and evaluating a video

Settings are made on this card which concern the section of a video visible in the video window which is to be evaluated.

"Play": Under "Play" you can choose between the settings **"Frame"** and **"Field"**. A transferred complete image (frame) consists of two single images produced in sequence (fields) in each of which only every second image pixel is shown; the image pixels are shifted so that the two superimposed fields form the complete image. Whether the frames or the individual fields are played back and evaluated depends on the speed at which the drop is produced. With a high drop formation speed we recommend the choice of "Fields"; because the number of images per time interval is doubled and also because the time-displaced creation of the two fields could result in the frames being less sharp. At slow speeds you should choose evaluation by frames because the sharpness of the image then does not depend so much on the drop production speed and the evaluation is more accurate because of the doubled number of pixels.

"Calculation": The section of the video to be evaluated is defined here. With **"play start to play end"** when calculation is started with the calculation symbol button (see Section 14.3.2) the video will be evaluated up to the end, not automatically from the first frame onwards but only from the position at which the sliding controller finds itself in the video window (see Section 14.3.1). Under "from frame ... to ..." you can define a section to be evaluated if the whole video is not to be calculated. The first and last frame of the required section are entered in the boxes. The necessary frame numbers can be obtained from the video image in the video window (see Section 14.3.1).

"Wait for user interaction every ...th frame/filed" You may not want to evaluate a complete section, but rather several single sections. In this case you have the possibility of interrupting the evaluation by means of a dialog in which you can decide which of the following frames are to be evaluated and which are to be skipped. The number entered here applies to both the number of frames to be evaluated between the interruptions and to the number of frames which are to be skipped. This is described in more detail in Section 0.

14.1.4 Programming several recording steps ("REC-Adv. Timing")

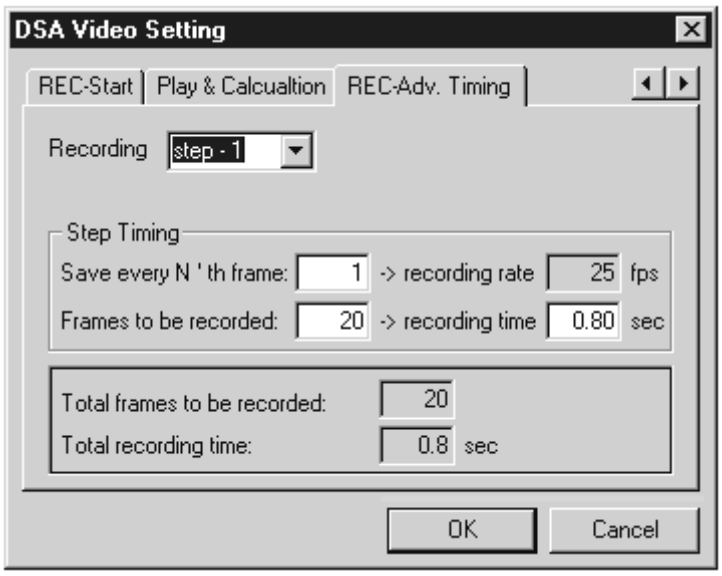


Fig. 14.4: Options for recording a video sequence in several steps

In the fourth recording and evaluation parameters card ("REC-Adv. Timing") you have the possibility of programming a video sequence in several steps. You can divide the sequence into a maximum of five steps. The parameters have the same meaning as in programming a single step in the "Recording Parameter" card (see Section 14.1.1).

By using the arrow key

you can program the steps one after the other; the sequence during programming does not matter. The total number of frames to be recorded ("Total frames to be recorded") and the total recording time for all steps ("Total recording time") is shown in the lower section of the card.

"OK" accepts the entries in this card; "Cancel" rejects the alterations.

14.2 Recording a video

When all the settings have been made and the image settings have been optimized you can start to record a video. Drop formation is first started and the video recording is switched on at the required moment. In principle you have the choice between starting the video manually or automatically with the aid of the trigger line. Recording can only start when the **FG window** is opened as the active window and the camera has been switched to the **live mode**.

When the video recording is finished the video cannot be evaluated immediately; it must first be stored and then loaded with the video window open. This is why a window for storing the video appears automatically when the recording is finished. Storage and selection of the required directory are the same as in other standard Windows programs. The video is stored in AVI-format; this format can be played back and processed in most standard video programs.

If you decide that the video is not to be stored immediately it will remain in the working memory. When the DSA1 program is exited a safety inquiry will be made as to whether the video is to be stored or not. If it is not stored at this point then the video will no longer be available once the program has been exited.

14.2.1 Manual start of video recording

If the setting "immediately" has been selected under "Options"→"Video options..."→"Recording start" then recording will start as soon as the recording button is operated

You must therefore wait for the right moment for starting the recording.

14.2.2 Starting the video recording by means of the trigger function

The recording can be started automatically by using a trigger line. The option "Use the software trigger line..." must be selected under "Options"→"Video options..."→"Recording start". After the start button is operated recording will only begin when an alteration in the grey level occurs at the height of the set trigger line or the set pixel level.

14.2.3 Positioning the trigger line/pixel level

In the frame grabber image there is a total of three horizontal lines. The two upper lines are intended for determining the scale; the lowest line is the trigger line and it appears in a different color from the scale lines. It is not possible to position the scale lines below the trigger line; this means that confusion is almost impossible.

In the FG window the mouse pointer turns into cross hairs. The line is moved to the required height by placing the cross hairs on the line and moving it with the left-hand mouse key pressed down. Alternatively the line can be moved upwards and downwards by using the cursor keys. The cursor left/right keys can also be used to define the **slope** of the line. A double-click on the trigger line returns it to the **horizontal position**.

If the setting "at...pixels" is chosen under "Options"→"Video options..."→"Recording start" then the set trigger line will be ignored at the start; the start then depends on the alteration to the grey level value set under **pixel height**. The current position of the mouse pointer in the FG window is shown in the status line, this means that it is easy to read off which mouse position corresponds to which pixel height (Y-value).

14.2.4 Stopping the video recording

During the video recording it is possible that you may realize that you do not require the full set length of the video recording or that the video is unusable. In this case you can interrupt the recording with the stop button

The video recorded up to this point will not be rejected, but can be stored in exactly the same way as a normally recorded video; the storage window opens automatically.

14.3 Playing back and evaluating a video

Playing back and evaluating a video is only possible in the video window. The video window can be opened either with the help of the

button or via the menu "File"→ "Open Video Window". A video which has just been recorded and is still in the working memory cannot be played back or evaluated immediately but must first be stored and then loaded with the video window open. Loading is carried out via the menu item "File"→"Open".
Control of the recording, playback and evaluation functions is carried out via the

buttons, which have the following functions (from left to right):

Playback – Stop - Calculate.

The recording function (not shown in the above illustration) should only be used in the FG window.

14.3.1 Video playback

Fig. 14.5: The video window

The video loaded in the video window can be played back with the play button. Parts of the video can be observed by moving the sliding controller (see Fig. 14.5) to the required video starting position. The playback then begins at the sliding controller position. The stop button can be used to stop the playback prematurely. If you want to move backwards or forwards

image by image this is done by using the arrow buttons to the left and right of the sliding controller.

In the upper part of the window the information belonging to the video is shown: the first line shows the number of frames (SO), the total time and the time of the recording (date and time); in the second line you will find information belonging to the individual image: frame number, drop age (Time) and image size in Kbytes (Size). If the option "Field" has been selected under "Options"→"Video options..."→"Play and calculation" then the two fields will be shown in sequence for each frame; the frame numbers then receive the suffix o (odd) and e (even).

14.3.2 Evaluating a video

Before the calculation of a video image can take place the baseline must first be determined manually; an automatic determination in the video image is not possible. The baseline should be the same for the whole video and therefore does not need to be calculated for each individual image. When the

button is operated the calculation of the video is carried out according to the conditions set down under "Options"→"Video options..."→"Play and calculation". The default method is automatically used for calculating the contact angle. Altering the "Default method" is carried out in the menu "Options"→"Drop window option..."→ "Contact angle measurement". The results of the calculation are automatically transferred to the result window.

Just like the recording and playback, the calculation can also be interrupted with the stop button. Values calculated up to this point are retained.

Evaluating the complete video

If the complete video is to be calculated, then the option "play-start to play-end" is selected in the menu "Options"→"Video options..."→"Play and calculation". When the calculation button is operated a contact angle calculation is carried out for each individual image (either frame-wise or field-wise, depending on the setting). The calculation does not start with the first image, but with the image currently shown in the video window. If the calculation is to start at the first image then the sliding controller must be moved fully to the left.

Evaluating a section

If the option "from frame...to..." has been selected under "Options"→"Video options..."→"Play and calculation" then the calculation is carried out automatically for each individual frame (or field) in the chosen section. In this case the position of the sliding controller in the video window is irrelevant.

Controlling the evaluation

If neither the complete video nor all the frames/fields in a section are to be calculated then you have the possibility of controlling the calculation via a dialog. This function can be found under "Options"→"Video options..."→"Play and calculation" in the field "Wait for user interaction every ...th frame/filed". If this option is selected then after the calculation button is operated the calculation will start either from the sliding controller position (if "play start to play end" has been selected) or with the first frame to be calculated (if "from frame...to..." has been selected). However, the following dialog window opens before the calculation starts:

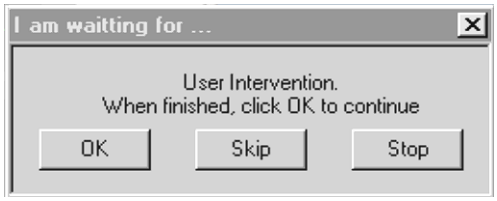


Fig. 14.6: Dialog window for user invention during a video calculation

If the first value is to be calculated then this is confirmed with "OK". The number of frames entered under "every ...th frame/filed" will then be calculated. The inquiry will then be repeated. With "Skip" the same number of frames will be skipped without any calculations being carried out. This process is repeated until the end of the video is reached, or the frame number entered under "from Frame...to..." is reached. "Stop" interrupts the process; all values calculated up to this point are retained

15 Basic settings

Under "Drop Window Option“ in the pull-down menu "Options“ in the menu bar (“Option“→“Drop Window Option“) a range of basic settings for all the evaluation methods of the program can be carried out.

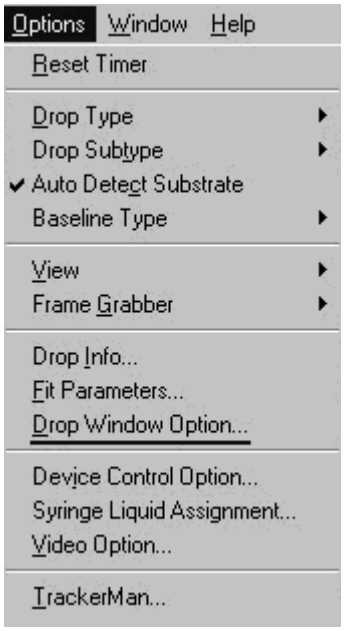


Fig. 15.1: Pull-down menu under "Option“

Settings for the following menu items are described:

- Drop Window Option... (sect.15.1)
- Frame Grabber (Selection of and settings for frame grabber and camera); sect. 15.2,
- Fit Parameters (settings for the Young-Laplace Fit (= “Sessile Drop Fitting“); sect.15.3.

15.1 Settings in the drop window

After selecting the menu item "drop window" a menu with 5 tab sheets appears. The tab sheets will be describe in the following subsections

15.1.1 "General"

Fig. 15.2: Tab-Sheet "Drop Window Option"→"General"

"Stretch Image..." Width and height of the video image will be scaled in a way that the image will always completely appear inside the "Frame Grabber Window".The image could look distorted, depending on the x- and y scaling factors: This has no effect on the following image analysis.
If this function is deactivated the image will be shown in 1:1 scale. The image must then be rolled up with the help of the scroll bars. The image appears undistorted. In this case the contact angle can already be estimated from the image.

"Check Drop Type automatically" If the automatic drop type check is activated the program uses the recorded drop image to determine the sub-type of the drop automatically, i.e. in which direction the drop is pointing. The setting of the general drop type (pendant or sessile) must be carried out manually in each case. For rapid serial measurements this option should be deactivated as it takes a lot of time.

"Show extracted profile" When this option is activated, the drop profile according to the grey level analysis will be shown. The degree of correspondence of the line with the visible drop image is a measure for the image quality and the suitability of the frame gabber settings.

"Show Fitted Profile" The activation of this option makes sense for checking the extent to which a sensible profile adaptation has been carried out. For numerical reasons, e.g. if an unfavorable starting value is selected, the fitted profile may vary from the actual contour line. For rapid serial measurements this option should be deactivated as it takes a lot of time.

"Update profiles..." When this option is activated all shown profiles will be updated for every single image of a video being recorded or played. This option should only be used when you are equipped with a fast and powerful computer.

"Warning for Loss..." In this setting a warning is given that images could be lost if they are not stored. An automatic possibility of storing the image is offered.

15.1.2 "Contact Angle Measurement"

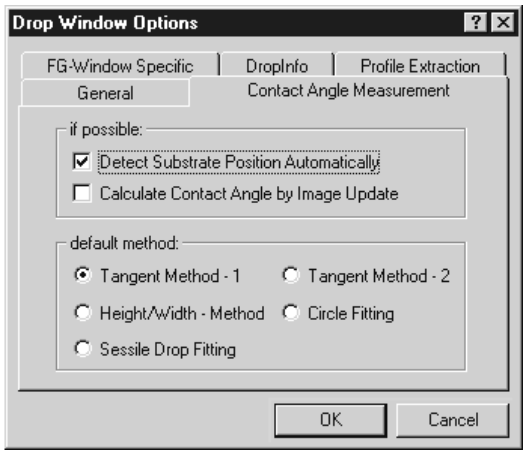


Fig. 15.3: Tab sheet "Drop Window Option"→"Contact Angle Measurement"

Automatic baseline determination ("Detect Substrate Position Automatically")
This setting is used for the automatic determination of the position of the baseline for contact angle measurement. If this setting is active the position of the baseline is determined automatically when a new image is loaded in the FG-window. The determination of the position can also be carried out by the selection of "Option | Substrate" detection activated and triggered and is suitable for contact angles $< 90°$. For contact angles $> 90°$ the baseline must be determined manually.

"Calculate Contact Angle by Image Update"If this option is activated then the contact angle is determined automatically by the default method when an image is imported into the window. This applies both to snaps (on-line measurement) and bitmaps (evaluation of stored images).

Preset evaluation method ("Default Method") The selection of the evaluation method for determining the contact angle is carried out here; this is used as the basic setting for the calculation. If in a measurement a different method is to be used to determine the contact angle then this must be carried out by direct selection of the required method after an image has been loaded into the window (drop window or FG-window) and the baseline has been determined. The selection and contact angle determination are carried out by "Profile | Contact Angle Using ..." and selecting the required method.

15.1.3 "FG-Window Specific"

Fig. 15.4: Tab sheet "Drop Window Option"→"FG-Window-Specific"

"Update Window´s Image Automatically" If automatic update of the contents of the FG-window has been selected then during serial measurements with the Trackerman the old contents of the window will be overwritten by the new recording which will then be visible in the FG-window. For rapid serial measurements this option should be deactivated as it takes a lot of time. The display of the current image can be carried out at any time manually "Image | Update Image".

"Tracking Contact Angle by Live Image" This allows the contact angle to be determined on-line. If this option is activated the contact angle is continually determined by switching on "Live-Image" (F5). The contact angle will be redetermined as rapidly as the computer and measuring board allow. This function can be terminated during the measurement by "Snap" (F7).

"Set image ROI" (Region of interest) The setting of the region of interest is described in detail in section 9.1.2.

15.1.4 "DropInfo"

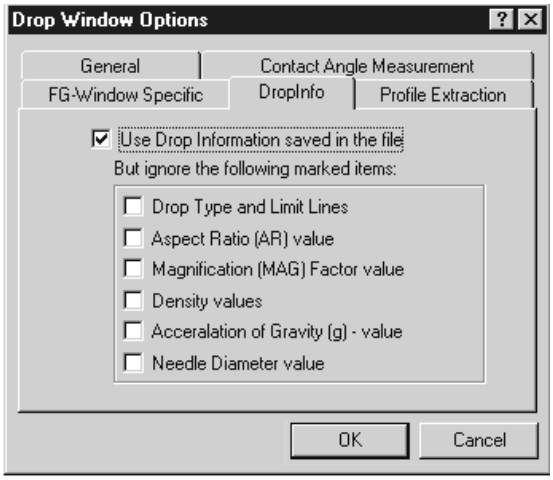


Fig. 15.5: Tab sheet "Drop Window Option"→"DropInfo"

Individual information about drop images and the particular measurement can be specified under "DropInfo"; this information is ignored when the images are stored and thus must be re-entered when the images are downloaded again.

15.1.5 "Profile Extraction"

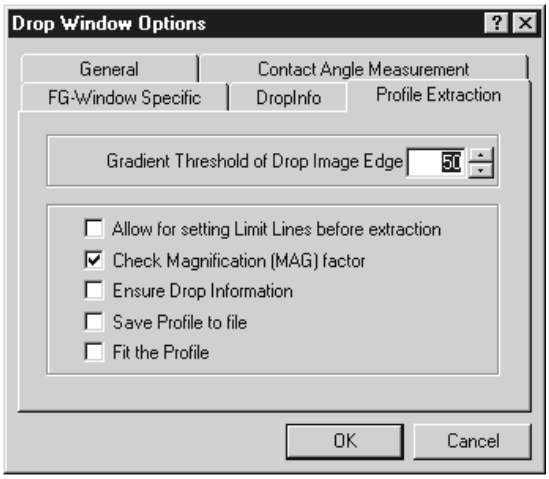


Fig. 15.6: Tab sheet "Drop Window Option"→"Profile Extraction"

Under "Profile Extraction" various functions can be determined which can also be carried out automatically from a digitized drop image during a profile determination. By "Profile"→"Extraction" or by clicking the icon the following functions will be carried out if they have been activated in the dialog window "Profile Extraction".

"Gradient threshold of drop image edge" Here the relative limit for the recognition of the drop edge can be selected in grey levels. The default value is 50. It may be possible to make alterations to obtain a better recognition of the contour. For example, a lower value can lead to the better recognition of low-contrast images. A higher value can reduce interference from lower grey levels.

"Allow for setting Lines before Extraction" If this option is activated then before the profile extraction is carried out a query is made with the information that it is now possible to reset the limit lines in the drop image.

"Check Mag Factor" If this option is activated then an automatic check and calculation of the magnification factor (MAG) is carried out before profile extraction using the limit lines set at the needle.

"Ensure Drop Information" If this option is activated then before profile extraction the dialog window "DropInfo" appears so that the entries can be checked and altered if necessary.

"Save Profile" After the determination of the contour (digitising) a menu for storing the contour is called up. The contour can be stored here under a name given by the operator and is then available for subsequent analyses.

"Fit Profile" An automatic fit of the Young-Laplace equation will be made to the contour line after the contour has been determined (profile extraction) if "Profile"→ "Extraction" or the icon FIT has been selected.

15.2 Frame grabber selection and setting

Under the menu item "Options"→"Frame Grabber" the following a pull down menu with two menu items opens:

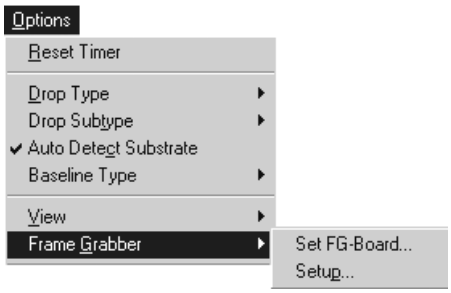


Fig. 15.7: Menu item "Frame Grabber"

Various parameters for setting the video frame grabber board, which also affect the image quality, are carried out in a dialog window which is opened by "FG"→"Setup...". Most setting only have to be altered when the hardware (frame grabber, camera) is changed. Exceptions are settings for brightness and contrast of the frame grabber to optimise the image quality (see section 7).

15.2.1 Selection of the frame grabber

When the frame grabber card is exchanged for a different model the new card has to be selected under the menu item „Set FG-Board“.

Fig. 15.8:Selection of the frame grabber under „Set FG-Board“

After the selection has been made and confirmed with „OK“, the DSA1 program must be restarted before the new frame grabber can be worked with.

15.2.2 Settings for Falcon frame grabber

Under the menu item „Setup...“ a menu with three tab sheets (respectively four with the Matrox board) opens.

„Input Channel“: The Falcon frame grabber board is equipped with several input channels. In this tab sheet the DSA1-Program must be „told“ which input channel is in use for the camera. Usually the channel in use is channel 1 (“Composite video – 1“), but it may be possible to select another channel with a connection cable different from that provided by KRÜSS. Because this rarely happens, the settings in this tab sheet don’t have to be changed in most cases.

Fig 15.9: Selection of the camera input channel

„Camera Format“

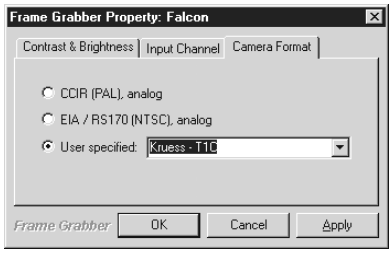


Fig. 15.10: Selection of the camera model

The settings in this tab sheet only have to be changed for the initial installation of the DSA1 and if the camera is exchanged for a different model.

15.3 Fit parameters

The program contains a range of default settings which concern the adaptation algorithm of the Young-Laplace equation to the drop contour and which can be altered if required. A subdivision is made into general parameters ("General Parameters“) and advanced parameters ("Advanced Parameters“). Adjustment is made by clicking “Options“→“Fit Parameters...“:

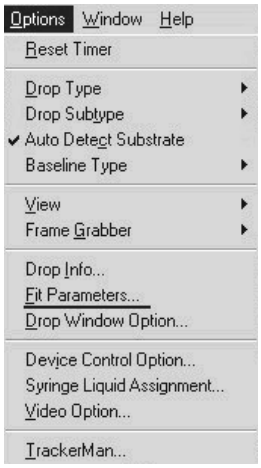


Fig. 15.11: Pull-down menu "Option“ for calling up the fit parameters

15.3.1 "General Parameters"

In the parameter menu the general parameters are displayed under "General“ and can be altered if necessary:

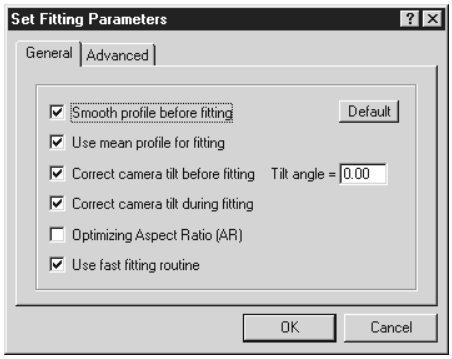


Fig. 15.12: Setting the general program parameters

"Smooth profile before fitting" Previous smoothing generally improves the accuracy and reliability of the measurement of the recorded contour of the drop. This function is active in the default setting. However, it takes a lot of time.

"Use mean profile..." A mean profile is obtained by comparison of the two halves of the recorded drop profile. In this way small tilts of the pendant drop are compensated and better results obtained during fitting. This function is active in the default setting. If problems occur with asymmetrical drops or incorrectly shown fit profiles this option should be switched off.

"Correct camera tilt..." The images produced by a tilted camera can be corrected both before and during the adaptation process (fitting). Under "Tilt Angle" the tilt value at the start of the measurement can be entered.

"Optimizing Aspect Ratio..." Depending on the CCD camera used there may be a slight distortion of the digitized image caused by the pixels shown not having a completely square shape. The so-called Aspect Ratio (AR) is a measure of the deviation of the pixel shape from a geometrically square shape. The ratio of height to width of a pixel designed by the "Aspect Ratio" can be determined and taken into account during the measurement. The determination requires a lot of computer calculation time and should only be carried out in special cases, e.g. for determining the AR of a newly purchased measuring system. It is determined by recording as large a drop as possible with a particularly good image quality and known interfacial tension. If the standard components supplied are used this function should be switched off.

"Use fast fitting..." Various optimizing and a fitting routines with different calculation speeds can be used. Because the PCs used today have higher calculation speeds than previously this option is becoming less important. As a result the default value provides as accurate a fit as possible.

15.3.2 "Advanced Parameters"

The advanced parameters are shown under "Advanced" in the parameter menu and can be altered if necessary:

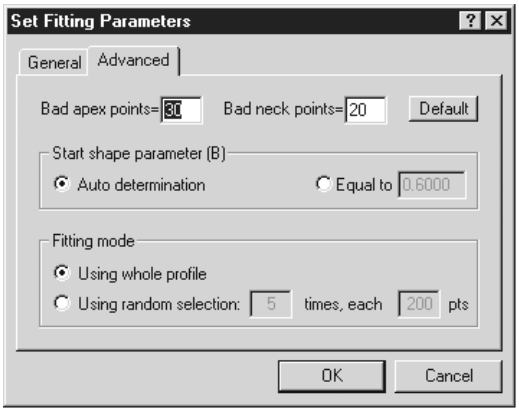


Fig. 15.13: Setting advanced fit parameters

"Bad apex points..." At the lower edge of a pendant drop, the drop apex, the image quality may be poorer as a result of light reflections and vibrations. By leaving out these "endangered" image points the fitting algorithm still provides unfalsified interfacial tension values. In this option the number of image points which are not to be taken into account during fitting can be set. The default value is 30 image points.

"Bad neck points..." A number of image points at the drop neck can be ignored in a similar way to the contour line at the drop apex. The default value is 20 image points.

"Start shape parameter..." The initial value of the drop shape parameter for iterative fitting can be set manually. The initial value can be decisive for an efficient and correct fit of the drop contour. The pre-set automatic start shape determination normally allows a problem-free evaluation of the drop contour; however, this takes a lot of time. For rapid serial measurements the initial value for the shape parameter should be set manually.

"Fitting mode..." Either all image points of the drop contour or a random selection of N image points (pts) can be used for the fitting process. The latter process is repeated M times. As M increases the time required for this option also increases; this should be taken into account when making rapid serial measurements.

16 Theory

In this section we first provide an introduction to the model considerations upon which interfacial tension is based (Section 16.1). This is followed by an explanation of the relationship between the contact angle and the surface energy of a solid upon which the individual methods for calculating the surface energy are based (Section 16.2). In addition, various methods of measuring the contact angle are described and an introduction is given to the theoretical background of the methods used in the DSA1 program for calculating the contact angle from the video images of sessile drops (Section 16.3). A further section deals with the theory of surface tension measurements using the images of pendant drops (Section 16.4).

16.1 Model considerations concerning interfacial tension

DUPRÉ defined the **work of cohesion** W_{ii} as the work done in dividing a homogeneous liquid per parting surface produced. As during division two individual parting surfaces 2A are produced, W_{ii} can be calculated from the surface tension σ (which is defined as the work per surface difference) according to the following equation:

$$W_{ii} = 2\sigma \qquad \text{Equation 1}$$

If a liquid column consists of 2 immiscible liquids then, when the column is separated, 2 new parting surfaces are formed at the interface and the boundary surface disappears. Therefore, according to DUPRÉ, the following relationship exists for the **work of adhesion** :

$$W_{ij} = \sigma_i + \sigma_j - \gamma_{ij} \qquad \text{Equation 2,}$$

where γ_{ij} represents the interfacial tension between the two phases.

ANTONOW has calculated the interfacial tension from the difference between the surface tensions of the individual phases:

$$\gamma_{12} = \left|\sigma_1 - \sigma_2\right| \qquad \text{Equation 3}$$

with the surface tensions σ_1, σ_2 of the individual components (this observation also forms the basis for the method according to ZISMAN described below (see Section 16.2.1)). However ANTONOW's approach proved to be an approximation that was not sufficiently accurate.

GOOD and GIRIFALCO describe the work of cohesion as being dependent on the geometric mean of the interactive energies between the particles of the two individual phases:

$$W_{12} = 2\Phi\sqrt{\sigma_1 \cdot \sigma_2} \qquad \text{Equation 4.}$$

By combining Equations 2 and 4 and transposition for $\gamma_{12}$the following relationship is obtained.

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2\Phi\sqrt{\sigma_1 \cdot \sigma_2}\gamma \qquad \text{Equation 5}$$

The interaction parameter Φ introduced here is a complex function of molecular quantities and initially could only be determined empirically.

FOWKES was the first to prepare the way for the calculation of interfacial tensions from surface tension data. He specified the interactions represented by the parameter Φ by assuming that only the same types of interactions could occur between the phases. For example, according to this only a nonpolar substance, i.e. a **purely disperse** interactive substance, can interact with the disperse fractions of the surrounding second phase:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^D \cdot \sigma_2^D} \qquad \text{Equation 6}$$

The disperse character of the interactions is expressed by the index D.

While dispersion forces exist in all atoms and molecules, polar forces are only found in certain molecules. Polar forces have their source in the differing electronegativity of different atoms in the same molecule. For polar liquids OWENS, WENDT, RABEL and KAELBLE (1969) assumed that there was a **polar fraction of the surface tension**. According to their model, the surface tension was the sum of the disperse and polar fractions:

$$\sigma = \sigma^D + \sigma^P \qquad \text{Equation 7.}$$

For the interfacial tension between two phases with polar fractions the following Equation (8) is obtained as an extension of Equation 6:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2(\sqrt{\sigma_1^D \cdot \sigma_2^D} + \sqrt{\sigma_1^P \cdot \sigma_2^P}) \qquad \text{Equation 8.}$$

In the "Extended FOWKES" method a further interactive fraction is also differentiated; the interactions caused by **hydrogen bondings**:

$$\sigma = \sigma^D + \sigma^P + \sigma^H \qquad \text{Equation 9}$$

with the corresponding extension of Equation 8 for the calculation of the interfacial tension by a further square root term:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2(\sqrt{\sigma_1^D \cdot \sigma_2^D} + \sqrt{\sigma_1^P \cdot \sigma_2^P} + \sqrt{\sigma_1^H \cdot \sigma_2^H}) \quad \text{Eq. 10.}$$

Equations 6, 8 and 10 use the **geometric mean** of the particular surface tension components of the individual phases. They produce satisfactory results throughout a wide range of surface energies.

The model according to OSS and GOOD is also based on the geometric mean, but the polar fraction is described with the help of the **Acid-Base-Model** according to LEWIS. The polar fraction is divided into an acid part σ^+ and a base part σ^-; this leads to the following equation:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+}) \qquad \text{Gl. 11.}$$

For low-energy systems (surface energies up to ≈35mN/m) the method according to WU can be used as an alternative. WU uses the **harmonic mean** instead of the geometric mean and limits it to the disperse and polar fractions.

$$\gamma_{12} = \sigma_1 + \sigma_2 - 4(\frac{\sigma_1^D \cdot \sigma_2^D}{\sigma_1^D + \sigma_2^D} + \frac{\sigma_1^P \cdot \sigma_2^P}{\sigma_1^P + \sigma_2^P}) \qquad \text{Equation 12}$$

In this way WU obtained more accurate results for low energy systems. However, the use of the harmonic mean is not suitable for high-energy materials (e.g. mercury, glass, metal oxides, graphite, polar polymers).

With the aid of the methods described here it is possible to calculate the interfacial tensions between liquids, provided that their surface tensions and disperse and polar fractions (and, if applicable, their hydrogen bridge fractions) are known. In addition the surface energies of solids can also be calculated. A requirement for this is the knowledge of the **contact angles** of the corresponding liquids during phase contact with the solid surface.

16.2 Contact angle and surface energy

In 1805 YOUNG had already formulated a relationship between the interfacial tensions at a point on a 3-phase contact line.

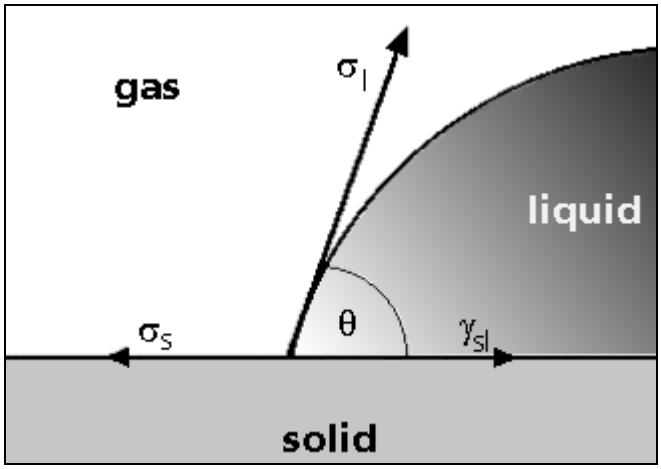


Fig. 16.1: Contact angle formation on a solid surface according to YOUNG

Indices s and l stand for "solid" and "liquid"; the symbols σ_s and σ_l describe the surface tension components of the two phases; symbol γ_{sl} represents the interfacial tension between the two phases, and θ stands for the contact angle corresponding to the angle between vectors σ_l and γ_{sl}. YOUNG formulated the following relationship between these quantities:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 13.}$$

The methods implemented in the DSA1 program allow the determination of the surface energy of solids from contact angle data. They are mainly based on combining various starting equations for γ_{sl} with the equation from YOUNG to obtain equations of state in which $\cos\theta$ represents a function of the phase surface tensions and, if applicable, the (polar and disperse) tension components $\sigma_{l,D}$, $\sigma_{l,P}$, $\sigma_{s,D}$ and $\sigma_{s,P}$. As liquids with known surface tension data and known polar and disperse fractions are used it is possible to include $\sigma_{l,D}$ and $\sigma_{l,P}$ in the equations. All methods assume that the interactions between the solid and the gas phase (or the liquid vapour phase) are so small as to be negligible. The methods are described in the following sections.

16.2.1 The ZISMAN method

In the ZISMAN method the surface energy of the solid is determined by using the **critical surface tension** (explained below) of the liquid. This method is based on a revised version of the ANTONOW method (see p. 121), it is implemented in the DSA1 program primarily for historical reasons and should not be used for routine measurements.

The method is based on the following consideration:
A liquid wets a solid completely when the work of cohesion for the formation of a liquid surface W_{ll} is smaller than the work of cohesion for the formation of the interface boundary W_{sl}. The difference between these two quantities is known as the spreading pressure $S_{l/s}$:

$$S_{l/s} = W_{sl} - W_{ll}$$ Equation 14.

The solid will be wetted completely when the spreading pressure is positive; at a negative spreading pressure the solid will not be wetted completely.

In addition, the following relationship exists between the work of cohesion W_{sl}, the contact angle θ and the surface tension of the liquid (see also 16.2.3.2):

$$W_{sl} = \sigma_l(\cos\theta + 1)$$ Equation 15

As the work of cohesion W_{ll} is defined as $2 \cdot \sigma_l$ according to DUPRÉ (see p. 121) then, for a contact angle of 0° ($\cos\theta = 0$) the work of cohesion will be the same as the work of adhesion; this results in a spreading pressure of 0. This means that the contact angle of 0° can be called the limiting angle for spreading (=complete wetting). Theoretically, a positive spreading pressure corresponds with negative contact angles which cannot be measured in practice.

The method according to ZISMAN uses this relationship by plotting $\cos\theta$ against the surface tension for various liquids and extrapolating the compensation curve to $\cos\theta = 1$. The corresponding value for the surface tension is known as the critical surface tension σ_{crit}.

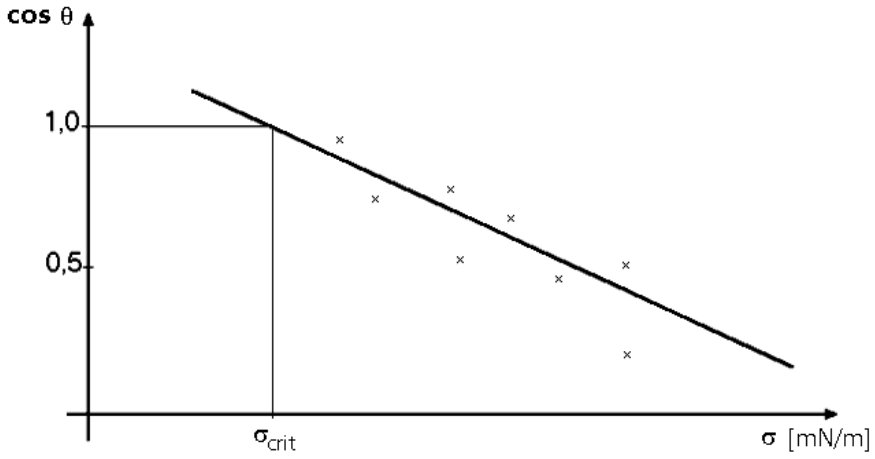


Fig. 16.2: Determining the critical surface tension according to ZISMAN

ZISMAN equates this value with the surface energy of the solid σ_s. Setting up a linear relationship between $\cos\theta$ and the surface tension σ_l is based on the now outdated assumption of ANTONOW that the interfacial tension is determined by the difference between the surface tensions. In fact this linear relationship only applies when the relationship between the disperse and polar interactions is the same between the solid and the liquid. This practically only occurs when a purely disperse interactive solid and liquid are involved; i.e. only under exceptional circumstances. This means that other methods should normally be used for determining the surface energy.

16.2.2 Equation of state

The equation of state was obtained during the search for a method of determining the surface energy of a solid from a single contact angle measurement by using a liquid with known surface tension.

Starting with the equation of Young

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 16}$$

it can be seen that a second equation is required which also describes the surface energy of the solid as a function of the interfacial tension solid/liquid and the surface tension of the liquid:

$$\sigma_s = f(\gamma_{sl}, \sigma_l) \qquad \text{Equation 17}$$

From thermodynamic considerations it was first demonstrated that such an equation valid for all systems must exist. By using an enormous volume of contact angle data the required equation of state was determined empirically:

$$\gamma_{sl} = \sigma_l + \sigma_s - 2\sqrt{\sigma_l \cdot \sigma_s} \cdot e^{-\beta(\sigma_l - \sigma_s)^2} \qquad \text{Equation 18}$$

The value 0.0001247 was determined for the constant β in the exponent. If the equation of state is inserted in Young's equation then a new equation is obtained which allows the calculation of the surface tension of the solid σ_s from a single contact angle if the surface tension σ_l is known:

$$\cos\theta = -1 + 2\sqrt{\frac{\sigma_s}{\sigma_l}} \cdot e^{-\beta(\sigma_l - \sigma_s)^2} \qquad \text{Equation 19}$$

In the calculation of the surface energy with the help of the equation of state the type of interactions which lead to the formation of the interfacial tensions (polar or disperse interactions) are not taken into account. However, the assumption that the knowledge of the surface tension of the liquid alone is sufficient has been disproved by experiments in which the contact angles of liquids with similar high surface tensions and differing fractions of polar interactions were measured. It appears that the disperse and polar fractions of the surface tensions must be taken into account; this means that the equation of state only provides useful results when only disperse interactions are present or when these are in the majority.

16.2.3 The method according to FOWKES

By using the FOWKES method the polar and disperse fractions of the surface free energy of a solid can be obtained. Strictly speaking this method is based on a combination of the knowledge of FOWKES on the one hand and that of OWENS, WENDT, RABEL and KAELBLE on the other, as FOWKES initially determined only the disperse fraction and the latter were the first to determine both the components of the surface energy. The difference between the FOWKES method used by KRÜSS and the OWENS, WENDT, RABEL and KAELBLE method is that in the **FOWKES method** the **disperse and the polar fractions are** determined in succession, i.e. **in two steps**, while in the OWENS, WENDT, RABEL and KAELBLE method both components are calculated by using a single linear regression.

The calculation steps described below are only intended to explain the methods. When calculating the surface energy according to FOWKES you do not have to proceed in several steps; when the calculation is carried out these steps are processed internally by the program. The same applies for the "Extended FOWKES" method described in Section 16.2.4.

16.2.3.1 Step 1: Determining the disperse fraction

In this first step the disperse fraction of the surface energy of the solid is calculated by making contact angle measurements with at least one purely disperse liquid.

By combination of the surface tension equation of FOWKES for the disperse fraction of the interactions

$$\gamma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^D \cdot \sigma_l^D} \qquad \text{Equation 20}$$

with the YOUNG equation (Equation 16) the following equation for the contact angle is obtained after transposition:

$$\cos\theta = 2\sqrt{\sigma_s^D} \cdot \frac{1}{\sqrt{\sigma_l^D}} - 1 \qquad \text{Equation 21}$$

and, based upon the general equation for a straight line,

$$y = mx + b \qquad \text{Equation 22}$$

$\cos\theta$ is then plotted against the term $1/\sqrt{\sigma_l^D}$ and $2\sqrt{\sigma_s^D}$ can be determined from the slope m. The straight line must intercept the ordinate at the point defined as b=-1 (0/-1). As this point has been defined it is possible to determine the disperse fraction from a single

contact angle: however, a linear regression with several purely disperse liquids is more accurate.

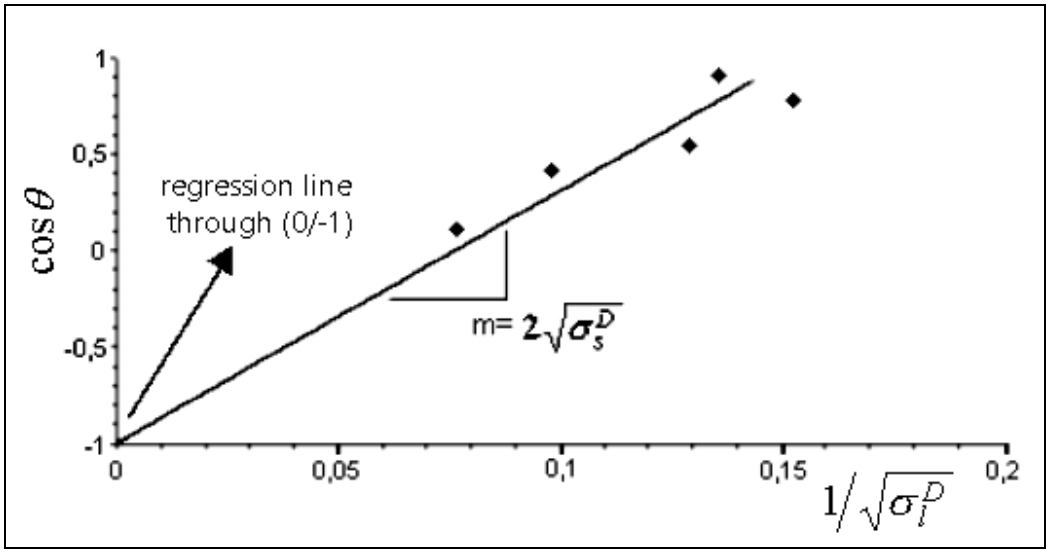


Fig. 16.3: Determining the surface energy according to FOWKES (1)

16.2.3.2 Step 2: Determining the polar fraction

For the 2nd step, the calculation of the polar fraction, Equation 20 is extended by the polar fraction:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}) \qquad \text{Equation 23.}$$

It is also assumed that the work of adhesion is obtained by adding together the polar and disperse fractions:

$$W_{sl} = W_{sl}^D + W_{sl}^P \qquad \text{Equation 24}$$

and then as a third step YOUNG's equation

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 25}$$

is added to the equation of DUPRÉ

$$W_{sl} = \sigma_s + \sigma_l - \gamma_{sl} \qquad \text{Equation 26}$$

to obtain the following relationship for the work of adhesion:

$$W_{sl} = \sigma_l(\cos\theta + 1) \qquad \text{Equation 27}$$

Now all the components required for the calculation of the polar fraction of the surface energy have been assembled. A combination of Equations 23, 24 and 27 produces

$$W_{sl}^P = \sigma_l(\cos\theta + 1) - 2\sqrt{\sigma_s^D \cdot \sigma_l^D} \qquad \text{Equation 28.}$$

Based upon this relationship the contact angles of liquids with known polar and disperse fractions are measured and W_{sl}^P is calculated for each liquid. In this case a single liquid with polar and disperse fractions would be sufficient, although the results would again be less reliable.

As according to Equation 23 the polar fraction of the work of adhesion is defined by the geometric mean of the polar fractions of the particular surface tensions

$$W_{sl}^P = 2\sqrt{\sigma_l^P} \cdot \sqrt{\sigma_s^P} \qquad \text{Equation 29,}$$

then, by plotting W_{sl}^P against $2\sqrt{\sigma_l^P}$ and following this with a linear regression, the polar fraction of the surface energy of the solid can be determined from the slope. As in this case the ordinate intercept b is 0, the regression curve must pass through the origin (0;0).

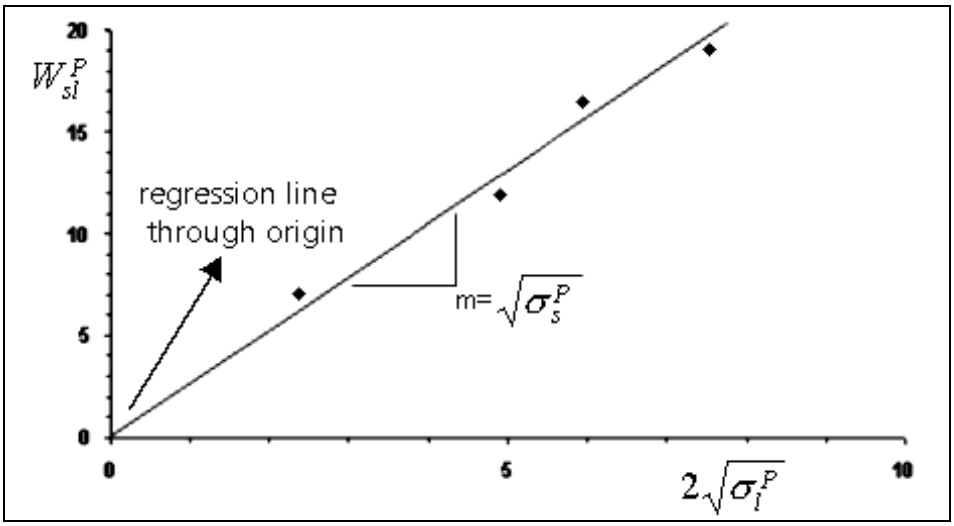


Fig. 16.4: Determining the polar surface energy according to FOWKES (2)

16.2.4 The Extended FOWKES method

In the Extended FOWKES method the work of adhesion is not split up into just two fractions but into three: the **disperse** and **polar** fractions as well as the fraction W_{sl}^H resulting from the **hydrogen bridges**:

$$W_{sl} = W_{sl}^D + W_{sl}^P + W_{sl}^H \qquad \text{Equation 30.}$$

The calculation of the surface energy accordingly is carried out in **three steps** instead of two.

As in the **first step** of the FOWKES method the disperse fraction of the surface energy of a solid is determined from the contact angle data of a purely disperse liquid (see 16.2.3.1).

In the **second step** liquids with known polar and disperse surface tension fractions are selected (σ_l^D and $\sigma_l^P > 0$) with a hydrogen bridge fraction σ_l^H of 0. In this way, as in the second step of the FOWKES method (see 16.2.3.2), the polar fraction of the surface free energy is first obtained with the aid of contact angle measurements (by subtracting the disperse fraction from the total work of adhesion).

$$W_{sl}^P = \sigma_l(\cos\theta + 1) - 2\sqrt{\sigma_s^D \sigma_l^D} \qquad \text{Equation 31.}$$

The determination of the polar fraction of the surface free energy of the solid is carried out as in the FOWKES method.

In a **third step** work is again carried out in a similar manner for the calculation of the hydrogen bridge fraction. Contact angles of liquids with known polar, disperse and hydrogen

bridge fractions ($\sigma_l^H > 0$) of the surface tension are measured. By extending Equation 23 by the hydrogen bridge fraction we obtain

$$\gamma_{12} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P} + \sqrt{\sigma_s^H \cdot \sigma_l^H}) \quad \text{Eq. 32}$$

As in Equation 28 the required fraction of the work of adhesion, i.e. the fraction W_{sl}^H resulting from the hydrogen bridges, can be calculated for each contact angle by subtracting the known fractions (by including the YOUNG Equation (25)):

$$W_{sl}^H = \sigma_l(\cos\theta + 1) - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}) \quad \text{Equation 33.}$$

Finally the hydrogen bridge fraction σ_s^H of the surface energy of the solid can now be determined as described in Step 2 of the FOWKES method. According to Equation 32 the following relationship applies to W_{sl}^H:

$$W_{sl}^H = 2\sqrt{\sigma_l^H} \cdot \sqrt{\sigma_s^H} \quad \text{Equation 34.}$$

If W_{sl}^H is plotted against $2\sqrt{\sigma_l^H}$ then $\sqrt{\sigma_s^H}$, i.e. the hydrogen bridge fraction of the surface energy of the solid, is obtained from the slope of the regression curve.

16.2.5 **The Owens, Wendt, Rabel and Kaelble method**

According to OWENS, WENDT, RABEL and KAELBLE the surface tension of each phase can be split up into a polar and a disperse fraction:

$$\sigma_l = \sigma_l^P + \sigma_l^D \qquad \text{Equation 35}$$

$$\sigma_s = \sigma_s^P + \sigma_s^D \qquad \text{Equation 36.}$$

The FOWKES method for calculating the surface energy has already been developed from this relationship. In contrast to the FOWKES method, in the OWENS, WENDT, RABEL and KAELBLE method the calculation of the surface energy of the solid takes place in a single step.

OWENS and WENDT took the equation for the surface tension

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}) \qquad \text{Equation 37}$$

as their basis and combined it with the YOUNG equation

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 38.}$$

The two authors solved the equation system by using the contact angles of two liquids with known disperse and polar fractions of the surface tension. KAELBLE solved the equation for combinations of two liquids and calculated the mean values of the resulting values for the surface energy. RABEL made it possible to calculate the polar and disperse fractions of the surface energy with the aid of a single linear regression from the contact angle data of various liquids. He combined Equations 37 and 38 and adapted the resulting equation by transposition to the general equation for a straight line

$$y = mx + b \qquad \text{Equation 39}$$

The transposed equation is shown below:

$$\underbrace{\frac{(1+\cos\theta)\cdot\sigma_l}{2\sqrt{\sigma_l^D}}}_{y} = \underbrace{\sqrt{\sigma_s^P}}_{m}\underbrace{\sqrt{\frac{\sigma_l^P}{\sigma_l^D}}}_{x} + \underbrace{\sqrt{\sigma_s^D}}_{b} \qquad \text{Equation 40.}$$

In a linear regression of the plot of y against x, σ_s^P is obtained from the square of the slope of the curve m and σ_s^D from the square of the ordinate intercept b.

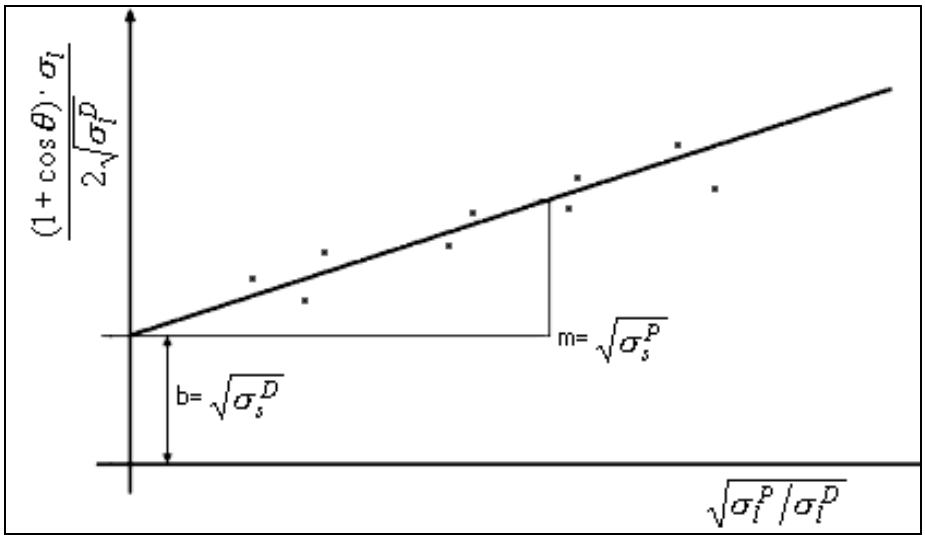


Fig. 16.5: Determination of the disperse and polar fractions of the surface tension of a solid according to RABEL

16.2.6 The WU method

In his observations on interfacial tension WU also started with the polar and disperse fractions of the surface energy of the participating phases. However, in contrast to FOWKES and OWENS, WENDT, RABEL and KAELBLE, who used the geometric mean of the surface tensions in their calculations, WU used the **harmonic** mean. In this way he achieved more accurate results, in particular for high-energy systems.

At least two test liquids with known polar and disperse fractions are required for this method; at least one of the liquids must have a polar fraction >0.

WU's initial equation for the interfacial tension between a liquid and a solid phase is as follows:

$$\gamma_{12} = \sigma_l + \sigma_s - 4\left(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P}\right) \qquad \text{Equation 41.}$$

If YOUNG's equation is inserted in Equation 41

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 42}$$

then the following relationship is obtained:

$$\sigma_l(\cos\theta + 1) - 4\left(\frac{\sigma_l^D \cdot \sigma_s^D}{\sigma_l^D + \sigma_s^D} + \frac{\sigma_l^P \cdot \sigma_s^P}{\sigma_l^P + \sigma_s^P}\right) = 0 \qquad \text{Equation 43.}$$

In order to determine the two required quantities σ_s^D and σ_s^P, WU determined the contact angles for each of two liquids on the solid surface and then, based on Equation 43, he drew up an equation for each liquid. After a factor analysis the resulting equations were as follows:

$$(b_1 + c_1 - a_1)\sigma_s^D\sigma_s^P + c_1(b_1 - a_1)\sigma_s^D + b_1(c_1 - a_1)\sigma_s^P - a_1b_1c_1 = 0 \qquad \text{Eq. 44}$$

$$(b_2 + c_2 - a_2)\sigma_s^D\sigma_s^P + c_2(b_2 - a_2)\sigma_s^D + b_2(c_2 - a_2)\sigma_s^P - a_2b_2c_2 = 0 \qquad \text{Eq. 45}$$

The variables a_1, b_1, c_1 for the first liquid and a_2,b_2,c_2 for the second liquid express the following terms:

a_1	$\frac{1}{4}\sigma_{l,1}(\cos\theta_1 + 1)$
b_1	$\sigma_{l,1}^{D}$
c_1	$\sigma_{l,1}^{P}$
a_2	$\frac{1}{4}\sigma_{l,2}(\cos\theta_2 + 1)$
b_2	$\sigma_{l,2}^{D}$
c_2	$\sigma_{l,2}^{P}$

The solution of the equations produces the surface energy of the solid σ_s and its polar end disperse components σ_s^P and σ_s^D. However, the following point must be taken into consideration: as quadratic equations are involved this means that two solutions are obtained for both σ_s^P and σ_s^D; only one of these solutions describes the actual surface energy.

16.2.6.1 Selecting the correct solution

The user now has the problem that, from the two solutions obtained above, the one which supplies the physically correct result for the system under investigation must be selected. This is very easy when one of the solutions has a negative sign. As negative values for the surface energy do not make sense from a physical point of view, in this case the second solution (with a positive sign) provides the result of the measurement.

For example:

	Solution 1	***Solution 2***
Surface energy of the solid	35.2 mN/m	15.7 mN/m
Disperse fraction	37.2 mN/m	12.2 mN/m
Polar fraction	**-2.0** mN/m	3.5 mN/m

In this example Solution 1 can be rejected as it supplies a negative polar fraction of the surface energy. Solution 2 is the correct result. In such a case the DSA1 program automatically ignores the negative solution and presents the positive solution as the result.

However, it is often the case that both solutions make sense from a physical point of view. In such cases the decision can be simplified by including further information:

- Which of the two solutions has the order of magnitude which is to be expected from a knowledge of the properties of the substance?
- Which of the two solutions agrees best with the results obtained with other pairs of liquids?
- Which of the two solutions is closest to results obtained by calculations according to FOWKES, or OWENS, WENDT, RABEL and KAELBLE?

16.2.6.2 Measurements with more than two liquids

Although the equation system drawn up by WU can be solved with the contact angle data obtained with two liquids, as in other methods the selection of a larger number of test liquids increases the reliability of the measurements. As WU uses two equations for two liquids to calculate the surface energy, a part-result is obtained for each of the possible pairings of the test liquids.

For example: The surface energy of a solid is to be determined by using the contact angles of 4 test liquids: water, diiodomethane, ethylene glycol and benzyl alcohol. The calculation is carried out for each of the six possible pairings:

	Liquid 1	***Liquid 2***
1st pair	water	diiodomethane
2nd pair	water	ethylene glycol
3rd pair	water	benzyl alcohol
4th pair	diiodomethane	ethylene glycol
5th pair	diiodomethane	benzyl alcohol
6th pair	ethylene glycol	benzyl alcohol

This means that the 4 test liquids supply 6 part-results; as described above, each of these results has two solutions. This means that the choice of the right solution must be made for each individual pair of liquids. The pairing of two purely disperse liquids ($\sigma_l^P = 0$) produces no solution for the equation system; they are not included in the calculation.

The final result of the surface energy determination is the arithmetic mean of the selected part-results.

16.2.7 The SCHULTZ method

The method for calculating the surface energy according to SCHULTZ is only intended for use with high-energy solid surfaces. In the DSA1 program there are two methods implemented which are based on SCHULTZ: "SCHULTZ 1" and "SCHULTZ 2". The theoretical requirements are the same for both methods; the difference lies in the test arrangement. As a result this section first described the theoretical principles and only then explains the differences between the two SCHULTZ methods.

16.2.7.1 Theoretical principles for the two SCHULTZ methods

High-energy solids are normally completely wetted by all liquids, so that their surface energy cannot be determined by using conventional contact angle measurements. In order to be able to investigate such systems at all the test arrangement must be altered: instead of being measured in air, the contact angle of a liquid drop ("drop phase") on a solid is measured in a surrounding liquid phase ("bulk phase").

The calculation of the surface energy assumes that the YOUNG equation also applies to a liquid/liquid/solid system:

$$\sigma_s = \gamma_{sl_{drop}} + \gamma_{ll\,drop/bulk} \cdot \cos\theta \qquad \text{Equation 46.}$$

In this case $\gamma_{sl_{bulk}}$ represents the interfacial tension between the solid and the surrounding phase; $\gamma_{sl_{drop}}$ the interfacial tension between the solid and the drop phase; and $\gamma_{ll\,drop/bulk}$ the interfacial tension between the two liquids.

With the equations of FOWKES and OWENS, WENDT, RABEL and KAELBLE (Equation 37, p.133) adapted for a liquid/liquid/solid system, the following equations are obtained for the drop phase and the surrounding phase:

$$\gamma_{sl\,drop} = \sigma_s + \sigma_{l\,drop} - 2\sqrt{\sigma_s^D \cdot \sigma_{l_{drop}}^D} - W_{sl_{drop}}^P \qquad \text{Equation 47}$$

$$\gamma_{sl\,bulk} = \sigma_s + \sigma_{l\,bulk} - 2\sqrt{\sigma_s^D \cdot \sigma_{l_{bulk}}^D} - W_{sl_{bulk}}^P \qquad \text{Equation 48}$$

W_{sl}^P is the polar fraction of the work of adhesion, i.e. the interactions between the particular liquid and the solid.

If Equations 46, 47 und 48 are combined then the following relationship is obtained:

$$\sigma_{l_{drop}} - \sigma_{l_{bulk}} + \gamma_{ll_{drop/bulk}} \cdot \cos\theta = 2\sqrt{\sigma_s^D} \cdot (\sqrt{\sigma_{l_{drop}}^D} - \sqrt{\sigma_{l_{bulk}}^D}) + W_{sl_{drop}}^P - W_{sl_{bulk}}^P \quad \text{Eq. 49}$$

16.2.7.2 SCHULTZ 1

In the "SCHULTZ 1" method only a single drop liquid is used and the surrounding phase is changed instead. The drop liquid used is normally water; the bulk phase is a liquid which is immiscible with water and with a lower density than water.

As in the FOWKES method (see Section 16.2.3) the calculation of the **polar** and **disperse** fractions of the surface energy is carried out in **two steps**.

At first the contact angle of water on the solid is measured in a range of purely disperse interacting liquids. Owing to the nonpolar character of the surrounding phase the term $W^P_{sl_{bulk}}$ can be deleted from Equation 49. Equation 49 can then be adapted to conform with the general equation for a straight line:

$$y = mx + b \qquad \text{Equation 50}$$

to give:

$$\underbrace{\sigma_{l_{drop}} - \sigma_{l_{bulk}} + \gamma_{ll_{drop/bulk}} \cdot \cos\theta}_{y} = \underbrace{2\sqrt{\sigma_s^D}}_{m} \cdot \underbrace{(\sqrt{\sigma^D_{l_{drop}}} - \sqrt{\sigma^D_{l_{bulk}}})}_{x} + \underbrace{W^P_{sl_{drop}}}_{b} \qquad \text{Eq. 51}$$

If the term y is plotted against x then the disperse fraction of the surface energy of the solid σ_s^D is can be calculated directly from the slope and $W^P_{sl_{drop}}$ from the y-axis intercept.

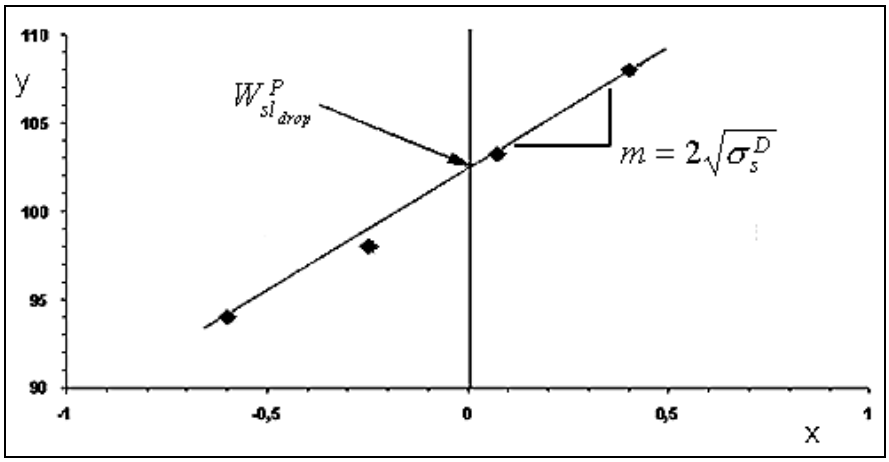


Fig. 16.6: Determining the surface energy according to SCHULTZ

In the **second step** the **polar fraction** of the surface energy of the solid is determined by using several surrounding phases which have polar fractions. As the term $W^P_{sl_{drop}}$ from Equation 49 is now known, the polar fraction of the adhesion energy between the solid and the surrounding phase $W^P_{sl_{bulk}}$ can be calculated for each individual surrounding phase.

According to FOWKES, this adhesion energy can be calculated from the geometric mean between the polar fractions of the surface tensions of the participating phases:

$$W_{sl_{bulk}}^{P} = 2 \cdot \sqrt{\sigma_s^P} \cdot \sqrt{\sigma_{l_{bulk}}^P} \qquad \text{Equation 52}$$

As a result, if $W_{sl_{bulk}}^{P}$ is plotted against $\sigma_{l_{bulk}}^{P}$ then the required term σ_s^P can be obtained from the slope of the regression curve.

16.2.7.3 SCHULTZ 2

In the SCHULTZ 2 method it is not the heavier liquid which is used as the drop liquid but the lighter one; the heavier liquid forms the surrounding phase. In order for this to be possible the test arrangement must be inverted: the drop is not present as a sessile drop on the solid but is suspended from it as a pendant drop:

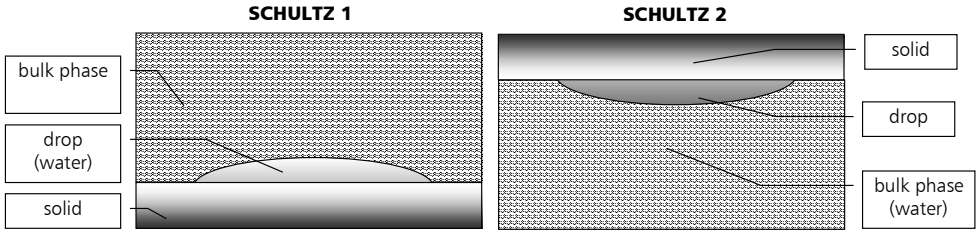


Fig. 16.7: Test arrangements for the SCHULTZ method; left SCHULTZ 1, right SCHULTZ 2

In this arrangement the surrounding phase is retained and the contact angles of various drop liquids are measured. The advantage when compared with the SCHULTZ 1 method is that the contact angles of the drop phase to be measured are larger and can therefore be measured more accurately.

As in SCHULTZ 1 the disperse fraction of the surface energy of the solid σ_s^D is measured first by using purely disperse interacting liquids. The difference from the calculation for SCHULTZ 1 is that the term $W_{sl_{bulk}}^{P}$ is obtained from the intercept of the regression curve with the y-axis (see Fig. 16.7) on the plot, whereas the term $W_{sl_{drop}}^{P}$ is deleted from Equation 49.

In the second step the term $W_{sl_{drop}}^{P}$ in Equation 49 is calculated from the contact angles of drop liquids with polar fractions for each test liquid. The polar of the surface energy of the solid σ_s^P is obtained in a similar way to SCHULTZ 1 by using the equation

$$W_{sl_{drop}}^{P} = 2 \cdot \sqrt{\sigma_s^P} \cdot \sqrt{\sigma_{l_{drop}}^P} \qquad \text{Equation 53.}$$

16.2.8 The acid-base method according to OSS & GOOD

OSS and GOOD also differentiate between a polar and a disperse fraction of the surface energy. However, in contrast to the previously described authors, they describe the polar fraction with the help of the a**cid-base model according to Lewis**. According to this model, the polar fraction of the surface energy of the solid and the surrounding drop liquid is split into an electron acceptor fraction corresponding to a Lewis acid (="electron receiving" fraction) $\sigma^+$and an electron donor corresponding to a Lewis base (="electron donor" fraction) σ^-. Owing to the attraction of opposite charges there are interactions between the particular counter poles of the polar components of the solid and the liquid. The Equation for the surface tension of FOWKES and OWENS, WENDT, RABEL, KAELBLE (Equation 37) is adapted accordingly:

$$\gamma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+}) \qquad \text{Eq. 54.}$$

In order to calculate the 3 fractions of the surface energy of a solid from contact angle data Equation 54 is combined with YOUNG's Equation:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos\theta \qquad \text{Equation 55}$$

to obtain

$$(1 + \cos\theta)\sigma_l = 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^+ \cdot \sigma_l^-} + \sqrt{\sigma_s^- \cdot \sigma_l^+}) \qquad \text{Eq.56}$$

In order to solve this equation, i.e. to determine the disperse fraction σ_s^D, the acid fraction σ_s^+ and the base fraction σ_s^- of the solid, contact angle data from at least 3 test liquids are required; at least 2 of these must have a known acid and base fraction >0.

Moreover, at least one of the liquids must have equal basic and polar parts. Usually water is chosen for this purpose because it serves as neutral point in the LEWIS scale.

16.2.9 Predicting the wetting behavior: the "wetting envelope"

The "wetting envelope" is not an independent calculation method for the polar and disperse fractions of the surface energy of a solid, but only a special type of presentation. It can be used for all surface energy calculation methods which provide a polar fraction and a disperse fraction in the result.

With the help of the wetting envelope and a knowledge of the polar and disperse fractions of the surface energy of a solid it is possible to **predict whether a particular liquid**, whose surface tension components are also known, will **wet** the solid completely. The following relationships make this possible:

A liquid will wet a solid surface completely when the work of adhesion W_{sl} between the solid surface and the liquid is greater than work of cohesion W_{ll} within the liquid. The difference between these two quantities is known as the spreading pressure $S_{l/s}$:

$$S_{l/s} = W_{sl} - W_{ll}$$ Equation 57;

this means that a liquid will wet a solid when the spreading pressure is positive.

The work of cohesion can also be described with the help of the contact angle between the liquid and the solid and surface tension of the liquid:

$$W_{sl} = \sigma_l(\cos\theta + 1)$$ Equation 58

As according to DUPRÉ W_{ll} is defined as $2 \cdot \sigma_l$ (see p. 121); this means that for a contact angle of 0° ($\cos\theta = 1$) the spreading pressure $S_{l/s}$ is 0 and the liquid will wet the solid completely.

The following figure shows the connection between contact angle and wettability:

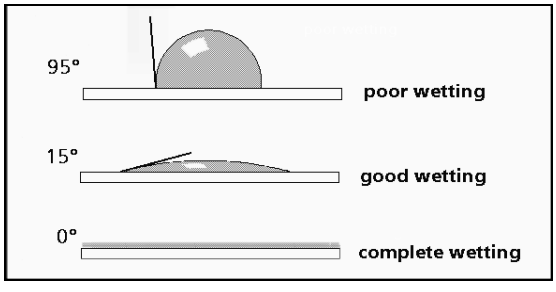


Fig. 16.8: contact angle and wettability

In order to represent the wetting envelope the methods described for the determination of the disperse and polar fractions of the surface energy (FOWKES; OWENS, WENDT, RABEL and KAELBLE; WU) are reversed: disperse and polar fractions of the solid are known (from a

measurement or from the literature); the corresponding equations are used instead to calculate the polar and disperse fractions of the liquid which have a value of $\cos\theta = 1$ for the solid under investigation. By plotting the polar fraction against the disperse fraction a curve is produced for $\cos\theta = 1$ which starts at the origin (0/0), attains a maximum value and then returns to the X-axis. The area enclosed within this curve is the wetting envelope or wetting range; all liquids whose data lie within this enclosed area will wet the corresponding solid.

The procedure is demonstrated below using two liquids as an example:

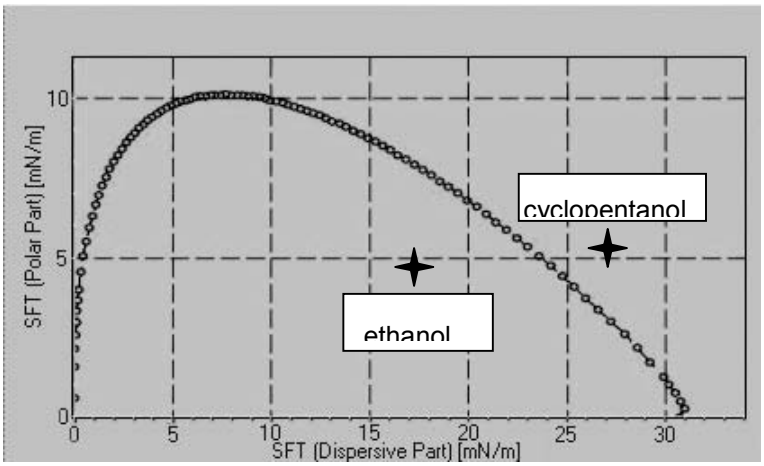


Fig. 16.9: Predicting the wetting behavior by using the wetting envelope

The following Table shows the data used for Fig. 16.9, this was taken from the DSA1 liquid database. The values for ethanol lie within the wetting envelope; this means that we can expect that ethanol will wet the solid. In contrast, cyclopentanol lies outside the envelope and should therefore not wet the solid.

Liquid	***Disperse fraction***	***Polar fraction***	***Wetting behavior***
Ethanol	17.5	4.6	wetted completely
Cyclo-pentanol	27.2	5.5	not wetted completely

16.3 Measuring the contact angle

The previous section explained the various methods of calculating the surface energy from contact angle data. In this section the theory of contact angle measurement is explained. All calculation methods (except for SCHULTZ 2) are based on the sessile drop method, i.e. drops of liquid are deposited on a solid surface (as smooth and horizontal as possible).

A differentiation is made between the various ways of measuring the drop:

- A contact angle can be measured on **static drops**. The drop is produced before the measurement and has a constant volume during the measurement.
- A contact angle can be measured on **dynamic drops**. The contact angle is measured while the drop is being enlarged or reduced; the boundary surface is being constantly newly formed during the measurement. Contact angles measured on increasing drops are known as "**advancing angles**"; those measured on reducing drops as "**retreating angles**".

16.3.1 Static contact angles

In a static contact angle measurement the size of the drop does not alter during the measurement. However, this does not mean that the contact angle always remains constant; on the contrary, interactions at the boundary surface can cause the contact angle to change considerably with time. Depending on the type of time effect the contact angle can increase or decrease with time.

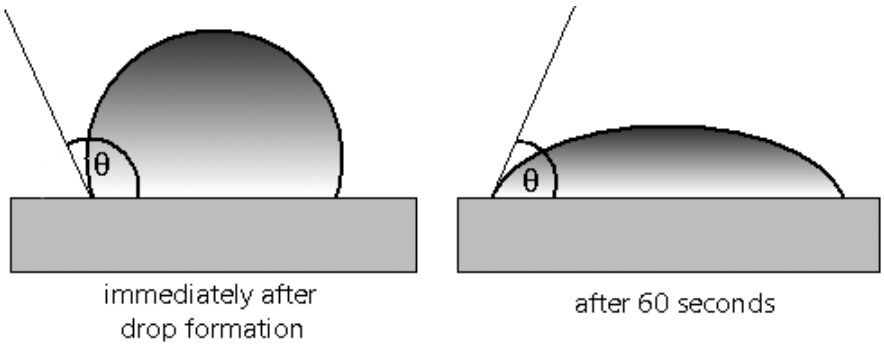


Fig. 16.10: Alteration of the static contact angle as a function of time

For example, these interactions could be:

- Evaporation of the liquid
- Migration of surfactants from the solid surface to the liquid surface
- Substances dissolved in the drop migrating to the surface (or in the opposite direction),
- Chemical reactions between the solid and liquid,

- The solid being dissolved or swollen by the liquid.

It may be a good idea to choose to measure the static contact angle when its variation as a function of time is to be studied. A further advantage of static contact angle measurement is that the needle does not remain in the drop during the measurement. This prevents the drop from being distorted (particularly important for small drops). In addition, when determining the contact angle from the image of the drop it is possible to use methods which evaluate the whole drop shape and not just the contact area.

Certain materials which don't show a fully rigid surface (e.g. rubber) are better being tested with static measurements. In such cases, dynamic contact angles are poorly reproducable.

However, changes with time often interfere with the measurement. There is also a further source of error: as the static contact angle is always measured at the same spot on the sample any local irregularities (dirt, inhomogeneous surface) will have a negative effect on the accuracy of the measurement. This error can be averaged out in dynamic contact angle measurements.

16.3.2 Dynamic contact angle

Dynamic contact angles describe the processes at the liquid/solid boundary during the increase in volume (advancing angle) or decrease in volume (retreating angle) of the drop, i.e. during the wetting and dewetting processes.

A boundary is not formed instantaneously but requires some time before a dynamic equilibrium is established. This is why a flow rate which is too high should not be selected for measuring advancing and retreating angles, as otherwise the contact angle will be measured at a boundary which has not been completely formed. However, it should also not be too slow as the time effects mentioned above will then again play a role. In practice flow rates between 5 and 15 µl/min can be recommended; higher flow rates should only be used for the simulation of dynamic processes.

For high-viscosity liquids (e.g. glycerol) the rate will tend to approach the lower limit.

16.3.2.1 Advancing angle

During the measurement of the advancing angle the syringe needle remains in the drop throughout the whole measurement. In practice a drop with a diameter of about 3-5 µl (with the needle of 0.5 mm diameter which is used in KRÜSS measurement systems) is formed on the solid surface and then slowly increased in volume. At the beginning, the contact angle measured is not independent from the drop size because of the adhesion to the needle. At a certain drop size the contact angle stays constant; in this area the advancing angle can be measured properly. (Fig. 16.11).

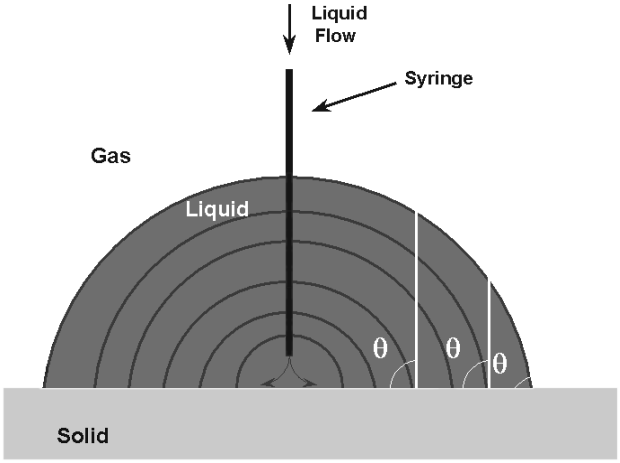


Fig. 16.11: Measuring advancing angles

As a result of the wetting process, advancing angles always simulate a fresh surface for the contact angle; this is formed immediately after the creation of the contact between the liquid and the surface. This type of measurement is therefore the most reproducible way of measuring contact angles. As a result, advancing angles are normally measured in order to determine the surface free energy of a solid.

16.3.2.2 Receding angle

During the measurement of the receding angle the contact angle is measured as the size of the drop is being reduced, i.e. as the surface is being de-wetted. By using the difference between the advancing and the receding angles it is possible to make statements about the roughness of the solid or chemical inhomogeneties; however, the receding angle is not suitable for calculating surface energies.

In practice a relatively large drop with a diameter of approx. 6 mm is deposited on the solid and then slowly reduced in size with a constant flow rate.

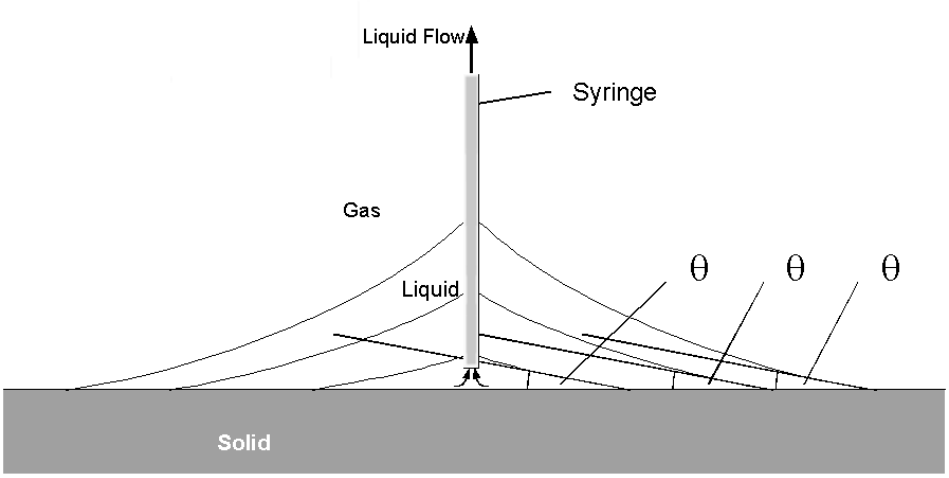


Fig. 16.12: Measuring receding angles

The same guiding limits and conditions apply here as for the measurement of the advancing angle (see Section 16.3.2.1).

16.3.3 Methods of evaluating the drop shape

The basis for the determination of the contact angle is the image of the drop on the drop surface. In the DSA1 program the actual drop shape and the contact line (baseline) with the solid are first determined by the analysis of the grey level values of the image pixels. To describe this more accurate, the software calculates the root of the secondary derivative of the brightness levels to receive the point of greatest changes of brightness. The found drop shape is adapted to fit a mathematical model which is then used to calculate the contact angle. The various methods of calculating the contact angle therefore differ in the mathematical model used for analyzing the drop shape. Either the complete drop shape, part of the drop shape or only the area of phase contact are evaluated. All methods calculate the contact angle as $\tan\theta$ at the intersection of the drop contour line with the solid surface line (base line).

In the following sections the different drop shape analysis methods are briefly described.

16.3.3.1 Tangent method 1

The complete profile of a sessile drop is adapted to fit a general conic section equation. The derivative of this equation at the intersection point of the contour line with the baseline gives the slope at the 3-phase contact point and therefore the contact angle. If dynamic contact angles are to be measured, this method should only be use when the drop shape is not distorted too much me the needle.

16.3.3.2 Tangent method 2

That part of the profile of a sessile drop which lies near the baseline is adapted to fit a polynomial function of the type ($y=a+bx+cx^{0,5}+d/lnx+e/x^2$). The slope at the 3-phase contact point at the baseline and from it the contact angle are determined using the iteratively adapted parameters.

This function is the result of numerous theoretical simulations. The method is mathematically accurate, but is sensitive to distortions in the phase contact area caused by contaminants or surface irregularities at the sample surface.

As only the contact area is evaluated, this method is also suitable for dynamic contact angles. Nevertheless, this method requires an excellent image quality, especially in the region of the phase contact point.

16.3.3.3 Height-width method

In this method the height and width of the drop shape are determined. If the contour line enclosed by a rectangle is regarded as being a segment of a circle, then the contact angle can be calculated from the height-width relationship of the enclosing rectangle. The smaller drop volume, the more accurate the approximation for smaller drops are more similar to the theoretically assumed spherical cap form.

As the drop height cannot be determined accurately when the needle is still in the drop, the height-width method is not suitable for dynamic drops. This method also has the disadvantage that the drops are regarded as being symmetrical, so that the same contact angle is obtained for both sides, even when differences between the two sides can be seen in the actual drop image.

16.3.3.4 Circle fitting method

As in the height-width method, in this method the drop contour is also fitted to a segment of a circle. However, the contact angle is not calculated by using the enclosing rectangle, but by fitting the contour to a circular segment function. The same conditions apply to the use of this method as to the height-width method with the difference that a needle remaining in the drop disturbs the result far less.

16.3.3.5 Young-Laplace (sessile drop fitting)

The most complicated, but also the theoretically most exact method for calculating the contact angle is the YOUNG-LAPLACE fitting. In this method the complete drop contour is evaluated; the contour fitting includes a correction which takes into account the fact that it is not just interfacial effects which produce the drop shape, but that the drop is also distorted by the weight of the liquid it contains. After the successful fitting of the YOUNG-LAPLACE Equation the contact angle is determined as the slope of the contour line at the 3-phase contact point.

If the magnification scale of the drop image is known (determined by using the syringe needle in the image) then the interfacial tension can also be determined; however, the calculation is only reliable for contact angles above 30°. Moreover, this model assumes a symmetric drop shape. Therefor it cannot be used for dynamic contact angles where the needle remains in the drop.

The physical-mathematical principles of the YOUNG-LAPLACE method are described in more detail in Section 16.4.1, which is concerned with the calculation of the surface tension of pendant drops.

16.4 Measuring the surface tension of pendant drops

If a drop of liquid is hanging from a syringe needle then it will assume a characteristic shape and size from which the surface tension can be determined. A requirement is that the drop is in hydromechanical equilibrium.

When in hydromechanical equilibrium the force of gravity acting on the drop and depending on its particular height corresponds to the LAPLACE pressure, which is given by the curvature of the drop contour at this point. The LAPLACE pressure results from the radii of curvature standing vertically upon one another in the following way:

$$\Delta p = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$ Equation 59

This equation describes the difference between the pressure below and above a curved section of the surface of a drop with the principal radii of curvature r_1 and r_2. The pressure difference Δp is the difference in pressure between the outside of the drop and its inside.

16.4.1 The basic drop contour equation

For a pendant drop which is rotationally symmetrical in the z-direction then, based on Equation 59, it is possible to give an analytically accurate geometric description of the principal radii of curvature. The tangent at the intersection of the z-axis with the apex of the drop forms the x-axis. The drop profile is given by pairs of values (x,z) in the x-z-plane.

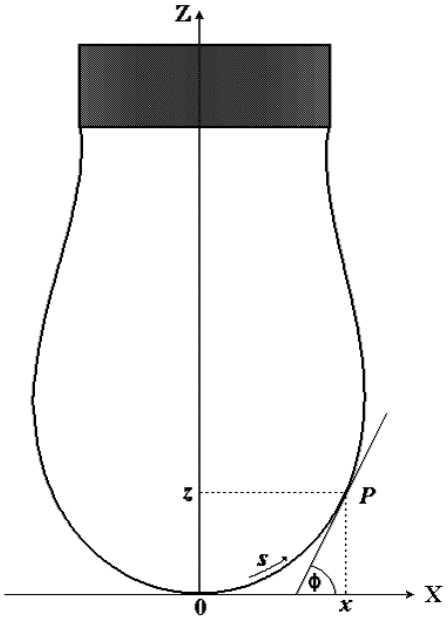


Fig. 16.13: Geometry of the pendant drop

In hydromechanical equilibrium the following relationship applies

$$\Delta p_{apex} - \Delta p_P = z \cdot \Delta\rho \cdot g \qquad \text{Equation 60}$$

(Δp_{apex} = pressure difference at apex; Δp_P = pressure difference at Point P (x,z); $\Delta\rho$ = difference in density between the drop liquid and its surroundings; g = acceleration due to gravity)

With the principal curvatures k (reciprocal value of principal curvature radius r) and the YOUNG-LAPLACE Equation (Equation 59) we obtain:

$$\Delta p_{apex} = \sigma \cdot \left(k_{apex,1} + k_{apex,2}\right) \qquad \text{Equation 61}$$

$$\Delta p_p = \sigma \cdot \left(k_{p,1} + k_{p,2}\right) \qquad \text{Equation 62}$$

$k_{apex,1(2)}$ = principal curvatures at apex

$k_{P,1(2)}$ = principal curvatures at Point P (x,z)

Because of the axial symmetry of the drop, the principal curvatures at the apex are the same in all directions (→ k_{apex}). From differential geometry the analytical expressions for the curvatures of the principal normal sections at Point P (x,z) are known:

$$k_{p,1} = \frac{d\Phi}{ds} = \left(\frac{d^2 z}{dx^2}\right) \cdot \left(1 + \left(\frac{dz}{dx}\right)^2\right)^{-3/2} \qquad \text{Equation 63}$$

$$k_{p,2} = \frac{\sin\Phi}{x} = \left(\frac{dz}{dx}\right) \cdot \frac{1}{x} \cdot \left(1 + \left(\frac{dz}{dx}\right)^2\right)^{-1/2} \qquad \text{Equation 64}$$

From Equations 60 to 64 we obtain:

$$\frac{d\Phi}{ds} = 2k_{apex} - \frac{z \cdot \Delta\rho \cdot g}{\sigma} - \frac{\sin\Phi}{x} \qquad \text{Equation 65}$$

(s = length of arc along the drop profile, Φ = angle between the tangents at Point P (x,z) and the x-axis (see Fig. 16.13)

Equation 65 describes the profile of a pendant drop in hydromechanical equilibrium. The Equation is converted into a dimensionless form to solve it. The following definitions are used:

$$X = \frac{x}{a};\ Z = \frac{z}{a};\ S = \frac{s}{a};\ B = \frac{1}{a \cdot k_{apex}};\ \text{with: } a = \sqrt{\frac{\sigma}{\Delta\rho \cdot g}}$$

B = dimensionless form parameter of the pendant drop

a = capillary constant

With these definitions Equation 65 can also be expressed in the following way:

$$\frac{d\Phi}{dS} = \frac{2}{B} - Z - \frac{\sin\Phi}{X};\ \frac{dX}{dS} = \cos\Phi;\ \frac{dZ}{dS} = \sin\Phi \qquad \text{Equation 66}$$

At the apex the limiting conditions X = Z = S = Φ = 0 apply. This results in:

$$\frac{\sin\Phi}{X} = \frac{1}{B} \qquad \text{Equation 67}$$

B is the only parameter to determine the shape of the drop profile. It is therefore known as the **form parameter**. In addition, it can be seen that the surface tension σ can be calculated for

a known difference in density $\Delta\rho$ if the relative size ratio a of a measured drop can be determined for the corresponding theoretical drop profile.

Equation 67 is, together with the limiting conditions from Equation 66, known as the **fundamental equation for a pendant drop**.

By varying the form parameter B it is possible to calculate theoretical drop profiles after carrying out a numerical integration method. If the theoretical drop profile corresponds to the measured drop profile then the surface tension can be calculated. The problem in measuring the interfacial tension therefore consists in determining the correct theoretical drop profile for the measured drop exactly and rapidly.

16.4.2 The robust shape comparison method

Various groups of methods exist for solving the problem mentioned above. In the DSA1 program the robust shape comparison method is used. This method is a statistical method which is characterized by its stability against "outliers". In this way even low-quality drop images can still be evaluated.

A series of drop profile co-ordinates is used for the evaluation. The measured profile is compared with the theoretical profile. The comparison is not made directly via the profile points, but via their vectors. An advantage of this method is that it is possible to optimize the individual parameters used independently.

For a more accurate observation of the mathematical details of the individual optimization steps and correction methods please refer to the technical publications (see Section 17.2). The error function E used in the optimization is a function of the form parameter B, the capillary constant a (which includes the surface tension), the position of the apex (x_0, z_0) (co-ordinate origin) and the angular variation Θ of the drop from the plane of symmetry.

$$E = E\left(B, a, \left(x_0, z_0\right), \Theta\right) \qquad \text{Equation 68}$$

The angular variation Θ of the drop from the plane of symmetry describes the variation of the vertical drop axis from the normal axis (z-axis). For small variations (± 0.1°) the correction does not cause any problems.

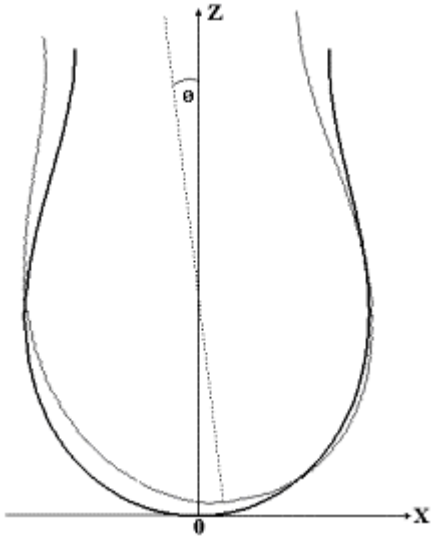


Fig. 16.14: Angular variation Θ of the drop from the plane of symmetry

In the evaluation of the image a further quantity appears which also needs to be taken into consideration: the height-width ratio AR (**A**spect **R**atio) of the image pixels in the drop image. By adaptation of the described parameters B, θ and AR the error function E_{rsc} (**r**obust **s**hape **c**omparison) from Equation 68 can be minimized by the robust shape comparison:

$$E_{rsc} = E\left(B, \left(x_0(\Theta), z_0(\Theta)\right), AR\right) \qquad \text{Equation 69}$$

17 Appendix

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17.3 Glossary

The glossary contains terms which are used in the DSA program and the manual. They are arranged alphabetically and provided with a short explanation. Within the glossary cross-references are made to other terms in the form (→ Term).

Apex

Apex of a pendant drop.

ASCII

Abbreviation for "American Standard Code for Information Interchange". Standard character code which is understood by many other programs.

Aspect Ratio

is one of the fitting parameters (→ Fitting Parameters) which you can set. It defines the X/Y-ratio (horizontal : vertical) of the drop image to be evaluated. The "Aspect Ratio" of a total measuring system depends on the "Aspect Ratios" of the individual components, consisting of

- the optical system
- the video camera
- the video frame grabber board.

The error of this parameter forms part of the error of the drop contour analysis and thus influences the values of the surface tension (→ Surface Tension) or interfacial tension (→ Interfacial Tension) obtained.

Bad Neck Points

is one of the fitting parameters (→ Fitting Parameters) which you can set. This parameter determines the number of contour points in the region of the neck of the drop which are not to be used in the evaluation.

Baseline

Projection of a flat solid surface, on which a sessile drop is located, in the two-dimensional image plane. Baseline for calculation of the contact angle.

Batch

Functions which are automatically processed in sequence are stored in a batch; these are carried out automatically in sequence as soon as the batch is called up.

Bitmap

Pixel-oriented format for storing images (abbreviation: BMP).

BMP-RLE

Subtype of BMP format (run-length-encoded bitmap) format. For saving memory capacity pixels with the same values are consolidated in this format.

Context menu

Menu in which important commands for an active window are gathered together. Called up by the right-hand mouse key while the mouse cursor is located in the window.

Decimal separator

Separator used in decimals. In Germany: "," (comma) is usual; otherwise: "." (stop).

Density

This parameter describes the difference in density between the drop and the surrounding phase in g/cm³. In the determination of surface tension (→ Surface Tension) this value corresponds quite accurately with the absolute density of the drop liquid, as the density of the surrounding phase (normally air) is virtually zero.

Digitisation threshold

Grey level above which the video digitizer recognises an image point as "black". Used for recognizing the drop contour.

Drop Window

DSA window for processing stored drop images.

Enhanced Metafile

Memory format which can be read by other Windows programs. (e.g. Word 97)

Extraction Parameter

These parameters are used for the recognition and evaluation of the drop contour. The needle diameter is of particular importance for the evaluation.

Field

The video image (frame) created and transferred to the computer consists of two partial images produced in rapid sequence each with half the pixel density. These partial images are known as "Fields".

Fitting Parameter

These parameters have a direct influence on the evaluation of the drop image. They define the points on the drop contour which are to be used for evaluation.

Frame

Single video image. A frame consists of two fields produced in rapid sequence each with half the pixel density; when these are superimposed they produce the complete image, the frame.

Frame grabber

This is the video frame grabber board which it used to digitise photographic recordings and show them on the screen as pixel images.

Frame grabber Window

DSA-window for controlling drop recording and evaluation of live images.

Histogram

Representation of the grey level distribution for the black/white recognition of a digitized video image.

Icon

(or command icon) is a patch panel with an pictogram on the user interface of the program. Icons are shown raised (3D). If you click an icon then you press the switch which is shown graphically. By clicking an icon you trigger the function allocated to it.

IFT

Abbreviation for "Interfacial Tension".

Installation

Installation and setup of a system/software.

Interfacial tension

In this manual this term refers to the force between two liquid phases.

ISA-slot

Standardised socket for PC plug-in boards, e.g. for video frame grabber boards.

Iteration Start Value (B0)

is one of the fitting parameters (→ Fitting Parameters) which you can set. It defines the initial value of the shape parameter (B) (→ Shape Parameters) in the Young-Laplace equation (→ Young-Laplace Equation). The evaluation process is accelerated if a good starting value is selected.

Limit Lines

belong to the extraction parameters (→ Extraction Parameters). They limit the image sections to be used for the evaluation.

Live Image

Directly transmitted image via video camera and frame grabber. The live image is visible on the second (video) monitor.

LUT

Abbreviation for "Look-Up Table". A "Look-Up Table" is a conversion table for transferring an incoming grey or color level into an outgoing value

Magnification

abbreviated MAG, is the factor for converting the pixel presentation of the video frame grabber to the drop image in millimetres. This factor depends on the magnification of the video image which has been set. In the DSA program the diameter of the syringe needle is used as the scale.

Mean Profile

is a fitting parameter (→ Fitting Parameters) which you can set. If the drop is not symmetrical a mean profile is calculated.

Multi Document Interface

Program and screen arrangement in which the available menus and menu items depend on the particular active window.

PCI-slot

Standardised socket for PC plug-in boards, e.g. for video frame grabber boards.

Pendant Drop

The name of a method for determining the surface tension by recording a pendant drop.

Pixel

Image point on the computer screen. During the digitising of photographic recordings there is a conversion to a pixel matrix. The individual pixels are allocated particular color or grey levels.

Sessile Drop

Name of a method for determining the contact angle and the interfacial tension by recording a drop placed on a solid surface.

SFT

Abbreviation for "Surface Tension".

Shape parameter

This parameter is used in the Young-Laplace equation (→Young-Laplace Equation) in drop contour analysis. It characterises the drop shape.

Smoothing

is a fitting parameter (→ Fitting Parameters) which you can set. Smoothing smoothes the drop shape and thus reduces errors in the fitting process.

Substrate Position

Position of the solid surface during the measurement of the contact angle of a sessile drop.

Surface Tension

In this manual this term refers to the force between a vapour phase (usually air) and a liquid phase.

Theta Correction

is a fitting parameter (→ Fitting Parameter) which you can set. This parameter is used to check whether and to what extent a drop does not hang vertically and to carry out a correction before the fitting process is carried out.

Threshold Gradient

is one of the extraction parameters (→ Extraction Parameters). This value defines the minimum grey level of an image pixel at which this point will be recognized as the (drop) edge.

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