Dynamic Contact Angle Analyzer Tutorial

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Introduction

Understanding the characteristics of a liquid-solid interface is important to virtually every manufacturing industry, from bio-materials and pharmaceuticals to paints and textiles. Knowledge of how sheet metal is wetted by different paints, for example, is as important to the automotive industry as is knowledge of the hydrophicity (or water absorption) of orally-ingested drugs to the pharmaceutical industry.

Over the past 100 years, a number of techniques have been developed to measure these characteristics. Methods for determining the wettability of solid surfaces, the tensiometry of liquids, and the absorption of liquids into solids have given researchers the information they need to more fully understand and control their production process.

Various techniques have been developed over the last few decades to obtain the surface properties of the liquid and solid. These methods include sessile drop (goniometer), tilted plate, Wilhelmy plate, capillary rise, maximum bubble pressure, drop weight, ring, and pendent drop. The parameters that are obtained by those techniques are contact angle between a solid and liquid, surface tension of a liquid, interfacial tension between two immiscible liquids, and surface energy of solid.

Among all of the techniques that are available, the Wilhelmy plate technique provides the most accurate and repeatable measurements. In the Wilhelmy plate technique, the solid sample is hanged perpendicular to the liquid's surface. When the solid is partially immersed in the liquid, the equilibrated force can be expressed as:

$$F \times g = F(\text{liquid-solid interaction}) - F(\text{buoyancy})$$

Or

$$F \times g = \gamma \times PR \times \cos\theta - \rho \times V \tag{1}$$

Where F is the interaction force between solid and liquid, g is the gravitational constant, γ is the surface tension of the liquid, PR is the wetted perimeter of the solid, θ is the contact angle between the solid and liquid, ρ is the density of the liquid, and V is the volume of solid immersed underneath the liquid.

When the solid is right at the liquid's surface, the F(buoyancy) term, $\rho \times V$, equals to zero. Then, the final equation for calculation will be:

$$F \times g = \gamma \times PR \times \cos\theta \tag{2}$$

Since the equation involves in force measurement, with a high-precision balance, the measurement can then be done with high accuracy and repeatability.

The Thermo Cahn Dynamic Contact Angle (DCA) analyzer is an instrument used to measure the surface properties of solid and liquid samples, by using the Wilhelmy technique. It consists of a highly sensitive balance, a moving stage mechanism, and a control station.

Hardware

Upon the purchase of a Thermo Cahn DCA system, it is necessary to set-up the hardware per the detailed instruction in the hardware set-up manual.

Sample Compartment Set-up

By setting up the DCA, it can be seen that there might be one, two, or three diamond shape loops in the DCA, based upon the DCA model. For DCA 312, which has one loop, the loop will be the place for putting the sample holder and sample. For DCA 315, there are two loops. The one on the left is for the sample holder and sample, and the one on the right is for counterweighs. There are three loops in DCA 322, named as loop A, loop B, and loop C, start from left to right. Loop C is always used for counterweighs, and loops A and B are for samples.

When the DCA is set-up, its sample compartment will look like the following picture. Picture shows the in-line stirrup and sample, and counterweights.

Balance Counterweighing

In the balance of the DCA 315 and DCA 322, there is a counter-weight side, which is the loop at the far right hand side, loop C. The counter-weight side is used to counter balance the sample's weight, so that the maximum weighing sensitivity and weighing range is obtained. Please refer to the instruction manual for further detailed information about the balance specifications.

For DCA 322, it is necessary to note that there are two sample loops, loop A and loop B. Before performing the counterweighing, please make sure that the active method selects the correct loop of operation. It is also worthy to mention that the ratio of the weighs on three loops of DCA 322, loop A: loop B: loop C, is 1: 5: 1. This means that 100 mg weigh on loops A or loop C creates the same amount of torque as that of 500 mg weigh on loop B.

By using the DCA/Record function of the DCA software, the counterweighing procedure is described as follows:

1. Make sure that the correct loop is selected in the current loaded method.
2. Put on stir-ups (stir-up and in-line stir-up) onto the balance. With NO weights on the stir-ups, tare the balance.
3. Start the Record function on the program to monitor the weight as the function of time.
4. Put on sample and necessary holder onto the sample loop, loop A or B.
5. Put on the stirrup on the counter-weight side, loop C.
6. Put on counter weight to make weight reading close to zero.
7. Remove sample holder and/or sample as needed.

NOTE: It is necessary to make sure that the maximum sample capacity of the balance is not exceeded during this procedure. Following table shows the specifications for the balances in each DCA model.

	DCA 322		DCA 315
	A-loop	B-loop	
Maximum Balance Capacity	1.5 g	3.5 g	100 g
Dynamic Weighing Range	± 150 mg	± 750 mg	± 10 g
Balance Sensitivity	0.1 µg	1 µg	1 µg

Software Operation

WinDCA is a Windows based software program used to control the DCA system, collect data, and perform data analysis. It is designed in such a way that the DCA experiments are controlled through experimental steps.

There are various sampling techniques in the WinDCA program. Since each sampling technique serves a different purpose, there are different experimental steps involved. It is also necessary to understand that the experimental steps are only one part of the WinDCA method. For detailed information about this software, please refer to the software manual.

General Note

During the deduction of the equation (2), F x g = γ x PR x cosθ, it is noted that F in the equation represents the interaction force between the liquid and solid at the zero buoyancy point, or touching point, or Zero Depth Of Immersion (ZDOI) point.

However, during the practical data collection, it is important to know that the interested solid surface is vertical to the liquid. Therefore, it's necessary to immerse the solid sample into the liquid deep enough so that the "side" surfaces of solid sample will interact with the liquid. When this is occurring, the solid is in the liquid and buoyancy will be measured by the system. It is then necessary to do something to correct the buoyancy term in the equation.

Since the buoyancy is directly proportional to the volume of immersed solid, it is then mathematically to fit a line across the collected data (in force vs immersed volume or immersion depth), so that it can be extrapolated to the ZDOI line. The intercept of such fitted line and the ZDOI line then represents zero volume and zero buoyancy, or true force at ZDOI.

Based upon the above discussion, it is then noted that the solid sample should be immersed in the liquid deep enough so that the vertical "sides" of the solid will interact with the liquid. After that, the software will allow user to specify a linear region to "eliminate" the buoyancy term and perform the correct calculation, which will be performed automatically by the software.

CALIBRATION

In order to obtain accurate measurements, it is always recommended that the DCA system be calibrated regularly. There are two parts that need to be calibrated. One is the balance, and the other is the stage motor. The balance calibration ensures that an accurate weight reading will be recorded, and the motor calibration guarantees that the correct sample position and motor speed will be attained. Since the WinDCA software allows the calibration results to be saved into the same calibration files, the following procedure should be used in order to ensure that the correct calibration factors are used:

- Create a new method file with the correct system configuration, or load an existing method file, or edit the loaded or created method and save the changed method file.
- Making sure the balance is correctly counter-weighed. If not sure, please refer to the section about balance counter-weighing on page 3.
- Calibrate the balance and/or the motor of the DCA system. Save the new calibration file and update it into the current method file.
- Perform the experiments.

Important: The calibration of the DCA system should be performed AFTER the method file has been loaded or created. It is also recommended, to ensure that the weight readings are correct, that you check them by using the DCA/Record or DCA/Weight function prior to running the experiments.

Making a DCA Run

Contact Angle

When collecting the contact angle data, from the Wilhelmy equation, $F \times g = \gamma \times PR \times \cos\theta$, it can be seen that $\cos\theta$ can only be obtained if the other parameters are known or measured. Therefore, in the method, it's necessary to enter g, γ, and dimension of the solid probe correctly.

Under this sampling technique, both advancing and receding contact angles are measured. Typically, three different methods are utilized. The first method performs experiments with one cycle (multiple experimental steps) and one loop (a set of advancing and receding steps). The second method has one cycle with multiple loops. The third method consists of multiple cycles and loops. The recommended steps for these three methods are listed as follows:

	Single Cycle and Single Loop (default method)	Single Cycle and Multiple Loops	Multiple Cycles and Loops
Recommended Experimental Steps	Set Speed Tare Balance Detect ZDOI Advance Dwell (optional) Recede Return to Zero Position	Same as the Single Cycle and Single Loop method, but with more than one advance/recede loops before the "Return to Zero Position" step.	different cycles which can be a combination of the previous two methods.

The first method is sufficient for most applications. The later two are useful for many other applications, such as the testing of a sample's cleanliness, or the re-orientation of the molecules on the sample's surfaces. In addition, the operator can create special experimental conditions for certain applications.

Following is an exemplary contact angle run of a piece of polymer against distilled water, by using the default single cycle single loop method.

It can be seen that the advancing and receding traces have a negative slope in them. This is caused by the increase of the buoyancy force, as the solid enters the liquid deeper. The boxes on the advancing and receding parts of the curves show the ranges of data that are used for linear regression to perform line fit and extrapolation to "eliminate" buoyancy force. The final results for advancing and receding are shown in the upper left corner, in the order of $\cos\theta$, θ, and regression factor. It is necessary to mention that the range of data that are used for calculation can be modified in the software. Please refer to the software for operation procedure.

CA-ONE.DCD - Auto Analysis - 1996

Advancing (0.5838 , 54.28° , 0.9570)
Receding (0.8961 , 26.35° , 0.9638)
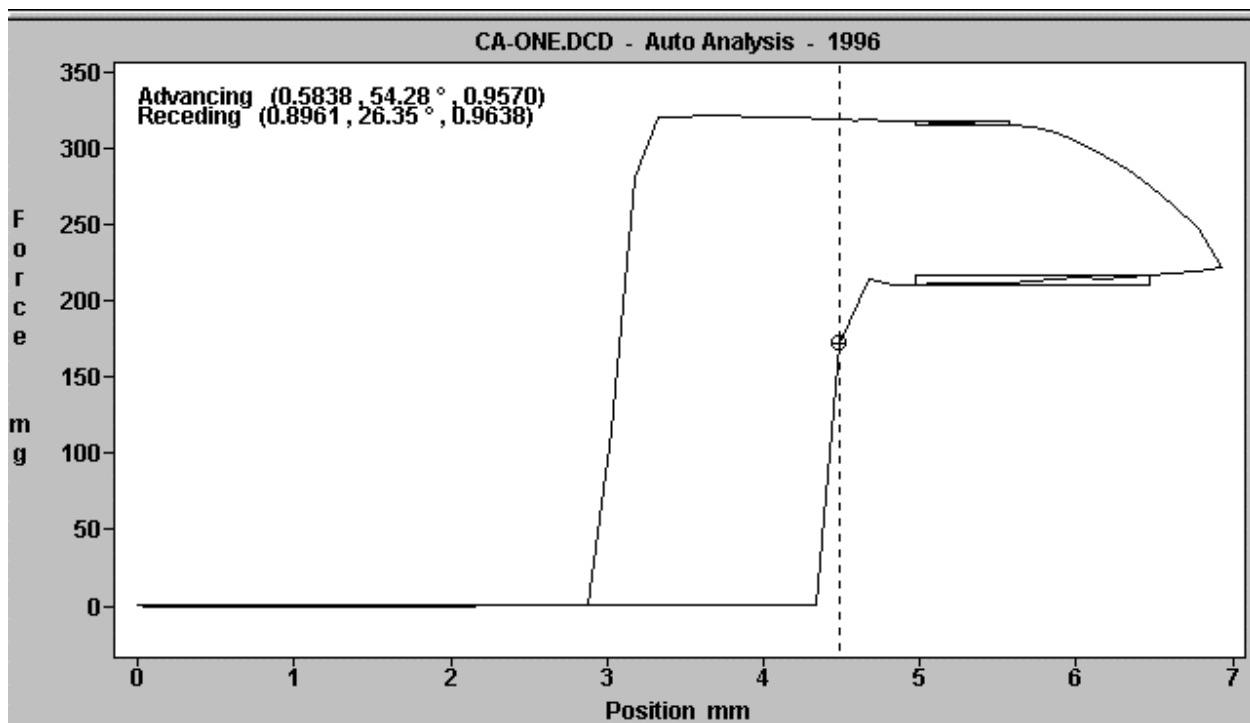
Surface Tension

To measure the surface tension of liquid, there are two different types of solid probes that can be used. One is a Wilhelmy Plate, made of glass or platinum. Another is the Du Nouy ring, made of platinum-iridium.

When using a Wilhelmy plate, the Wilhelmy equation, $F \times g = \gamma \times PR \times \cos\theta$, is used again. However, it's necessary to use standard solid probes which will provide known contact angle values. This standard solid probes can be clean glass plate or platinum plate, which will give a 0° contact angle, or $\cos\theta = 1$, because of the very high surface energies of these two materials when they are clean. This turns the Wilhelmy equation into:

$$F \times g = \gamma \times PR$$

Or

$$\gamma = F \times g \, / \, PR$$

Another commonly used surface tension measurement method is using a Du Nouy ring. In this method, a Platinum-Iridium ring is immersed into the testing liquid, and pulled out of the surface. The force needed to bring the ring out of the liquid is directly related to the surface tension value of the liquid. The equation used to calculate the surface tension of the liquid is expressed as follow:

$$\gamma = \gamma^* \times cF$$

Where γ* is the raw surface tension reading from the measurement, and cF is the correction factor, which is used to correct for the amount of liquid attached to the bottom of the ring during the pulling process of the experiment.

$$cF = 0.7250 + \sqrt{\frac{1.452\gamma^*}{C^2(D-d)} + 0.04534 - \frac{1.679}{R/r}}$$

Where C is the mean circumference of the ring, D is the density of the heavier liquid, d is the density of the lighter liquid, R is the radius of the ring, and r is the radius of the wire of ring.

When using a Wilhelmy plate, two different methods can be used. One method has a simple advance and recede cycle where the surface tension value is taken from the receding step. Another, more accurate and recommended method, has a "Read Weight/Time until Weight Stable" step at the ZDOI (Zero Depth Of Immersion) position which gives the surface tension value. A simple advance and recede loop method is used with the Du Nouy ring. The following table provides an example of the method steps.

	Wilhelmy Plate		Du Nouy Ring
	Simple	Recommended (default method)	
Experimental Steps	Set Speed Tare Balance Detect ZDOI Advance* Dwell (optional) Recede Return to Zero Position	Set Speed Tare Balance Detect ZDOI Advance* Dwell (optional) Recede to ZDOI Read Weight/Time until Weight Stable Return to Zero Position	Set Speed Tare Balance Detect ZDOI Advance* Dwell (optional) Return to Zero Position

* The solid probe should be advanced into the liquid deep enough so that the Wilhelmy plate is partially, or the Du Nouy ring is completely, immersed.

When using the plate method for measuring the surface tension, it's necessary to be sure that the solid probes are cleaned well. This can be done by using an oxidizing flame to clean the surface of solid probes, for example, a propane torch or Bensen burner with blue flame. For Platinum plate, burning it to dull red, after it's cleaned by chemicals, is a good sign of good cleaning. For glass plate, however, it's necessary to run it in and out of the flame very quickly for at least 6 times on each side. It's also important to visually check the cleaned glass plate to make sure that the surface is not wrapped or bent, and the edges of the plate is not dull or deformed.

With correctly cleaned plate, the advancing data line and the receding data line should superimpose and the curve of a surface tension run should be looked like this:

Surface Tension - A - Operator Unknown - Tue Sep 08 15:37:04 1998

newst8.dcd - Surface Tension - A - Operator Unknown - Tue Sep 08 15:37:04 1998

Read Weight/Time until Weight Stable (st = 31.6578 mN/m)
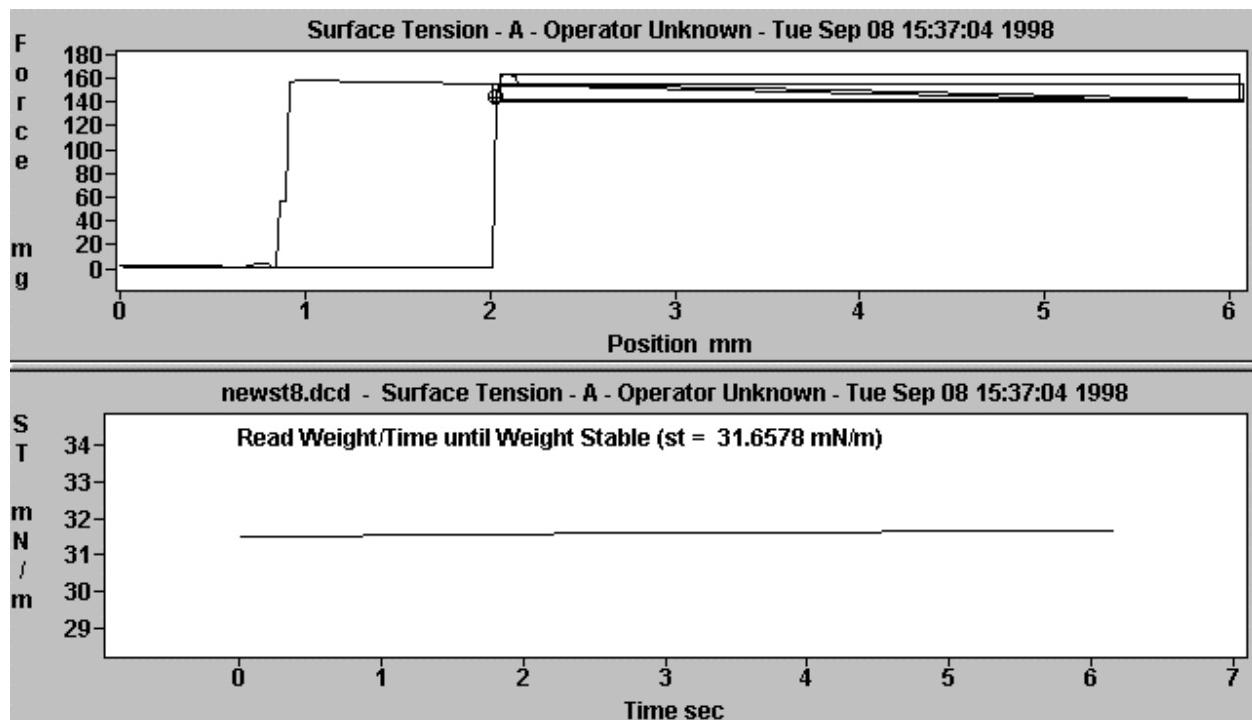
For the surface tension measurement performed with a Du Nouy ring, the data should be looked like the following plot. It is necessary to mention that there are two different standards for picking the point for calculating surface tension, ASTM and DIN. The ASTM standards will use the break point to calculate the surface tension, while the DIN standards will use the max pull point to calculate. It's our recommendation that the DIN standards should be used.

newst.dcd - Auto Analysis - Wed Jul 22 10:20:11 1998

(st = 34.2804 mN/m)
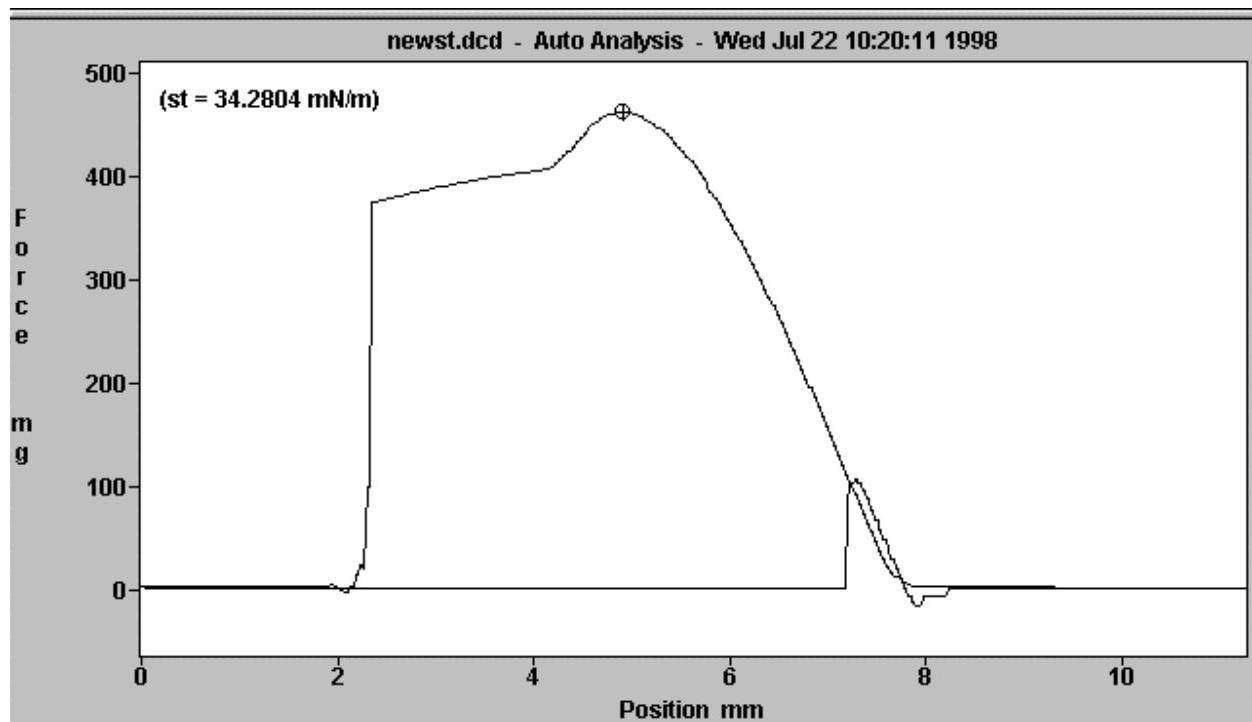
Even though both the Wilhelmy plate and Du Nouy ring can be used for many kinds of liquids, we recommend you use the Du Nouy ring method with highly viscose liquids (viscosity of 1000 cP or higher). However, when the Du Nouy ring method is used, it is also necessary to know the density of the liquid.

Interfacial Tension

Similar to the Surface Tension technique, both the Wilhelmy plate and Du Nouy ring can be used as the solid probe to measure the interfacial tension between two liquids, a light liquid on top of a heavier liquid. It is required that the solid probe pass only once between the interface of the two liquids, typically from the heavier to the lighter liquid.

The experimental steps, however, are more complicated than those of a surface tension measurement. We recommend you use two beakers for the experiment and use the following experimental procedure:

Step	DCA Method Step	PC Screen	Operator
1	Set Speed		
2	Wait for Operator Ready	Press the OK button, once the operator finishes the step(s) in the right column	Immerse the solid probe totally[*] inside the light liquid (beaker 1), by using the manual stage height adjustment.
3	Tare Balance		
4	Wait for Operator Ready	Press the OK button, once the operator finishes the step(s) in the right column	Remove the solid probe, have it cleaned and reinstalled. Remove beaker 1 and replace with beaker 2 containing the heavier liquid underneath the solid probe.
5	Detect ZDOI		
6	Advance (make sure that the solid probe breaks the surface of the heavier liquid, so that the Wilhelmy plate is partially, or the Du Nouy ring is completely, immersed)		
7	Wait for Operator Ready	Press the OK button, once the operator finishes the step(s) in the right column	Pour the light liquid slowly into beaker 2. Make sure there is enough light liquid to allow the solid probe to be completely immersed in the light liquid after the next step(s).
8	Return procedures are the same as those of a surface tension measurement. For Wilhelmy plate probe, use Recede and Return to Zero Position for the simple method, or Return to ZDOI, Read Weight/Time until Weight Stable and Return to Zero Position under the recommended method. For Du Nouy ring probe, use Return to Zero Position.		

*   If a Wilhelmy plate is used, all of the plate should be immersed in the light liquid. Only the ring itself should be immersed in the liquid, if a Du Nouy ring is used. This is to ensure that the probe returns to the same position once it's pulled out of the heavier liquid and returned to the zero position.

Steps 1 and 2 can be interchanged. Step 2 can even be eliminated from the method, but the solid probe must be immersed in the light liquid prior to the start of the data collection. It is also suggested that several trial runs be made in order to optimize the experimental conditions and the amount of liquids needed for the experiment.

The above experimental steps should be used in most cases. However, when the heavier liquid has a much smaller surface tension than that of the lighter liquid, the solid probe should pass through the interface from the lighter liquid to the heavier liquid. Under this circumstance, the experimental steps for the interfacial tension run is then the same as that of the standard surface tension measurements, and only the advancing data will be analyzed by using the manual analysis mode.

Figure: IT.dcd - Auto Analysis - 1996. Force (mg) vs. Position (mm). (it = 36.3538 mN/m)
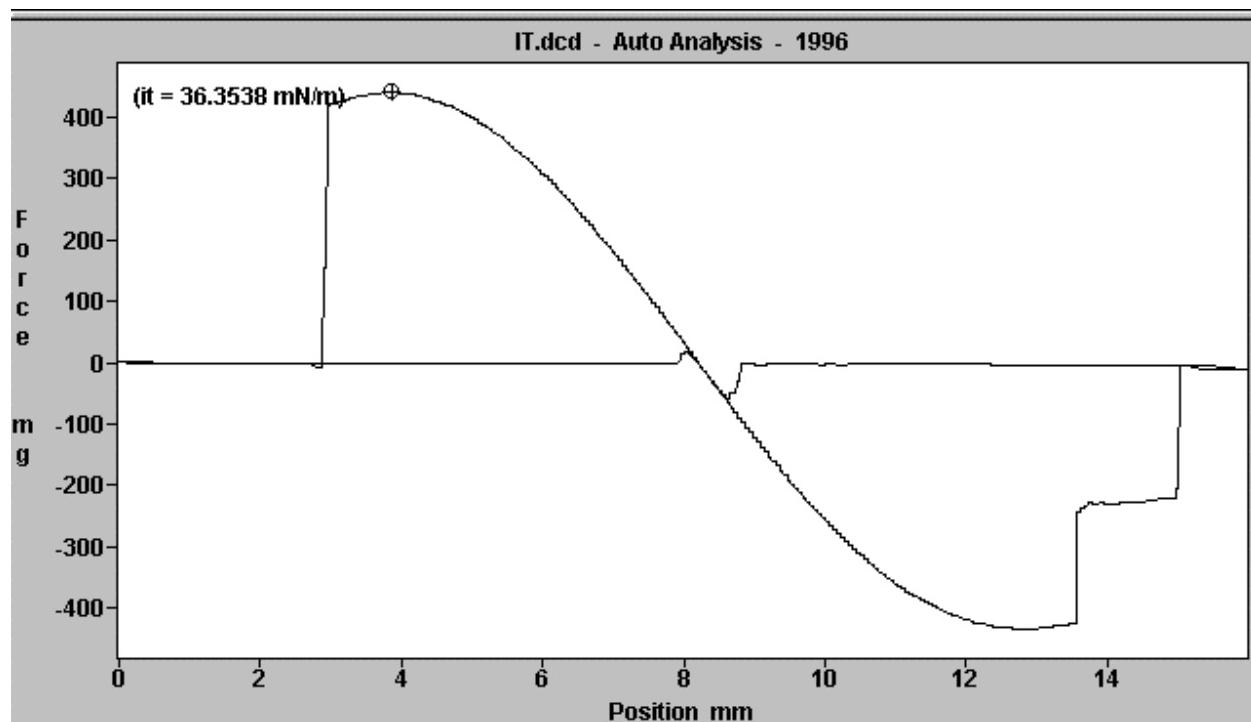
Wicking

When the amounts of liquid being adsorbed by solid samples, porous or powder, are of interest, you will perform a wicking experiment. Under this technique, solid samples will be immersed and held just below the liquid's surface and the weight change recorded as a function of time. Therefore, the experimental steps are: Set Speed, Tare Balance, Detect ZDOI, Advance, Tare Balance (optional but recommended), Read Weight/Time until Weight Stable, Return to Zero Position.

The motor speed should be set to a high value in order to immerse the solid into the liquid quickly. The distance for the advance step should be set to a low value large enough to ensure

that solid will be in contact with liquid throughout the run, since the liquid level will drop due to adsorption by the solid sample.
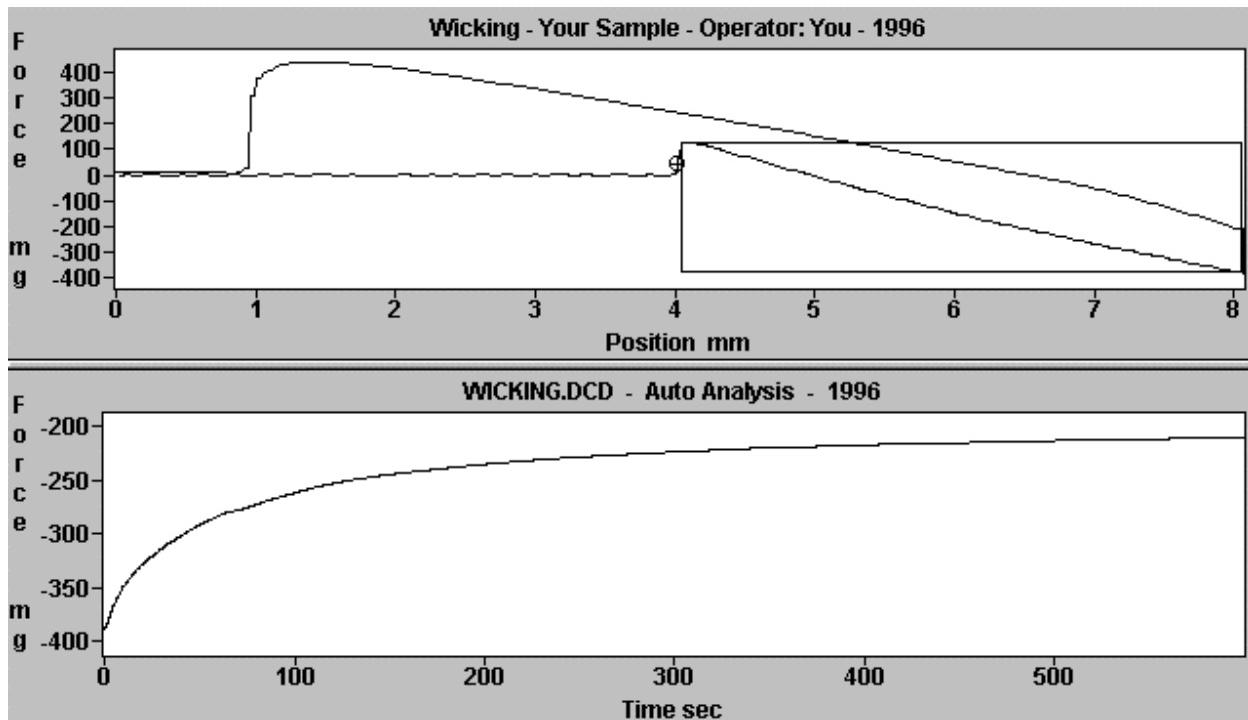
Fiber Diameter

For fiber samples, it's very difficult to measure its diameter, since it's usually very small, about a few micrometers. Even though a microscope can be utilized for this purpose, it's very time-consuming, and the apparatus can be expensive. The result obtained from microscopic methods can still be not accurate, since the measuring direction and the measuring point are varying among the fibers and within one single fiber.

For DCA, however, it's very simple and fast, and an accurate averaged diameter can be obtained, since the Wilhelmy equation contains the information about the fiber diameter.

$$F \times g = \gamma \times \pi \times \text{Diameter} \times \cos\theta$$

When a very low surface tension liquid is used, the contact angle should then be 0°, or $\cos\theta = 1$. Then the fiber diameter can be obtained as:

$$\text{Diameter} = F \times g / (\gamma \times \pi)$$

During the measurement, it's necessary to use a liquid with low surface tension, such as hexane, and acetone. This will then ensure the total wetting angle, or 0°, or $\cos\theta = 1$, is obtained.

The experimental steps are the same as those of the contact angle sampling technique, with single cycle single loop. Since most of the low surface tension liquids are volatile, it's highly possible that the sample or the attachment may absorb the vapor. Therefore, only the advancing data will be used for calculating the fiber's diameter. A typical fiber diameter run is illustrated as follows:
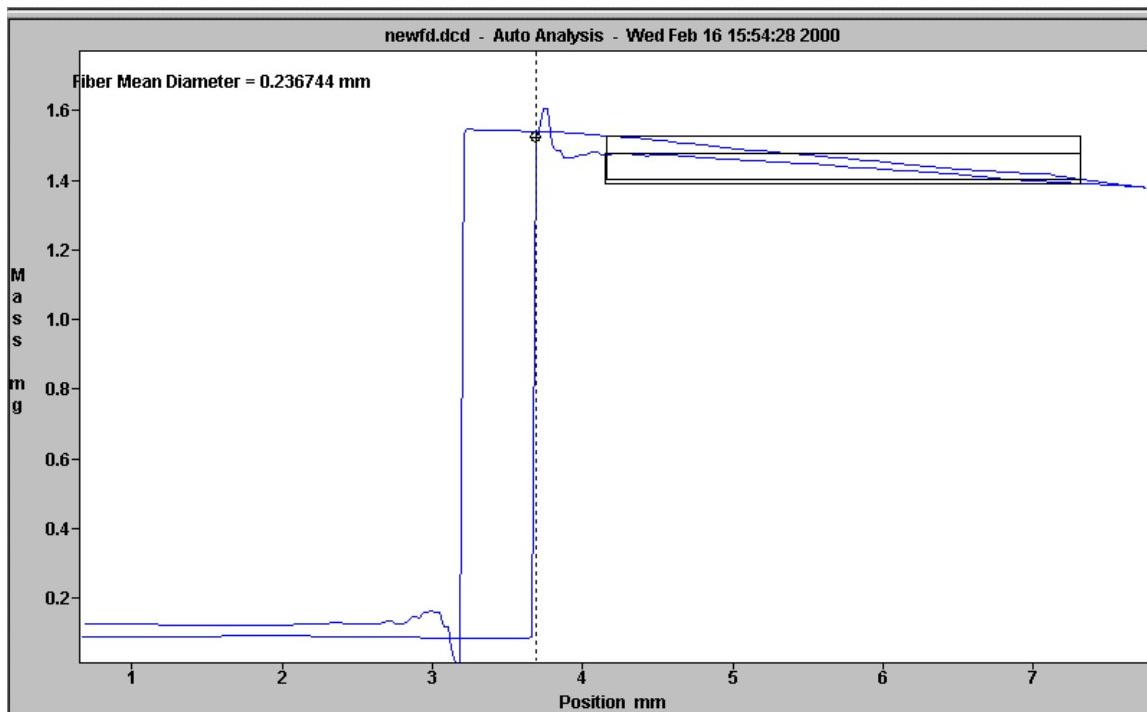
Solid Volume

For irregular shaped solid samples, the most common way to obtain its volume is the immersion method. This means that the sample is immersed into a liquid, and the volume of the solid is measured by either knowing the difference of the volume change of the liquid before and after the immersion, or the buoyancy force occurred on the solid after it's immersed in the liquid. By following the above logic, the solid's volume can be calculated as:

$$V = \text{Buoyancy Force} / \text{Liquid's density}$$

During the solid volume measurement, it's necessary to use a known-density liquid, and use very thin wire or small-volume sample holder to hold the sample. Otherwise, the experimental steps will be steps that ensure the solid is fully immersed into the liquid. The following graph shows a typical run of the solid volume.

Solid Volume - Sample Unknown - Operator Unknown - Fri Mar 24 12:53:20 2000

Solid Volume.dcd - Auto Analysis - Wed Aug 02 08:52:04 2000

Read Weight/Time until Weight Stable (sv = 1.1842 ml.)
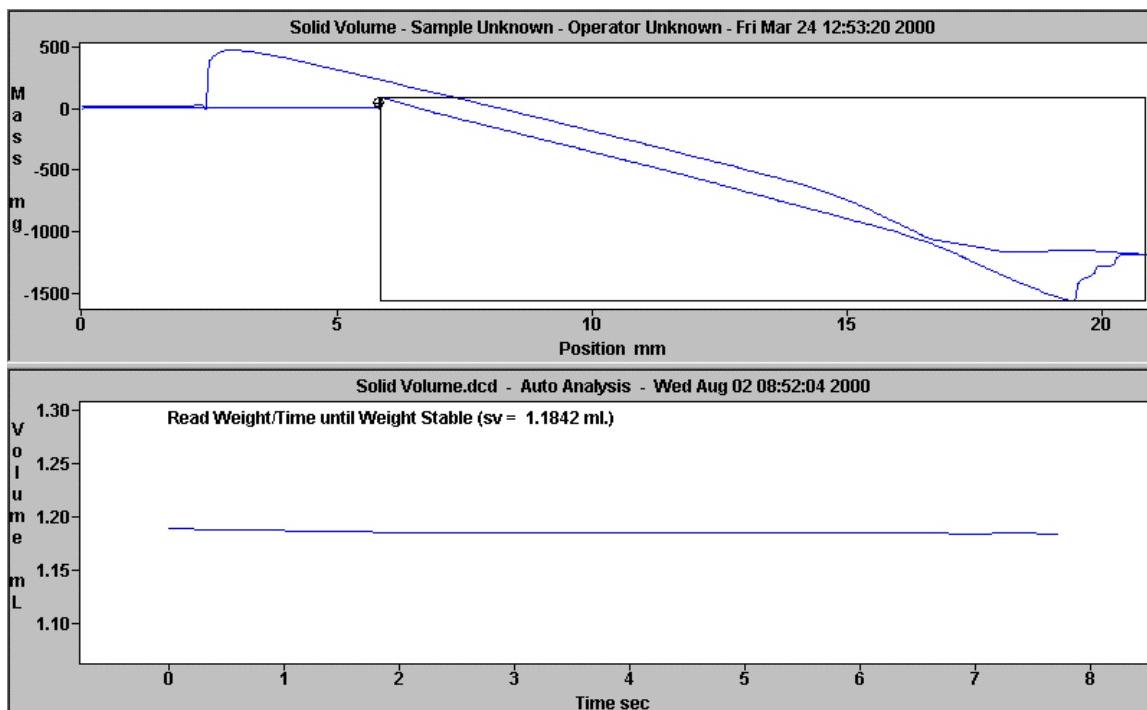
Liquid Density

The theory of measuring the liquid density is to obtain the buoyancy force of a known-volume solid inside the testing liquid. By knowing the buoyancy force and the volume of the solid, the density can be calculated as:

Liquid density = Buoyancy Force / Volume of solid

By using the Thermo Cahn supplied liquid density kit, which the volume of the solid is known, or can be measured by using the above solid volume sampling technique, the liquid's density can then be measured. However, it's necessary to be sure that the whole solid with partial support wire is immersed into the liquid. Also, if the liquid has a higher density than that of the solid, it might be necessary to put extra weight on top of the solid to push it into the liquid.

Typical experimental curves looks as follows:

Liquid Density - Sample Unknown - Operator Unknown - Fri Mar 24 13:26:47 2000

Liquid Density.dcd - Auto Analysis - Wed Aug 02 08:47:51 2000

Read Weight/Time until Weight Stable (ld = 1.1431 Denisty g/mL)
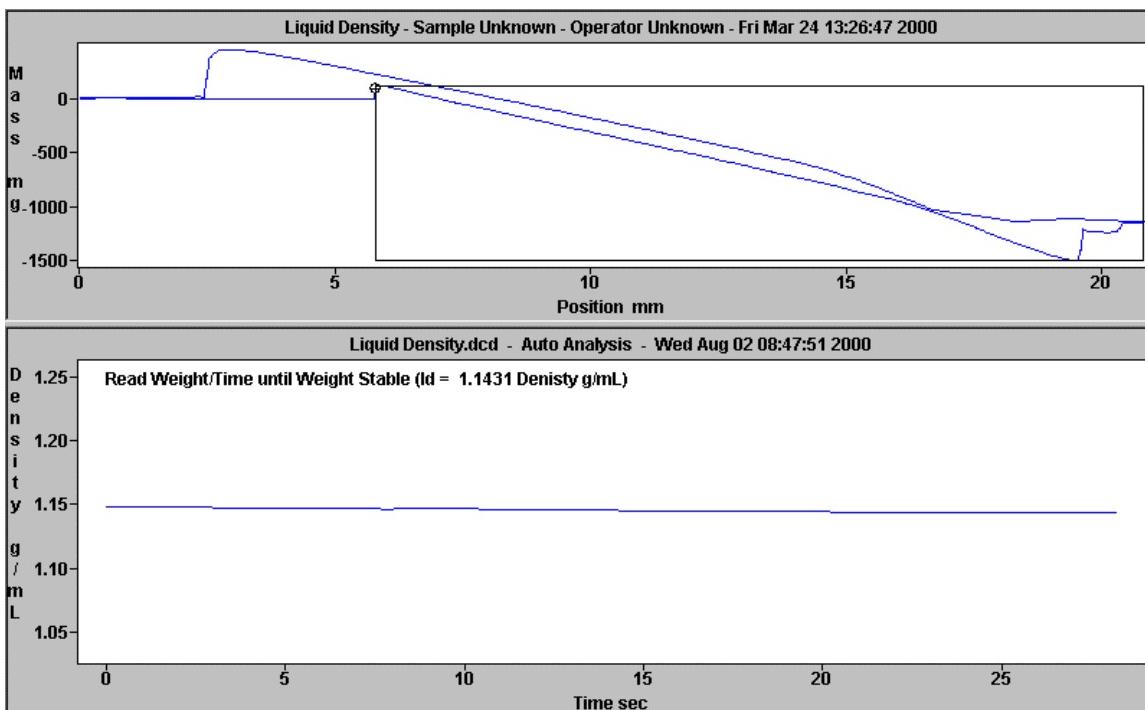
Solid Density

The density of a material is defined as:

$$\text{density} = \text{weight} / \text{volume}.$$

For solid, the weight can be measured by a balance. The volume can be measured by using the buoyancy force of the solid inside a known-density liquid, or

$$\text{volume of solid} = \text{buoyancy force} / \text{liquid density}.$$

Therefore, the final equation for calculation is:

$$\text{Solid Density} = \text{Liquid Density} \times \text{Solid Weight} / \text{Buoyancy Force}$$

In the data collection, the solid weight will be obtained at the beginning of the run, the buoyancy force will then be obtained by immersing the solid into the liquid, which the density is known. It's necessary to immerse the whole solid into the liquid for accurate measurement.

To accomplish the necessary steps to collect all of the needed data, the experimental steps are: set speed, tare balance (without solid sample), load solid sample, read weight/time until stable (to get the solid weight), detect ZDOI, advance (deep enough to immerse the whole solid sample), read weight/time until stable (to obtain the buoyancy force), and return to zero position. By performing the above steps, a run will look like:

Solid Density - Sample Unknown - Operator Unknown - Thu Feb 17 08:19:20 2000

Solid Density.dcd - Auto Analysis - Wed Aug 02 08:51:04 2000

Read Weight/Time until Weight Stable (sd = 8.3213 Denisty g/mL)
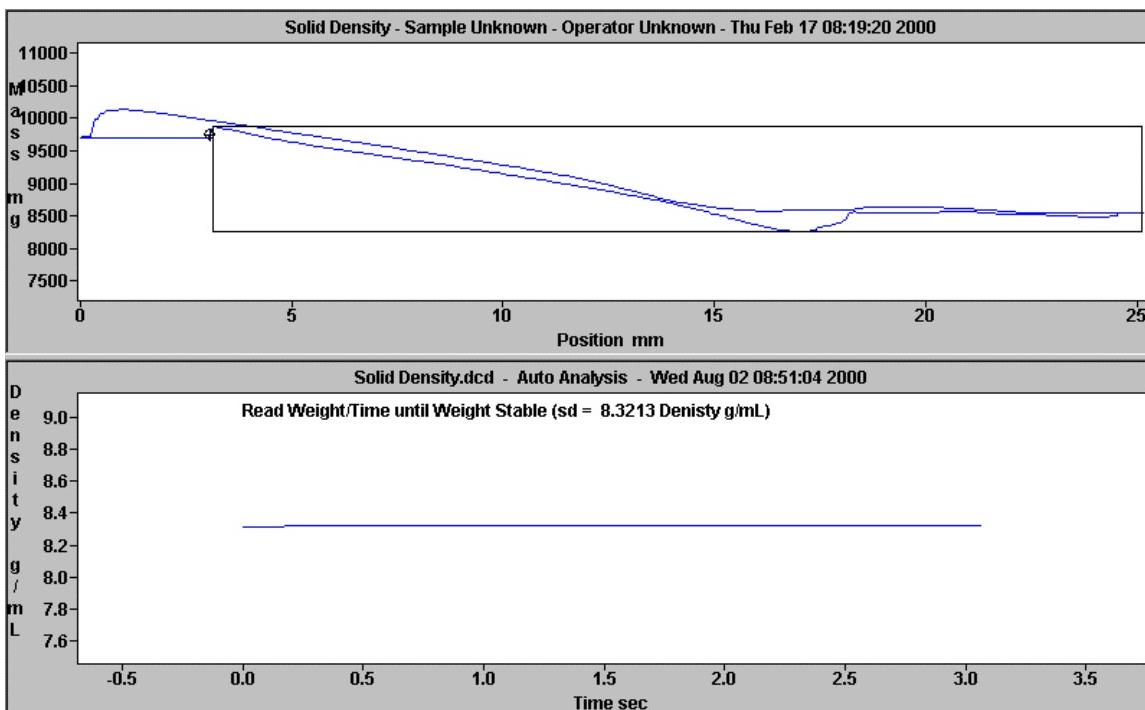
CMC

When adding the surfactant into a solvent, the threshold concentration at which micellization begins is known as the critical micelle concentration (CMC). With optional CMC accessory, the system will be capable of finding the CMC of surfactant in a solvent. A CMC experiment is a series of experiments where a surface tension measurement is performed after making a surfactant concentration change. With an understanding of the surface tension measurement steps (please refer to the surface tension section), it is easy to create the CMC experimental steps by adding the proper dosing related commands.

There are three modes for dosing, linear (default), fast, and manual (*show the screen capture*). It is recommended you use the fast mode to optimize the dosing parameters, once the surface tension measurement steps are optimized. After the optimum parameters are obtained, the linear or manual dosing method can then be used for a CMC measurement.

Since the CMC experiment is a series of surface tension measurements at different surfactant concentrations, the final CMC curve then looks like:

db1.dcd - CMC - Sample Unknown - Operator Unknown - Wed Mar 03 13:00:38 1999

CMC Plot for sample DB-45.

CMC = 0.8332g/L
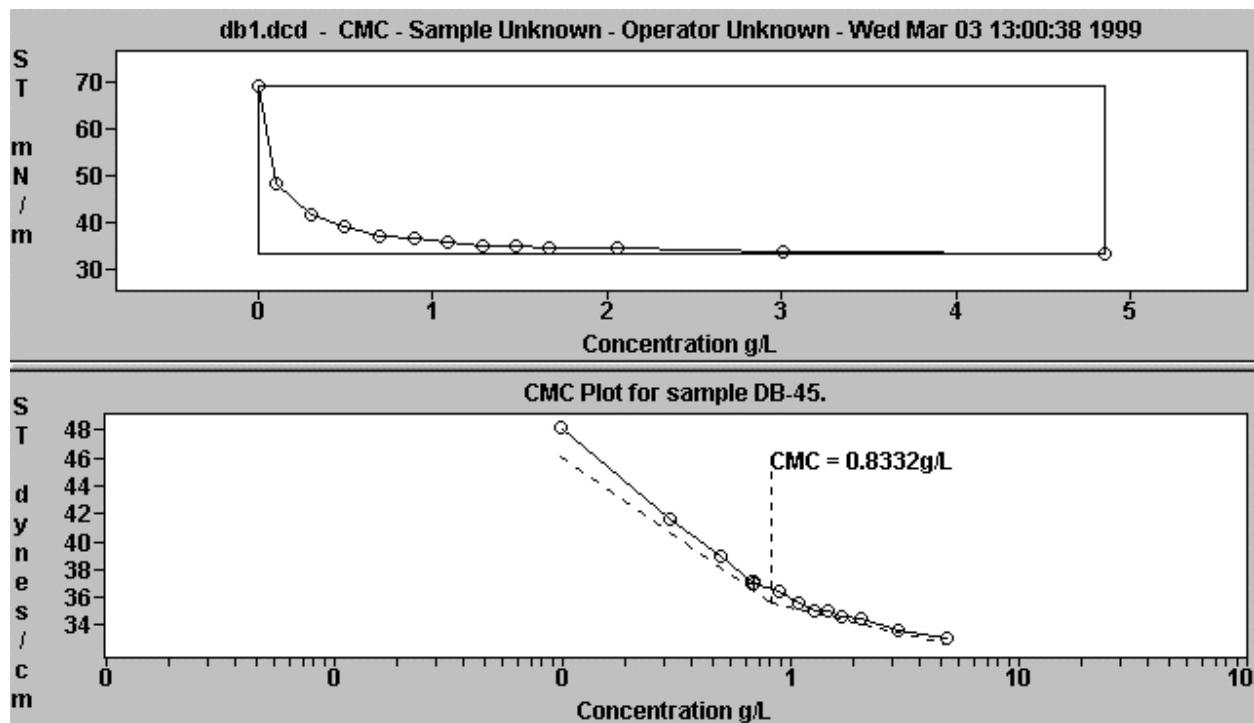
It's necessary to make sure that there are enough data points before and after the CMC. Otherwise, the software won't be able to locate the CMC automatically.

Special Sample Handling and Preparation

Thin Film Samples

Thick film samples can be easily handled by using a clip. However, for thin film samples, it may not be rigid enough to penetrate into the liquid, and no meaningful data will be obtained. It's then necessary to use the Thermo Cahn Thin Film sample holder for this purpose.

In order to make the film piece rigid, the Thermo Cahn Thin Film sample holder has a blunt "V" shape tip to bend the film sample. By also cutting the sample short, this will enable the sample to penetrate into the liquid and be measured.
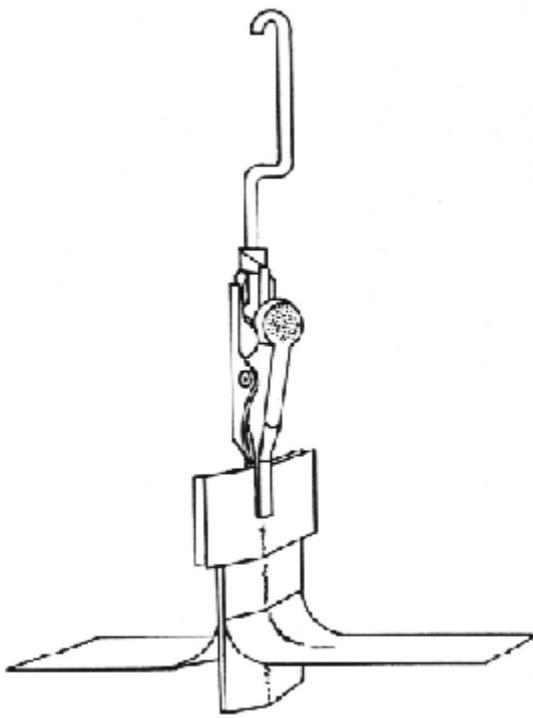
Single Sided Samples

When the sample is only coated on one side, or one side of the sample is of interest, this presents a challenge for DCA technique, since during a DCA experiment, the wetted solid surface should be the same. It's then necessary to prepare the sample in such a way that the interested side of the solid is exposed and will contact liquid.

To achieve this, it is recommended to use double-sided tape or apply glue to stick the sample back-to-back and only expose the interested surface. This way the interested side will be exposed to the liquid. However, since the single-sided sample has a certain thickness, by using the double-side tape or glue won't be able to cover the edges of the sample. It's then necessary

to prepare a wider sample so as to minimize the contribution of the edges with respect to the overall wetting perimeter of the sample.

Single Fiber Sample

For the DCA 322, single fiber samples are very commonly measured. Single fiber samples normally have a diameter ranging from a few microns to about 30 microns. Handling fibers this small is very tricky and can be time-consuming. Mounting the fiber sample to perform DCA experiments is even more difficult. The following steps are recommended by Thermo Cahn and have been proven to work very successfully and efficiently:

1. Prepare a set of metal wire support. The metal wire support should be bent into "7" shape, so that one end can be attached to the balance loop, and the other straight end will be used to attach the fiber.
2. Mounting the single fiber sample onto the metal wire support, by using glue, or small pieces of tape. It's important to make sure the glue or tape won't adsorb the liquid that will be used for testing. At the mean time, it may be necessary to expose a very short piece of single fiber sample, about 2 to 4 mm, in order to gain rigidity.

During the data collection, it's recommended to use a slow stage moving speed.

Powder Sample

Wettability of powder samples are often needed for various industries. In order to quantitatively obtain the wettability, the contact angle experiments should be performed. However, as you know already, DCA is utilizing the Wilhelmy plate technique, which requires a plate. Therefore, for powder samples, sample preparation needs to be performed prior to the experiments.

Generally speaking, there are three different ways to measure the wettability of powder samples.

1. Press the powder into pellet, and then treat it as a disc, or cut it into rectangle shape and treat it as a plate. However, the pressing procedure can easily introduce unknown factor to the surface properties of the powder sample. Therefore, this technique is not commonly practiced, or recommended.
2. Using double-side tape or a rectangle shape substrate coated with spray glue, coat the powder onto its surface. It will then be treated as a plate. However, during the preparation, it's necessary to make sure that the tape or substrate is totally and uniformly coated with powder, and powder particles have to be small enough so that there is no tape or substrate exposed. This technique has been commonly practice, and proved to be very easy and fairly repeatable. However, practice is needed for preparing the sample, and the powder sample has to be fairly fine.
3. Using the Powder accessory (mention in the later part), the powder is packed into a tube, which has a fritted opening at the end. Wicking experiments will then be performed on this packed tube, and Washburn equation will be applied to obtain the contact angle values. This

technique can handle powders of any particle size, however, this technique is fairly time-consuming, and many experiments have to be performed to optimize the experimental conditions. Also, for a powder that doesn't wet a certain liquid, the experiments can't be carried out.

Applications Software

As a surface analyzer, a standard DCA can provide surface related information, such as the contact angles between solids and liquids, liquid surface tension, and liquids interfacial tension. However, for the surface energy of solid, liquid surface tension components, and contact angle of porous materials, the applications software has to be used.[1] The following discusses each of the functions.

Surface Energy - Zisman Plot method

The value obtained by using this method is often known as the "Critical Surface Tension" of the solid. The technique was proposed by Zisman and Fox[2] who found a quasi-linear relationship between the cosine of the advancing contact angle and the liquid surface tension of a series of liquids. This technique is often applied to low energy, non-polar solids, such as polymers.

Surface Energy - Geometric Mean and Harmonic Mean methods

Surface energy or surface tension of a substance (γ) is often time described to be consisted of two components, polar (γ^p) and dispersive (γ^d), and expressed as:

$$\gamma = \gamma^p + \gamma^d$$

When two surfaces meet, substance i and j, the combination result can be expressed as:

$$\gamma = \gamma_i + \gamma_j + - f(\gamma_i^p, \gamma_i^d, \gamma_j^p, \gamma_j^d)$$

The term, $f(\gamma_i^p, \gamma_i^d, \gamma_j^p, \gamma_j^d)$, is then studied by various researchers, and two different groups of theories were proposed by different researchers.

One is called Geometric mean method, and was proposed by Girafalco and Good[3], and extended by Fowkes[4], Owens and Wendt[5], and Kaeble[6]. In this method, it is assumed that the ionization potentials of the two phases are dominated by dipole-dipole interactions. The equation for calculation is expressed as:

$$\gamma_L \times (1 + \cos\theta) = 2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^p \gamma_S^p}$$

Due to the assumption, it's better utilized to deal with solid surfaces that are polar. Since most of the solids have some polarities on their surfaces, it is the most often used method.

Another method is called Harmonic mean method, and was proposed by Wu[7]. The theory assumed that the polarizabilities of the two phases are equal (and assuming that the polar component has the same form as the dispersive component). This results in the following equation:

$$\gamma_L \times (1 + \cos\theta) = 4\frac{\gamma_L^d \gamma_S^d}{\gamma_L^d + \gamma_S^d} + 4\frac{\gamma_L^p \gamma_S^p}{\gamma_L^p + \gamma_S^p}$$

This method is often used by many polymer scientists who are dealing with much less polar surfaces, and want to know the polarity of the sample. However, due to the mathematical difficulties in solving for the values, it is not as commonly utilized as the Geometric mean method.

Surface Energy - Polar +/- or Lewis Acid/Base method

Based on the Lewis acid and base theory, a different approach, other than Geometric Mean and Harmonic Mean methods, was proposed by Good, van Oss and Chaudhury[8]. This method yields the Lifshitz-van der Waals component (γ^{LW}), the Lewis acid (γ^+) and the Lewis base (γ^-) components of the solid surface energy. The surface energy is expressed as:

$$\gamma = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-}$$

and the equation for interaction between two phases is:

$$\gamma_L \times (1 + \cos\theta) = 2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^+} + \sqrt{\gamma_s^-\gamma_l^-})$$

Due to the consideration of the bonding between the molecules, this method is more applicable for hydrogen bonding systems. Since it's still at its early stage, the usage of this method is not as wide as the Geometric mean and Harmonic mean method.

Liquid Surface Tension Components

In a solid-liquid system, the solid surface properties can be studied by using any of the above functions. For liquid, however, the DCA can find out its total surface tension, not the polarity or the liquid surface tension components. This liquid surface tension components function uses a well-characterized non-polar solid, such as polyethylene or Teflon, as the reference to obtain the contact angle value against the liquid. The liquid surface tension components is then calculated by means of both the Geometric mean and Harmonic mean equations.

Wicking Rate

While the wicking experiment provides the weight pick-up information for porous or powder samples, the wicking rate will provide the information about the rate of the weight pick-up. The derivative of the wicking curve will be presented.

Powder Option – Washburn method

The wettability of porous materials, such as paper, wood, and powder, is always important information to obtain. However, obtaining the wettability information is a challenge. DCA utilizes the Washburn[9] theory to calculate the contact angle between the interested solid against a certain liquid. The Washburn equation that is utilized in the calculation is as follows:

$$\cos\theta = \frac{w^2}{t} \times \frac{\eta}{\rho^2 \times \gamma \times C}$$

where θ is the contact angle, w is the measured weight, t is time, C is a dimension constant that is related to the porosity and/or packing of the solid sample, and η, γ, and ρ are the viscosity, surface tension and density of the liquid, respectively.

By using a standard liquid which has low enough surface tension that gives $\cos\theta = 1$, the contact angle between the solid against the interested liquid can then be calculated.

For detailed information, please refer to the Product Note about the DCA Applications Software, and the reference papers listed below.

1. Thermo Cahn Instruments, Inc., Product Note "*Solid Surface Energy Analysis: Yesterday and Today*", CHN 19, 8/91.
2. Fox, H. W. and Zisman, W. A., *J. Colloid Science*, **1950**, *5*, 514.
3. Girafalco, L. A. and Good, R. J., *J. Phys. Chem.*, **1957**, *61*, 904.
4. Fowkes, F. M., *J. Phys. Chem.*, **1962**, *66*, 382.
5. Owens, D. K. and Wendt, R. C., *J. Appl. Polym. Sci.*, **1969**, *13*, 1741.
6. Kaele, D. H., *J. Adhesion*, **1970**, *2*, 66.
7. Wu, S., *J. Polym. Sci.*, **1971**, *19*, 34.
8. van Oss, C. J., Good, R. J. and Chaudhury, M.K., *J. Colloid Interface Sci.*, **1986**, *111*, 378.
9. E. W. Washburn, *Physics Review*, **1921**, 17(3), 273-282.

Accessories for DCA

CMC Accessory

As a common phenomenon, when there is impurity in the liquid, its physical properties will change. One of the physical properties, surface tension, will also change. For surfactant industries, this change is related to the surfactant's concentration. There is always a critical concentration that when adding more surfactant, the surface tension of the system is not

changing or not changing as much. This concentration is often time called critical micelle concentration, or CMC.

To obtain the CMC, there are many different apparatus, based upon different changing physical properties. As part of the function of DCA, surface tension can be easily measured and therefore the CMC can be obtained by varying the concentration of the surfactant in solvent. This is then the purpose of the CMC accessory, which will make the CMC measurement automatic.

More detailed information about this accessory can be obtained from the manual for CMC accessory.

Powder Accessory

As mentioned in the special sample handling techniques, one way to measure the wettability of powder samples is to use the Powder accessory. This accessory consists of glass tubes with fritted bottom. The powder sample will be packed into the tube, and wicking experiments will be performed. With Washburn technique, the contact angle or wettability will then be obtained. Further information can be found in the Applications software section.

Temperature Module

As any other physical constants, the surface tension of the liquids and solids are highly dependent upon the temperature. It's therefore necessary to control and measure the temperature of the experiments. The temperature module accessory allows the user to control the temperature of the liquid and its surroundings, while the software will record temperature of the liquid. More detailed information can be obtained from Thermo Cahn Instruments.

Troubleshooting

Communication

When there is an error message about not finding the DCA, most commonly seen causes for this communication problem are:

- Wrong RS232 cable is used.
- Wrong power setting is set on the back of DCA.
- Wrong DCA model selected in the method's system configuration.
- Wrong communication port selected in the method's system configuration screen.
- DCA stage is still moving back to its zero position.
- Balance is not correctly counterweighed.

The simplest way to check is to turn off and DCA, and exit the WinDCA software. Then, turn on the DCA with NO weights on the balance. Wait for a few seconds, and make sure that only one light is on at the front of the DCA panel. Now, launch the WinDCA software, and make sure the communication setting in the current method is correct. Select DCA/Diagnostics/DCA Test to check for the communication. If this fails as well, please contact Thermo Cahn service department.

Stage kept on moving at Detect ZDOI step

When this happens, the stage will keep on moving to its maximum travel distance, even though the sample may have been immersed into the liquid. There are two possible causes:

- Wrong ZDOI threshold is used in the current method. Usually means the current ZDOI threshold is too large.
- Wrong counter-weight is used.

The following steps will allow the user to check the both situations:

1. Use Method/Edit function to open the method editor. On the main editor page, click on Experiment setup. Now, in this dialog, locate the field for ZDOI threshold. Decease the ZDOI threshold, and try the run again.

NOTE: since the ZDOI threshold can be different for different combination of sample size, and liquid, it's very hard to come up with a "good" value to use for all of the conditions. It's recommended to create different method for different kinds of samples or conditions.

2. When balance is over counter-weighed on the sample size, or the tare side, the balance will be locked into a "saturated" value all the time. This will show no live weight reading during the run. The problem can be fixed by performing the balance counter-weighing process, on page 3, again with the sample and holder.

Balance shows ZERO weight reading all the time

When this occurs, it normally means that the system is over counter-weighed. It happened in Radian DCA 322 the most often. In this case, please refer the balance counter-weighing procedure located on page 3.

Balance shows 1/5 or 5 times of the actual weight

This happened only in Radian DCA 322 model. It's mostly caused by the fact that wrong loop was selected in the method. Please check the system configuration of the current method, and make sure the correct loop is selected AND used.

Balance performance test

Since the accuracy of the weigh reading is very critical for a DCA measurement, it's then necessary to perform the following two tests to verify the correct operation of the DCA balance.

- Balance stability test
1. Remove every thing from the hang-downs of the balance loops. Make a run to make sure that the balance is stable all by itself.
2. Put samples and counterweights on and make another run without liquid sample. Make sure the weight is stable.
3. Then put on liquid sample and make another run. If unstable weight is seen, it's caused by the liquid and/or solid/liquid interaction.

- Accuracy of weight reading
  It's necessary to perform calibration with the samples and counterweights hanged on balance loops. The amount of calibration should be in the same range of the expected weight change. Using the DCA/Record function to make sure the accurate weight reading is obtained.

Values obtained are off from expected

When the measured value is not as expected, such as the surface tension of distilled water, often time, there are two possible causes. One is related to the accuracy of the balance reading, and another is related to the sample. It is recommended to check the above two in order.

DCA is utilizing the Wilhelmy plate theory. Therefore, all of the measurements and calculation are dependent upon the accuracy of the balance reading. By doing the balance performance test mentioned above, the balance performance can be checked and corrected.

When the balance is assured to be performing OK, then the problem has to come from the sample side. The samples, both liquid and solid, should then be examined, such as the cleanliness of samples, cleanliness of containers, accuracy of measured solid dimension, etc. In some cases, different liquids or solids should be tried to ensure the correct measurements.