

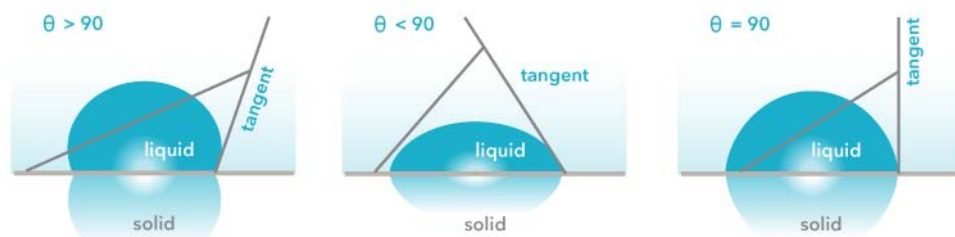
Application note #1:

Contact angle and its measurement techniques

This application note provides a brief introduction to the use and measurement of contact angles. The techniques used for measurement are discussed and compared.

What is contact angle?

Contact angle, θ , is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown below:



It can be seen from this figure that low values of θ indicate that the liquid spreads, or wets well, while high values indicate poor wetting. If the angle θ is less than 90° the liquid is said to wet the solid, with a contact angle of zero representing complete wetting. If it is greater than 90° it is said to be non-wetting. A static contact angle measurement depends on the recent history of the interaction. When the drop has recently expanded an advanced contact angle is measured. When the drop has recently contracted a receded contact angle is measured. These angles fall within a range with advanced angles approaching a maximum value and receded angles approaching a minimum value.

If the is actually in motion, that is if the three phase (liquid/solid/vapor) boundary is in actual motion, the angles measured are called dynamic contact angles and are referred to as advancing and receding angles. The difference between advanced and advancing (or receded and receding) is that in the first case motion is about to appear and in the latter case the drop is actually moving.

Hysteresis

The difference between the maximum and minimum contact angle values is called the contact angle hysteresis. A great deal of research has gone into analysis of the significance of hysteresis. It has been used to help characterize surface heterogeneity, roughness and mobility.

Non-homogeneous surfaces have domains on the surface which present barriers to the motion of the contact line. For the case of chemical heterogeneity these domains represent areas with different contact angles than the surrounding surface. For example when wetting with water, hydrophobic domains will pin the motion of the contact line as the liquid advances thus increasing the contact angles. When the water recedes the hydrophilic domains will hold back the draining motion of the contact line thus decreasing the contact angle. From this analysis it can be seen that, when testing with water, advancing angles will be sensitive to the hydrophobic domains and receding angles will characterize the hydrophilic domains on the surface.

For situations in which surface roughness generates hysteresis the actual microscopic variations of slope on the surface create the barriers which pin the motion of the contact line and alter the macroscopic contact angles.

Contact angle can also be considered in terms of the thermodynamics of the materials involved. This analysis involves the interfacial free energies between the three phases and is given by:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

where γ_{lv} , γ_{sv} and γ_{sl} refer to the interfacial energies of the liquid/vapor, solid/vapor and solid/liquid interfaces respectively.

How is contact angle measured?

Two different approaches are commonly used to measure contact angles of non-porous solids, optical tensiometry (goniometry) and force tensiometry. Optical tensiometry involves the observation of a sessile drop of test liquid on a solid substrate. Force tensiometry involves measuring the forces of interaction as a solid is contacted with a test liquid. Both techniques are described below with comments on the choice of either technique for particular research applications.

In the case of porous solids, powders and fabrics another approach is commonly used. This technique involves using a force tensiometer, such as an Attension Sigma, and the Washburn method. It is the method of choice when your sample contains a porous architecture which absorbs the wetting liquid.

Optical tensiometry

Analysis of the shape of a drop of test liquid placed on a solid is the basis for optical tensiometry. The basic elements of an optical tensiometer include a light source, sample stage, lens and image capture device. Contact angle can be assessed directly by measuring the angle formed between the solid and the tangent to the drop surface.

The production of drops with advanced and receded contact angles involves one of two strategies. Drops can be made to have advanced edges by the addition of liquid. Receded edges may be produced by withdrawing liquid from the drop or by allowing sufficient evaporation. Alternately, both advanced and receded edges are produced when the stage on which the solid is held is tilted to cause the drop to roll off. Using an instrument with high speed image capture capabilities shapes of drops in motion may be analyzed.

Advantages

Optical tensiometry can be used in many situations where force tensiometry cannot. You can use a great variety of solid substrates provided they have a relatively flat portion for testing, and can fit on the stage of the instrument. Substrates with regular curvature, such as contact lenses are also easily analyzed. Testing can be done using very small quantities of liquid. It is also easy to test high temperature liquids such as polymer melts.

Limitations

The assignment of the tangent line which will define the contact angle is a factor which can limit the reproducibility of contact angle measurements. Conventional optical tensiometry relies on the consistency of the operator in the assignment of the tangent line. This can lead to significant error, especially subjective error between multiple users. Attension Theta removes this problem by using computer analysis of the drop shape to generate consistent contact angle data.

The conditions which produce advanced and receded angles are sometimes difficult to reproduce. Although drops in motion can produce data on dynamic contact angles the velocity of motion cannot be controlled. It is also less suited, when compared to force tensiometry, to analysis of the effects of wetting on changes in contact angle.

In addition the amount of surface sampled for each measurement is limited and multiple measurements should be used to characterize a surface. Fibers are not easily studied by optical tensiometry, unless you can use the meniscus measurement method.

Force tensiometry

Force tensiometers measure the forces that are present when a sample of solid is brought into contact with a test liquid. If the forces of interaction, geometry of the solid and surface tension of the liquid are known then the contact angle can be calculated. The user first makes a measurement of the surface tension of the liquid using either a Wilhelmy plate or a Du Noüy ring. The sample of the solid to be tested is hung on the balance and tared. The liquid is raised to contact with the solid. When the solid contacts the liquid the change in forces is detected and this elevation is set as zero depth of immersion. As the solid is pushed into the liquid the forces on the balance are recorded. The forces on the balance are:

$$F(\text{total}) = \text{wetting force} + \text{weight of probe} - \text{buoyancy}$$

Attension Sigma uses the tare weight of the probe and removes the effects of buoyancy by extrapolating the graph back to zero depth of immersion. The remaining force component is the wetting force which is defined as:

$$\text{Wetting force} = \gamma_{lv} P \cos \theta$$

where γ_{lv} is the liquid surface tension, P is the perimeter of the probe and θ is the contact angle. With a known liquid the surface tension is known and the perimeter of the sample probe is also known. Wetting force is measured, and the contact angle can be calculated from the data obtained at any depth of immersion. This contact angle, which is obtained from data generated as the probe advances into the liquid, is the advancing contact angle. The sample is immersed to a set depth and the process is reversed. As the probe retreats from the liquid data collected is used to calculate the receding contact angle.

Advantages

The use of force tensiometry for measurement of contact angle has several advantages over conventional optical tensiometry. At any point on the immersion graph, all points along the perimeter of the solid at that depth contribute to the force measurement recorded. Thus the force used to calculate θ at any given depth of immersion is already an averaged value. You may calculate an averaged value for the entire length of the sample or average any part of the immersion graph data to assay changes in contact angle along the length of the sample.

This technique allows the user to analyze contact angles produced from wetting over an entire range of velocities from static to rapid wetting. Because the contact angles are determined from the forces measured by the instrument there is no possibility of subjective error.

The graphs produced by this technique are very useful in studying hysteresis. Variations of contact angles, both advancing and receding, for the entire length of the sample tested, are visualized on the same graph. In addition variations generated over multiple wetting/dewetting cycles can yield information on changes caused by wetting (such as absorption or surface reorientation).

Analysis of fibers, sometimes problematic for optical tensiometers, is handled easily by force tensiometry.

Limitations

There are two major limitations for the application of this technique. Firstly the user must have enough of the liquid being tested available so that he can immerse a portion of his solid in it. Secondly the solid in question must be available in samples which meet the following constraints. The sample must be formed or cut in a regular geometry such that it has a constant perimeter over a portion of its length. Rods, plates or fibers of known perimeter are ideal. The sample must have the same surface on all sides which contact the liquid. The sample must also be small enough so that it can be hung on the balance of a Sigma, and weigh less than the maximum of the balance.

It is also more difficult to use this technique in systems which are measured at high temperatures. Temperatures at or below 100 °C are easily handled but for measurements above this range optical tensiometry is recommended.

Washburn method

This method is chosen when the solid sample to be tested contains a porous architecture which leads to absorption of the wetting liquid. The solid is brought into contact with the testing liquid and the mass of liquid absorbed into the solid is measured as a function of time. The amount absorbed is a function of the viscosity, density and surface tension of the liquid, the material constant of the solid, and the contact angle of the interaction. If the viscosity, density and surface tension of the liquid are known the material constant and contact angle can be solved for. Attension Force tensiometers can be used to determine contact angles *via* the Washburn technique.

Utilization of contact angle data

The primary focus of contact angle studies is in assessing the wetting characteristics of solid/liquid interactions. Contact angle is commonly used as the most direct measure of wetting. Other experimental parameters may be derived directly from contact angle and surface tension results. Some examples are:

Work of Adhesion: defined as the work required to separate the liquid and solid phases, or the negative free energy associated with the adhesion of the solid and liquid phases. Used to express the strength of the interaction between the two phases. It is given by the Young-Dupre equation as:

$$W_a = \gamma (1 + \cos \theta)$$

Work of Cohesion: defined as the work required to separate a liquid into two parts, it is a measure of the strength of molecular interactions within the liquid. It is given by;

$$W_c = 2 \gamma$$

Work of Spreading: the negative free energy associated with spreading liquid over solid surface. Also referred to as Spreading Coefficient it is given as:

$$W_s = \gamma (\cos \theta - 1)$$

Wetting Tension: a measurement of force/length defined as:

$$\tau = F_w / P = \gamma \cos \theta$$

This value, wetting force normalized for length, also represents the product of the cosine of the contact angle and the surface tension. It allows for a characterization of the strength of the wetting interaction without separate measurement of surface tension. It is helpful in situations, such as multicomponent systems, where surface tension at the interface may not equal equilibrium surface tension. It is also referred to as adhesion tension or as work of wetting.

Characterization of the solid surface

Measurements of surface tension yield data which directly reflect thermodynamic characteristics of the liquid tested. Measurement of contact angles yield data which reflect the thermodynamics of a liquid/solid interaction. If you wish to characterize the wetting behavior of a particular liquid/solid pair you only need to report the contact angle. It is also possible to characterize the wettability of your solid in a more general way. Various methods are used but the same basic principle applies for each. The solid is tested against a series of liquids and contact angles are measured. Calculations based on these

measurements produce a parameter (critical surface tension, surface free energy, etc...) which quantifies a characteristic of the solid which mediates wetting. Four different approaches are mainly used for determining the energy of solid substrates.

Critical Surface Tension (Zisman): Using a series of homologous nonpolar liquids of differing surface tensions a graph of $\cos \theta$ vs γ is produced. It will be found that the data forms a line which approaches $\cos \theta = 1$ at a given value of γ . This value, called the critical surface tension, can be used to characterize a solid surface. It is often presented as the highest value of surface tension of a liquid which will completely wet a solid surface. This approach is most appropriate for low energy surfaces which are wetted by nonpolar liquids. See references for details on procedure and limitations.

Another way to characterize a solid surface is by calculating surface free energy (sometimes referred to as solid surface tension). This approach involves testing the solid against a series of well characterized wetting liquids. The liquids used must be characterized such that the polar and dispersive components of their surface tensions are known.

Geometric Mean (Fowkes): This approach divides the surface energy into two components, dispersive and polar, and uses a geometric mean approach to combine their contributions. The resulting equation when combined with Young's equation yields:

$$\gamma_l (1 + \cos \theta) = 2 [(\gamma_{lp}\gamma_{sp})^{1/2} + (\gamma_{ld} \gamma_{sd})^{1/2}]$$

This equation can be rearranged as by Owens and Wendt to yield:

$$\gamma_l (1 + \cos \theta) / (\gamma_{ld})^{1/2} = (\gamma_{sp})^{1/2} [(\gamma_{lp})^{1/2} / (\gamma_{ld})^{1/2}] + (\gamma_{sd})^{1/2}$$

where θ is the contact angle, γ_l is liquid surface tension and γ_s is the solid surface tension, or free energy. The addition of d and p in the subscripts refer to the dispersive and polar components of each respectively. The form of the equation is of the type $y = mx + b$. You can graph $(\gamma_{lp})^{1/2} / (\gamma_{ld})^{1/2}$ vs $\gamma_l (1 + \cos \theta) / (\gamma_{ld})^{1/2}$. The slope will be $(\gamma_{sp})^{1/2}$ and the y-intercept will be $(\gamma_{sd})^{1/2}$. The total free surface energy is merely the sum of its two component forces.

Harmonic Mean (Wu): This method utilizes a similar approach but uses a harmonic mean equation to sum the dispersive and polar contributions. Contact angles against two liquids with known values of γ_d and γ_p are measured. The values for each experiment are put into the following equation;

$$(1 + \cos \theta) \gamma_l = 4(\gamma_{ld} \gamma_{sd} / \gamma_{ld} + \gamma_{sd} + \gamma_{lp} \gamma_{sp} / \gamma_{lp} + \gamma_{sp})$$

where γ refers to surface tension (surface free energy), the subscripts l and s refer to liquid and solid, and the superscripts d and p refer to dispersive and polar components. You then have two equations with two unknowns and can solve for γ_{sd} and γ_{sp} .

Acid-Base (van Oss): Contact angles against at least three liquids with known values of γ_d , γ_+ and γ_- are measured. The values for each experiment are put into the following equation:

$$0.5(1 + \cos \theta) \gamma_l = (\gamma_{sd} \gamma_{ld})^{1/2} + (\gamma_{s-} \gamma_{l+})^{1/2} + (\gamma_{s+} \gamma_{l-})^{1/2}$$

where γ refers to surface tension (surface free energy), the subscripts l and s refer to liquid and solid, and the superscripts d, + and - refers to dispersive, acid and base components. You then have three equations with three unknowns and can solve for γ_{sd} , γ_{s+} and γ_{s-} . The total surface free energy of the solid is then given by:

$$\gamma_s = \gamma_{sd} + \gamma_{sAB} \quad , \quad \text{where } \gamma_{sAB} = 2(\gamma_{s+} \gamma_{s-})^{1/2}$$

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