Primer on liquid-solid interfaces

Understanding the characteristics of a liquid solid interface is important to virtually every manufacturing industry, from biomaterials 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 absorbtion) of orally-ingested drugs to the pharmaceutical industry.

Defining the Interface

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 absorbtion of liquids into solids have given researchers the information they need to more fully understand and control their production processes.

When a liquid comes in contact with the surface of a solid, the liquid will either spread out and "wet" the surface, or it will form droplets that "repel" from the surface. The angle formed at the edge of these droplets where the liquid contacts the solid surface and the surface energy that affects this angle form the basis of modem liquid-solid interface technology.

Contact Angle

For a fully wetted surface, this contact angle is zero, while for nonwetted surfaces it can vary between ∞and 180°. Contact angles can vary greatly depending upon the wetting liquid and the characteristics of the substrate. Data on the relationship of some liquids to some substrate surfaces have been generated and tabulated. For the most part, researchers rely on experimental data when evaluating non-ideal applications.

Techniques for measuring contact angles include the goniometer, an optical device for viewing a silhouette of the droplet and aligning a tangent to the angle of contact with cross hairs on the instrument; photographic images of a meniscus inside a cylindrical tube and a microbalance that records the forces required to move a liquid past a fiber or plate, which then is mathematically correlated to the contact angle.

Surface Tension

The thermodynamic definition of wetting is rooted in the concept of surface energy or surface tension. At the surface of a liquid, the molecules are attracted to each other and create forces that pull themselves together. High surface tension means the molecules tend to interact strongly, such as in water which has a high degree of hydrogen bonding. Organic molecules have weaker bonds and lower surface tensions. A number of techniques have been developed for determining surface tension, including methods that involve measurements of capillary height, maximum bubble pressure, drop weight, sessile drop, spinning drop, stalagmometer, and vibrating jets. The most prevalent techniques, however, are the Wilhelmy plate and du Nouy ring methods.

Wilhelmy/du Nouy

The easy-to-use Wilhelmy plate method, developed by L. Wilhelmy in 1863, is especially suited to the measurement of surface tensions over long time intervals. It employs a thin vertical plate, usually a platinum blade of known perimeter, attached to a microbalance. Surface tension of the liquid, assuming a zero contact angle, is determined by direct measurement of the weight of the meniscus formed on the perimeter of the plate divided by the plate's perimeter.

The du Nouy ring method for measuring surface tension eliminates any wetting questions or conditions of the surface or interface. Since the adhesion of a liquid to a metal ring is greater than the cohesion of the liquid itself, the force required to detach a ring from the surface of a liquid is directly related to the size of the ring and the surface tension of the liquid, with the addition of a correction factor to adjust for liquid still remaining on the ring.

Characterizing the Liquid-Solid Interface

Measurement of contact angle and surface tension properties provide the primary basis for characterizing liquid-solid interfaces. The most accepted, well respected, and easiest to use technique for these measurements is the Wilhelmy plate method. In its initial configuration, however, it only measures static contact angles and relies on a fully wetted solid surface. Extending this technique to the measurement of dynamic contact angles is not trivial because of complex hydrodynamic modeling issues in moving contact lines. Measuring dynamic contact angles, nevertheless, is important because in the real world, solid surfaces are rarely homogeneous. Real-world surfaces are exposed to contaminants in the form of naturally occurring oxide layers, lubricants, and other airborne substances. These contaminated surfaces need to be fully characterized to understand the real-world effects on liquid-solid interfaces.

Dynamic Contact Angle

Automated dynamic contact angle (DCA) instruments overcome the limitations of static contact angle measurement devices. They let you measure larger surfaces and liquid solutions rather than single drops on a plate which often concentrate contaminants or provide incomplete pofiles.

DCAs operate by holding a Wilhelmy like plate in a fixed vertical position, attaching it to a microbalance and moving a probe liquid contained in a beaker at a constant rate up and down past the plate. A unique contact angle hysteresis curve is produced by the microbalance as it measures the force exerted by the moving contact angle in advancing and receding directions. The dynamic contact angle is then calculated from a modified Young's equation COSq = Force / (surface tension x wetted perimeter).
This system can be applied to most any solid surface, including single fibers as small as 1pm in diameter. Contact angle measurements obtained by commercial instruments range from ∞to 180° with a precision of ± 0.001°.
Wetting is an effect commonly characterized by a zero or close to zero contact angle that allows a liquid to easily spread over a solid surface. For absorbent porous materials, classical analyses are not useful. In these cases, specialized techniques to simultaneously measure solid absorption and wetting properties must be used.

Surface/Interfacial Tension

The surface tension of a certain liquid and the interfacial tension between two immiscible liquids can be measured by a DCA system. DCAs can be used either with known liquids to probe unknown solid surfaces (surface energy method) or with known solid surfaces to probe unknown liquid solutions (surface tension method). Automated DCAs often provide both the Wilhelmy plate and du Nouy ring measurement capabilities. The surface/interfacial tension measurements obtainable by automated DCAs range from 0.1 mN/m to 1,000 mN/m Since temperature changes can affect surface/interfacial tension characteristics, these instruments can operate with probe liquids at -l0 °C to 100 °C.

Critical Micelle Concentration

The unique ability of surface active agents, or surfactants, to diffuse to the surface of a liquid and dramatically lower the surface tension of a solution has resulted in their wide spread use in product as diverse as shampoos and baby diapers.
A surfactant molecule works by orienting its polar and apolar head and tail groups at the air/liquid or liquid/liquid interface. In sufficient quantities, surfactant molecules can aggregate to form clusters or micelles which prevent further changes in the surface tension of the liquid solution.
The concentration of surfactant present when micelle formation occurs is characteristic of the „critical micelle concentration“ or CMC of the solution. Adding more surfactant past the CMC can not only destroy the effectiveness of the product, but it can also significantly increase the cost of the formulation.
Calculating the CMC of a dilution can be performed with a DCA instrument by using an accessory to dispense the surfactant and a magnetic stirrer to mix the solution. Automated dispensing, calculation of the CMC, and storing and reporting of data can be performed with „smart“ software packages.

Surface Energy Analyses

The objective of many DCA experiments is to determine the surface energy of a solid. Working with commercial software applications, DCAs can provide this information using a variety of probe liquids with different surface tensions.

- Critical surface tension - Zisman Plot

An empirical linear relationship between the cosine of the contact angle and the surface tension of a sessile drop on lowenergy polymer substrates was found by W.A. Zisman at the Naval Research Laboratory. Extrapolation of this relationship for a zero contact angle provides a critical surface tension of the substrate, or the surface tension of a liquid that just spreads on the surface.

- Surface Energy - Geometric/ Harmonic Means

The results of two or more contact angle analyses are used to extract the liquid surface tension components from a constant table.
A calculation based on the geometric/harmonic mean method then yields the polar and dispersive components of the solid surface energy, along with the total solid surface energy.

- Surface Energy - Lewis Acid/Base

Using contact angle results, this calculation yields the Lifshitzvan der Waals component and the Lewis acid and base components of the solid surface energy.

Glossary

Contact angle
Angle formed at a droplet's edge where the liquid contacts the solid surface.

Critical micelle concentration (CMC)
Concentration at which the rate of change of surface tension with an increase in concentration levels off or proceeds at a slower rate.

Dynamic contact angle (DCA)
Advancing and receding contact angle of a Wilhelmy plate dipped or pulled from a solution.

du Nouy ring method
Traditional method for determining surface/interfacial tension. Performed by measuring the force required to pull a ring from a liquid surface.

Goniometer
Optical device for measuring the contact angle 01 a droplet on a solid surface.

Interfacial tension
Contractile force of a liquid-liquid interface.

Micelle
The product of spontaneous association of solute molecules.

Sessile drop method
Optical method for determining contact angle. Determined by mea-suring the angle between the base-line of a liquid drop and the tangent at the drop boundary.

Spread
To „wet“ a surface with a liquid such that full and complete coverage is obtained. It is characterized by a contact angle that approaches 0°.

Stalagmometer
Apparatus for determining surface tension by counting and weighing individual liquid drops.

Surfactant (surface active agent)
Soluble or colloidal substance having the property of affecting the surface tension of solutions.

Surface tension
Property, due to molecular forces, existing at the boundary of surface films that tends to prevent the liquid from spreading.

Wetting (thermodynamic)
Reduction in interfacial free energy when a liquid is placed in contact with a solid surface, resulting in a contact angle of less than 90.

Wetting agent
Substance that reduces the surface tension of a liquid.

Wilhelmy method
Universal method for determining surface/interfacial tension and contact angle. Measured by the force needed to pull a thin plate from a liquid surface

Zisman plots
Relationship between the cosine of the contact angle versus the surface tension of various wetting liquids on a given solid.

Applications

Biomaterials
Advances in medical and dental technologies utilize the information obtained from DCA instrumentation Surface-modified biomaterials are being employed to create disposable contact lenses, IOLs, catheters, dental prosthetics, and biocompatible implants.

Coatings
New formulations for use in environmental protection and wear applications continue to push the DCA instrumentation envelope. The adhesion of a pesticide to a plant surface is just one example of a unique coating that protects a plant from pests and the environment.

Composites
Fiber-reinforced polymer composites are better understood and explained with the use of DCA instrumentation adapted for measuring individual or bundled reinforcing fibers. The „work of adhesion“ at the fiber/matrix interface is an important contribution of the DCA system. Composites are found in a wide range of products used in aerospace, automotive, and sporting goods applications.

Cosmetics
Cleanliness and adhesiveness of human hair fibers is a critical factor in the development of shampoos that can be measured with the single fiber capabilities of the DCA. Hair conditioners, soaps, and skin creams can also be evaluated with DCA instruments.

Paints
DCA analyses find especially broad use in applications involving paints and coatings. With the increased use of composite body panels and new fluorocarbon and waterbased paint systems with special surfactant additives, new substrate preparation and application systems are continuously being developed.

Paper,Film & ink Products
Improved water-based ink adhesion and recycling efforts benefit from the information provided by DCA analyses Adhesion of inks and protective coatings to polymer film products used in the production of photographic and electronic media and in the packaging of food and electronic products also are enhanced.

Pharmaceuticals
The hydrophiobicity/hydrophilicity of orally ingested or transdermally applied drug products can be readily identified with DCA techniques. Many individual drugs may have the need for characterizing several liquid-solid interfaces, from the beginning of the production/mixing process all the way through the oral ingestion stages.

Powders
Porous materials are often highly absorbent preventing classical optical techniques for contact angle measurements. Accessories for measuring both absorption and wetting properties simultaneously now solve this problem.

Textiles
The application of water and stain or staticresistant coatings is wide-spread in the textile industry. Everything from carpet fibers to surgical gowns to crosscountry ski apparel involves the use of surface treat-ments applied to textile materials that can be characterized by DCA instrumentation.

Thermo Scientific DCA RADIAN 300 series

DCA are versatile enough to characterize complex wettability systems.

- Unique single fiber range capability for textiles and composites
- Dynamic contact angles by continuous surface scanning
- Programmable automatic cycling and looping capabilities
- Windows user interface
- Features CMC (critical micelle concentration)
- Automatically calculated advancing and receding angles
- Multi and two-liquid method solid surface energy calculations

Thermo Fisher Scientific
Process Instruments

International/Germany
Dieselstr. 4,
76227 Karlsruhe
Tel. +49(0)721 40 94-444
info.mc.de@thermofisher.com

Benelux
Tel. +31 (0) 76 5 87 98 88
info.mc.nl@thermofisher.com

China
Tel. +86 (21) 68 65 45 88
info.mc.china@thermofisher.com

France
Tel. +33 (0) 1 60 92 48 00
info.mc.fr@thermofisher.com

India
Tel. +91 (22) 27 78 11 06
info.mc.in@thermofisher.com

United Kingdom
Tel. +44 (0) 1785 81 36 48
info.mc.uk@thermofisher.com

USA
Tel. 603 436 9444
info.mc.us@thermofisher.com

www.thermo.com/mc

C001_30.07.2008