

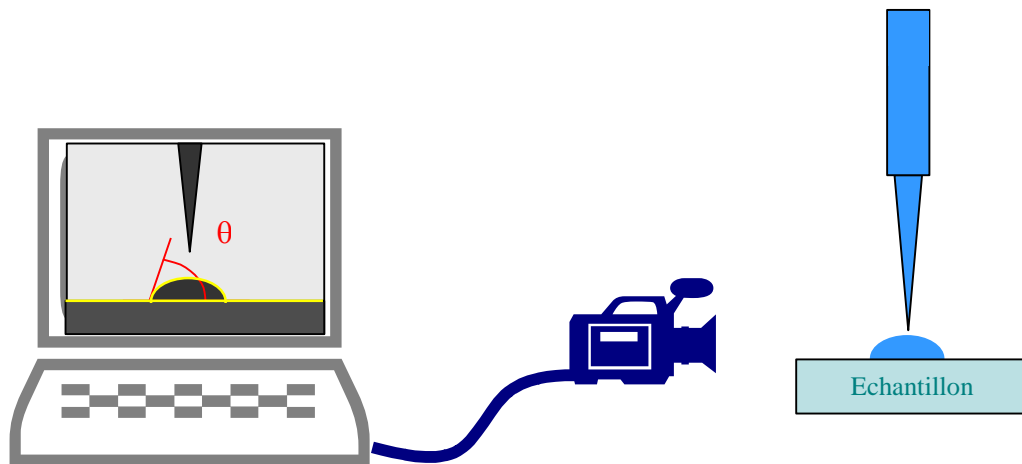
## CONTACT ANGLE MEASUREMENT

### I.1 Introduction

The contact angle is a measure of the ability of a liquid to spread on a surface. The method consists to measure the angle between the outline tangent of a drop deposited on a solid and the surface of this solid. The contact angle is linked to the surface energy and so one can calculate the surface energy and discriminate between polar and apolar interactions.

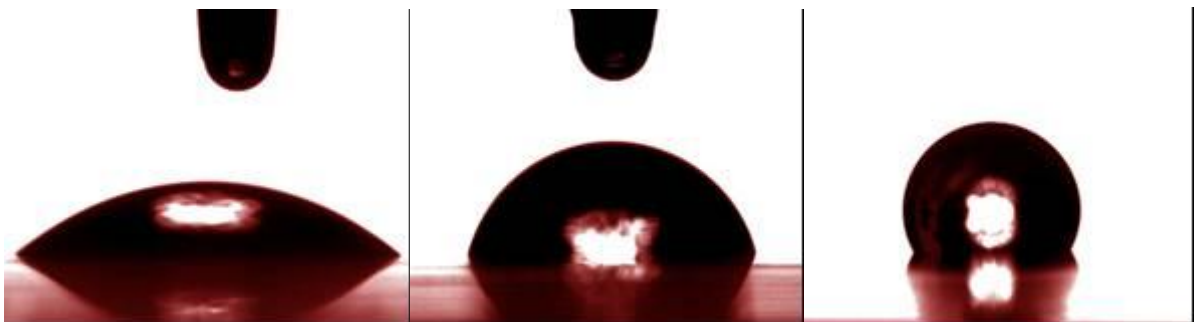
### I.2 Principle

A drop of liquid is deposited on a planar solid surface. A picture of the drop is captured at grazing angle. After numerization of drop, the angle between the outline tangent of the drop at the contact location and the solid surface is calculated. This angle is called contact angle ( $\theta$ ).



More the material get affinities with the liquid, more the liquid spread and the contact angle is weak. Less there are affinities between the material and the liquid, more the drop stays spherical and the contact angle is great. Examples of various drop shapes are shown on Figure 1

*Figure 1 : Water drop shape according to hydrophobicity*



The contact angle measurements give 3 informations :

- The affinity of a liquid to a solid surface : if water is used to measure the contact angle one can deduce the hydrophobic (great angle, low surface energy) or hydrophilic (small angle, high surface energy) character of the surface.
- If several standard liquids are used, the surface energy of the solid can be calculated, discriminating between polar and dispersive components. The most common models used are Good & Van Oss model or Owens & Wendt model.
- The measure of the hysteresis between advancing angle and receding angle give informations on non homogeneity of the surface (rugosity, contamination,...).

### I.3 Surface energy calculations

Three parameters influence the shape of drop at solid surface is :

- Solid-Liquid interfacial tension  $\gamma_{SL}$
- Solid-Vapour interfacial tension  $\gamma_{SV}$  ( $\gamma_S$ )
- Liquid-Vapour interfacial tension  $\gamma_{LV}$  ( $\gamma_L$ )

These three parameters are linked with the contact angle  $\theta$  by the Young equation :

$$-\gamma_{SV} + \gamma_{SL} + \gamma_{LV} \cos \theta = 0$$

Solely  $\gamma_{LV}$  and  $\theta$  are measurable, so additional equations are required to determine  $\gamma_{SL}$  and  $\gamma_{SV}$ . Several models were developed to calculate these parameters.

#### I.3.1 Neumann Model:

In this model there is no distinction between the various components of surface energy and there also no relation with the material physico-chemical properties. The contact angle equation is written as :

$$\cos \theta = \frac{(0.015\gamma_S - 2)\sqrt{\gamma_S\gamma_L} + \gamma_L}{\gamma_L(0.015\sqrt{\gamma_S\gamma_L} - 1)}$$

This equation is limited to system with low polar components like fluorinated surface and it is difficult to compare values obtained with different liquid.

#### I.3.2 Owens & Wendt Model

The OW model considers that surface energy can be expressed as :

$$\gamma_S = \gamma_S^d + \gamma_S^{nd} \text{ with :}$$

- $\gamma_S^d$  dispersive component (Lifshitz-Van der Waals interactions)
- $\gamma_S^p$  non-dispersive component (polar interactions, Lewis acid-base)

The equation between tension components and contact angle is then :

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

In this model the measure of contact angle of two different liquids are necessary to calculate the surface energy. One of them must be apolar. However there is an approximation on non dispersive interactions (polar) considering that it is the geometrical mean of  $\gamma_S^{nd}$  and  $\gamma_L^{nd}$ . This approximation can not predict the behavior of polar polymer in aqueous environment.

### I.3.3 Good Van Oss Model

In the Good & Van Oss model the surface energy is written as :

$$\gamma_s = \gamma_s^d + 2\sqrt{\gamma_s^+ \gamma_s^-} \quad \text{with :}$$

- $\gamma_s^d$  dispersive component (Lifshitz-Van der Waals interactions)
- $\gamma_s^+$ ,  $\gamma_s^-$  polar components (polar interactions, Lewis acid-base)

The relation between surface energy components, liquid components and contact angle is written as:

$$\gamma_L(1 + \cos \theta) = 2\left(\sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_L^+ \gamma_s^-}\right)$$

Depositing a drop of 3 different liquids with known dispersive and polar components, one can calculate the solid surface energy. One of the liquid must be apolar, the 2 others must have polar components >0 and one of them must have the equal acid and polar components. In most of cases water is used for this because it is considered as neutral point in Lewis scale. The Table 1 gives values of components of typical liquids used in the determination of surface energy (C.J. Van Oss - Interfacial forces in aqueous media - Marcel Dekker, Inc – 1994).

Table 1 : Energy components of typical liquids

Liquides	$\gamma_L$ (mJ/m <sup>2</sup> )	$\gamma_L^d$ (mJ/m <sup>2</sup> )	$\gamma_L^p$ (mJ/m <sup>2</sup> )	$\gamma_L^{p+}$ (mJ/m <sup>2</sup> )	$\gamma_L^{p-}$ (mJ/m <sup>2</sup> )
Eau	72.8	21.8	51	25.5	25.5
Glycerol	64.0	34.0	30.0	3.92	57.4
Formamide	58	39	19	2.28	39.6
Ethylene Glycol	48.0	29	19	1.92	47
a-Bromonaphtalene	44.4	44.4	≈0	0	0
Diiodomethane	50.8	50.8	0	0	0
Cis-decaline	32.2	32.2	≈0	0	0

## I.4 Apparatus

A typical apparatus is shown on the following picture :



The liquid drops are deposited with a micro-syringe on the surface. The angle measurements are made on the digital pictures. The software determines the drop shape and calculates the contact angle by interpolation methods.