

Surface free energy - theory and calculations

This technology note explains the concepts of surface free energy and how it can be calculated by using contact angle data.

Introduction

Precise characterization of solid material surfaces plays a vital role in research and product development in many industrial and academic areas. Wettability of the surface is important in processes like painting and printing, and has been utilized in the study of cell - biomaterial interactions to name a few. Wettability can be studied by measuring contact angle of the substrate with a given liquid. The Young equation describes the balance at the three phase contact of solid, liquid and gas.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta_v \quad (1)$$

The interfacial tensions, γ_{sv} , γ_{sl} and γ_{lv} , form the equilibrium contact angle of wetting, many times referred to as Young contact angle θ_v . The Young equation assumes that the surface is chemically homogenous and topographically smooth. One of the important applications of the contact angle measurement is the assessment of the surface free energy (SFE) of the solid. Surface free energy of the solid is equivalent to surface tension of the liquid and the unit is the same mN/m (= dynes/cm). Although contact angle itself also gives indications on the wetting properties of the surface, contact angle always depends also on the liquid used for the measurements.

In equation (1), the surface free energy of the solid is described by using the contact angle θ_v , surface tension of the liquid γ_{lv} and interfacial tension between solid and liquid γ_{sl} . The first two are easily measured but the problem is the unknown γ_{sl} which cannot be measured directly. To be able to solve the equation, more assumptions of the relationship between γ_{sv} , γ_{sl} and γ_{lv} has to be made. To be able to understand the different methods, term "work of adhesion" has to be explained. Thermodynamic adhesion is the work required to separate surfaces into two new surfaces (see Figure 1(a)). The equation for work of adhesion can be written as

$$W_A = \gamma_A + \gamma_B - \gamma_{AB} \quad (2)$$

where γ_{AB} is the interfacial tension between two phases, γ_A is the surface tension of phase A and γ_B is the surface tension of phase B. Now, if the other phase is solid and other liquid the equation can be written as

$$W_{sl} = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \quad (3)$$



Attension Theta

Attension Sigma

Equations (1) and (3) can be combined into Young-Dupré equation

$$W_{sl} = \gamma_{lv} (1 + \cos\theta_v) \quad (4)$$

In a similar way the work of cohesion can be defined as shown in the Figure 1(b).

$$W_C = \gamma_A + \gamma_A - 0 = 2\gamma_A \quad (5)$$

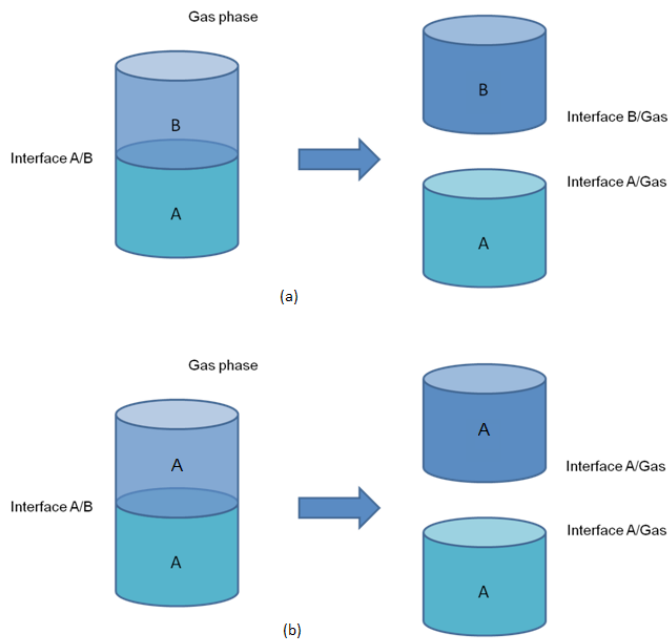
Berthelot initiated the direction to surface free energy calculations at the end of 19th century. He assumed that the work of adhesion (W_A) between the solid and liquid is equal to the geometric mean of the cohesion work of a solid and the cohesion work of the measuring liquid.

$$W_{sl} = \sqrt{(W_{ss}W_{ll})} \quad (6)$$

And then combining with the equations (4), (5) and (6)

$$W_{sl} = \sqrt{2\gamma_{lv}2\gamma_{sv}} = 2\sqrt{\gamma_{lv}\gamma_{sv}} = \gamma_{lv}(1 + \cos\theta_v) \quad (7)$$

Equation (7) is the basis of SFE theories [1, 2]. All the SFE theories are semi-experimental which is why the used theory has to always be stated.



[Figure 1] (a) Schematic of adhesion process (b) Schematic of cohesion process.

Equation of state

Although there are few different formulas based on Equation of state (EQS), the best known is one described by Neumann [3]:

$$\cos\theta_Y = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (8)$$

Here the coefficient $\beta = 0.0001247$ is determined experimentally. In principle the equation of state requires the measurement to be done only by using one liquid and regardless which liquid is chosen the surface free energy result should be the same. There is a lot of criticism against this theory. The controversy deals with the question whether the constant β is universal constant of the materials or just quantity obtained as a result if the iterative procedures applied. Equation of state theory also does not divide the surface tension into different components as the other theories. This is also the only theory which allows the calculations to be done by using just one probe liquid.

OWRK/Fowkes

The idea of division of the SFE into individual components includes the assumption that γ_{sl} is determined by various interfacial interactions that depend on the properties of both the measured substrate and the measurement liquid. Fowkes assumed that surface free energy of a solid (and surface tension of a liquid) is a sum of independent components, associated with specific interactions:

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p + \gamma_{sv}^h + \gamma_{sv}^i + \gamma_{sv}^{ab} + \gamma_{sv}^o \quad (9)$$

where γ_{sv}^d , γ_{sv}^p , γ_{sv}^h , γ_{sv}^i and γ_{sv}^{ab} are the dispersion, polar, hydrogen, induction and acid-base components, respectively. γ_{sv}^o refers to all remaining interactions. Fowkes investigated mainly systems containing substance (solid or liquid) in which only the dispersion interactions appear. According to Fowkes, dispersion interactions are connected with London interactions, arising from the electron

dipole fluctuations. Owen and Wendt continued the Fowkes idea stating that all the components in the right side of the equation (9), except γ_{sv}^d can be considered to be polar (γ_{sv}^p). Consequently, leading to equation (10):

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}^d \gamma_{lv}^d} - 2\sqrt{\gamma_{sv}^p \gamma_{lv}^p} \quad (10)$$

And if equation (10) is combined with Young equation (1), equation called OWRK can be written as:

$$\sqrt{\gamma_{sv}^d \gamma_{lv}^d} + \sqrt{\gamma_{sv}^p \gamma_{lv}^p} = 0.5 \gamma_{lv} (1 + \cos\theta_Y) \quad (11)$$

Because there are two unknowns, γ_{sv}^d and γ_{sv}^p , in equation (11), two liquids with the known dispersive and polar components are needed to solve it. The liquid with the dominant polar component should be chosen as one measuring liquid and dispersive liquid as other one. Water, glycerol and formamide can be used as polar liquids and diiodomethane and α -bromonaphtalene as dispersive. Water and diiodomethane are most often utilized. The OWRK is one of the most common methods for SFE calculations.

Wu

Wu accepted to idea of Owen and Wendt to divide the SFE into polar and dispersive components. Instead of using the geometric mean as in equation (10), he used the harmonic one:

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 4 \left[\frac{\gamma_{sv}^d \gamma_{lv}^d}{(\gamma_{sv}^d + \gamma_{lv}^d)} + \frac{\gamma_{sv}^p \gamma_{lv}^p}{(\gamma_{sv}^p + \gamma_{lv}^p)} \right] \quad (12)$$

And if combined with Young equation (1), Wu equation can be written as:

$$\left[\frac{\gamma_{sv}^d \gamma_{lv}^d}{(\gamma_{sv}^d + \gamma_{lv}^d)} + \frac{\gamma_{sv}^p \gamma_{lv}^p}{(\gamma_{sv}^p + \gamma_{lv}^p)} \right] = 0.25 \gamma_{lv} (1 + \cos\theta_Y) \quad (13)$$

As in the OWRK method, the Wu method requires the use of at least two liquids, one mainly polar and one dispersive. Water and diiodomethane are again often used. From a theoretical point of view, the geometric mean is more accurate than the harmonic one.

Acid-base

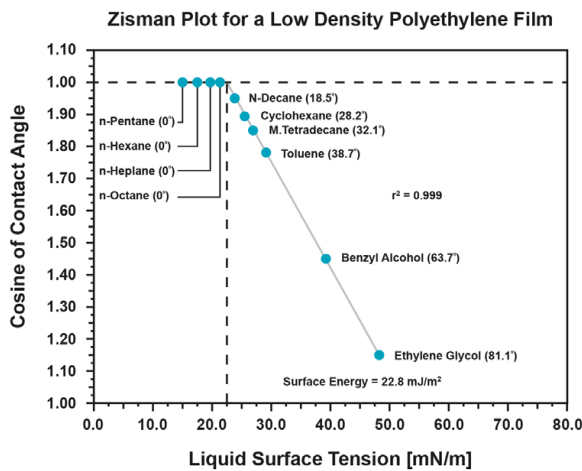
By using the acid-base approach, sometimes called Van Oss-Chaudhury-Good method, the polar component is further divided into acid and base components and the equation can be written as:

$$\sqrt{\gamma_{sv}^d \gamma_{lv}^d} + \sqrt{\gamma_{sv}^{acid} \gamma_{lv}^{base}} + \sqrt{\gamma_{sv}^{base} \gamma_{lv}^{acid}} = 0.5 \gamma_{lv} (1 + \cos\theta_Y) \quad (14)$$

Since there are three unknown, γ_{sv}^d , γ_{sv}^{acid} and γ_{sv}^{base} , at least three liquids with known properties are needed to solve the equation. One dispersive (e.g. diiodomethane) and two polar (e.g. water glycerol) should be used. Acid-base method is one of the most recent developments in the field of SFE calculations. It has a potential to give more in depth information about surface properties of the solid but has been criticized by its sensitivity to even small variations in the contact angle measurements or properties of liquids used.

Zisman plot

The Zisman plot is used to define so-called critical surface tension which is the surface tension of the liquid needed to completely wet the solid (contact angle between the solid and liquid is zero). This critical surface tension value differs from the surface free energy of the solid, and is not divided into dispersive and polar components. In practice, critical surface tension is defined by measuring the contact angle between several different probe liquids and the studied surface. The results are then plotted by having $\cos\theta$ in y-axis and the surface tension of the liquid in x-axis. Straight line is fitted to these measurement points and extrapolated to point $\cos\theta=1$ which will give the critical surface tension value for the surface. In theory, only two measurement points would be needed but in practice using just few different liquids will lead to incorrect results, even negative values are often seen.



[Figure 2] Zisman plot.

References

- [1] C. D. Volpe, D. Maniglio, M. Brugnara, S. Siboni and M. Morra, "The solid surface free energy calculation I. In defence of the multicomponent approach", *Journal of Colloid and Interface Science* 271 (2004) 434.
- [2] S. Siboni, C. D. Volpe, D. Maniglio and M. Brugnara, "The solid surface free energy calculation II. The limits of the Zisman and of the "equation-of-state" approaches", *Journal of Colloid and Interface Science* 271 (2004) 454.
- [3] D. Y. Kwok and A. W. Neumann, "Contact angle measurements and contact angle interpretation", *Advances in colloid and interface science* 81 (1999) 167.