The Measurement of surface energy of polymer by means of contact angles of liquids on solid surfaces
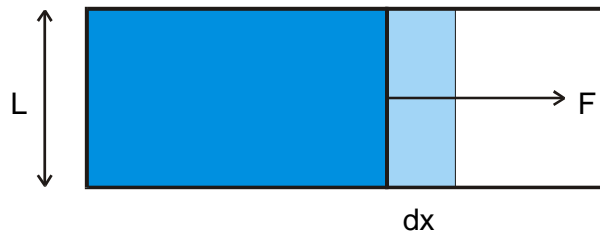
A short overview of frequently used methods

by

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Definitions

Surface tension and surface energy

Surface tension form force:

The force, F, involved in stretching a film is: $F = \gamma L$ γ = surface tension (constant)

This means: $\gamma = F/L$ i.e. <u>force/unit length</u>   Units: N/m or mN/m (= dyn/cm in c.g.s units)
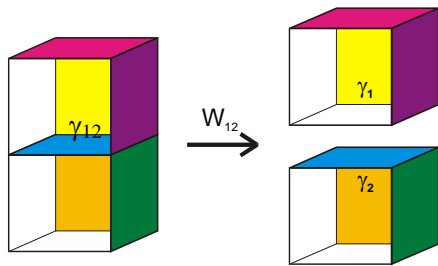
Surface energy from work:

The work, dW, involved in increasing the surface by a length dx is: $dW = dG = \gamma L \, dx = \gamma \, dA$

This means: $\gamma = dG/dA$ i.e. <u>free energy/unit area</u> Units: $J/m^2 = N/m$

<u>Surface tension and surface energy are interchangeable definitions with the same units</u>

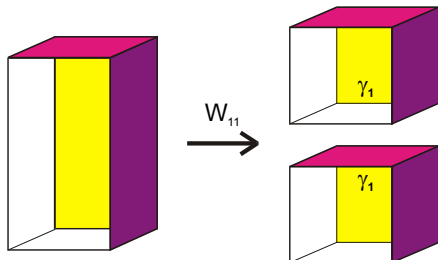## Work of adhesion and work of cohesion

Work of adhesion

The **work of adhesion** between 2 (incompatible) substances is:

$$W^a = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$

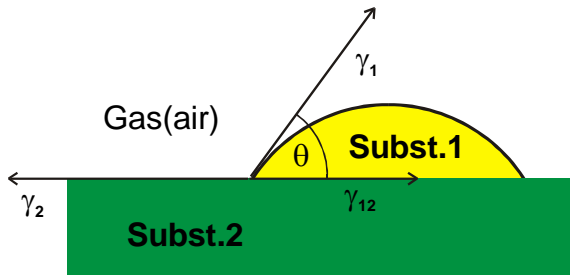or: $\gamma_{12} = \gamma_1 + \gamma_2 - W^a$

Work of cohesion

The **work of cohesion** of a single substance is:

$$W^c = W_{11} = \gamma_1 + \gamma_1 - 0 = 2 \gamma_1$$

I.e.   <u>$\gamma_{12} = 0.5 (W^c_1 + W^c_2) - W^a$</u>

Young's equation

When the liquid does not spread, a drop has a contact angle on the surface. The balance between the forces on the surface gives:

Youngs Equation: $\gamma_2 = \gamma_{12} + \gamma_1 \cos \theta$

NB: Only valid in "dry wetting"

In cases with "wet wetting", the surface pressure of the liquid vapor on the solid is substantial. In these cases, γ_2 becomes lowered by the surface vapor pressure π.

So that: $\gamma_2 = \pi + \gamma_{12} + \gamma_1 \cos \theta$

Expressed by the work of adhesion we can write:

$W^a = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_1 + \gamma_1 \cos \theta = \gamma_1(1+\cos \theta)$ **This is the Young - Dupree equation**

Critical surface tension - Zisman plot

Zisman et al. (1950)[1] found an empirical connection between $\cos\theta$ and γ_1:

If we measure the contact angle of many liquids on the same surface, and plot $\cos\theta$ against γ_1, we get a curve that can be extrapolated to $\cos \theta = 1$.

The extrapolated value is called the **critical surface tension** of the solid surface.

Note: This is not necessarily the same as the surface tension of the solid, γ_2.
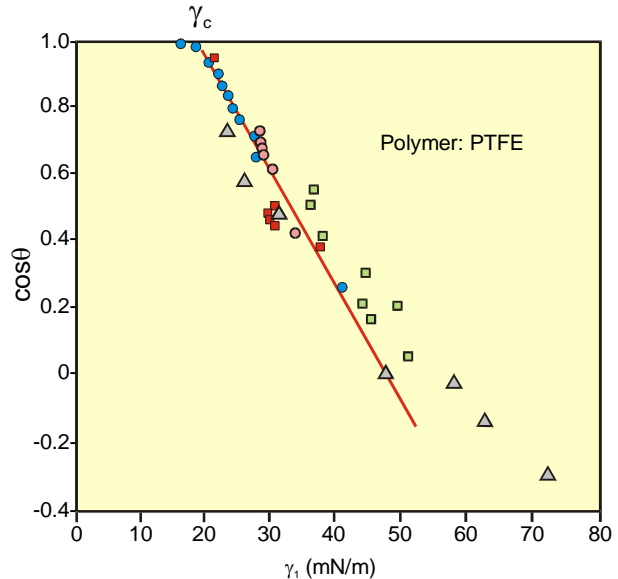
There are 2 problems: 1. The line is not really straight (it is more hyperbolic)
2. γ_c is not the same as γ_2 (only if $\gamma_{12}= 0$ when $\theta = 0$)

In DROPimage the Zisman Plot tool performs an ordinary linear Zisman plot.

The interaction parameter and the work of adhesion

The work of adhesion has been expressed by Good and Girifalco (1960)[2] by the geometric mean of the surface tensions in the same way as the Hamaker constant:

$$W^a = 2\Phi\left(\gamma_1\gamma_2\right)^{1/2} \quad \text{where } \Phi \text{ is the } \textbf{Interaction parameter}, 0.5 < \Phi < 1.15$$

Φ is a function of the molar volumes of substance 1 and 2:

$$\Phi = \frac{4r_1r_2}{\left(r_1+r_2\right)^2}\frac{\sum A_{12}}{\left(\sum A_{11} + \sum A_{22}\right)^{1/2}} \quad \text{where } r_1, r_2 = \text{molecular radii}$$

and ΣA is the sum of London constants (or corresponding) for all types of intermolecular forces (dispersive, polar, acid-bas, etc.)

If we insert for W^a in the Young-Dupree equation, we get:

$$W^a = 2\Phi\left(\gamma_1\gamma_2\right)^{1/2} = \gamma_1\left(1+\cos\theta\right) \quad \text{or} \quad \gamma_2 = \gamma_1\frac{\left(1+\cos\theta\right)^2}{4\Phi^2}$$

Φ has been calculated theoretically, but the results have often been misleading.

It is possible to calculate empirical values for Φ by using values of Φ measured by liquid/liquid interactions in systems of similar polarity.

In a recent publication, Kwok and Neumann (K&N)[3] have argued for using an analytical expression, i.e. and equation of state for Φ. Their expression is:

$$\Phi = \exp\left[\beta\left(\gamma_1 - \gamma_2\right)^2\right]$$

It is easily seen that if $\gamma_1 = \gamma_2$ then $\Phi = 1$. The magnitude of β is therefore crucial in giving a universally correct work of adhesion, if such an expression is possible. K&N have determined this experimentally from an extensive amount of measurements of low energy polymer surfaces. They found $\beta = 0.0001247$ $(m^2/mJ)^2$ to give the best all-over results, although it varied some.

This method has been implemented in DROPimage's Surface Energy (One Liquid) tool.

Fowkes' theory

Fowkes' theory is based on 2 fundamental assumptions: Additivity and the geometric mean

1. Surface forces (energies) are additive: $\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^i + \gamma^{ab} + ...$

where d = dispersion force
        p = polar force
        h = hydrogen bonding force
        i = induction force (Debye)
        ab = acid/base force
        … etc.

2. Geometric mean is used for the work of adhesion for each type of force (energy):

$$W^d_{12} = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} \, , W^p_{12} = 2\left(\gamma_1^p \gamma_2^p\right)^{1/2}, \; W^h_{12} = 2\left(\gamma_1^h \gamma_2^h\right)^{1/2} \, , \text{etc.}$$

The general expression for W_{12} is: $W_{12} = \gamma_1 \left(1 + \cos\theta\right) = W^d_{12} + W^p_{12} + ...$

And for γ_{12} thus: $\underline{\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} - 2\left(\gamma_1^p \gamma_2^p\right)^{1/2} - ...}$

By using a liquid that only interacts with the surface by dispersion forces, we can write:

$$W_{12} = \gamma_1 \left(1 + \cos\theta\right) = 2\left(\gamma_1 \gamma_2^d\right)^{1/2} \qquad (\gamma_1 = \gamma_1^d) \qquad \text{and} \qquad \gamma_2^d = \frac{\gamma_1 \left(1 + \cos\theta\right)^2}{4}$$

Extended Fowkes' theory

The combination of additivity and geometric mean has been used by many:

$$W_{12} = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} + 2\left(\gamma_1^p \gamma_2^p\right)^{1/2} + 2\left(\gamma_1^h \gamma_2^h\right)^{1/2} \quad \text{(Kitazaki and Hate, 1972)}[4]$$

$$W_{12} = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} + 2\left(\gamma_1^n \gamma_2^n\right)^{1/2} \quad \text{(n = all non-dispersive componenets)}$$

By doing measurements with m number of liquids on the same surface, we can calculate m different components of the surface energy, if the corresponding components of the liquids are known.

By using 2 liquids, A and B, we can write

$$W_{12A} = \gamma_{1A}\left(1+\cos\theta_A\right) = 2\left(\gamma_{1A}{}^d\gamma_2{}^d\right)^{1/2} + 2\left(\gamma_{1A}{}^p\gamma_2{}^p\right)^{1/2}$$

$$W_{12B} = \gamma_{1B}\left(1+\cos\theta_B\right) = 2\left(\gamma_{1B}{}^d\gamma_2{}^d\right)^{1/2} + 2\left(\gamma_{1B}{}^p\gamma_2{}^p\right)^{1/2}$$

The 2 equations can be linearized to give:

$$\frac{\left(\gamma_{1A}{}^d\right)^{1/2}}{\gamma_{1A}}\left(\gamma_2{}^d\right)^{1/2} + \frac{\left(\gamma_{1A}{}^p\right)^{1/2}}{\gamma_{1A}}\left(\gamma_2{}^p\right)^{1/2} = \frac{1+\cos\theta_A}{2}$$

$$\frac{\left(\gamma_{1B}{}^d\right)^{1/2}}{\gamma_{1B}}\left(\gamma_2{}^d\right)^{1/2} + \frac{\left(\gamma_{1B}{}^p\right)^{1/2}}{\gamma_{1B}}\left(\gamma_2{}^p\right)^{1/2} = \frac{1+\cos\theta_B}{2}$$

These equation set is solved for $(\gamma_2{}^d)^{1/2}$ and $(\gamma_2{}^p)^{1/2}$.

Usually, one polar (water) and one unpolar (methylene iodide) liquid are used. **This is the so-called two-liquid method.** In the solution, care must be taken to check if a square root is negative. This indicates errors in the measurements. This procedure is used in DROPimage's Surface Energy (Two Liquids) tool (Geometric Mean)[5].

The question of geometric or harmonic mean

Fowkes' assumption of the geometric mean is based on Berthelot's hypothesis, again based on London's theory of dispersive forces.

The London (Lennard-Jones) attraction constants between like and dislike substances are

$$A_{12}{}^d = \left(\frac{3}{2}\right)\hbar\left(\frac{\nu_1\nu_2}{\nu_1+\nu_2}\right)\alpha_1\alpha_2, \quad A_{11}{}^d = \left(\frac{3}{4}\right)\hbar\nu_1\alpha_1{}^2, \quad A_{22}{}^d = \left(\frac{3}{4}\right)\hbar\nu_2\alpha_2{}^2$$

where $\hbar$ = Planck's constant, ν = frequency of vibration, α = polarizability

If α is eliminated, we obtain

$$A_{12}{}^d = \frac{2(\nu_1\nu_2)^{1/2}}{\nu_1+\nu_2}(A_{11}{}^d A_{22}{}^d)^{1/2}, \text{ and if } \nu_1 = \nu_2, \text{ then } A_{12}{}^d = (A_{11}{}^d A_{22}{}^d)^{1/2}$$

After Girifalco and Good, the works of adhesion are expressed by

$$W_{12} = \frac{n_1 n_2 A_{12}}{6d_{12}{}^2}\left(\frac{1}{2}-\frac{1}{m-4}\right), \quad W_{11} = \frac{n_1{}^2 A_{11}}{6d_{11}{}^2}\left(\frac{1}{2}-\frac{1}{m-4}\right), \quad W_{22} = \frac{n_2{}^2 A_{22}}{6d_{22}{}^2}\left(\frac{1}{2}-\frac{1}{m-4}\right)$$

where n = molecular density, d = equilibrium distance between the phases, m = the repulsion constant (Lennard-Jones). By eliminating n, and using the expressions for A_{ij} above, we obtain:

$$W_{12}{}^d = \frac{d_1 d_2}{d_{12}{}^2}(W_{11}{}^d W_{22}{}^d)^{1/2}$$ (There are only dispersion energies here)

If then $d_{12} = (d_{11}d_{22})^{1/2}$ we obtain: $W_{12}{}^d = (W_{11}{}^d W_{22}{}^d)^{1/2}$ and therefore $\underline{W_{12}{}^d = 2(\gamma_1{}^d \gamma_2{}^d)^{1/2}}$

These are therefore the assumption involved in using the geometric mean.

It is, however, possible that some of these assumptions are less acceptable. It is possible to derive another mean, based on slightly different assumptions[6]:

If we eliminate ν instead of α from the equations above, we obtain

$$A_{12}{}^d = \frac{2A_{11}{}^d A_{22}{}^d}{A_{11}{}^d(\alpha_1/\alpha_2)+A_{22}{}^d(\alpha_1/\alpha_2)}$$

If now $\alpha_1 = \alpha_2$ then the expression for A_{12} is: $A_{12}{}^d = \frac{2A_{11}{}^d A_{22}{}^d}{A_{11}{}^d + A_{22}{}^d}$, i.e. a **harmonic mean**

By using the same equations for W_{ij} as above, we now obtain

$$W_{12}{}^d = \frac{2W_{11}{}^d W_{22}{}^d \frac{d_{11}}{n_1}\frac{d_{22}}{n_2}\frac{d_1 d_2}{d_{12}{}^2}}{W_{11}{}^d(d_{11}/n_1)^2 + W_{22}{}^d(d_{22}/n_2)^2}$$

If now again $d_{12} \cong (d_{11}d_{22})^{1/2}$ and in addition $n_1/d_{11} \cong n_2/d_{22}$, the work of adhesion becomes

$$W_{12}{}^d = \frac{2W_{11}{}^d W_{22}{}^d}{W_{11}{}^d + W_{22}{}^d}, \quad \text{and therefore} \quad \underline{W_{12}{}^d = \frac{4\gamma_{11}{}^d \gamma_{22}{}^d}{\gamma_{11}{}^d + \gamma_{22}{}^d}}$$

This is the harmonic mean for the work of adhesion. Wu has claimed that the harmonic mean is better suited for low energy surfaces, such as polymers[6].

On the next page are shown two figures of the work of adhesion plotted as a function of the dispersive and polar surface energy components. The plot using the harmonic mean is seen to give generally lower values for the work of adhesion than the geometric mean.
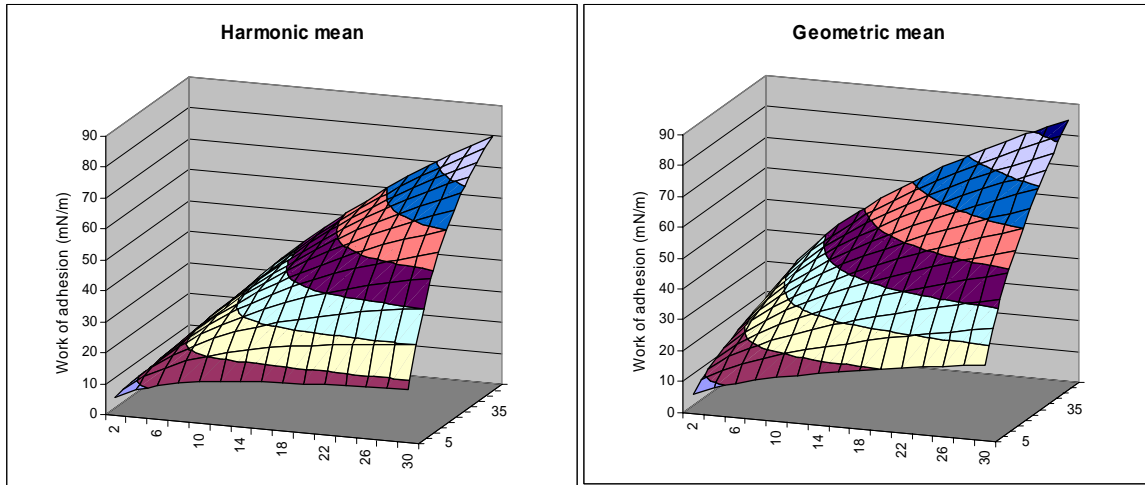
Measuring surface energies with 2 liquids by the harmonic mean

In the same way as with using the geometric mean, the harmonic mean may be used to calculate the dispersive and polar components of the surface energy by measuring the angles of two liquids, A and B.

The two equations are then:

$$W_{12A} = \gamma_{1A}\left(1+\cos\theta_A\right) = \frac{4\gamma_{1A}{}^d\gamma_2{}^d}{\gamma_{1A}{}^d + \gamma_2{}^d} + \frac{4\gamma_{1A}{}^p\gamma_2{}^p}{\gamma_{1A}{}^p + \gamma_2{}^p}$$

$$W_{12B} = \gamma_{1B}\left(1+\cos\theta_B\right) = \frac{4\gamma_{1B}{}^d\gamma_2{}^d}{\gamma_{1B}{}^d + \gamma_2{}^d} + \frac{4\gamma_{1B}{}^p\gamma_2{}^p}{\gamma_{1B}{}^p + \gamma_2{}^p}$$

Here, the harmonic mean is used also for the polar components. The justification of this assumption is not necessarily solid, but is necessary here to obtain an analytical solution. This set of equations may be converted to two second degree equations as given below.

$$a^d\left(\gamma_2{}^d\right)^2 + b^d\gamma_2{}^d + c^d = 0$$

$$a^p\left(\gamma_2{}^p\right)^2 + b^p\gamma_2{}^p + c^p = 0$$

Where the constants are

$a^d = A_B B_A - A_A B_B$ $a^p = A_B C_A - A_A C_B$

$b^d = C_B B_A - C_A B_B - D_A A_B + D_B A_A$ and $b^p = B_B C_A - B_A C_B - D_A A_B + D_B A_A$

$c^d = D_B C_A - D_A C_B$ $c^p = D_B B_A - D_A B_B$

$$A_i = \gamma_{1i}(3 - \cos\theta)/4$$

and
$$B_i = \gamma_{1i}{}^P \left[\gamma_{1i}{}^d - \gamma_{1i}(1 + \cos\theta_i)/4\right]$$
$$C_i = \gamma_{1i}{}^d \left[\gamma_{1i}{}^P - \gamma_{1i}(1 + \cos\theta_i)/4\right]$$
for i = A and B, respectively
$$D_i = \gamma_{1i}{}^d \gamma_{1i}{}^P \gamma_{1i}\left((1 + \cos\theta_i)/4\right)$$

The roots of the second degree equations are found in the usual way, taking care to obtain the correct, positive, roots. This procedure is used in DROPimage's Surface Energy (Two Liquids) tool (Harmonic Mean).

Combinations of means

Different combinations of geometric and harmonic means have also been proposed, for instance the following combination[6]:

$$W_{12} = 2(\gamma_1{}^d \gamma_2{}^d)^{1/2} + \frac{4\gamma_1{}^P \gamma_2{}^P}{\gamma_1{}^P + \gamma_2{}^P}$$

Wu proposed that this equation should be used for high energy surfaces, such as mercury, glass, oxides and graphite, while the harmonic mean also should be uses for the dispersive components in the case of polymer surfaces.

Acid-base interactions

Also, even if these types of relationships fit for the dispersion forces, and possibly also for some polar (Debye and Keesom forces), they are not so good for acid/base and hydrogen bonding. For this, Van Oss and coworkers[7-9] have proposed other combination of surface energies.

The argument is that often, the polar (Keesom and Debye) forces are weak, and can be included in the dispersive contribution. The "combined" contribution is denoted by LW – Lifschitz-van der Waals. In addition, there is a short-range interaction (SR), that is caused by acid-base interactions (hydrogen bonding is a type of acid-base).

We can write: $\gamma = \gamma^{LW} + \gamma^{AB}$

W^{LW} can be expressed by the geometric mean (after Fowkes): $W_{12}{}^{LW} = 2\left(\gamma_1{}^{LW}\gamma_2{}^{LW}\right)^{1/2}$

However, W^{AB} can not be expressed in this way, as the basic components of the surface only interact with the acid components of the liquid, and vice versa.

Therefore, Van Oss and coworkers write: $\underline{W_{12}{}^{AB} = 2\left(\gamma_1{}^+ \gamma_2{}^-\right)^{1/2} + 2\left(\gamma_1{}^- \gamma_2{}^+\right)^{1/2}}$

where γ_i^+ is the acidic part and γ_i^- the basic part. Some substances that have only acidic or only basic properties are classified as **monopolar**, while substances with both types of properties are **bipolar**.

Calculation

By measuring the contact angle of three different liquids, A, B, and C, with known LW, acidic and basic components, the corresponding surface energies of the solid can be calculated.

$$W_{12A} = \gamma_{1A}\left(1 + \cos\theta_A\right) = 2\left(\gamma_{1A}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1A}{}^+\gamma_2{}^-\right)^{1/2} + 2\left(\gamma_{1A}{}^-\gamma_2{}^+\right)^{1/2}$$

$$W_{12B} = \gamma_{1B}\left(1 + \cos\theta_B\right) = 2\left(\gamma_{1B}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1B}{}^+\gamma_2{}^-\right)^{1/2} + 2\left(\gamma_{1B}{}^-\gamma_2{}^+\right)^{1/2}$$

$$W_{12C} = \gamma_{1C}\left(1 + \cos\theta_C\right) = 2\left(\gamma_{1C}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1C}{}^+\gamma_2{}^-\right)^{1/2} + 2\left(\gamma_{1C}{}^-\gamma_2{}^+\right)^{1/2}$$

These equations are solved in the same way as the 2-equaions set above. We may express the set in matrix form:

Coefficient vector: $\quad \mathbf{a} = [(\gamma_2{}^{LW})^{1/2} \quad (\gamma_2{}^-)^{1/2} \quad (\gamma_2{}^+)^{1/2}]$

The x-matix: $\quad \boldsymbol{\alpha} = \begin{bmatrix} \dfrac{(\gamma_{1A}{}^{LW})^{1/2}}{\gamma_{1A}} & \dfrac{(\gamma_{1A}{}^+)^{1/2}}{\gamma_{1A}} & \dfrac{(\gamma_{1A}{}^-)^{1/2}}{\gamma_{1A}} \\[2mm] \dfrac{(\gamma_{1B}{}^{LW})^{1/2}}{\gamma_{1B}} & \dfrac{(\gamma_{1B}{}^+)^{1/2}}{\gamma_{1B}} & \dfrac{(\gamma_{1B}{}^-)^{1/2}}{\gamma_{1B}} \\[2mm] \dfrac{(\gamma_{1C}{}^{LW})^{1/2}}{\gamma_{1C}} & \dfrac{(\gamma_{1C}{}^+)^{1/2}}{\gamma_{1C}} & \dfrac{(\gamma_{1C}{}^-)^{1/2}}{\gamma_{1C}} \end{bmatrix}$

The y-vector: $\quad \boldsymbol{\beta} = \begin{bmatrix} (1 + \cos(\theta_A))/2 \\ (1 + \cos(\theta_B))/2 \\ (1 + \cos(\theta_C))/2 \end{bmatrix}$

The solution is then obtained from the solution: $\mathbf{a} = \boldsymbol{\beta}\,\boldsymbol{\alpha}^{-1}$ by the usual matrix inversion and multiplication. This procedure is used by DROPimage's Acid-Base tool.

Using more than 2 liquids in Fowkes' method

In the modified Fokes' theory only two liquids are used to calculate the dispersive and polar components of the surface energy. If more than two liquids are used, all combination of liquid pairs may be used to calculate the components, and then the average of these may be taken. However, there is also another method that has been proposed in the literature[10] by using a regression line.

The extended Fowkes' equation

$$\gamma_1 (1 + \cos\theta) = 2\left(\gamma_1^{d}\gamma_2^{d}\right)^{1/2} + 2\left(\gamma_1^{p}\gamma_2^{p}\right)^{1/2}$$

is modified by dividing by $2\left(\gamma_1^{d}\right)^{1/2}$ and we obtain

$$(1 + \cos\theta)\frac{\gamma_1}{2\left(\gamma_1^{d}\right)^{1/2}} = \left(\gamma_2^{d}\right)^{1/2} + \left(\gamma_2^{p}\right)^{1/2}\left(\frac{\gamma_1^{p}}{\gamma_1^{d}}\right)^{1/2}$$

If we plot the left side of this equation as a function of $\left(\dfrac{\gamma_1^{p}}{\gamma_1^{d}}\right)^{1/2}$ we get a straight line with the slope equal to $\left(\gamma_2^{p}\right)^{1/2}$ and intercept on the y-axis equal to $\left(\gamma_2^{d}\right)^{1/2}$. With only two liquids the result is the same as with the Surface Energy (Two Liquids) method, using the geometric mean. But the advantage with the regression is that more liquids may be used, and that by this method it also possible to do a realistic evaluation of the errors involved. This procedure is implemented in the DROPimage Surface Energy (Multi Liquids) tool.

One should be careful not to accept negative slopes in this regression because the square always comes out positive. A negative slope is clearly caused by errors in the contact angle data or the surface energies of the liquids.

Measurements of high energy surfaces

As most liquids are spread on a high energy surface, the contact angle cannot be measured. However, Shultz (1977)[11] has developed a method where these angles may be measured by submerging the surface in one liquid and using a second liquid to measure the contact angle. Usually, hydrocarbons like n-hexane, n-octane, n-decane, and n-hexadecane are used as the submerging liquids and water as the contact angle liquid.

We can show this by the following derivation (using the geometric mean)

For the hydrocarbon: $\gamma_{SH} = \gamma_S + \gamma_H - 2(\gamma_S^{d}\gamma_H)^{1/2}$

For the water drop: $\gamma_{SW} = \gamma_S + \gamma_W - 2(\gamma_S^{d}\gamma_W^{d})^{1/2} - E_{SW}$

where S denotes solid, H hydrocarbon, and W water. The parameter E_{SW} is the excess interaction energy, i.e. the polar part. By subtracting the second from the first equation, we obtain

$$\gamma_{SH} - \gamma_{SW} = \gamma_H - \gamma_W + 2(\gamma_S^{d})^{1/2}[(\gamma_W^{d})^{1/2} - (\gamma_H)^{1/2}] + E_{SW}$$

From Young's equation $\gamma_{SH} - \gamma_{SW} = \gamma_{WH}\cos\theta$, we obtain

$$\gamma_{WH}\cos\theta = \gamma_H - \gamma_W + 2(\gamma_S^d)^{1/2}[(\gamma_W^d)^{1/2} - (\gamma_H)^{1/2}] + E_{SW}, \text{ or}$$

$$\gamma_W - \gamma_H + \gamma_{WH}\cos\theta = 2(\gamma_S^d)^{1/2}[(\gamma_W^d)^{1/2} - (\gamma_H)^{1/2}] + E_{SW}$$

By plotting the left side against $(\gamma_W^d)^{1/2} - (\gamma_H)^{1/2}$ we get a straight line with the slope $2(\gamma_S^d)^{1/2}$ and intercept E_{SW}.

Using the geometric mean, E_{SW} is expressed according to the extended Fowkes' theory as $E_{SW} = 2(\gamma_S^p \gamma_W^p)^{1/2}$.

Knowing the polar part of the surface tension of water, the solid's polar component can be easily calculated and thus the total surface energy of the solid. The figure to the left shows an example of this type of plot.
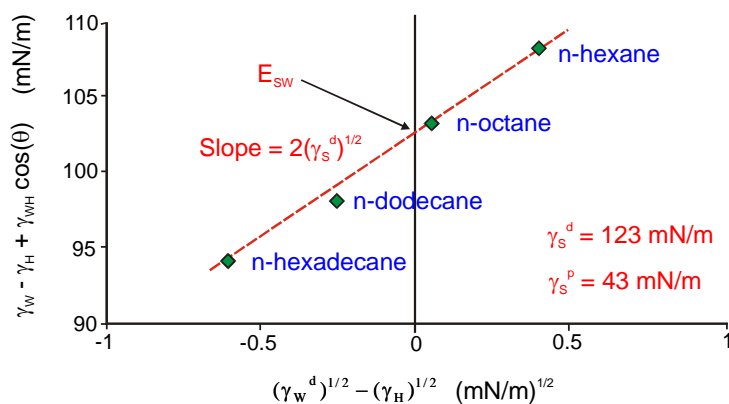
The described method is applied in the Solid-Liquid-Liquid (SLL) Surface Energy tool in DROPimage.

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