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Interfacial Chemistry

Introduction into Methods of Measuring and Analyzing Contact Angles for the Determination of Surface Free Energies of Solids

1 Introduction

Already at the beginning of the last century Young realized, that the equilibrium of forces at the edge of a resting drop can be described by the interfacial energies of the corresponding surfaces. The geometric situation is shown in fig. 1.

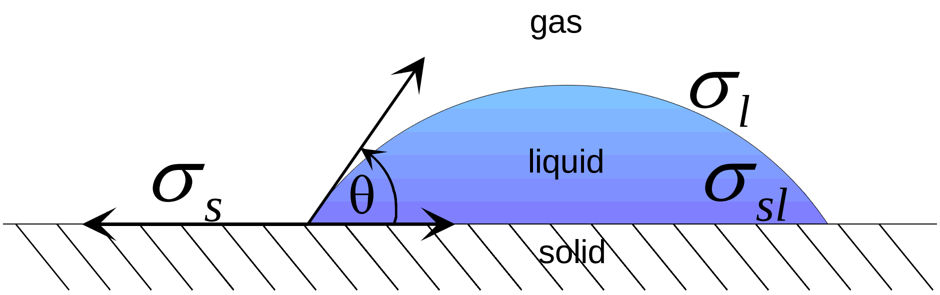


Fig. 1 Drop on the surface of a solid.

From the equilibrium of the forces one obtains for the surface and interfacial tensions::

$$\sigma_s = \sigma_{ls} + \sigma_l \cdot \cos\theta \tag{1}$$

Here σ_s, σ_{ls} and σ_l represent the surface tensions between the solid and the saturated vapor of the liquid, the interfacial tension between the drop and the solid and the surface tension of the drop versus the saturated vapor.

Experimentally in most cases the surface energy of the solid is of interest, while initially also the interfacial tension between the liquid and the solid is unknown. The surface energy of the solid is equal to its surface tension because of the stiffness of the solid. The surface tension of the liquid is assumed to be known. Additionally, depending on the method, the components of the surface tension (polar and disperse, see below) of the used liquid must be known.

The analyzing methods described below aim at the determination of the surface energy of solid surfaces. Depending on the employed method the contact angles of two or more liquids on the solid will be measured. Within each method different models for the description of the interfacial tension between liquid and solid are employed.

2 Measurement of Contact Angles

In the past, contact angles were mainly determined in a geometry, where the light source and the sensor lie on opposite sides of the drop. In the simplest case the measurement is done with a goniometer eyepiece, where the result can be influenced by the subjective impression of the operator and therefore will lead to rather irreproducible results. In recent times more and more video based systems are employed. This became possible by the availability of powerful frame grabber boards and powerful inexpensive computers.

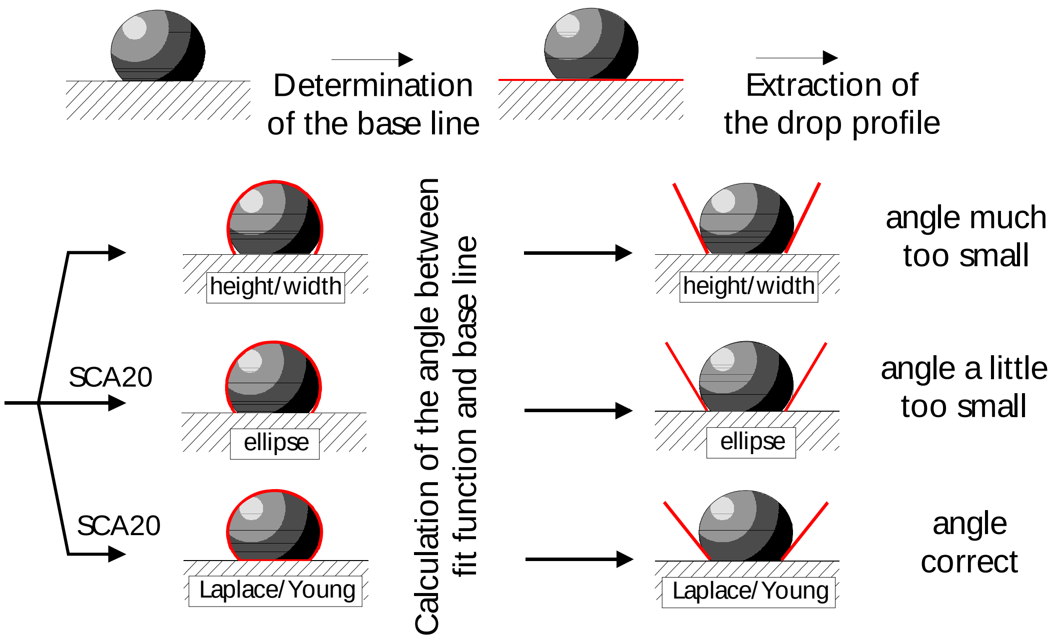


Fig. 2 Schematic presentation of the measurement of a contact angle.

In these system the eyepiece is mostly exchanged by a CCD-camera. For the determination of the contact angle the imaging software has to fulfill the following tasks, which are schematically represented in fig. 2:

- determination of the base line at the phase boundary solid/liquid
- determination of the drop profile
- measurement of the contact angle

Initially a digital image of the drop is stored by the help of the CCD-Camera. The position of the base line and also the drop contour line is determined by calculating the difference between the brightness of one pixel and the neighboring pixels for the whole image. The contour line of the drop and the base line then result from the positions of the maximum difference in brightness, e.g. the maximum contrast.

Before a contact angle can be determined a mathematical function has to be fitted to the measured contour line. Different functions can be used, resulting in highly different accuracies, but also costing highly different computational time.

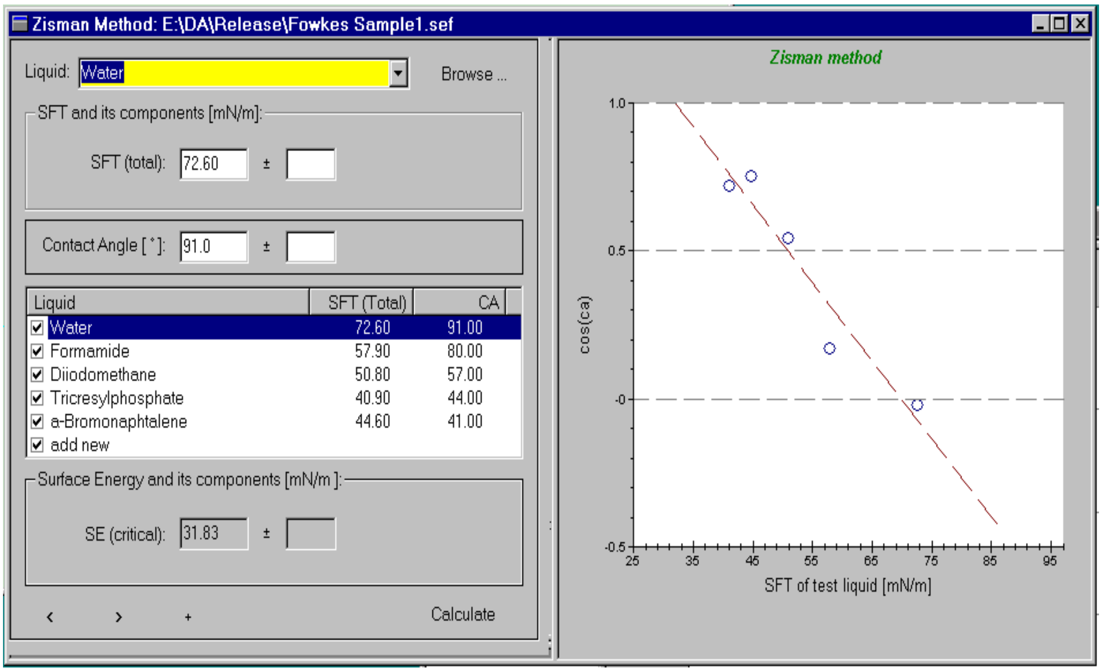
1. In the height/width method a segment of a circle is fitted to the drop shape. With larger drops this method leads to drastic errors, because the larger mass of larger drops results in a large deviation of the shape from a circle.
2. In the ellipse method the drop contour is approximated by a line of an ellipse. Here, the deviations from the true drop shape are in the range of a few per cent.
3. In the Young-Laplace-Method a line is fitted to the drop contour, which exactly represents the contour of the drop. The drop shape is determined by the force balance of surface tension and the force of gravity. In the Young-Laplace-method the corresponding equation is solved numerically fitting the solution to the drop shape by varying a parameter.

A comparison between the different methods shows, that only the ellipse and the Young-Laplace-Method lead to a satisfying accuracy in the contact angle. The ellipse method holds the advantage, that the result is available within fractions of a second, while the Young-Laplace-Method takes 1-2 seconds depending on the computational speed. For fast absorption processes this method can be used only very limited.

3 Analyzing Methods and their Applications

3.1 Analyzing Method after Zisman

For at least two liquids with known surface tensions the contact angle is measured on the unknown solid. Then the cosine of the measured angles is plotted versus the surface tension of the corresponding liquid. Approximately a straight line is obtained, which can be extrapolated to a value of cos Θ = 1 by using a linear regression line. This point corresponds to an angle of 0 degrees, e.g. complete wetting. This value is assigned to the so called critical surface tension σ_{crit} . The critical surface tension represents the surface energy of solid only if mere disperse interactions are present. e.g. with non-polar solids. This conditions is fulfilled by many polymers like PE or PTFE. The method is demonstrated in Fig. 3, where a respective computer program is shown. The main properties of the method after Zisman are summarized in table 1.



Zisman Method: E:\DA\Release\Fowkes Sample1.sef

Liquid: Water

SFT and its components [mN/m]:

SFT (total): 72.60 ±

Contact Angle [°]: 91.0 ±

Liquid	SFT (Total)	CA
☑ Water	72.60	91.00
☑ Formamide	57.90	80.00
☑ Diiodomethane	50.80	57.00
☑ Tricresylphosphate	40.90	44.00
☑ a-Bromonaphtalene	44.60	41.00
☑ add new		

Surface Energy and its components [mN/m]:

SE (critical): 31.83 ±

Fig. 3 Analyzing method after Zisman, determination of the critical surface tension.

Table 1 Properties of the method after Zisman.

Method	Information	Number of Fl., Min.	Application	Examples of application	Comment
Zisman	critical surface tension	2	non-polar solids	PE, PTFE, waxes	time consuming, little information

3.2 Analyzing Method after Owens, Wendt, Rabel and Kaelble

Owens, Wendt, Rabel and Kaelble developed for the first time the idea, that the interfacial tension can be separated according to the underlying interactions between the molecules. They distinguished between disperse interactions and polar interactions. Here, polar interactions contain Coulomb interactions between permanent dipoles and the ones between permanent and induced dipoles. The interaction because of the time fluctuations of the charge distribution within the molecules is called disperse interaction. Polar and disperse contributions to the surface energy and surface tension respectively are combined by forming the sum of both parts. Therefore one obtains:

$$\sigma_l = \sigma_l^d + \sigma_l^p \qquad \sigma_s = \sigma_s^d + \sigma_s^p \tag{2}$$

Here σ_l^d and σ_l^p represent the disperse and polar parts of the liquid, while σ_s^d and σ_s^p stand for the respective contributions of the solid. The interfacial energy can be calculated according to Owens, Wendt, Rabel and Kaelble from the contributions of the liquid and the solid by forming the geometric mean.

For σ_{sl} one obtains

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p}\right) \tag{3}$$

Substituting this term for σ_{sl} in equation (1) and solving for the unknown quantities gives an equation of a straight line of the form

$$y = a \cdot x + b \tag{4}$$

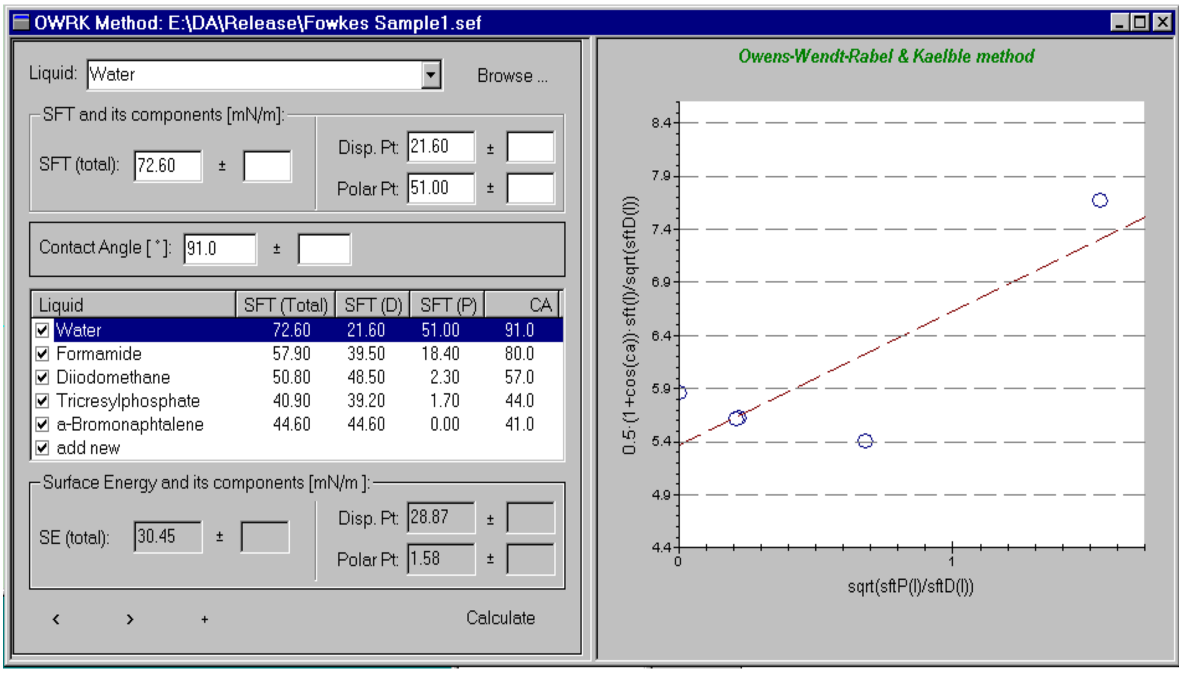
with

$$y = \frac{1+\cos\theta}{2} \cdot \frac{\sigma_l}{\sqrt{\sigma_l^d}} \qquad x = \sqrt{\frac{\sigma_l^p}{\sigma_l^d}}$$
$$a = \sqrt{\sigma_s^p} \qquad b = \sqrt{\sigma_s^d} \tag{5}$$

Therefore, by plotting y versus x allows to calculate σ_s^p from the slope of the fitted line and σ_s^d from the intersection with the vertical axis. To achieve this, the contact angle of at least two liquids on the unknown solid must be determined.

If a suitable computer program is available the solution is calculated within fractions of a second after entering the measured contact angles and surface tension data of the liquids. By using suitable data bases with data of liquids the procedure is simplified even further. A typical analysis with a computer is shown in fig. 4.

The properties of this method are summarized in table 2.



Liquid: Water

SFT and its components [mN/m]:

SFT (total): 72.60 ±

Disp. Pt: 21.60 ±

Polar Pt: 51.00 ±

Contact Angle [°]: 91.0 ±

Liquid	SFT (Total)	SFT (D)	SFT (P)	CA
☑ Water	72.60	21.60	51.00	91.0
☑ Formamide	57.90	39.50	18.40	80.0
☑ Diiodomethane	50.80	48.50	2.30	57.0
☑ Tricresylphosphate	40.90	39.20	1.70	44.0
☑ a-Bromonaphtalene	44.60	44.60	0.00	41.0
☑ add new				

Surface Energy and its components [mN/m]:

SE (total): 30.45 ±

Disp. Pt: 28.87 ±

Polar Pt: 1.58 ±

Fig. 4 Analysis after OWRK, determination of polar and disperse contributions to the surface energy.

Table 2 Properties of the method after Owens, Wendt, Rabel and Kaelble.

Method	Information	Number of Fl., Min.	Application	Examples of application	Comment
OWRK	polar and disperse parts of the surface energy	2	universal	Polymers, Aluminum, Coatings, Varnishes..	simple, fast results

3.3 Analyzing method after Fowkes

Similar to the method after Owens, Wendt, Rabel and Kaelble, Fowkes also distinguishes between disperse and non-disperse parts of the surface energy. In contrast to the above mentioned method Fowkes does not give a description of the polar interaction, which is denoted I_p . After Fowkes one gets

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^d \cdot \sigma_l^d} - I_p \tag{6}$$

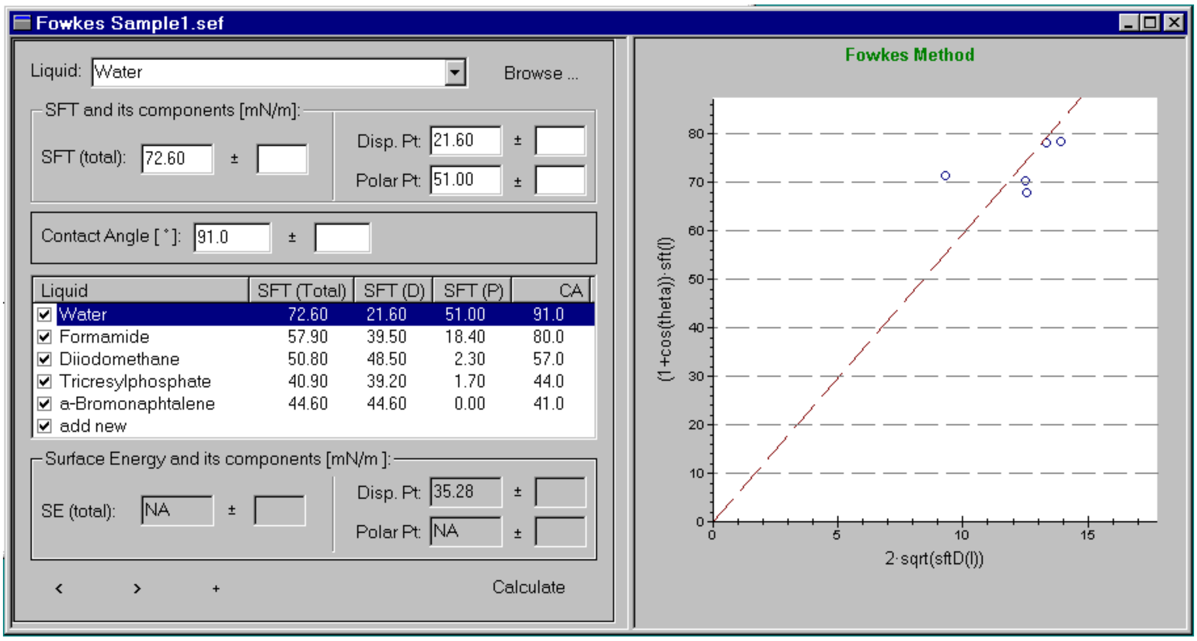
Because no further information is available about I_p , an analysis after Fowkes is only possible if I_p is zero. This is true for solely disperse liquids or completely disperse solids. In the first case the disperse contribution to the surface energy of a solid with additional polar contributions can be determined. Again the expression for σ_{sl} is substituted into equation (1). After some transformations again an equation of a straight line is obtained:

$$\sigma_l\left(1 + \cos\theta\right) = 2 \cdot \sqrt{\sigma_s^d} \cdot \sqrt{\sigma_l^d} \tag{7}$$

Therefore the disperse part of the surface energy can be calculated by evaluating the slope of the line:

$$2\cdot\sqrt{\sigma_s^d} \tag{8}$$

Here, the straight line must run through the origin, because according to equation (7) the intersection with the vertical axis is zero. An analysis with a computer is shown in fig. 5. Again, the properties of this analyzing method are summarized in table 3.



Fowkes Sample1.sef

Liquid: Water

SFT and its components [mN/m]:

SFT (total): 72.60 ±

Disp. Pt: 21.60 ±

Polar Pt: 51.00 ±

Contact Angle [°]: 91.0 ±

Liquid	SFT (Total)	SFT (D)	SFT (P)	CA
☑ Water	72.60	21.60	51.00	91.0
☑ Formamide	57.90	39.50	18.40	80.0
☑ Diiodomethane	50.80	48.50	2.30	57.0
☑ Tricresylphosphate	40.90	39.20	1.70	44.0
☑ a-Bromonaphtalene	44.60	44.60	0.00	41.0
☑ add new				

Surface Energy and its components [mN/m]:

SE (total): NA ±

Disp. Pt: 35.28 ±

Polar Pt: NA ±

Fig. 5 Analyzing method after Fowkes.

Table. 3 Properties of the method after Fowkes.

Method	Information	Number of Fl., Min.	Application	Examples of application	Comment
Fowkes	disperse parts of the surface energy	1	non-polar systems	PE, PTFE, waxes	little contents of information

The treatment of the surface for example in the production of polymer foils with oxygen plasma has a great influence especially on the polar parts of the surface energy. The same is true for various cleaning techniques in semiconductor technology. Since with the procedure after Fowkes only disperse interactions are taken into account, the application of the method is quite restricted.

3.4 Analyzing method after Wu

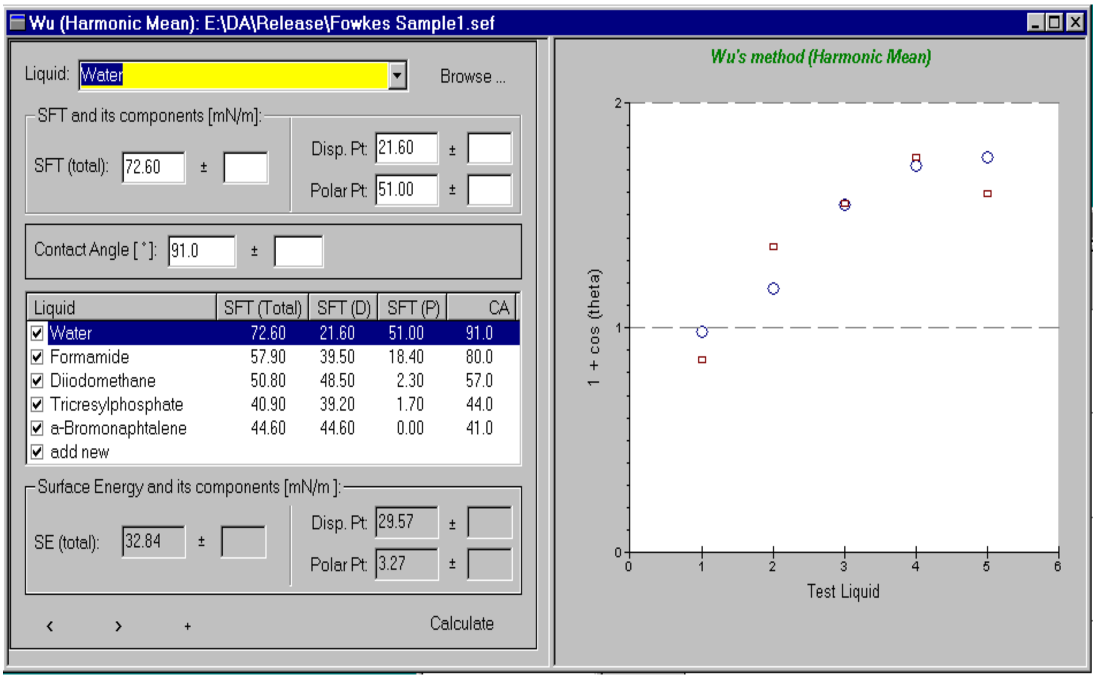
Wu proposed another method for evaluating contact angles. After Wu the interface energy between liquid and solid can be calculated by forming the harmonic mean (compare OWRK: geometric mean).

For σ_{sl} one obtains

$$\sigma_{sl} = \sigma_s + \sigma_l - \frac{4 \cdot \sigma_l^d \cdot \sigma_s^d}{\sigma_l^d + \sigma_s^d} - \frac{4 \cdot \sigma_l^p \cdot \sigma_s^p}{\sigma_l^p + \sigma_s^p} \tag{9}$$

Again this expression for σ_{sl} is substituted in Young´s equation (1) resulting in two linear equations in the unknown σ_s^d and σ_s^p . After solving the system of equations one obtains for one of the two unknowns a quadratic equation, which in general has two solutions. Therefore also for the other unknown two solutions are obtained. Thus, two sets of solutions are calculated, of which only one is the true solution, of course. Normally one of the sets can easily be rejected as not reasonable, if for example negative values or unreasonable high values for the surface energy are calculated. With this method drops of at least two liquids must be determined. At least one of the liquids must have a polar part greater than zero.

In practice the solutions are calculated with the aid of computers by using algorithms employing non-linear regression. The physically reasonable solution is determined by allowing only reasonable starting values in the regression. The analysis with a respective software is shown in fig. 6. The features of this analyzing method are compiled in table 4.


Wu (Harmonic Mean): E:\DA\Release\Fowkes Sample1.sef

Liquid: Water

SFT and its components [mN/m]:

SFT (total): 72.60 ±

Disp. Pt: 21.60 ±

Polar Pt: 51.00 ±

Contact Angle [°]: 91.0 ±

Liquid	SFT (Total)	SFT (D)	SFT (P)	CA
☑ Water	72.60	21.60	51.00	91.0
☑ Formamide	57.90	39.50	18.40	80.0
☑ Diiodomethane	50.80	48.50	2.30	57.0
☑ Tricresylphosphate	40.90	39.20	1.70	44.0
☑ a-Bromonaphtalene	44.60	44.60	0.00	41.0
☑ add new				

Surface Energy and its components [mN/m]:

SE (total): 32.84 ±

Disp. Pt: 29.57 ±

Polar Pt: 3.27 ±

Fig. 6 Analysis after Wu, the correspondence of circles and rectangles is a measure for the accuracy of the non-linear regression.

The analyzing method after Wu has proven to be especially suited for low energetic systems.

Table 4 Properties of the analyzing method after Wu.

Method	Information	Number of Fl., Min.	Application	Examples of application	Comment
Wu	disperse and polar parts of the surface energy	2, at least one polar	low energetic systems	org. Solutions, polymers, org. Pigments	time consuming without computer

3.5 Analyzing method after Schultz

In practice often the surface energies of high energetic surfaces are of interest. For example metal surfaces belong to this class of systems, where the wetting behavior when applying paint to the surface is of crucial importance. Metal surface generally have a high surface energy and therefore show the tendency to be completely wetted by any liquid. In this case the measurement of the contact angle in air is not possible and therefore also the determination of the surface energy is excluded. The solution to the problem can be reached by measuring the contact angle of one liquid drop under a second liquid. This situation is shown in fig. 6.

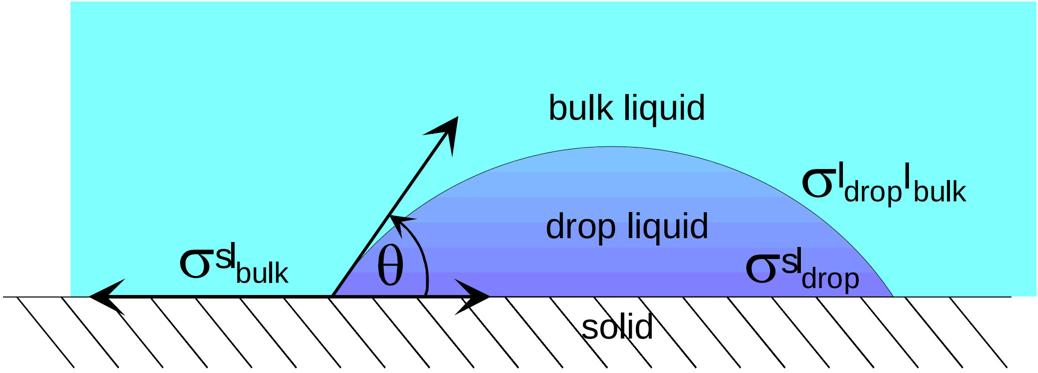


Fig. 6 Measurement after Schultz, determination of the contact angle of a drop under a second liquid.

Assuming that Young´s equation equally holds for this situation, one gets:

$$\sigma_{sl_{bulk}} = \sigma_{l_{drop}l_{bulk}} \cdot \cos\theta + \sigma_{sl_{drop}} \tag{10}$$

After Fowkes one obtains

$$\begin{aligned} \sigma_{sl_{drop}} &= \sigma_s + \sigma_{drop} - 2\cdot\sqrt{\sigma_s^d \cdot \sigma_{l_{drop}}^d} - I_{sl_{drop}}^{nd} \\ \sigma_{sl_{bulk}} &= \sigma_s + \sigma_{bulk} - 2\cdot\sqrt{\sigma_s^d \cdot \sigma_{l_{bulk}}^d} - I_{sl_{bulk}}^{nd} \end{aligned} \tag{11}$$

I_{sl}^{nd} represents the non-disperse part of each liquid. Like in the analysis after Fowkes in this term all polar interactions are summarized, including the interactions due to hydrogen bonds.

Substituting equation (11) in equation (10) yields

$$\underbrace{\sigma_{drop} - \sigma_{bulk} + \sigma_{l_{drop}l_{bulk}} \cdot \cos\theta}_{y} = 2\cdot\underbrace{\sqrt{\sigma_s^d}}_{a}\cdot\underbrace{\left(\sqrt{\sigma_{l_{bulk}}^d} - \sqrt{\sigma_{l_{bulk}}^d}\right)}_{x} + \underbrace{I_{sl_{drop}}^{nd}}_{b} - \underbrace{I_{sl_{bulk}}^{nd}}_{0} \tag{12}$$

For the common case of a drop consisting of water and the surrounding liquid of a n-alcane, the last term in equation (12) can be neglected. Again an equation of a straight line is obtained as indicated in equation (12). Plotting y versus x yields the disperse part of the solid from the slope of the line. Since again no information about the non-disperse part is available, only an interaction energy can be stated. The properties of this method are compiled in table 5.

Table 5 Properties of the analyzing method after Schultz.

Method	**Information**	**Number of Fl., Min.**	**Application**	**Examples of application**	**Comment**
Schultz	disperse parts of the surface energy	2	high energetic solids	metals, metal coated surfaces	high energetic surfaces can be determined

4 Final Remarks

In recent times additional methods have been developed. Here, above all an extension of the method after Fowkes should be mentioned, which takes into account the interaction originating from hydrogen bonds. This method is called the ´extended Fowkes´ method.

A modification of the above described method after Schultz is the measurement of the contact angle of a non-polar liquid drop within a polar surrounding liquid. This method is called ´Schultz 2´ method, while the procedure introduced in chapter 3.5 is denoted ´Schultz 1´.

Yet another approach was chosen by van Oss & Good. Here, the interaction between liquid and solid is interpreted as interaction between an acid and a base. With this procedure, being called Acid/base-method, exclusively Lewis-acids and Lewis-bases are considered. This approach is not commonly used and not quite undisputed. Mainly this comes from the fact, that an arbitrary value for the acid/base contribution is assign to water. This value serves as reference for values of different substances, which therefore only represent relative values.