Q&A for Theory

Great expectation is put to surface free energy analysis as one of effective techniques to evaluate or analyze the surface / interfacial phenomena like natures of wetting and adhesion. Actually, articles reporting this technique are not a few.

However, surface free energy analysis is not established technique as a technique to evaluate surface by any means. Trial and error of experiment / analysis should be necessary depending on the corollary, and you have to pay much attention for interpretation of their results. Then, we summarize the general questions and points for attention about surface free energy analysis hereafter.

On the other hand, FAMAS software shows statistical information, but figures of statistics do not tell the truth. A quantity of statistics should inflect as assistance of data analysis strictly. Correct interpretation will be given on the basis of technical knowledge about target materials and their physical properties.

Points to notice for measuring / evaluating surface property

As general, since the actions of measurement / evaluation themselves will change conditions of corollary, and it will be rare that “true” measurement / evaluation is enabled. For example, the temperature of water may change at the moment of putting a stick-thermometer in it. An external micrometer may change the length of object when nipping the object to measure.

In the case of contact angle measurement, the solid surface may adsorb the vapor of droplet or change its quality after depositing droplet. When blower is applied to a solid surface before measurement, static electricity may occur. Besides, if we need to characterize solid surface including the case of contamination, cleaning surface with solvent must remove the contamination and the experiment may be in vain. Polishing the surface is also the same.

Therefore, in measurement and evaluation, it is significant to define objective and fully examine effects of pre-processes and actions for measurement on the corollary.

Points to notice for surface free energy analysis

It has passed over 40 years since Fowkes announced the first topic of dividing components along the theory of surface free energy, but various kinds of theories flood still and a decisive analysis theory is not given. Some might be popular of the times, but it might not be a conclusion fairly evaluated the reliability.

As evaluation of surface characteristic, surface free energy analysis sometimes gives useful information, but sometimes it does not.

Considering the current status of surface free energy analysis, it is necessary to avoid swallowing the results of surface free energy analysis. Simultaneously applying analyses of other techniques (e.g. XPS: X-ray Photoelectron Spectroscopy) is desirable. Thus, it is realistic that results of surface free energy are used as one of back up data to support leading expectation and conclusion. In the event that a conclusion has to be lead in the step without any extra information, sufficient attention is needed.

Kinds of intermolecular forces

Theories of surface free energy refer idea of dividing the energy into components. These components are based on the intermolecular forces essentially. The intermolecular forces argued by theory of surface free energy are Orientation force, Inductive force, Dispersion force, and Hydrogen bonding force. Among them Orientation force, Inductive force, and Dispersion are generally said *van der Waals force*.[*1]

Depended on interpretation of these intermolecular forces, means to divide energy into components seems varied.

Orientation force

Even if a molecule is electrically neutral, there is the case that it has partially both the positive and the negative electric charges (permanent dipole) due to deflection of electric charge density. When the molecules which have the permanent dipoles (they are called polarity molecules) come close to each other, positive and negative electric charges orient as if they are facing each other, and static electricity force works.

Inductive force

When a polar molecule comes close to a non-polar molecule which does not have permanent dipole, electric dipole is inducted to this non-polar molecule. As the result, static electricity force works. Generally, it is said that this inductive force is very tiny and is ignored in the theory of surface free energy.

Dispersion force

Molecules are always vibrating, and even a non-polar molecule causes a condition of non-symmetric distribution of electrons temporarily, and electric dipole is generated. When such non-polar molecules come close, interaction between dipoles is generated and they pull at each other. This force works between all molecules regardless of polarity / non-polarity.

Hydrogen bonding force

Hydrogen bonding force is a force working between a hydrogen atom and an atom of high donatives. F-H, O-H, N-H are typical. If hydrogen and oxygen are bonded in a molecule for instance, deflection in electron density is generated. As the result, electrification of oxygen as negative and hydrogen as positive occurs and the hydrogen atom pulls at the atom in the other molecule which is electrified as negative (hydrogen bonding between molecules). The hydrogen bonding is interaction stronger than *van der Waals* force, since it has similar nature with covalent bond.

[*1] There is a case that *van der Waals* specifies only dispersion force component.

The differences of various theories of surface free energy analysis

Young-Dupré equation

As introduction, it is necessary to understand young-Dupré equation in order to analyzing surface free energy by use of contact angle data.

Here defines surface free energy of liquid as γ_L and solid as γ_S, interfacial free energy as γ_{SL}, and contact angle as θ, then, Young equation as below is given.

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{L}} \cos\theta + \gamma_{\mathrm{SL}} \quad \text{……………………………………………………..} \quad (1)$$

On the other hand, work of adhesion; a required energy to separate a solid and a liquid at their interface, is defined as W_{SL}, Dupré equation as below is given.

$$\gamma_{\mathrm{S}} + \gamma_{\mathrm{L}} = W_{\mathrm{SL}} + \gamma_{\mathrm{SL}} \quad \text{…………………………………………………….} \quad (2)$$

Dupré equation is applicable to work of adhesion not only between solid - liquid, but also liquid - liquid and solid - solid. The equation can be expressed as below generally, if two different kinds of matters are described with figures as 1 and 2.

$$\gamma_1 + \gamma_2 = W_{12} + \gamma_{12} \quad \text{……………………………………………………} \quad (3)$$

If γ_{SL} is erased from the equations (1) and (2) above, Young-Dupré equation as below is given.

$$W_{\mathrm{SL}} = \gamma_{\mathrm{L}}(1 + \cos\theta) \quad \text{…………………………………………………….} \quad (4)$$

The theories of surface free energy analysis have been developed in the trials to express the components of W_{SL} by using the components of solid and liquid energies. About concrete ways of expression of W_{SL}, various theories are suggested. And the components of surface free energy can be obtained based on those theories if contact angles θ are obtained with practice of measurement. Various theories and their fundamental equations are summarized in the table-1 and -2 followed.

On the contrary, if components of surface free energy are known, W_{SL} can be calculated out. In addition, interfacial free energy γ_{12} also can be calculated out from the equation (3), and θ from the equation (4) above.

Theories of *Kaelble, Owens, Kitazaki*

Kaelble, Uy[2] divide surface free energy into dispersion and polar component and use sign *d*, *p* for each. They do not describe about contribution of hydrogen bonding force.

Owens, Wendt[3] use signs *d, h* and divide surface free energy into 2 components. γ^h is defined as “the component of surface energy due to hydrogen bonding and dipole - dipole interactions”, which seems to include hydrogen bonding and orientation force. On the other hand, they describe "Although hydrogen bonding interactions are more than geometric mean, but dipole - dipole interactions (to which hydrogen bonding is similar) take the form of a geometric mean".

Kitazaki, Hata[4] use signs *a, b, c* and divide surface free energy into 3 components in their article issue in 1972. But they do not clarify what those mean. There are simply suggestion in the later part of their article that the *a*-component and *b*-component for each of the extended Fowkes theory. The *c*-component is described. “it cannot be treated approximation of geometric mean of interaction as far as regarding it as contribution of hydrogen bonding…(omission)…Nevertheless we applied geometric mean about the *c*-component as a trial. The *c*-component thus described should be regarded as a term of correction for hydrogen bonding.”

Even their article issued in 1983 also uses signs *a, b, c*. However, their article issued in 1987 uses signs *d, p, h*, and it is clarified that the signs means dispersion, polar and hydrogen bonding components. (But hydrogen bonding is seemed a position to be considered “according to necessity.”) Taking this into account, our analysis software FAMAS uses signs *d, p, h*.

As for the theories mentioned above, every interaction of dispersion, polar and hydrogen bonding component is treated as geometric mean approximation. It is considered adequate that geometric mean approximation is applied to dispersion component theoretically, but there seems to be many objections to apply geometric mean to polar and hydrogen bonding components.

For example about hydrogen bonding, *Fowkes*[7] describes, “The extension of equations to try to predict hydrogen-bonding with a geometric mean expression is quite incorrect, for hydrogen-bond acceptors such as ethers, esters, or aromatics cannot themselves form hydrogen-bonds, and therefore γ^h is zero for such materials, even though these materials have a large W^h with hydrogen-donors”.)

Theory of *Wu*

Wu uses signs *d, p* and also divides surface free energy into dispersion and polar components. His article issued in 1971 describes, “The polar interactions may include dipole – dipole, dipole – induced dipole and others”. But his article[9] issued in 1973 says, “The polar component includes various dipole interactions and hydrogen bonding”.

A theoretical characteristic of *Wu* is pointing approximation of harmonic mean instead of geometric mean in interaction of these. He leads that dispersion component can be applied geometric mean approximation theoretically. And even for polar component, if it is controlled by dipole – dipole interaction, he says that geometric mean approximation is applied it theoretically. Nevertheless, he states, "Empirically, we found that the geometric mean is not applicable, while the ‘reciprocal’ mean gives accurate results."

He also describes range of theory applicable as “The ‘reciprocal-mean’ non-polar term is based on the assumption that the ploarizabilities of the interacting elements of the two phases are not too different. This assumption appears to be applicable to polymers, organic liquids and water systems. It is however, not expected to apply to systems involving phases with widely different polarizabilities, such as water and mercury.”

Theory of acid-base

The theory of acid-base uses signs *LW* and *AB*, which are sorted by *Lifshits - van der Waals (LW)* component and a *Lewis acid-base (AB)* component.

According to *van Oss*, the equation as below is given.

$$\gamma^{\mathrm{LW}} = \gamma^{\mathrm{d}} + \gamma^{\mathrm{i}} + \gamma^{\mathrm{p}} \quad (5)$$

d is defined a component caused by dispersion force, *i* as orientation force and *p* as inductive force. However, these are not treated individually, and γ^{LW} is one component to the last.

On the other hand, acid-base component is divided into electron acceptor component (acid component) γ^{+} and electronic donor component (base component) γ^{-} and these components are treated numerically individual.

In the case of hydrogen bonding force, γ^{+} is proton donor component (Brønsted acid) and γ^{-} is proton acceptor component (Brønsted acid), and it is a special case in acid-base interaction treaty.

Although the component caused by orientation force has been treated as a polar component, acid-base theory defined *LW* component as non-polar component, and acid-base component as a polar component. Therefore, orientation force should be a part of non-polar component.

Geometric mean approximation is applied to interaction of *LW* and acid-base component respectively. *Kloubek* says “It seems that the idea of the acid-base interaction can help to remove the objections against the previously used terms for the polar and hydrogen bond interactions”, but ground of theory to apply geometric mean approximation to acid-base component seems insufficient. In addition, base component tends to be evaluated excessively, and there are arguments for determination of surface free energy value of probe liquid.

Table 1: Theories of Surface Free Energy Analysis

The “average of quantities of A and B” generally specifies “Arithmetical mean”, and it is described by:

$$\frac{A+B}{2} \quad \text{……………………………………………………………………..} \quad (6)$$

Whereas “Geometric mean” and “Harmonic mean” are described by the following equations respectively:

$$\sqrt{AB} \quad \text{……………………………………………………………………} \quad (7)$$

$$\frac{2}{\frac{1}{A}+\frac{1}{B}} = \frac{2AB}{A+B} \quad \text{………………………………………………………} \quad (8)$$

Theory	Assumption	Work of Adhesion	Young-Dupré equation
Owens Wendt	$\gamma^{total} = \gamma^{d} + \gamma^{h}$	$W_{SL} = 2\sqrt{\gamma_S{}^{d}\gamma_L{}^{d}} + 2\sqrt{\gamma_S{}^{h}\gamma_L{}^{h}}$	$\sqrt{\gamma_L{}^{d}\gamma_S{}^{d}} + \sqrt{\gamma_L{}^{h}\gamma_S{}^{h}} = \frac{\gamma_L{}^{total}(1+\cos\theta)}{2}$
Kaelble Uy	$\gamma^{total} = \gamma^{d} + \gamma^{p}$	$W_{SL} = 2\sqrt{\gamma_S{}^{d}\gamma_L{}^{d}} + 2\sqrt{\gamma_S{}^{p}\gamma_L{}^{p}}$	$\sqrt{\gamma_L{}^{d}\gamma_S{}^{d}} + \sqrt{\gamma_L{}^{p}\gamma_S{}^{p}} = \frac{\gamma_L{}^{total}(1+\cos\theta)}{2}$
Kitazaki Hata	$\gamma^{total} = \gamma^{d} + \gamma^{p} + \gamma^{h}$	$W_{SL} = 2\sqrt{\gamma_S{}^{d}\gamma_L{}^{d}} + 2\sqrt{\gamma_S{}^{p}\gamma_L{}^{p}} + 2\sqrt{\gamma_S{}^{h}\gamma_L{}^{h}}$	$\sqrt{\gamma_L{}^{d}\gamma_S{}^{d}} + \sqrt{\gamma_L{}^{p}\gamma_S{}^{p}} + \sqrt{\gamma_L{}^{h}\gamma_S{}^{h}} = \frac{\gamma_L{}^{total}(1+\cos\theta)}{4}$
Wu	$\gamma^{total} = \gamma^{d} + \gamma^{p}$	$W_{SL} = \frac{4\gamma_S{}^{d}\gamma_L{}^{d}}{\gamma_S{}^{d}+\gamma_L{}^{d}} + \frac{4\gamma_S{}^{p}\gamma_L{}^{p}}{\gamma_S{}^{p}+\gamma_L{}^{p}}$	$\frac{\gamma_L{}^{d}\gamma_S{}^{d}}{\gamma_S{}^{d}+\gamma_L{}^{d}} + \frac{\gamma_L{}^{p}\gamma_S{}^{p}}{\gamma_S{}^{p}+\gamma_L{}^{p}} = \frac{\gamma_L{}^{total}(1+\cos\theta)}{4}$
acid-base	$\gamma^{total} = \gamma^{LW} + \gamma^{AB}$ $\left(\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}}\right)$	$W_{SL} = 2\sqrt{\gamma_S{}^{LW}\gamma_L{}^{LW}} + 2\sqrt{\gamma_S{}^{+}\gamma_L{}^{-}} + 2\sqrt{\gamma_S{}^{-}\gamma_L{}^{+}}$	$\sqrt{\gamma_S{}^{LW}\gamma_L{}^{LW}} - \sqrt{\gamma_S{}^{+}\gamma_L{}^{-}} + \sqrt{\gamma_S{}^{-}\gamma_L{}^{+}} = \frac{\gamma_L{}^{total}(1+\cos\theta)}{2}$

Table 2. Calculation Process of Components of Solid Surface Free Energy

The solutions x, y (, z) are searched so that difference between both the left and the right sides of equation shall be minimum within the range of non-negative value. (Optimizing reckon under the condition of non-negative restriction)

Theory	Assumption	Replacement	Equation	Result
Owens Wendt	$\gamma^{total} = \gamma^d + \gamma^h$	$x \equiv \sqrt{\gamma_S{}^d},\ y \equiv \sqrt{\gamma_S{}^h}$ $a_1 \equiv \sqrt{\gamma_{L_1}{}^d},\ b_1 \equiv \sqrt{\gamma_{L_1}{}^h},\ \frac{\gamma_{L_1}{}^{total}\left(1+\cos\theta_{L_1}\right)}{2}$ $a_2 \equiv \sqrt{\gamma_{L2}{}^d},\ b_2 \equiv \sqrt{\gamma_{L_2}{}^h},\ \frac{\gamma_{L2}{}^{total}\left(1+\cos\theta_{L_2}\right)}{2}$	$\begin{cases} a_1x + b_1y = d_1 \\ a_2x + b_2y = d_2 \\ x \ge 0,\ y \ge 0 \end{cases}$	$\gamma_S{}^d = x^2$ $\gamma_S{}^h = y^2$
Kaelble Uy	$\gamma^{total} = \gamma^d + \gamma^p$	$x \equiv \sqrt{\gamma_S{}^d},\ y \equiv \sqrt{\gamma_S{}^p}$ $a_1 \equiv \sqrt{\gamma_{L_1}{}^d},\ b_1 \equiv \sqrt{\gamma_{L_1}{}^p},\ \frac{\gamma_{L_1}{}^{total}\left(1+\cos\theta_{L_1}\right)}{2}$ $a_2 \equiv \sqrt{\gamma_{L2}{}^d},\ b_2 \equiv \sqrt{\gamma_{L_2}{}^p},\ \frac{\gamma_{L2}{}^{total}\left(1+\cos\theta_{L_2}\right)}{2}$	$\begin{cases} a_1x + b_1y = d_1 \\ a_2x + b_2y = d_2 \\ x \ge 0,\ y \ge 0 \end{cases}$	$\gamma_S{}^d = x^2$ $\gamma_S{}^p = y^2$
Kitazaki Hata	$\gamma^{total} = \gamma^d + \gamma^p + \gamma^h$	$x \equiv \sqrt{\gamma_S^d},\ y \equiv \sqrt{\gamma_S^p},\ z \equiv \sqrt{\gamma_S^h}$ $a_1 \equiv \sqrt{\gamma_{L_1}{}^d},\ b_1 \equiv \sqrt{\gamma_{L_1}{}^p},\ c_1 \equiv \sqrt{\gamma_{L_1}{}^h},\ d \equiv \frac{\gamma_{L_1}{}^{total}\left(1+\cos\theta_{L_1}\right)}{2}$ $a_2 \equiv \sqrt{\gamma_{L2}{}^d},\ b_2 \equiv \sqrt{\gamma_{L_2}{}^p},\ c_2 \equiv \sqrt{\gamma_{L_2}{}^h},\ d \equiv \frac{\gamma_{L_2}{}^{total}\left(1+\cos\theta_{L_2}\right)}{2}$ $a_3 \equiv \sqrt{\gamma_{L_3}{}^d},\ b_3 \equiv \sqrt{\gamma_{L_3}{}^p},\ c_3 \equiv \sqrt{\gamma_{L_3}{}^h},\ d \equiv \frac{\gamma_{L_3}{}^{total}\left(1+\cos\theta_{L_3}\right)}{2}$	$\begin{cases} a_1x + b_1y + c_1z = d_1 \\ a_2x + b_2y + c_2z = d_2 \\ a_3x + b_3y + c_3z = d_3 \\ x \ge 0,\ y \ge 0,\ z \ge 0 \end{cases}$	$\gamma_S{}^d = x^2$ $\gamma_S{}^p = y^2$ $\gamma_S{}^h = z^2$
Wu	$\gamma^{total} = \gamma^d + \gamma^p$	$x \equiv \gamma_S{}^d,\ y \equiv \gamma_S{}^p$ $a_1 \equiv \gamma_{L_1}{}^d,\ b_1 \equiv \gamma_{L_1}{}^p,\ d_1 = \frac{\gamma_{L_1}{}^{total}\left(1+\cos\theta_{L_1}\right)}{4}$ $a_2 \equiv \gamma_{L_2}{}^d,\ b_2 \equiv \gamma_{L_2}{}^p,\ d_2 = \frac{\gamma_{L_2}{}^{total}\left(1+\cos\theta_{L_2}\right)}{4}$	$\begin{cases} \frac{a_1x}{a_1+x} + \frac{b_1y}{b_1+y} = d_1 \\ \frac{a_2x}{a_2+x} + \frac{b_2y}{b_2+y} = d_2 \\ x \ge 0,\ y \ge 0 \end{cases}$	$\gamma_S{}^d = x$ $\gamma_S{}^p = y$
acid-base	$\gamma^{total} = \gamma^{LW} + \gamma^{AB}$ $\left(\gamma^{AB} = 2\sqrt{\gamma_L^+\gamma_L^-}\right)$	$x \equiv \sqrt{\gamma_S^{LW}},\ y \equiv \sqrt{\gamma_S^+},\ z \equiv \sqrt{\gamma_S^-}$ $a_1 \equiv \sqrt{\gamma_{L_1}{}^{LW}},\ b_1 \equiv \sqrt{\gamma_{L_1}{}^-},\ c_1 \equiv \sqrt{\gamma_{L_1}{}^+},\ d \equiv \frac{\gamma_{L_1}{}^{total}\left(1+\cos\theta_{L_1}\right)}{2}$ $a_2 \equiv \sqrt{\gamma_{L2}{}^{LW}},\ b_2 \equiv \sqrt{\gamma_{L_2}{}^-},\ c_2 \equiv \sqrt{\gamma_{L_2}{}^+},\ d \equiv \frac{\gamma_{L_2}{}^{total}\left(1+\cos\theta_{L_2}\right)}{2}$ $a_3 \equiv \sqrt{\gamma_{L_3}{}^{LW}},\ b_3 \equiv \sqrt{\gamma_{L_3}{}^-},\ c_3 \equiv \sqrt{\gamma_{L_3}{}^+},\ d \equiv \frac{\gamma_{L_3}{}^{total}\left(1+\cos\theta_{L_3}\right)}{2}$	$\begin{cases} a_1x + b_1y + c_1z = d_1 \\ a_2x + b_2y + c_2z = d_2 \\ a_3x + b_3y + c_3z = d_3 \\ x \ge 0,\ y \ge 0,\ z \ge 0 \end{cases}$	$\gamma_S{}^{LW} = x^2$ $\gamma_S{}^+ = y^2$ $\gamma_S{}^- = z^2$ $\gamma_S{}^{AB} = 2yz$

Calculation procedure of solid surface free energy

Solid surface free energy can be calculated out in the following procedures.

1. Prepares probe liquids (liquid of surface free energy components are known) as many as the number of components supposed to be obtained. For example, since acid-base theory supposes 3 kinds of components γ^{LW}, γ^{+}, γ^{-}, 3 kinds of probe liquids are needed.
2. Measure contact angles between each 3 probe liquids and a solid sample to be analyzed.
3. Calculate out surface free energy components based on desired theory.

Choice of theory

Comparing the theory of *Owens/Wendt* and *Kaelble/Uy*, they are simply different in interpretation of hydrogen bonding component and polar component. Therefore, if same data is applied to analysis, at all same data must be obtained because there is not substantial difference in calculation technique. (FAMAS treats them as the other theories.)

Fowkes[15] persisting in acid-base theory states, "*Owens* and *Wendt's* 'extended *Fowkes* equation', and *Wu*'s harmonic mean equations are erroneous' and furthermore states, "There must always be a contribution to surface tension of the solid due to the heat of solidification. This surface energy contribution should be present in all solids, and it cannot be measured with contact angles."

Kloubel[12] who reviews results for 40 years of surface free energy analysis (including acid-base theory) come to conclusion in 1992 "During this time a great many ideas and concepts, their alteration and modification, and also a large number of greater or smaller errors appeared. …A definite and definitive solution is still not available."

On the other hand, *M. Imoto*[16] says, "I object to the idea of dividing component. But I cannot say that I am right. The readers had better have ones own opinion."

In the field of interfacial chemistry, since there are comparatively many articles lacking in objectivity, logic and calmness, we are unable to take authors' insistences everything seriously. As for the surface free energy theory, even an expert cannot come to a conclusion of its theoretical right or wrong after all. User oneself has to make trial and error to investigate the best method. (It may be completely worthless method for another user.)

"2 component model" or "3 component model", which is the better?

There are 2 models for surface free energy analysis in the point of dividing components; "2 component model" which suggests only dispersion and polar components, and "3 component model" which suggests hydrogen bonding in addition to the above 2 components. [*2]

The idea to assume that "3 component model" is superior due to larger number of

---

[*2] Before assumption a model, it should be needed to pay attention that, as *Fowkes* specifies, hydrogen bonding component will be occurred after bonding even one of two matters does not have hydrogen bonding.

components is wrong.

First of all, we would like to consider a case to evaluate the relation of causing and result between physical property and its surface free energy.

If hydrogen bonding component does not exist in the matters, 2 component model should be applied for analysis without hesitation. If 3 component-models are applied in spite of no hydrogen bonding component, an erroneous analysis result must be lead as if hydrogen bonding component is available. (The FAMAS may analyze the hydrogen bonding component as “0” in that condition, but it should be considered an occasional result and should not be reliable result.) In the data analysis, a proverb “Greater hides the less.” cannot be applied.

If it is unknown whether hydrogen bonding component is available, the availability should be checked with referring to literatures, chemical directory, etc.

On the other hand, in case to evaluate the correlation between physical property and its calculated result of surface free energy, it may be one of technique to try to analyze “2 component model” and “3 component model” and then use either model which can show more characterized correlation. (Even if correlation is clarified, causing and result are not always clarified. In this case, it may have no meaning to consider physically. (Roughly speaking, clarification of components simply as No.1, No.2,… may be sufficient instead of expressing as dispersion, polar,…)

Under the present condition that the theory is not established sufficient, treating of polar component and hydrogen bonding component is not clear and it will not be needed to remark the contents of components.

Why analysis results are varied depended on the combination of probe liquid?

It cannot but admit the fact that the results of analysis vary when changing the combination of probe liquid. Before proceed the surface free energy analysis, it is needed to recognize the above fact enough. The followings are conceivable reasons that results vary depended on probe liquid combination.

1. Theories of surface free energy analysis are not perfect.
2. Energy values of probe liquids have bias (Statistical error).
3. Measured results of contact angle have dispersion (random error).

   → In this case, the effect of dispersion can be removed theoretically by repeating measurement.
4. Measured results of contact angle have bias.

   → Even if superior method to analyze contact angle is applied, actual resolution is limited. And there is no theory that describes correctly about the interfacial phenomena effective to contact angle. Thus, it will be almost impossible to remove completely bias of contact angle that is caused by the measurement of actual droplet.

Even repeating measurement cannot remove bias. [*3]

5. Depended on combination of probe liquids and energy of solid, there is possibility that the errors mentioned above are effective much to the analysis results.

   → To ease these matters, FAMAS evaluates the combination of probe liquid with a value det' (refer to next page) and restricts the combination. But even these evaluation, there is still possibility that the errors are effective much.

What does "det' value" mean?

Kaelble[17] describes about "*D*" (determinant value of simultaneous equation in the calculation process) as below, but mathematical grounds are not clear, however, it seems to come from a personal experience.

D=0 : analysis disabled

0<$|D|$<1 : Extremely big values are analyzed

The value $|D|$ is difficult to be treated because it changes much depended on energy value of probe liquid and is resulted in the range from 0 to infinite. The value "det'" is the standardized value so that the maximum becomes 1.

As far as our simulation to use the probe liquids included in our surface energy kit, we have confirmed trend that the accuracy becomes worse[*4] when the value det' is extremely small. Therefore, the FAMAS is programmed so that analysis is disabled when det' ≤ 0.05 in the case of 3 component model.[*5] These ranges are also set up from our experiences and grounds of mathematics are not available.

When selecting probe liquids, it is necessary to consider sufficiently whether the probe liquid does change solid surface or not, and whether contact angle does not become 0 (spreading wet) or not, etc. But also check the det' value in advance so that the measured data is resulted in vain due to analysis disabled range of det' value.

Why several values are reported for probe liquid?

For example, *Fowkes*[18] reported that dispersion component is 21.8 ± 0.7mJ/m^2 figured out with use of liquid-liquid interfacial tension data. On the other hand, *Kitazaki* et al[4] reports it as 29.1 ± 3.1 mJ/m^2 with use of liquid-solid contact angle data. *Kitazaki* et al refer *Fowkes's* report and describe on this matter, "it is unfavorable that the resulted values are varied depended on the method in the process, but it is unavoidable matter considering the different constructions of the interfaces between liquid-liquid and liquid-solid.

After all, no answer is given to solve on this matter clearly, Using average of several reported data may be one of method. In this case, obtaining the standard deviation among several reported values is recommended. The FAMAS figures out the standard deviation on the analysis results of surface free energy for reference of effect.

[*3] Applying maximum square method by using a lot of probe liquids and their contact angle data may be able to convert bias into dispersion and remove effect of bias theoretically. (This function is not adopted on the FAMAS.)

[*4] Errors of probe liquids and contact angle data affect much to analysis results.

[*5] The ideas of *D* or det' are not applied to the theory of *Wu*.

Examples that surface free energy analysis are efficient.

We described the matters to pay attention for surface free energy analysis, but efficient practical examples are not a little. Please be introduced as follows.

Wettability between polymer solid surface and saturated hydrocarbon liquid

Kitazaki et al[4] report about wetting between polymer solid surface and saturated hydrocarbon liquid that contact angle of a saturated hydrocarbon liquid are varied even on solids of which total surface free energy is similar, if the rates of energy components are varied.

Nature of adhesion

Sumiya et al[19] analyzed the adhesion between several kinds of polymer substrates and sputtered cobalt thin film. They found out that dispersion components were not effective to work of adhesion, but polar components had good correlation with work of adhesion. Furthermore, they analyzed alkali treated sample by FTIR (Fourier transform infrared spectroscopy method) and found out the correlation between work of adhesion and polar component.

On the other hand, *Nakamae et al*[20] report about adhesion between EVA film (substrate adhered) and PVA (adhesive agent) that dispersion component on EVA film surface hardly contributes the strength for repelling, but hydrogen bonding component on it greatly contributes for it. And it is proved by their report of surface analysis obtained by XPS.

Sliding angle

Kawai[21] researched the correlation between the sliding angle of water droplet on inorganic thin film and the surface free energy of the thin film, and describes that changing polarity of surface can control the sliding angle.

Wettability of paper

Matsunaga et al[22] report about wetting of paper that interaction based on non-dipersive components between water and the cellulose (hydrophilic matter), a component of paper, is large.

Wu theory restricts probe liquids to be usable.

Wu theory needs to solve quadric equation in its calculation process. Generally quadric equation should have two real roots. But it is not understood which solution is proper physically at present since even the articles written by Wu himself do not describe on this matter.

Therefore, we simulated the calculation with several kinds of probe liquids and solid surface free energy, and examined the correlation between true solution and results of analysis. As the results based on this simulation, we restrict the probe liquids usable for Wu theory as follows:

The surface free energy should be in the following ranges:

Liquid – 1: $16 \le \gamma^d \le 36 \mathrm{mJ/m^2}$ and $38 \le \gamma^d \le 58 \mathrm{mJ/m^2}$

Liquid – 2: $36 \le \gamma^d \le 100 \mathrm{mJ/m^2}$ and $0 \le \gamma^d \le 12 \mathrm{mJ/m^2}$

Typical probe liquid applicable to the above liquid-1 is water and the liquid-2 is diiodemethane or 1-brononaphtalene (α-brononaphtalene).

The later two liquids are included in our surface energy kit at option.

Possibility to generate negative value in the calculation process of energy analysis

In the process of calculating surface free energy analysis, we had cases that values not to be negative were resulted negative and troubled how we should interpret physically. This problem is caused by several kinds of error factor, and is unavoidable since the calculations have to be done with the data including errors (energy value of probe liquid and contact angle results) based on the theory “which is believed o be correct”.

But as the FAMAS adopts the mathematical technique to search a solution (optimizing calculation under the condition of non-negative restriction), calculation is not fallen into impossible and a physically efficient result can be obtained.

Fundamental method of that calculation is as follows:

There is a difference ε caused by various kinds of error factors between a calculation result f(x) processed by an analysis theory (theoretical calculation model) and a value y_{obs} demanded by experiment and observation. That is;

$$\varepsilon = y_{\text{obs}} - f(x) \quad \text{(9)}$$

Generally it is calculated regarding as;

$$\varepsilon = y_{\text{obs}} - f(x) = 0 \quad \text{(10)}$$

Therefore, as a result of calculation, a case $x < 0$ is happened. But if the restriction “to search a solution among the range $x \geq 0$” is given in that equation and the calculation is made so as to minimize $|\varepsilon|$, a solution $x \geq 0$ can be obtained. Thus, the FAMAS recognizes the existence of errors, then obtain a solution in the range $x \geq 0$ and that minimizing error.

The part treated as “error” is equivalent to “shifting the strain of calculation” to correct a valued resulted as negative into a non-negative value, and is expressed by a quantity “Residual” (Resid.) in the FAMAS.

Interpretation of “Residual”

As described above, “Residual” is equivalent to “shifting the strain of calculation” to correct a value resulted as negative into non-negative. In the FAMAS, the residual is expressed equivalent to the unit “mJ/m^2.

In addition, the FAMAS can figure out standard deviation (S.D.) of energy values, if the errors (standard deviation) of probe liquids and contact angle data are given. By comparison of the standard deviation of energy value with the residual, adequacy of results can be evaluated qualitatively with rough. If the total[*6] of standard deviations of energy component value is equal to or larger than the residual, it can be explained that “shifting the strain” is caused from the errors of probe liquids and contact angle results. But if the residual is far larger than the total of standard deviations of energy component values, it is conceivable that the applied theory was not adequate or the applied data had large errors than estimation.

On the other hand, resulting the residual as zero can be explained that “shifting the strain” was not needed. But it does not always mean a result of high liability. There is possibility that various kinds of error factors happen to make the residual resulted as zero.

[*6] There may be a discussion to point a value whether of simply mathematic total or square root of square total, but precise analysis equivalent to discussing the problem of these differences cannot be evaluated. Comparison of the standard deviation and the residual in the range of same order is the best.

Compatibility between conventional result and result by optimizing calculation under the condition of non-negative restriction

When the result to be non-negative had become negative number in a calculation process of surface free energy analysis, the conventional analysis software did not make any mathematical adjustment. Therefore, if non-negative result was obtained as even a component, it made effect to the other results of components to be “positive”.

On the other hand, the optimizing calculation under the condition of non-negative restriction is rational method, and effects to other components are smaller than the conventional method does (held down to 1/2 ~ 1/3). As a result, there is possibility that the results by the optimizing calculation are completely different from those by the conventional method.

Thus, compatibility is apt to be considered as problem, but it is nonsense to find compatibility since accuracy of analysis should be better by use of the optimizing calculation.

It is natural that a new know-how overturns an old opinion in accordance with improvement of measurement and analysis technologies, and improvement of them will not have any meaning without such matters.

In addition, when non-negative result is obtained normally for the values to be non-negative, results by the FAMAS are completely as same as those by the conventional one.

Droplet continues spreading over.

As a typical example, it is seen as if ends of droplet stop spreading 1 or 2 seconds later after its deposition onto solid surface. (We call this state as “semi-static state” here under.) But in microscopic watching, there is a case that the droplet is still spreading, or is contrarily contracting due to evaporation. Accordingly a case completely static state of droplet (equilibrium) is hardly available. There is an opinion that contact angles generally measured are all advancing angles, but not angles in equilibrium.

It will take long time to get “semi-static state” depending on liquid sample property, and there is a case that liquid sample is evaporating while spreading over and the droplet is disappeared too soon.

Therefore, disregarding the state of droplet spreading, it should be impossible to have conclusion about “how contact angle is defined?” as a real problem.

On the other hand, the theories of surface free energy analysis are related to Young equation. But as Young equation should be applied to equilibrate state, we fall into a dilemma with the matter “contact angle measurement cannot be defined”. In addition, there is an opinion that receding angle is important to determine polar component.

In the real problem, the following 2 methods should be tried, and if the results are no good, the analysis should be given up. There will not be improvement of data quality without essential solution.

Standardize the interval of contact angle measurement after deposition of droplet on solid. (e.g. 1 sec. later)

Change the probe liquid (change condition of wetting to solid.)

Digit and tolerance of value of energy

FAMAS can display the energy value up to 9999.9mJ/m^2, but it does not mean possible to analyze a solid sample of such large energy.

The maximum range of energy value possible to analyze can be determined in a point whether a probe liquid has contact angle or not (zero as spreading wet). For example, if n-hexadecane ($\gamma^{total} = \gamma^{d} = 27.6$mJ/m^2) is used one of probe liquid for analyzing a solid sample of saturated hydrocarbon (composed with only dispersion component), the solid energy must be lower than $\gamma^{total} = \gamma^{d} = 27.6$mJ/m^2.

In the FAMAS, data range for contact angle possible to input is from 0.1 to 179.9.

Meaning of the standard deviation figured out by FAMAS

Contact angle data is accompanies with experimental errors since users themselves measure it. Also energy values of probe liquids have experimental errors since they have been obtained by experiment. These errors are treated as standard deviation of data, and the effect for analysis is displayed with standard deviations of energy components.

Generally, the standard deviation is expressed by σ. It is said that “95% data belongs to the range $\pm 2\sigma$”, but that should be said based on the condition that infinite repeated measurement were done and the data distribution was fit to a normal distribution. Actually measurement shall be repeated about 10 times at the best, and there is no guarantee that the data of contact angle and probe liquid follows a normal distribution. Even if the input data follows a normal distribution, since they are obtained in the process of complicated calculation, there is no guarantee that the energy data calculated out follows a normal distribution.

Therefore, it cannot be said that 95% data belongs to the range $\pm 2\sigma$ for the standard deviation figured out by the FAMAS. The expression “Almost data shall belong to the range $\pm 2\sigma$” may be rather proper. This “Almost” may be 99% by a case, or 80% by another case.

The standard deviation figured out by the FAMAS is rather to evaluate effect of input data errors giving to analysis results of solid surface free components.

Standard deviations of contact angle data are usually calculated out with the results of repeated measurement. But the standard deviations calculate out like that does not include bias (systematic error). Therefore, the standard deviation resulted with the analysis also does not include bias (systematic error). When requiring evaluation considering bias, considering bias in the standard deviation of input data is required.

Points for attention to calculate the standard deviation

For example, when energy component value of probe liquid is small, there is a case that the energy value becomes negative by applying its error. This does not have meaning physically. On the other hand, if the negative value is replaced with zero, its calculation may be fallen into impossible. When such negative energy data is caused, the FAMAS replaces it with 0.01mJ/m^2 and calculate.

Thus, when a standard deviation value larger than energy component value is input, results of error (standard deviation) will be uncertain.

In the case that contact angle data becomes smaller than 0 or larger than 180 by applying errors, each data is also replaced to 0 or 180 for calculation, and results of error will be uncertain, too.

Error of probe liquid energy value is unknown

Though energy value of probe liquid is picked up from the literature generally, there are cases that errors of them are not indicated. But please note that error is not zero even if not written. Besides, there are cases that values seemed to be errors are indicated but meaning of the values is not described. For example, there are many cases that it does not describe clearly whether the standard deviation has been obtained by straight data or simply by average.[*7] (Generally this should be called "standard error".)

The FAMAS calculates the standard deviation to evaluate effects that errors of input data give results of analysis. Even if errors are unknown, input of values meaning standard deviation can figure out quantity of effect, which is usable for interpretation of data.

Points for attention to analyze Work of Adhesion

For example, if the values of surface free energy components of Polyethylene and Polypropylene are known, Work of Adhesion between these matters can be calculated out.

But please note that the Work of Adhesion calculated as above is not the one in the case when they are adhered through an adhesive agent. When an adhesive agent exists among them, analyzing the surface free energy of the adhesive agent is needed.

[*7] Standard deviation of average is obtained by $\sigma\sqrt{n}$. Where n is number of data, is the average, σ is the standard deviation.

References

[1] D.H.Kaelble、J.Adhesion、2、66、(1970)
[2] D.H.Kaelble、K.C.Uy、J.Adhesion、2、50、(1970)
[3] D.K.Owens、R.C.Wendt、J.Appl.Polym.Sci.、13、1741、(1969)
[4] 北崎寧昭、畑敏雄、日本接着協会誌、8、131、(1972)
[5] 畑敏雄、高分子、32、648、(1983)
[6] T.Hata、Y.Kitazaki、T.Saito、J.Adhesion、21、177、(1987)
[7] F.M.Fowkes、Amer.Chem.Soc.Div.Org.Coat.Plast.Chem.Prepr.、40、13、(1979)
[8] S.Wu、J.Polymer.Sci.、C34、19、(1971)
[9] S.Wu、J.Adhesion.、5、39、(1973)
[10] R.J.Good、Contact Angle,Wettability and Adhesion、p.3、(Ed.K.L.Mittal、Utrecht、1993)
[11] L.H.Lee、Contact Angle,Wettability and Adhesion、p.45、(Ed.K.L.Mittal、Utrecht、1993)
[12] J.Kloubek、Advances in Colloid and Interface Science、38、p.99、(1992)
[13] L.H.Lee、Langmuir、12、1681、(1996)
[14] B.Bouali、J.Colloid Interface.Sci.、208、81、(1998)
[15] F.M.Fowkes、Colloid and Surface、43、367、(1990)
[16] 井本稔、表面張力の理解のために p.123、(高分子刊行会、1992)
[17] D.H.Kaelble、Physical Chemistry of Adhesion、p.149、(Ed.Wiley-Interscience、New York、1971)
[18] F.M.Fowkes、Ind.Eng.Chem.、56、40、(1964)
[19] 角谷賢二、泰井俊明、中前勝彦、松本恒隆、日本接着協会誌、18、346、(1982)
[20] 中前勝彦、宮田照久、山下晋三、松本恒隆、高分子論文集、40、65、(1983)
[21] A.Kawai、日本接着学会誌、34、191、(1998)
[22] T.Matsunaga、Y.Ikada、J.Colloid Interface.Sci.、84、8、(1981)

Database for the surface free energies of probe liquids

- The data below are in principle transcription of the reference value in literatures, but if the data shows 2 places of decimals, the place is rounded off to 1 place of decimal.
- The data of surface free energy and standard deviation not shown on the literatures are in blank.
- The literature of Fowkes (Ind. Eng. Chem., 1964) shows only the dispersion component.
- When adapting the data below, we recommend the original literature to be seen.

Liquid name	Component	Temp C	γ1	S.D1	γ2	S.D2	γ3	S.D3	Total	Reference literature
1,1,2,2-tetrabromoethane	d, p, h	20.0	44.3	1.0	3.2		0.0		47.5	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
1-bromonaphthalene	d, p		44.6		0.0				44.6	M.Mantel and J.P.Wightman, surface and interface analysis, 21, 595, (1994)
1-bromonaphthalene	d, p		44.8		0.0				44.8	E.J.Berger, J.Adhesion Sci. Technol, 4, 373, (1990)
1-bromonaphthalene	d, p, h	20.0	44.4		0.2		0.0		44.6	Kitazaki, Hata, J . Adhesion,8 , 131 , (1972)
1-bromonaphthalene	d, etc.	20.0	47.0	7.0					44.6	F.M.Fowkes, Ind.Eng.Chem., 56, 40, (1964)
1-bromonaphthalene	LW, +, -	20.0	43.5		0.0		0.0		44.4	L.H.Lee, Langmuir, 12, 1681, (1996)
1-bromonaphthalene	LW, +, -	20.0	43.5		0.0		0.0		44.4	L.H.Lee, Langmuir, 12, 1681, (1996)
dimethylformamide	d, p		32.4		4.9				37.3	M.Mantel and J.P.Wightman, surface and interface analysis, 21, 595, (1994)
n-undecane	d, p, h	20.0	24.7		0.0		0.0		24.7	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-octane	d, p, h	20.0	21.8		0.0		0.0		21.8	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-decane	d, p, h	20.0	23.9		0.0		0.0		23.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-tetradecane	d, p, h	20.0	26.7		0.0		0.0		26.7	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-dodecane	d, p, h	20.0	25.4		0.0		0.0		25.4	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-nonane	d, p, h	20.0	22.9		0.0		0.0		22.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-hexadecane	d, p	20.0	27.6		0.0				27.6	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-hexadecane	d, p, h	20.0	27.6		0.0		0.0		27.6	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
Transdecalin	d, p, h	20.0	29.9		0.0		0.0		29.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
Thiodiglycol	d, p, h	20.0	39.2	0.4	1.4	1.1	13.4		54.0	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
Aniline	d, p		41.2		2.0				43.2	E.J.Berger, J.Adhesion Sci. Technol, 4, 373, (1990)
ethylene glycol	d, p		29.4		18.3				47.7	A.Kawai, J. Adhesion, 34, 191 , (1998)
ethylene glycol	d, p		29.0		19.0				48.0	M.Mantel and J.P.Wightman, surface and interface analysis, 21, 595, (1994)
Ethyleneglycol	d, p, h	20.0	30.1	1.6	0.0		17.6		47.7	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
ethylene glycol	LW, +, -	20.0	29.0		1.9		47.0		48.0	L.H.Lee, Langmuir, 12, 1681, (1996)
ethylene glycol	LW, +, -	20.0	29.0		2.6		34.8		48.0	L.H.Lee, Langmuir, 12, 1681, (1996)
Glycerol	d, p	20.0	37.0		26.4				63.4	D.H.Kaelble, Physical Chemistry of Adhesion,Wiley-Interscience,John Wiley&Sons,Inc. (1971)
Glycerol	d, p		34.0		29.4				63.4	A.Kawai, J. Adhesion, 34, 191 , (1998)

Liquid name	Component	Temp C	γ1	S.D1	γ2	S.D2	γ3	S.D3	Total	Reference literature
glycerol	d，p		34.0		32.7				66.7	M.Luangtana-Anan and J.T.Fell，Powder Technology，52，215，(1987）
glycerol	d，p		34.0		30.0				64.0	M.Mantel and J.P.Wightman，surface and interface analysis，21，595，(1994)
glycerol	d，p	20.0	35.7		27.7				63.4	H.Y.Erbil and R.A.Meric，Colloids and Surfaces，33，85，(1988）
glycerol	d，p		33.9		29.8				63.7	E.J.Berger，J.Adhesion Sci. Technol，4，373，(1990）
glycerol	d，p，h	20.0	37.4	2.5	0.2	0.2	25.8		63.4	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
glycerol	d，etc.	20.0	37.0	4.0					63.4	F.M.Fowkes，Ind.Eng.Chem.，56，40，(1964）
glycerol	LW，+，-	20.0	34.0		3.9		57.4		64.0	L.H.Lee，Langmuir，12，1681，(1996）
glycerol	LW，+，-	20.0	34.0		5.3		42.5		64.0	L.H.Lee，Langmuir，12，1681，(1996）
diethyleneglycol	d，p，h	20.0	31.7	1.2	0.0		12.7		44.4	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
dipropyleneglycol	d，p，h	20.0	29.4	0.7	0.0		4.5		33.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
dimethyl siloxanes	d，etc.	20.0	16.9	0.5					19.0	F.M.Fowkes，Ind.Eng.Chem.，56，40，(1964）
dimethylsulfoxide	d，p		34.9		8.7				43.6	M.Mantel and J.P.Wightman，surface and interface analysis，21，595，(1994）
dimethylsulfoxide	LW，+，-	20.0	36.0		0.5		32.0		44.0	L.H.Lee，Langmuir，12，1681，(1996）
dimethylsulfoxide	LW，+，-	20.0	36.0		0.7		23.8		44.0	L.H.Lee，Langmuir，12，1681，(1996）
diiodomethane	d，h	20.0	49.5	1.0	1.3				50.8	D.K.Owens,and,R.C.Wendt，J.Appl.Polym.Sci.，13，1741，(1969）
diiodomethane	d，p	20.0	48.5		2.3				50.8	D.H.Kaelble，Physical Chemistry of Adhesion,Wiley-Interscience,John Wiley&Sons,Inc.，，，(1971）
diiodomethane	d，p		48.5		2.3				50.8	M.Mantel and J.P.Wightman，surface and interface analysis，21，595，(1994）
diiodomethane	d，p	20.0	42.9		7.9				50.8	H.Y.Erbil and R.A.Meric，Colloids and Surfaces，33，85，(1988）
diiodomethane	d，p		49.8		2.4				52.2	E.J.Berger，J.Adhesion Sci. Technol，4，373，(1990）
diiodomethane	d，p	20.0	44.1		6.7				50.8	S.Wu，J.Polymer.Sci，C，19，(1971）
diiodomethane	d，p，h	20.0	46.8	0.6	4.0		0.0		50.8	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
diiodomethane	d，etc.	20.0	48.5	9.0					50.8	F.M.Fowkes，Ind.Eng.Chem.，56，40，(1964）
diiodomethane	LW，+，-	20.0	50.8		0.0		0.0		50.8	L.H.Lee，Langmuir，12，1681，(1996）
diiodomethane	LW，+，-	20.0	50.8		0.0		0.0		50.8	L.H.Lee，Langmuir，12，1681，(1996）
tetrachloroethane	d，p，h	20.0	33.2	2.9	3.1		0.0		36.3	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
trichlorobiphenyl (Aroclor1242)	d，p	20.0	44.0		1.3				45.3	D.H.Kaelble，Physical Chemistry of Adhesion,Wiley-Interscience,John Wiley&Sons,Inc.，，，(1971）
arochlor1242	d，p，h	20.0	41.5		3.8		0.0		45.3	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
trichlorobiphenyl	d，etc.	20.0	44.0	6.0					45.3	F.M.Fowkes，Ind.Eng.Chem.，56，40，(1964）
fluorolube FCD-330	d，etc.	20.0	14.0	0.2					20.2	F.M.Fowkes，Ind.Eng.Chem.，56，40，(1964）
hexachlorobutadiene	d，p，h	20.0	35.8		0.2		0.0		36.0	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-hexane	d，p，h	20.0	18.4		0.0		0.0		18.4	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
n-heptane	d，p，h	20.0	20.3		0.0		0.0		20.3	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
polydimethylsiloxane	d，p，h	20.0	18.1		1.8		0.0		19.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
polyethyleneglycol 200	d，p，h	20.0	29.9	1.5	0.1	0.1	13.5		43.5	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)

Liquid name	Component	Temp C	γ1	S.D1	γ2	S.D2	γ3	S.D3	Total	Reference literature
polyglycol P-1200	d, p		23.0		8.2				31.2	M.Luangtana-Anan and J.T.Fell, Powder Technology, 52, 215, (1987)
polyglycol 15-200	d, p		27.5		8.5				36.0	M.Luangtana-Anan and J.T.Fell, Powder Technology, 52, 215, (1987)
polyglycol E-200	d, p		32.1		26.1				58.2	M.Luangtana-Anan and J.T.Fell, Powder Technology, 52, 215, (1987)
formamide	d, p	20.0	39.5		18.7				58.2	D.H.Kaelble, Physical Chemistry of Adhesion,Wiley-Interscience,John Wiley&Sons,Inc., , , (1971)
formamide	d, p		32.4		25.8				58.2	A.Kawai, J. Adhesion, 34, 191 , (1998)
formamide	d, p		32.3		26.0				58.3	M.Mantel and J.P.Wightman, surface and interface analysis, 21, 595, (1994)
formamide	d, p	20.0	38.7		19.5				58.2	H.Y.Erbil and R.A.Meric, Colloids and Surfaces, 33, 85, (1988)
formamide	d, p		31.8		25.7				57.5	E.J.Berger, J.Adhesion Sci. Technol, 4, 373, (1990)
formamide	d, p, h	20.0	35.1	2.6	1.6	0.3	21.5		58.2	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
formamide	d, etc.	20.0	39.5	7.0					58.2	F.M.Fowkes, Ind.Eng.Chem., 56, 40, (1964)
formamide	LW, +, -	20.0	39.0		2.3		39.6		58.0	L.H.Lee, Langmuir, 12, 1681, (1996)
formamide	LW, +, -	20.0	39.0		3.1		29.1		58.0	L.H.Lee, Langmuir, 12, 1681, (1996)
tricresyl phosphate	d, p	20.0	39.2		1.7				40.9	D.H.Kaelble, Physical Chemistry of Adhesion,Wiley-Interscience,John Wiley&Sons,Inc., , , (1971)
tricresyl phosphate	d, p, h	20.0	37.4	1.5	3.5		0.0		40.9	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
tricresyl phosphate	d, etc.	20.0	39.2	4.0					40.9	F.M.Fowkes, Ind.Eng.Chem., 56, 40, (1964)
phenol,liquefied	d, p		37.8		2.6				40.4	E.J.Berger, J.Adhesion Sci. Technol, 4, 373, (1990)
water	d, h	20.0	21.8	0.7	51.0				72.8	D.K.Owens,and,R.C.Wendt, J.Appl.Polym.Sci., 13, 1741, (1969)
water	d, p	20.0	21.8		51.0				72.8	D.H.Kaelble, Physical Chemistry of Adhesion,Wiley-Interscience, John Wiley&Sons,Inc., , , (1971)
water	d, p		20.7		52.1				72.8	M.Luangtana-Anan and J.T.Fell, Powder Technology, 52, 215, (1987)
water	d, p		21.6		51.0				72.6	M.Mantel and J.P.Wightman, surface and interface analysis, 21, 595, (1994)
water	d, p	20.0	28.9		43.9				72.8	H.Y.Erbil and R.A.Meric, Colloids and Surfaces, 33, 85, (1988)
water	d, p		21.7		50.2				71.9	E.J.Berger, J.Adhesion Sci. Technol, 4, 373, (1990)
water	d, p	20.0	22.1	0.6	50.7				72.8	S.Wu, J.Polymer.Sci, C, 19, (1971)
water	d, p, h	20.0	29.1	3.1	1.3	1.1	42.4		72.8	Kitazaki, Hata, J.Adhesion, 8 , 131 , (1972)
water	d, etc.	20.0	21.8	0.7					72.8	F.M.Fowkes, Ind.Eng.Chem., 56, 40, (1964)
water	LW, +, -	20.0	21.8		25.5		25.5		72.8	L.H.Lee, Langmuir, 12, 1681, (1996)
water	LW, +, -	20.0	21.8		34.2		19.0		72.8	L.H.Lee, Langmuir, 12, 1681, (1996)
mercury	d, etc.	20.0	200.0	7.0					484.0	F.M.Fowkes, Ind.Eng.Chem., 56, 40, (1964)