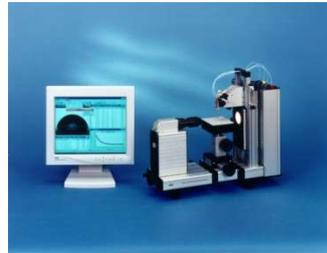


Application Report

Predicting the dispersability of particles

Application report: AR213e
Industry section: Pharmaceuticals, cosmetics, polymers/composites
Author: CR
Date: 01/2000



Drop Shape Analyzer DSA10



Force Tensiometer – K12

Method:   

Keywords: Wetting, dispersion, surface free energy, Good's equation, composite materials, carbon black, fumed silica, titanium dioxide, nylon 6.6

Two-Component Surface Energy Characterization as a Predictor of Wettability and Dispersability

Abstract

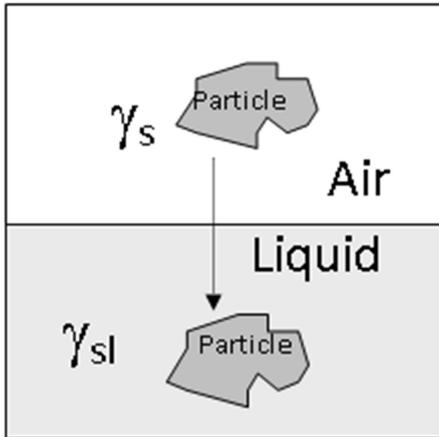
The dispersal of a solid in a liquid has been described as a three-fold process: (1) wetting the particles and displacing entrapped air, (2) deaggregation and/or fragmentation of the particle clusters, and (3) prevention of reaggregation of the dispersed particles.^{1,2,3} Of these, the first is most critical. Wetting must take place in order for the solid to become even partially dispersed in the liquid. Deaggregation and fragmentation of the particle clusters (step 2) may be encouraged by mechanical means and the prevention of reaggregation (step 3), by steric stabilization⁴, columbic⁵, and other effects. This is the subject of a vast amount of research in colloid and surface science. However, if wetting of the solid by the liquid is thermodynamically unfavorable (or only marginally favorable), then discussion of these latter steps in the dispersion process becomes irrelevant.

The focus of this note is the thermodynamics of wetting as related to dispersability of particles in liquids. Four case studies on dispersability problems solved in our laboratory will be discussed. In each case, we combined simple wetting thermodynamics with independent characterizations of the wetting liquid and the prospective dispersed solid to quantify the thermodynamic drive toward immersional wetting. As you will see, the value of such work goes beyond predicting whether or not a solid will wet. The two-component surface energy approach that is described also provides a "road map" for modification of either the solid or the liquid to enhance wetting in cases where it is unfavorable or only marginally favorable.

Theory

Definition of Immersional Wetting Thermodynamics

As discussed above, the first step toward dispersing a solid particle in a liquid is exchanging a solid/air surface for a solid/liquid surface, as depicted below.



Where:

γ_s = free energy associated with the air/solid interface per unit surface area of particle, commonly reported in units of mJ/m^2 , and referred to as "solid surface energy"

and

γ_{sl} = free energy associated with the liquid/solid interface per unit surface area of particle, also commonly reported in units of mJ/m^2 , and referred to as "solid/liquid interfacial energy"

From a thermodynamic standpoint the free energy of immersion of a solid in a liquid (which we will call ΔG_i), is thus:

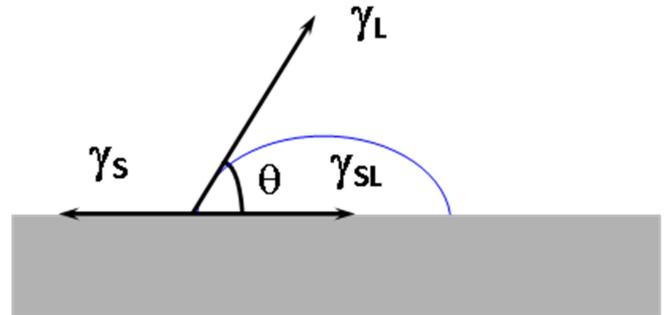
$$\Delta G_i = \gamma_{sl} - \gamma_s$$

Equation #1

If ΔG_i is a negative quantity for the solid and liquid in question, then immersional wetting is thermodynamically favored. If ΔG_i is a positive quantity for the solid and liquid in question, then immersional wetting is not favored thermodynamically. As such, an independent method to calculate ΔG_i for any solid particle/liquid combination would be quite useful. Each ΔG_i value could be used to predict the likelihood of successfully creating dispersion with that solid particle/liquid combination.

Young's equation and the quantities γ_s and γ_{sl}

It is obvious, from equation 1, that if we wish to independently calculate ΔG_i for an immersion process we must have values for γ_s and γ_{sl} . Unfortunately, there is no straightforward way to determine either of these values. However, their difference is defined by Young's equation⁶, which is a summation of the vector forces acting on a drop of liquid in contact with a solid surface:



$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta$$

Equation #2 (Young's equation)

Where:

γ_l = free energy associated with the air/liquid interface per unit surface area, commonly reported in units of mN/m , and referred to as "surface tension"

and

θ = contact angle between the liquid and the solid.

Young's equation mathematically links the two quantities that we seek (γ_s and γ_{sl}) to each other through two readily measurable properties (γ_l and θ). Methods used to determine surface tension of a liquid (γ_l) include: the Wilhelmy plate method⁷, the DuNouy ring method⁸, and the pendant drop method⁹. Methods to straightforwardly determine the contact angle between a liquid and a solid include: the sessile drop method¹⁰, the Wilhelmy dynamic contact angle technique¹¹, and the Washburn technique (for porous solids and dispersible particles¹²). Young's equation can also be combined with equation #1 above to yield another useful definition of ΔG_i :

$$\Delta G_i = -\gamma_l \cos \theta$$

Equation #3

A quick inspection of equation #3 leads to the conclusion that ΔG_i will be negative (immersional wetting will be favored) if the contact angle (θ) between the wetting liquid and the solid in question is less than 90° . Further, immersional wetting will be more strongly favored (ΔG_i will be a larger negative value) the lower the contact angle (θ) is, and the higher γ_i is.

Equation #3 is therefore the fundamental equation relating particle dispersability to contact angle. Our laboratory conducts many experiments to determine contact angle of a prospective dispersant liquid against a solid in order to predict its dispersability. The lower the contact angle, the more favorable dispersion is likely to be. Therefore, I do not want to make light of equation #3. However, our goal for this application note is bit more far reaching. We seek an independent method to calculate ΔG_i for the particles we wish to disperse, without need of an actual experiment that brings the liquid and the solid together. The calculation would be based solely on known (or easily measurable) properties of the particles themselves and the perspective dispersant liquid.

Why do we seek this? How will an independent method benefit us any more than a contact angle experiment done between the solid we need to disperse and the prospective dispersant liquid? The answer to this question will become clear as we go on. You will find that the independent method we develop provides guidance (ideas and options) for modification of either the solid or the liquid to enhance wetting in cases were wetting is unfavorable, or not favorable enough. By contrast, straightforward contact angle experiments done only between the liquid and the solid will only tell you how far you have come toward achieving your goal of good wetting. They do not suggest means for improvement.

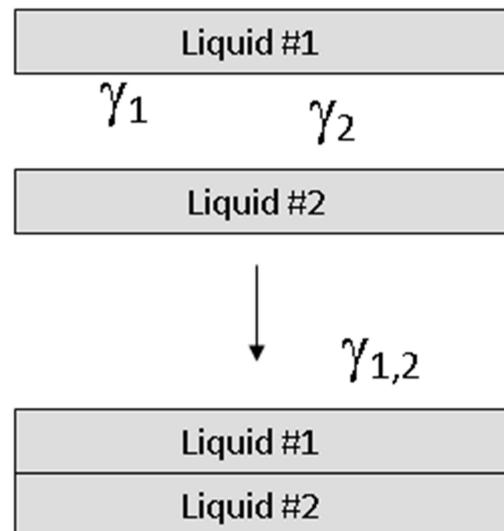
Good's equation and the quantities γ_s and γ_{sl}

Having Young's equation, which links the two quantities γ_s and γ_{sl} , yet still having no experimental means to separate the two quantities, Good¹³ decided that perhaps the interfacial free energy between a solid and a liquid (γ_{sl}) need not be such an elusive quantity. Formation of a solid/liquid interface can be considered analogous to the formation of a liquid/liquid interface. The difference is that in formation of a liquid/liquid interface, all the relevant interfacial energies can be directly measured by standard techniques. Methods, which will straightforwardly and independently determine the surface tension of each liquid (γ_1 and γ_2) have been discussed earlier. Methods for measurement of interfacial tension between two liquids ($\gamma_{1,2}$) include: the DuNouy ring method⁸, the pendant drop method⁹ and the drop volume method¹⁰.

It is clear from the picture shown below that the free energy for formation of a liquid/liquid interface can be expressed as:

$$\Delta G_{1,2} = \gamma_{1,2} - \gamma_1 - \gamma_2$$

Equation #4



Where

γ_1 = surface tension of liquid #1

γ_2 = surface tension of liquid #2

and

$\gamma_{1,2}$ = interfacial tension between the two liquids

Since all the above quantities are directly measurable, Good was quickly able to determine that free energy of formation for all liquid/liquid interfaces is negative.

Examples:

Hexane has a surface tension of 18.4 mN/m at room temperature.

Water has a surface tension of 72.8 mN/m at room temperature.

The interfacial tension between hexane and water at room temperature is 47.1 mN/m (when each phase is saturated with the other, that is, at equilibrium).

Therefore, $\Delta G_{\text{hex/wat}} = -44.1 \text{ mN/m (mJ/m}^2\text{)}$ at room temperature.

Benzene has a surface tension of 28.9 mN/m at room temperature.

Water has a surface tension of 72.8 mN/m at room temperature.

The interfacial tension between benzene and water at room temperature is 34.1 mN/m (when each phase is saturated with the other, that is, at equilibrium).

Therefore, $\Delta G_{\text{ben/wat}} = -67.6 \text{ mN/m (mJ/m}^2\text{)}$ at room temperature.

Benzyl alcohol has a surface tension of 39.0 mN/m at room temperature.

Water has a surface tension of 72.8 mN/m at room temperature.

The interfacial tension between benzyl alcohol and water at room temperature is 15.0 mN/m (when each phase is saturated with the other, that is, at equilibrium).

Therefore, $\Delta G_{\text{bza/wat}} = -96.8 \text{ mN/m (mJ/m}^2\text{)}$ at room temperature.

The formation of any liquid/liquid interface by elimination of two gas/liquid interfaces is thermodynamically favorable. This is because liquids exhibit cohesive interactions between their molecules while gases do not. The molecules that make up the surface of a liquid are therefore sacrificing cohesive interactions since they are in contact with a gaseous phase. This is what gives rise to liquid surface tension. Surface tension is the amount of work necessary to overcome liquid cohesive forces and form a unit area of liquid/gas interface. Molecules at the surface of a liquid favor any interaction with another liquid over having to interact with a gas. This is true even if the liquids are very incompatible.

Consider hexane and water for example. Hexane molecules are only capable of relatively weak van der Waals type interaction with other molecules. Water molecules are capable of van der Waals interactions as well. In addition, they are capable of much stronger hydrogen bonding interactions. Therefore, water molecules would far prefer to interact with each other than to interact with hexane molecules. However, water molecules at the surface of water are forced to interact with a gas. They would happily trade their interaction with a gas for interaction with any liquid offering at least some cohesive interactions. This is true even when the interaction offers only van der Waals forces, as is the case for hexane. For their part, hexane molecules at the hexane surface are less unhappy than water molecules at the surface of water. They are only sacrificing weak van der Waals interaction to be at the surface. However, they too would be happier to interact with water, since water offers cohesive interactions. Therefore, the free energy of formation of a hexane/water interface is negative (favorable).

The hexane/water interface ($\Delta G_{\text{hex/wat}} = -44.1 \text{ mJ/m}^2$) is an extreme example of two incompatible liquids in contact. When the liquids are more compatible, the free energy of interface formation is even more negative. Benzyl alcohol is capable of hydrogen bonding and π -cloud related dipole/dipole interactions. The free energy change when benzyl alcohol and water are put in contact (relative to each having a surface with a gas) is much more negative ($\Delta G_{\text{bza/wat}} = -96.8 \text{ mJ/m}^2$). Even the π -cloud related dipole/dipole interactions offered by benzene make the free energy of forming a benzene/water interface ($\Delta G_{\text{ben/wat}} = -67.6 \text{ mJ/m}^2$) even more favorable than forming a hexane/water interface.

A brief note would be prudent at this point before proceeding to discuss Good's theory. Stating that the free energy of formation for all liquid/liquid interfaces is negative or favorable, as I have done above may cause some confusion. One may mistakenly get the impression

that liquid/liquid interfaces form spontaneously in all situations (that, for example, emulsification of one liquid in another is thermodynamically favored). This is untrue, and not at all what is being stated here. The thermodynamics of dispersing one liquid in another are defined by an entirely different set of mathematics than those described in this note. The free energy of formation for a liquid/liquid interface is defined here relative to the situation of initially having two gas/liquid surfaces that are eliminated to form one liquid/liquid interface. This interaction is always thermodynamically favorable, for reasons discussed above.

After noting that free energy of formation for a liquid/liquid interface is more negative (favorable) if the two liquids are compatible (capable of similar cohesive interactions), Good had the idea that perhaps this free energy could be predicted. If one had information about whether or not strong cohesive interactions existed between molecules of each of the two liquids, then compatibility of the liquids, and thus free energy due to formation of an interface between them, might be predicted.

This is the basis of what we call two-component surface energy theory. Good noticed that every liquid with an overall surface tension of 30 mN/m, for example, does not have the same free energy of interface formation with water. He decided to assign component surface tensions to every liquid. He defined liquids that have only the capability of van der Waals interactions as "dispersive" because their entire surface tension is due to the loss of van der Waals interactions from the molecules on their surfaces. All other interactions were described as "polar", to include dipole/dipole interactions, hydrogen bonding, π -cloud π -cloud interactions, and so on. Liquids capable of such interactions are said to be both polar and dispersive, since all liquids exhibit van der Waals interactions between their molecules. Good reasoned that surface tensions of such liquids could be separated into two components, since molecules on their surfaces show a loss of both polar and dispersive interactions, relative to molecules in the bulk. Liquids such as water, benzyl alcohol, and even benzene are therefore said to have two components to their overall surface tension which, when added together, total their overall surface tension.

Free energy of formation for a liquid/liquid interface is likely to be most negative in cases where the two liquids are most compatible. Based on this assumption, Good proposed that surface tension components of various liquids be defined such that free energy of formation for an interface between two liquids could be predicted by the following equation:

$$\Delta G_{1,2} = -2 [(\gamma_1^D \gamma_2^D)^{1/2} + (\gamma_1^P \gamma_2^P)^{1/2}]$$

Equation #5

Where

- γ_1^D = dispersive component for the surface tension of liquid #1
- γ_2^D = dispersive component for the surface tension of liquid #2
- γ_1^P = polar component for the surface tension of liquid #1
- γ_2^P = polar component for the surface tension of liquid #2

Good chose the mathematical form given above on an empirical basis (based on fitting a variety of data), but also because it represents what is known in statistics as a “geometric mean” approach. This approach was natural for Good’s theories and observations that the free energy is lowest when the liquids are most compatible. If the liquids are completely incompatible (liquid one is completely dispersive $\gamma_1 = \gamma_1^D$ ($\gamma_1^P = 0$) and the other is completely polar $\gamma_2 = \gamma_2^P$ ($\gamma_2^D = 0$)), then the free energy of interface formation ($\Delta G_{1,2}$) is zero. This is never the case for real liquids however, since every liquid has a dispersive component to its surface tension. Therefore, this theory agrees with the observation that formation of all liquid/liquid interfaces is favorable ($\Delta G_{1,2}$ is always negative).

It can also be shown (albeit with more effort) that, for any pair of liquids having overall surface tensions of γ_1 and γ_2 , equation #5 predicts a minimum free energy for the case where $\gamma_1^P/\gamma_1 = \gamma_2^P/\gamma_2$. In other words, free energy is minimized when the two liquids have the same fractional surface polarity. Fractional surface polarity is defined as γ_1^P/γ_1 (and often reported as percent surface polarity = 100% * γ_1^P/γ_1). This is also in keeping with observations that free energy of formation for liquid/liquid interfaces is most favorable (most negative) where the liquids are capable of similar cohesive interactions.

Good combined equation #5 with equation #4 to further show that interfacial tension between two liquids can be predicted if one has prior knowledge of the polar and dispersive components of each liquid’s surface tension. This takes the form of equation #6.

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2 [(\gamma_1^D \gamma_2^D)^{1/2} + (\gamma_1^P \gamma_2^P)^{1/2}]$$

Equation #6

Equation #6 can also be used in reverse to calculate the component surface tensions of liquids. All that need be known is surface tensions of the liquids (γ_1 and γ_2) and interfacial tension between the two liquids ($\gamma_{1,2}$). An important example would be determining components for the surface tension of water (liquid 1) based on having measured interfacial tension between water and hexane (liquid 2). this case: $\gamma_1 = 72.8$ mN/m, $\gamma_1^P =$ unknown, $\gamma_1^D =$ unknown, $\gamma_2 = \gamma_2^D = 18.4$ mN/m, and $\gamma_{1,2} = 47.1$ mN/m as reported above. Since hexane is only capable of van der Waals interactions, $\gamma_2^P = 0$. Therefore, the polar component term drops out of equation #6, and γ_1^D can be calculated as 26.4 mN/m (equation #7).

$$47.1 = 72.8 + 18.4 - 2 (18.4 \gamma_1^D)^{1/2}$$

Equation #7 – Calculation of the dispersive component of the surface tension of water

The polar component for water is thus: $\gamma_1^P = (\gamma_1 - \gamma_1^D) = (72.8 - 26.4) = 46.4$ mN/m. In other words, 46.4/72.8 = 63.7% of the surface tension of water is due to its polar interaction capability.

The characterization of water given above will be used for further calculations shortly. However, we first need to reiterate the primary objective of this note. Our objective was to find a means of determining values for interfacial energy between a liquid and a solid (γ_{sl}) and values for solid surface energy (γ_s). We could then use equation #1 to predict solid particle wettability and dispersability. During our discussion, we found that values for γ_{sl} are not directly measurable. So, we considered that liquid/liquid interfaces might be analogous to liquid/solid interfaces, and followed Good’s observations and theories. This led us to equation #6 for interfacial tension between two liquids. Now we turn the analogy around (as Good did). If equation #6 applies to liquid/liquid interfacial tensions, it should also apply to liquid/solid interfacial energies. Therefore, Good has given us a definition of liquid/solid interfacial energy (γ_{sl}) which depends only on individual properties of the liquid and solid of interest (and not on properties which can only be determined by actually bringing the liquid and solid into contact). Good’s equation for solid/liquid interfaces is formally written as follows:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 [(\gamma_s^D \gamma_l^D)^{1/2} + (\gamma_s^P \gamma_l^P)^{1/2}]$$

Equation #8 – Good’s Equation

Where

- γ_l = overall surface tension of the liquid
- γ_l^D = dispersive component of surface tension for the liquid

- γ_l^P = polar component of surface tension for the liquid
- γ_s = overall surface energy of the solid
- γ_s^D = dispersive component of surface energy for the solid
- γ_s^P = polar component of surface energy for the solid

Two-component surface energy theories based on Good's equation

Owens and Wendt¹⁴ and also Fowkes¹⁵ showed us (in two mathematically equivalent, but philosophically different, theories) how to make use of Good's equation to determine the polar and dispersive components of both liquids and solids. They simply combined equation #8 with equation #2 (Young's equation) to produce the following primary equation for two-component surface energy characterization:

$$(\gamma_s^D \gamma_l^D)^{1/2} + (\gamma_s^P \gamma_l^P)^{1/2} = \gamma_l (\cos \theta + 1)/2$$

Equation #9 Primary equation for two component surface energy characterization

Characterization of liquids

Equation #9 can be used to separate the surface tension of liquids into dispersive and polar components. Contact angle of the liquid is measured against a standard reference surface, using either the sessile drop method¹⁰ or the Wilhelmy method¹¹. The accepted standard reference surface is poly(tetrafluoroethylene) (PTFE). Untreated PTFE is assumed to have a surface energy of 18.0 mJ/m², and is assumed to not be capable of polar interactions with liquids. In other words, $\gamma_s = \gamma_s^D = 18.0 \text{ mJ/m}^2$ for PTFE, and $\gamma_s^P = 0 \text{ mJ/m}^2$ for PTFE. Substituting these values into equation #9, followed by rearrangement yields:

$$\gamma_l^D = (\gamma_l^2 / 72) (\cos \theta_{\text{PTFE}} + 1)^2$$

Equation #10 Liquid surface tension component characterization

where

θ_{PTFE} = contact angle measured between PTFE and the liquid in question.

Equation #10 can be used to calculate the dispersive surface tension component (γ_l^D) of any liquid by measuring its surface tension (γ_l) and contact angle between that liquid and PTFE (θ_{PTFE}). The polar surface energy component for the liquid is then determined by difference ($\gamma_l^P = \gamma_l - \gamma_l^D$). Results are given on page 6 for a number of liquids (overall surface tensions determined by the Wilhelmy plate method⁷):

Surface Tension Components for Various Liquids				
Liquid	Room Temperature Surface Tension (mN/m)	Contact Angle on PTFE (degrees)	Dispersive Component of Surface Tension (mN/m)	Polar Component of Surface Tension (mN/m)
n-hexane	18.4	12.0	18.4	0.0
n-heptane	19.9	25.6	19.9	0.0
n-octane	21.3	33.0	21.3	0.0
n-decane	23.8	42.3	23.8	0.0
cyclohexane	25.5	47.1	25.5	0.0
n-tetradecane	26.4	49.4	26.4	0.0
toluene	28.4	58.2	26.1	2.3
nitromethane	36.5	84.8	22.0	14.5
methyl benzoate	37.2	79.3	27.0	10.2
benzyl alcohol	39.0	78.6	30.3	8.7
ethylene glycol	47.7	94.9	26.4	21.3
diiodomethane	50.8	79.0	50.8	0.0
formamide	57.0	107.2	22.4	34.6
glycerol	63.4	100.7	37.0	26.4
water	72.8	113.7	26.4	46.4

As you study the surface tension data above, you will note that surface tension of straight chain alkanes (and even cyclic alkanes such as cyclohexane), is entirely attributable to dispersive forces. None of these liquids has any polar component to its overall surface tension. This data is encouraging, since Good described dispersive forces as being non-site specific (van der Waals) forces, and we know these are the only molecular interactions possible for alkanes.

The remainder of the liquids in the list (aside from toluene) contain heteroatoms (nitrogen and/or oxygen) in the form of hydroxyl, carbonyl, amide, or nitrate functionality. These liquids are capable of polar interactions with surfaces to which they are applied. Each has a substantial polar component for its surface tension. Note also that the component surface energies calculated for water using PTFE contact angle testing are the same as those determined using hexane/water interfacial tension data. Water also has the greatest surface polarity (calculated as $100\% * \gamma^P/\gamma_l$) of any of the heteroatom containing liquids at 63.7%. This is due to hydrogen bonding between water molecules in the liquid. Diiodomethane is unique amongst the heteroatom containing liquids. Diiodomethane has a relatively high overall surface tension, 50.8 mN/m. Because of its molecular symmetry, the surface tension of diiodomethane has no polar component, so

$\gamma_l = \gamma_l^D = 50.8$ mN/m. This makes diiodomethane very useful as a probe liquid to characterize solid surfaces for component surface energies, as we will see shortly.

It is also interesting that toluene (a benzene ring with one methyl substituent) has a surface polarity of about 8%, although it has no heteroatom. The polarity can be attributed to polarizability of the π -cloud electrons on the benzene ring. This π -cloud effect also contributes to the 22% surface polarity obtained for benzyl alcohol.

The purpose of this section was to show that surface tension of and contact angle data for a dispersant liquid against PTFE is all the data needed to characterize the liquid part of a prospective solid/liquid wetting problem. Discussion of the various liquids given above is background information to give you a better understanding of two-component surface tension characterization.

Characterization of solids

Equation #9 can be used to characterize solids for overall, polar, and dispersive components of surface energy. The Owens and Wendt theory and the Fowkes theory differ on how to apply equation #9 to determine the values γ_s^D and γ_s^P . We will stick with the Fowkes theory in this text, for two reasons. First, we have had good success using the Fowkes theory for a number of dispersion problems, as the case studies will demonstrate. Second, the Fowkes theory is simpler to apply. If you are interested in learning more about the Owens and Wendt theory, an overview has been written.¹⁶

The first step in determining a solid surface energy using the Fowkes theory is to test the solid for contact angle using a liquid which has only a dispersive component to its surface tension (that is, a liquid for which $\gamma_l^P = 0$, so that $\gamma_l^D = \gamma_l$). In this case, equation #9 reduces to:

$$\gamma_s^D = (\gamma_l/4) (\cos \theta + 1)^2$$

Equation #11 Solid dispersive component characterization

and γ_s^D can be calculated directly from contact angle data for the probe liquid on the solid.

The second step is to test the solid for contact angle using another liquid which has both a dispersive component and a non-dispersive (polar) component to its surface tension. With data on surface tension components of the liquid, contact angle between the liquid and solid, and γ_s^D (as calculated in step 1), one can calculate γ_s^P as the only unknown in equation #9. Overall surface energy of the solid, γ_s , is then calculated as $\gamma_s = \gamma_s^P + \gamma_s^D$.

Typically, Fowkes theory is applied using contact angle data from only two liquids. The recommended liquids are diiodomethane and water. As stated above, diiodomethane has a relatively high surface tension of 50.8 mN/m, all of which arises from dispersive interactions. Since $\gamma_l = \gamma_l^D = 50.8$ mN/m for diiodomethane, it is used as probe liquid for the first step described above. Water

($\gamma_l^P = 46.4$ mN/m, and $\gamma_l^D = 26.4$ mN/m) is then used as test liquid for the second step.

Descriptions of methods by which contact angles are typically obtained for diiodomethane and water on solid particles are beyond the scope of this text. As noted previously, such methods include: the sessile drop method¹⁰, the Wilhelmy plate method¹¹, and, most notably for powder characterization, the Washburn method¹². All these methods have been described in other notes that are referenced in the footnotes. In the case studies that will be presented, the method used is noted for each diiodomethane and water contact angle obtained.

The Goal Realized – A Useful Guide to Immersional Wetting

Some pages ago we set the goal for this application note as finding an independent method to calculate the free energy of immersional wetting (ΔG_i) for solid particles we hoped to disperse in some liquid. We hoped to determine ΔG_i without actually doing an experiment that brought the liquid and the solid together. Instead, we wanted our value of ΔG_i to predict the likelihood of obtaining a good dispersion for the solid in the liquid. And, we wanted ΔG_i to be obtained from known (or easily measurable) properties of the particles themselves and the prospective dispersant liquid.

We thought such a method might benefit us more than results of a contact angle measurement between the solid we hoped to disperse and the perspective dispersant liquid. It should also provide direction for modifying either the solid or the liquid to enhance wetting in cases where it is not favorable. By contrast, contact angle data for the liquid and solid in question only tell us how far we have progressed toward achieving favorable immersional wetting. They provide no guidance as to how improvement might be achieved.

This goal has been achieved! In the previous two sections we have described methods which can be used to determine surface tension of any liquid, separated into polar and dispersive components. Using the same theories, surface energy of any solid, with polar and dispersive components can also be determined. Once we have this information about a liquid and a solid (which were tested independently on each other), we can use Good's equation (equation #8) to predict the interfacial free energy (γ_{sl}) between them when they are brought into contact. The fundamental thermodynamic definition of immersional wetting (equation #1) can then be used to predict free energy of immersional wetting (ΔG_i) for the solid being dispersed in the liquid. We can also combine equations #8 and #1 to produce a single master equation for immersional wetting (equation #12):

$$\Delta G_i = \gamma_l - 2 \left[(\gamma_s^D \gamma_l^D)^{1/2} + (\gamma_s^P \gamma_l^P)^{1/2} \right]$$

Equation#12

Recall that a negative ΔG_i means immersional wetting is thermodynamically favorable, and a positive ΔG_i means immersional wetting is thermodynamically unfavorable. The magnitude of ΔG_i indicates how favorable or unfavorable wetting will be.

As for suggesting how to alter the solid and/or the liquid to improve immersional wetting, our method provides this information in the form of liquid and solid component surface energies ($\gamma_l^P, \gamma_l^D, \gamma_s^P,$ and γ_s^D). Once we have those values, we can calculate percent surface polarity values for both the solid and liquid as follows:

$$\% \text{ surface polarity (liquid)} = 100\% * \gamma_l^P / \gamma_l$$

Equation#13

$$\text{surface polarity (solid)} = 100\% * \gamma_s^P / \gamma_s$$

Equation#14

Good's theory predicts that the closer these percentages match each other, the more compatible the liquid and solid are and the lower ΔG_i will be. Therefore, determining these percentages indicates why immersion is unfavorable or favorable. You will also know how to promote immersional wetting for cases where it is only marginal (either by modifying the solid surface to more closely match polarity of the liquid, or by modifying the liquid to more closely match polarity of the solid surface). An example of solid surface treatment is modifying a hydrophobic pigment to raise its surface polarity (hydrophilicity) so it is more dispersible in water. An example of modifying liquid polarity is adding surfactants or solvents to water so it will disperse hydrophobic particles of low surface polarity. You do this every time you wash your dishes or hair with soap.

Case Studies

Now that we have our theories in place, let's apply them. Let's look at some case studies of dispersability problems that have been investigated in our laboratory using these theories. I have chosen four from 1999, with emphasis on showing the methods applied in a variety of industries. For each case, the problem is presented and our characterization data are given for the solid(s) and liquid(s) in question. Immersional energy values are calculated next and related to the initial problem, and a solution to the problem (or our recommendation to the customer) is provided. Information provided in these examples is not subject to confidentiality agreements, and is publicized here with each customer's permission.

Case #1 – Pharmaceutical Dispersions

About a year ago, a researcher at a major pharmaceutical company presented us with a dispersion problem. The company was manufacturing a steroid-based compound for treatment of HIV and related diseases. The customer wanted the compound to be dispersible in water. There were three different manufacturing processes for the compound, only one of which resulted in a form of the compound that could be dispersed in water. We were asked to characterize each of the three products (which we'll call steroid process #1, steroid process #2, and steroid process #3), for surface energy and free energy of immersion in water. The customer hoped to gain insight as to what might be done to improve dispersability of the two non-dispersible products.

Solid Surface Characterization – Raw Data			
Solid	Liquid	Contact Angle (degrees)	Method of Obtaining Angle
Steroid Process #1	Diiodo methane	73.6	Washburn
Steroid Process #1	Water	95.0	Sessile Drop
Steroid Process #2	Diiodo methane	78.8	Washburn
Steroid Process #2	Water	88.8	Washburn
Steroid Process #3	Diiodo methane	73.0	Washburn
Steroid Process #3	Water	92.5	Sessile Drop

Solid Surface Characterization – Surface Energy Components				
Solid	Overall Surface Energy (mJ/m ²)	Polar Component (mJ/m ²)	Dispersive Component (mJ/m ²)	Surface Polarity (%)
Steroid Process #1	22.95	2.05	20.90	8.9
Steroid Process #2	23.14	5.04	18.10	21.8
Steroid Process #3	23.86	2.67	21.20	11.2

Calculated Immersion Energies (Water Only)		
Solid	Liquid	Immersion Energy (mJ/m ²)
Steroid Process #1	Water	6.31
Steroid Process #2	Water	-1.50
Steroid Process #3	Water	3.24

The immersion energy data clearly predict that the steroid from process #2 is the only one that will disperse in water, a fact the customer already knew. However, the data also indicate that process #1 steroid is further from being dispersible than the process #3 steroid. The surface energy data show that both process #1 and process #3 products are not easy to disperse due to their low surface polarities (8.9% and 11.2%) relative to the surface polarity of water (63.7%).

The choice of solutions to the problem was thus: (a) lower the polarity of water with some co-solvent or surfactant to more closely match polarities of the process #1 and #3 products, (b) somehow modify surface of the steroid, or (c) use only product from process #2.

Immersional energies for products #1 and #3 were not extremely positive, so we suggested adding some ethanol as a co-solvent to make both products dispersible. Adding small amounts of ethanol to water lowers overall surface tension and surface polarity of the solution while leaving the dispersive component relatively unchanged. The table on page 9 gives data for the surface tension components of low percentage ethanol and water solutions, in support of these statements.

Characterization of Ethanol-in-Water Solutions for Surface Tension Components					
Solution	Overall Surface Tension (mN/m)	Polar Component (mN/m)	Dispersive Component (mN/m)	Contact Angle Against PTFE (degrees)	Surface Polarity (%)
Pure Water	72.80	46.40	26.40	113.7	63.7
1.0% Ethanol	71.27	44.92	26.35	112.9	63.0
1.5% Ethanol	66.57	40.25	26.32	110.2	60.5
2.0% Ethanol	63.24	36.95	26.30	108.2	58.4
2.5% Ethanol	60.66	34.39	26.27	106.4	56.7
3.0% Ethanol	58.55	32.31	26.24	104.9	55.2

Overall surface tension values were determined by the Wilhelmy plate method
Contact angle data for solution on PTFE was done by the sessile drop method

If data in this table are combined with the surface energy component information given previously for the steroids, we can readily predict the ethanol percentage necessary for immersional wetting for the two non-water dispersible steroids (products #1 and #3). This is shown below.

Calculated Immersion Energies for Steroids in Ethanol/Water Solutions		
Solid	Liquid	Immersion Energy (mJ/m ²)
Steroid Process #1	1.0% Ethanol	5.14
Steroid Process #1	1.5% Ethanol	1.50
Steroid Process #1	2.0% Ethanol	-1.05
Steroid Process #1	2.5% Ethanol	-3.00
Steroid Process #1	3.0% Ethanol	-4.57
Steroid Process #3	1.0% Ethanol	2.11
Steroid Process #3	1.5% Ethanol	-1.39
Steroid Process #3	2.0% Ethanol	-3.83
Steroid Process #3	2.5% Ethanol	-5.69
Steroid Process #3	3.0% Ethanol	-7.19

The data suggest that adding 2.0% ethanol to water should be enough to make steroid product #1 dispersible. In actual dispersion tests, 2.5% ethanol in water was needed to disperse product #1. The data also suggest that only 1.5% ethanol added to water will be enough to disperse steroid product #3. (You will recall that we had originally predicted that steroid #3 was closer to dispersing in water versus steroid #1 in the first place, so this makes intuitive sense.) In actual dispersion tests, 2.0% ethanol in water was needed to disperse product #3.

No predictive theory matches reality perfectly, but I think you would now agree, based on this case, that the one developed in this note is worth using. For this case, the theory predicted the correct trend and was fairly accurate in predicting what could be done, and how much modification (of the liquid in this case) would be needed to fix the dispersion problem.

To conclude this case, I will tell you that the customer chose another method altogether to solve their problem. They wound up modifying the wetting liquid, and not the steroid surface, per se. They did so by adding a dispersant to the water. In our theory, such a dispersant gets credit for modifying the wetting liquid, because that is all it does prior to contact between the liquid and solid in question. However, dispersants primarily modify surface of the solid particles in suspension, typically by adsorbing to hydrophobic surfaces in what is called a "tail-down" configuration. This renders each particle more hydrophilic, and more wettable with water.

Case #2 – Dispersion of Particles in a Polymer Matrix

We have worked with a customer whose business is manufacturing conductive thermoplastic and thermoset polymers. They make the polymers conductive by dispersing additives such as carbon blacks and metal powders in the polymer matrix. As you might imagine, this type of dispersion (or as some might call it "conductive composite") must be formed in an extruder at temperatures above the melting point of the polymer (at least for thermoplastics). Conductivity of the product composite depends strongly on how well dispersed the conductive additive is within the polymer. The reason for our routine work with this customer, using the predictive techniques described in this note, stems from three important points concerning their process.

First, their primary conductive additive is carbon black. It provides better conductivity in most polymers compared to metal powders. However, untreated carbon black is extremely hydrophobic. It does not wet or disperse well in many polymer matrices. This is particularly true for polymers that contain heteroatoms, and thus have a fair amount of surface polarity. So, the customer is naturally concerned about dispersability every time they use carbon black.

Second, they have developed a proprietary technique to modify the surface of carbon black by depositing the emeraldine form of polyaniline on it. Emeraldine is an aromatic polymer with amine linkages in its backbone. When deposited on carbon black, it makes the surface more polar (without sacrificing conductivity), and therefore more dispersible in many polymers. The customer can also deposit a cationic form of emeraldine on a carbon black surface (which makes the carbon black even more polar). The degree of deposition for either form of the polymer on the carbon black can also be controlled. They are rightfully proud of this technology. However, not so much that they want to use it any more than is absolutely necessary to get carbon black dispersed in the polymer matrix of interest. Cost of the surface modification is expensive, both in terms of time and dollars, and the cost goes up almost exponentially with the degree of emeraldine deposition required.

Third, they work with a variety of polymer matrices, using trial and error to find the minimum surface modification on carbon black that will allow optimum dispersion into each. This is an expensive process. Some of you may have been reading this note and thinking, "forget the prediction theory he has been going on about for 9 pages now – just do a dispersion test with the liquid and solid in question". The dispersion in this case is made in an extruder with fairly expensive polymers (the liquid in this case) and even more costly solids (the modified carbon blacks). The test for a good dispersion is conductivity measurement on the cooled solid. We are talking about a lot of time, effort, and money for the trial and error approach.

For these reasons, the customer has been submitting samples of polymers and carbon blacks to our lab for independent testing. They rely on the theories described in this paper to calculate magnitude of the immersional energy that will result from dispersing the carbon blacks in various polymers. For the record, the customer likes to see immersional energies of at least 20 mJ/m² in his favor (that is, $\Delta G_i = -20 \text{ mJ/m}^2$) for good dispersion. This is a gross excess for customers producing low viscosity liquid dispersions, such as the pharmaceutical dispersions discussed in case #1. However, keep in mind that the liquid in this case is a polymer melt with a very high viscosity. You are therefore fighting viscosity effects to disperse the particles, so an excess thermodynamic drive toward wetting may be necessary. (I'll show other examples of this in cases #3 and #4).

Getting back to case at hand, let us look at some data obtained for our conductive polymer customer. The customer wants to add carbon black to melamine formaldehyde (a heterocyclic backboned polymer containing amide linkages, with a melting point of about 130°C). They have a choice of three carbon blacks. The first is untreated. The second is surface treated with non-ionic emeraldine. The third is treated with cationic emeraldine.

We investigated carbon blacks using the theories in the note, with the following results:

Carbon Black Characterization – Raw Data			
Treatment	Liquid	Contact Angle (degrees)	Method of Obtaining Angle
Untreated	Diiodo methane	79.1	Washburn
Untreated	Water	112.5	Sessile Drop
Nonionic Emeraldine	Diiodo methane	68.3	Washburn
Nonionic Emeraldine	Water	97.0	Sessile Drop
Cationic Emeraldine	Diiodo methane	59.0	Washburn
Cationic Emeraldine	Water	67.4	Washburn

Carbon Black Characterization – Surface Energy Components				
Solid	Overall Surface Energy (mJ/m ²)	Polar Component (mJ/m ²)	Dispersive Component (mJ/m ²)	Surface Polarity (%)
Untreated	17.97	0.01	17.96	0.06
Nonionic Emeraldine	24.86	1.03	23.83	4.1
Cationic Emeraldine	40.19	11.04	29.15	27.5

We investigated the melamine formaldehyde polymer as a melt at 140°C using the theories in the note, with the following results:

Characterization of the Melamine Formaldehyde Polymer as Melt at 140°C for Surface Tension Components					
Liquid	Overall Surface Tension (mN/m)	Polar Component (mN/m)	Dispersive Component (mN/m)	Contact Angle Against PTFE (degrees)	Surface Polarity (%)
Melamine Formaldehyde at 140°C	58.43	34.20	24.23	106.6	58.5

Overall surface tension value determined by the Wilhelmy plate method
Contact angle data on PTFE by the sessile drop method

Putting the surface energy component and surface tension component data for the various carbon blacks together with the melamine formaldehyde surface tension data yields the following immersional energy data:

Calculated Immersion Energies for Carbon Blacks in Melamine Formaldehyde Resin at 140°C		
Carbon Black	Liquid	Immersion Energy (mJ/m ²)
Untreated	Melamine Formaldehyde at 140°C	15.54
Nonionic Emeraldine	Melamine Formaldehyde at 140°C	-1.50
Cationic Emeraldine	Melamine Formaldehyde at 140°C	-33.58

Conclusion: Because the melamine formaldehyde has such a high surface polarity (58.5%) the consumer will likely have to use the cationic emeraldine treated carbon black to achieve a good dispersion. As we said, good dispersion is needed to yield good conductive properties for the polymer. Costs will be high to make melamine formaldehyde conductive. At last check, their consumer for the conductive melamine formaldehyde (the U.S. Department of Defense) was still considering whether or not they will fund the project.

Case #3 – Dispersion of Fumed Silica in an Aqueous Formulation

This case study speaks volumes about using two-component surface energy theories (which provide polar and dispersive components of surface energy) as opposed to one-component surface energy models that only return an overall surface energy from contact angle results.

Fumed silica is a low bulk density powder used in a variety of commercial products including adhesives and sealants, coatings, inks, rubbers, and even cosmetic products (perhaps most notably toothpastes). It is used primarily to impart favorable rheological properties to these products, including thixotropic thickening properties and anti-sag properties. Fumed silica is available with many different surface treatments, ranging from very hydrophobic to very hydrophilic.

We recently ran samples for a customer who had problems dispersing a certain grade of fumed silica in a moderate viscosity aqueous formulation (viscosity was about 2000 cP). He was buying fumed silica from two different major U.S. manufacturers, and was having a dispersion problem with only one of them. Of course, as luck would have it, the problematic fumed silica was the one he could buy at a lower price. Nonetheless, both manufacturers told him that the two fumed silicas tested at the same grade (overall surface energy).

He submitted the two fumed silicas (which we'll call Good and Bad as related to their relative dispersibilities) to our lab for surface energy analysis. Here are the results:

Fumed Silica Surface Characterization- Raw Data			
Fumed Silica	Liquid	Contact Angle (degrees)	Method of Obtaining Angle
Good	Diiodo methane	57.4	Washburn
Good	Water	79.0	Washburn
Bad	Diiodo methane	53.0	Washburn
Bad	Water	84.0	Washburn

From the raw contact angle results, it appears that the Good sample has a more hydrophilic surface. After all, not only is the contact angle for water lower on the Good sample versus the Bad, but contact angle with diiodomethane is actually higher on the Good sample. However, when we calculated surface energy data for the two fumed silicas, we were surprised to find that the manufacturers were actually providing our customer exceptionally accurate information.

Fumed Silica Surface Characterization- Surface Energy Components				
Fumed Silica	Overall Surface Energy (mJ/m ²)	Polar Component (mJ/m ²)	Dispersive Component (mJ/m ²)	Surface Polarity (%)
Good	35.05	4.98	30.07	14.2
Bad	35.13	2.55	32.59	7.3

The overall surface energies of the two fumed silicas were nearly identical. However, surface polarity of the Good fumed silica was almost double that of the Bad fumed silica. There's little secret why the Good fumed silica disperses better in a formulation that is based on water (which is 63.7% polar). Conclusion: The consumer is taking the data back to his fumed silica suppliers for comment.

We didn't test the customer's actual aqueous formulation, so there are no true application related immersion energy values to report here. However, just for fun, let's look at immersion energy values for pure water on these two fumed silicas.

Calculated Immersion Energies for Fumed Silicas in Water		
Fumed Silica	Liquid	Immersion Energy (mJ/m ²)
Good	Water	-14.0
Bad	Water	-7.6

Are you surprised to find that the Bad silica has such favorable immersion energy in water (-7.6 mJ/m²)? Why is there a dispersion problem with it? Actually, there could be one of two reasons for this result. (1) The liquid used for dispersion is not just water. It is most likely a solution having different surface properties than that of water. Therefore, I should have tested the actual dispersion medium and not shown you this meaningless immersion energy data for water. Point taken. However, it also possible that: (2) The customer requires a greater than expected negative immersion energy value to overcome viscosity effects for this 2000 cP formulation. I like reason 2. I think good dispersability requires more than just a negative immersion energy. My theory is that significantly more negative values are required for good wetting in viscous systems. Consider case #4.

Case #4 – Dispersion of TiO₂ Pigment in Molten Nylon 6,6

Titanium dioxide, TiO₂, is the most widely used white pigment. We recently had a customer who was trying to disperse TiO₂ as a colorant in Nylon 6,6. She was having some dispersion problems with one particular grade of TiO₂. The TiO₂ is dispersed in molten Nylon 6,6 at 270°C. Obviously, viscosity is a factor in the dispersion process. The customer submitted two TiO₂ samples and her Nylon 6,6 for immersion energy testing. We'll call the TiO₂ samples "Good" and "Problematic" for purposes of this discussion. They were characterized as follows:

TiO ₂ Surface Characterization – Raw Data			
TiO ₂	Liquid	Contact Angle (degrees)	Method of Obtaining Angle
Good	Diiodomethane	36.2	Washburn
Good	Water	78.5	Washburn
Problematic	Diiodomethane	50.9	Washburn
Problematic	Water	82.2	Washburn

TiO ₂ Surface Characterization – Surface Energy Components				
TiO ₂	Overall Surface Energy (mJ/m ²)	Polar Component (mJ/m ²)	Dispersive Component (mJ/m ²)	Surface Polarity (%)
Good	43.88	2.41	41.47	5.5
Problematic	36.60	2.83	33.77	7.7

The Nylon 6,6 was characterized at 270°C as follows:

Characterization of the Molten Nylon 6,6 at 270°C for Surface Tension Components					
Liquid	Overall Surface Tension (mN/m)	Polar Component (mN/m)	Dispersive Component (mN/m)	Contact Angle Against PTFE (degrees)	Surface Polarity (%)
Nylon 6,6 at 270°C	45.90	17.49	28.91	90.8	38.1
Overall surface tension value determined by the Wilhelmy plate method					
Contact angle data on PTFE by the sessile drop method					

Immersional energy values were then calculated as follows:

Calculated Immersion Energies for TiO ₂ 's in Nylon 6,6 at 270°C		
TiO ₂	Liquid	Immersion Energy (mJ/m ²)
Good	Nylon 6,6 at 270°C	-35.73
Problematic	Nylon 6,6 at 270°C	-30.12

Nylon 6,6 was found to have a surface polarity of 38.1%. Both the TiO₂ samples must have been hydrophobically modified grades, because their surface polarities are quite low (5.5% and 7.7% respectively). High dispersive component values for both TiO₂ samples show that the immersional energy values are favorable for dispersion of both. The dispersive component is particularly high for the "Good" TiO₂, which supports a more favorable immersional energy and keeps the data trend correct.

Based on this data, the customer has since switched to an even more hydrophilic (higher % surface polarity) grade of TiO₂ than either of the ones tested here, and is now having good success. I included this case because it is striking that she was having problems with a dispersion for which the immersion energy was -30.12 mJ/m². Again I attribute this to viscosity of the liquid, which is certainly high for Nylon 6,6 at 270°C. The customer needs a large negative immersion energy (thermodynamic driving force for wetting) to overcome the viscous resistance to wetting.

Perhaps someday I will have enough viscosity versus immersion energy data to write another note correlating the two in terms of what immersion energy is necessary to overcome what magnitude of viscous effect. However, that day is not here yet.

Summary

My intent in writing the application note was to show that a simple theory does exist to predict whether or not a solid particle can be dispersed in a liquid based only on easily measured properties of the liquid and solid. The theory may be used to predict dispersability for any liquid/solid pair. These predictions can prevent a great deal of expensive trial and error dispersion testing.

In addition, the method also serves as a guide for cases where dispersability is poor or completely unfavorable. It tells you, in the form of percent surface polarity values for the liquid and the solid, why the liquid and the solid are incompatible. You can then make an informed decision on which of the two phases you will alter to improve dispersability.

I hope this note is useful for those of you who form dispersions of solids in liquids. If you have questions or comments concerning the note, or you wish to have our laboratory study your dispersion problem, please me know.

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