İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

CONTACT ANGLE EVALUATION AND MODELING BY USING IMMISCIBLE FLUIDS

Ph.D. Thesis by Orkun ÖZKAN

Department : Chemical Engineering

Programme : Chemical Engineering

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BİRBİRİ İLE KARIŞMAYAN AKIŞKAN ÇİFTLERİ KULLANILARAK TEMAS AÇILARININ MODELLENMESİ

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FOREWORD

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ABBREVIATIONS

PP	: Polypropylene
PTFE	: Polytetrafluoroethylene
PC	: Polycarbonate
PMMA	: Poly(methyl methacrylate)
MMA	: Methyl methacrylate Monomer
PVA	: Polyvinyl Alcohol
PVC	: Poly(vinychloride)
SFA	: Semifluorinated Alkanes
PE	: Polyethylene
PS	: Polystyrene
IGC	: Inverse Gas Chromatograpy
САН	: Contact Angle Hysteresis
SFE	: Surface Free Energy
HC	: Hydrocarbon
W	: Water
Н	: n-Heptane
0	: n-Octane
D	: n-Decane
Ν	: n-Nonane
DD	: n-Dodecane
HD	: n-Hexadecane
С	: Carbon
Spr	: Spreading

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CONTACT ANGLE EVALUATION AND MODELING BY USING IMMISCIBLE FLUIDS

SUMMARY

Measurement of contact angles and surface tensions is an important practical approach for understanding of the interactions between solids and liquids or between two immiscible liquids. These interactions play a key role in understanding adhesion, material wettability, biocompatibility, lubricity of solid surfaces, as well as the wetting, washability, spreading and adsorption of liquids. Contact angle data can be used to calculate the surface free energy (SFE) of solids. This data also provides a key tool to development and modification of the solid surfaces and liquids.

The aim of the study is investigating the sources of the discrepancies from the ideal conditions, when combining one-liquid and two-liquid contact angle data on the same polymer and glass substrates and by using the same fluid couples. These discrepancies were explained according to the surface properties. In addition, these deviations were attributed to semi-empiric models. In this study, on FEP-Teflon, poypropylene (PP), poly(methyl methacrylate) (PMMA), polycarbonate (PC) and glass surfaces, one-liquid and two-liquid contact angle values were measured by using different liquids and immiscible fluid couples. Summation of both results was compared to examine deviations of difference from ideal condition, total of 180°, for the complementary cases. Experimental contact angle results were compared to literature values and found to be consistent. After testing Young-Dupre equations, the discrepancies were found to be in relation to spreading pressures of water and oil films, formed on the substrates. A new approach, named "complementary hysteresis", was tried for different immiscible fluids; γ_{WA} ($\cos\theta_2 - \cos\theta_1$) and γ_{OW} $(\cos\theta_6 - \cos\theta_5)$ values were observed as a specific material property, for the investigated surfaces. Here, γ_{WA} and γ_{OW} represent interfacial tensions of water/air and water/hydrocarbon (oil) and θ_2 , θ_1 and θ_6 , θ_5 represent contact angle values for cases of water/air and oil/water complementary cases, respectively. Contact angle hysteresis data, which was calculated from advancing and receding contact angles, were measured for the first time in literature for two-liquid setup, and these data were also investigated in terms of surface free energies of the substrates.

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BİRBİRİ İLE KARIŞMAYAN AKIŞKAN ÇİFTLERİ KULLANILARAK TEMAS AÇILARININ MODELLENMESİ

ÖZET

Temas açılarının ve yüzey gerilimlerinin ölçülmesi, katı ve sıvılar ile birbiri ile karışmayan iki sıvı/sıvı ara yüzeyi arasındaki etkileşimlerin daha iyi anlaşılmasını sağlar. Bu etkileşimler, yapışma, ıslatılabilirlik, biyouyumluluk, katı yüzeylerin kayganlığı, yayılma ve sıvıların adsorbsiyonunda önemli bir rol oynamaktadır. Temas açısı verileri, aynı zamanda, katıların serbest yüzey enerjilerinin hesaplanılmasında da kullanılmaktadır. Bu veriler aynı zamanda, sıvıların ve katı yüzeylerin geliştirilmesi ve modifikasyonunda yardımcı olacak bilgileri sağlamaktadır.

Bu calışmadaki amaç, aynı polimer ve cam yüzeyler üzerinde ve aynı sıvılarla, teksıvı ve iki-sıvı temas açısı ölçümlerinin toplamlarının ideal durumdan sapmaların kaynağının araştırılması ve geliştirilecek bir model ile bu sapmaların yarı-ampirik olarak denklemlerle ifade edilmesidir. Bu farklar, yüzey özelliklerine göre açıklanmıştır. Ayrıca bu farklar yarı-ampirik modellere dayandırılmışlardır. Bu calışmada, FEP-Teflon, polipropilen (PP), poli(metil metakrilat) (PMMA), polikarbonat (PC) ve cam yüzeyler üzerinde, farklı sıvı ve birbiri ile karışmayan akışkan çiftleri için tek-sıvı ve iki-sıvı temas açısı değerleri ölçülmüştür. Ölçülen teksıvı ve iki-sıvı temas açısı verileri karşılaştırılıp, toplamlarının, tamamlayıcı durumlar için, 180° ideal durumdan sapmaları incelenmiştir. Bu açıların toplamları, tamamlayıcı durumlarda ideal durumdan sapmaların anlasılması icin karsılastırılmıştır. Denevsel temas acısı verileri, literatür değerleri ile karsılaştırılarak literatur ile uyumlu bulunmuştur. Young-Dupre denklemleri test edilerek bu farklar, yüzeyde oluşan su ve yağ filmlerinin yayılma basınçlarına dayandırılmıştır. Yeni bir yaklaşım olan "tamamlayıcı hysteresis" yaklaşımında, farklı birbiri içerisinde karısmayan sıvılar denenerek, γ_{WA} ($\cos\theta_2$ - $\cos\theta_1$) ve γ_{OW} ($\cos\theta_6$ - $\cos\theta_5$) carpımlarının, aynı yüzey için spesifik bir materiyal özelliği ifade ettiği sonucuna varılmıştır. Burada γ_{WA} su-hava ve γ_{OW} hidrokarbon (yağ)-su ara yüzey gerilimlerini, θ_2 ila θ_1 ve θ_6 ila θ_5 ise, sırasıyla su/hava ve yağ/hava tamamlayıcı durumlarının temas açısı değerlerlerini ifade etmektedir. İlerleyen ve gerileyen temas açılarından elde edilen temas açısı histeresis değerleri, iki-sıvı durumu için literatürde ilk defa ölçülmüş olup, kullanılan yüzeylerin serbest yüzey enerjileri değişimlerine göre incelenmiştir.

1. INTRODUCTION

1.1 Surface Tension of Liquids

Surface Tension is the measurement of the cohesive (excess) energy present at a gas/liquid or gas/solid interface. The molecules of a liquid attract each other. The interactions of a molecule in the bulk of a liquid are balanced by an equally attractive force in all directions (Adamson, 1997). Molecules on the surface of a liquid experience an imbalance of forces as indicated in Figure 1.1.



Figure 1.1: Molecular interacting forces of a liquid.

The net effect of this situation is the presence of free energy at the surface. This excess energy is called "*surface free energy*" and can be quantified as a measurement of energy/area. It is also possible to describe this situation as having a line tension or "*surface tension*", which is quantified as a force/length measurement.

Polar liquids, such as water, have strong intermolecular interactions and thus high surface tensions. Any factor, which decreases the strength of this interaction, will lower surface tension. Thus, an increase in the temperature of this system will lower surface tension. Any contamination, especially by surfactants, will lower surface tension. Therefore, researchers should be very cautious about the issue of contamination.

1.2 Interfacial Tension of Liquids

When two immiscible phases are present, interfacial tension is a measurement of the cohesive (excess) energy present at an interface arising from the imbalance of forces between molecules at an interface (gas/liquid, liquid/liquid, gas/solid or liquid/solid). It can be quantified as the force acting normal to the interface per unit length (force/unit length, mN/m).

When two different phases (gas/liquid, liquid/liquid, gas/solid or liquid/solid) are in contact with each other, the molecules at the interface experience an imbalance of forces (Figure 1.2). This will lead to an accumulation of free energy at the interface (Couper, 1993).



Figure 1.2: Molecular interaction between two phases.

The excess energy is called "*interfacial free energy*" and can be quantified as a measurement of energy/area i.e. the energy required to increase the surface area of the interface by a unit amount. It is also possible to describe this situation as having a line tension or "*interfacial tension*", which is quantified as a force/length measurement. This force tends to minimize the area of the surface, thus explaining why for example liquid drops and air bubbles are spherical. The common units for interfacial tension are dyn/cm or mN/m. These units are equivalent.

This excess energy exists at any interface. If one of the phases is the gas phase of a liquid being tested, the measurement is normally referred to as "surface tension" because the gas molecules are so dilute that they interact with liquid or solid so weak that the gas phase can be accepted as being a vacuum phase. If the surface investigated is the interface of two immiscible liquids, the measurement is normally referred to as "interfacial tension". In either case, the more dense fluid is referred to herein as the "heavy phase" and the less dense fluid is referred to as the "light phase". Solid surfaces also may be described to have an interfacial tension normally

referred to as "*surface free energy*", but direct measurement of its value is not possible through techniques used for liquids because of the elastic restrains of the solid phase (Erbil, 2006).

1.3 Surface and Interfacial Tension Measurement Methods for Liquids

1.3.1 Drop Shape Analysis Method

This method uses a contact angle goniometer to measure surface and interfacial tensions. The shape of a drop of liquid hanging from a syringe tip is determined from the balance of forces which include the surface tension of that liquid (Hansen and Rodsrud, 1991). The surface or interfacial tension at the liquid interface can be related to the drop shape (Figures 1.3 and 1.4) through the following equation:

$$\gamma = \Delta \rho \, g \, R_o^2 / \beta \tag{1.1}$$

where;

 γ = surface tension

 $\Delta \rho$ = difference in density between fluids at interface

g = gravitational constant

 $R_o =$ radius of drop curvature at apex

 β = shape factor

 β , the shape factor can be defined through the Young-Laplace equation expressed as three dimensionless first order equations as shown in Figures 1.3 and 1.4.



Figure 1.3: Pendant drop method for surface interfacial and tensions.



Figure 1.4: Captive (raising) bubble method for determination of interfacial tensions of liquids.

Modern computational methods using iterative approximations allow solution of the Young-Laplace equation for β to be performed. Thus for any pendant drop where the densities of the two fluids in contact are known, the surface tension may be measured based upon the Young-Laplace equation.

1.3.2 Du Noüy Ring Method

This method utilizes the interaction of a platinum ring with the liquid interface being tested (Huh and Mason, 1975). The ring is submerged below the interface and subsequently raised upwards. As the ring moves upwards, it raises a meniscus of the liquid. Eventually this meniscus tears from the ring and returns to its original position. Prior to this event, the volume, and thus the force exerted, of the meniscus passes through a maximum value and begins to diminish prior to the actually tearing event. The process is shown in Figure 1.5.

At the position 1, the ring is above the surface and the force is zeroed. The ring hits the surface at position 2 and there is a slight positive force because of the adhesive force between the ring and the surface. The ring must be pushed through the surface (due to the surface tension) which causes a small negative force (position 3). Then the ring breaks through the surface and a small positive force is measured due to the supporting wires of the ring at position 4. When lifted through the surface the measured force starts to increase as shown in position 5. The force keeps increasing until the maximum force is reached at position 6. After the maximum, there is a small decrease in the force until the lamella breaks, as described in position 7 and 8.



Figure 1.5: Surface tension measurement by du Noüy ring method.

The calculation of surface or interfacial tension by this technique is based on the measurement of this maximum force (Figure 1.6). As an additional volume of liquid, which is raised due to the proximity of one side of the ring to the other mathematical corrections, are needed in order to obtain the correct surface/interfacial tension values.



Figure 1.6: Du Noüy ring method.

From the definition of surface tension, the force balance at the moment of detachment can be given as:

$$F_{\max} f_r = 2(2\pi r_{mean}) \gamma \cos\theta = 2\pi (r_{ext} + r_{int}) \gamma \cos\theta$$
(1.2)

where F_{max} is the maximum upward pull applied to the ring of mean radius, r_{mean} , $r_{\text{mean}} = (r_{\text{ext}} + r_{\text{int}})$, and f_r , is the correction factor for the small but significant volume of the liquid that remains on the ring after detachment, and also for the discrepancy between r_{mean} and the actual radius of the meniscus in the plane of rupture. The term F_{max} corresponds to the maximum weight of the meniscus over the liquid surface that can be supported by the ring. The contact angle between the liquid and the ring, θ decreases as the extension increases and has the value 0° at the point of maximum force, this means that the term $\cos \theta$ has the value 1 and considered to be complete wetting. The perimeter of the ring is multiplied by 2 because of the presence of two surfaces, created on both sides of the ring.

The calculation is made according to Equation (1.2) and surface and interfacial tensions of liquids can be expressed as maximum force per wetted length.

$$\gamma = \frac{F_{\max} f_r}{2\pi \left(r_{ext} + r_{int}\right)}$$
(1.3)

The f_r , factor is a function of the mean radius, thickness of the ring and also of meniscus volume, and varies between 0.75 and 1.05 numerically, according to the size and the shape of the ring, and the difference in the fluid density. The *f* values can be calculated by using the following approximate equation:

$$f = 0.725 + \left(\frac{9.075 \times 10^{-4} F}{\pi^3 \Delta \rho r^3} - \frac{1.679 r_{wire}}{r} + 0.04534\right)^{\frac{1}{2}}$$
(1.4)

Equation (1.2) can be applied in the range $[7.5 \ge \Delta \rho r^3/F \ge 0.045]$. In many modern computerized systems, the interfacial tension reading does not require separate calculation of *f*, since its calculation is incorporated within the software.

The weight of the volume of liquid lifted beneath the ring must be subtracted from the measured maximum force as it also affects the balance. A solution must also be found for a further problem: the curve of the film is greater at the inside of the ring than at the outside. This means that the maximum force at which the contact angle $\theta = 0^{\circ}$ is reached at different ring distances for the inside and outside of the ring; as a result the measured maximum force does not agree exactly with the actual value. The correction methods available apply to different ranges of values. The three possible correction methods are: Harkins and Jordan (1930) have drawn up tables of correction values by determining different surface tensions with rings of different diameters. This comprehensive program of measurements also provides the basic data for the corrections according to Zuidema and Waters (1941) and Huh and Mason (1975). The Harkins and Jordan correction offers the greatest accuracy, but it is possible to imagine liquid systems, which are outside the range of validity for the Harkins and Jordan method. However, in practice such a case is extremely rare. Zuidema and Waters needed correction values for small interfacial tensions. For this reason, they carried out interpolation calculation on the data from Harkins and Jordan in order to cover the range of small interfacial tensions more accurately. However, Zuidema and Waters corrections have the greatest deviation range of all corrections and should only be used for comparative measurements with values given in the literature. Huh and Mason have used mathematical methods to increase the range of application of the correction calculation; this means that this correction method has the largest range of validity while still possessing sufficient accuracy. This is this method is chosen as the standard one. If one wants to make measurements with the greatest possible accuracy, he should change to the Harkins and Jordan correction method but keep its range of validity in mind.

There are several advantages of the ring method over Wilhelmy plate method. Many values in the literature have been obtained with the ring method. This means that in many cases, the ring method should be preferred for comparison purposes. The wetted length of the ring exceeds that of the plate. This leads to a higher force on the balance and accordingly to a better accuracy. This effect does not influence the results of surface tension measurements, but small interfacial tensions can be carried out more accurately with the ring method. Some substances, e.g. cationic surfactants, show poor wetting properties on platinum. In such cases, the surface line between a ring and the liquid is more even than that of a plate.

1.3.3 Wilhelmy Plate Method

Wilhelmy plate method utilizes the interaction of a platinum plate, shown in Figure 1.7, with the liquid interface being tested. The calculations for this technique are based on the geometry of a fully wetted plate in contact with, but not submerged in, the liquid. In this method, the position of the probe relative to the surface is significant. Therefore the measurement is made at the so called zero depth of

immersion of the probe, and the force acting on the probe at this position is registered and can directly be used to calculate the surface tension of the liquid when the perimeter of the plate is accurately known (Pallas and Pethica, 1983).



Figure 1.7: Wilhelmy plate contacting liquid surface.

If only limited quantity of the liquid to be tested is available, one may consider using a thin round platinum rod as the probe. In such a case, the measurement is exactly the same as with the Wilhelmy plate, but the probe dimensions of the probe will be smaller which affects the accuracy of the measurement and hence also might affect the reproducibility of the results.



Figure 1.8: Wilhelmy plate method tension calculation.

The vessel carrying the liquid is lowered until the inserted plate is detached from the liquid surface, and the maximum vertical pull, F_{max} on the balance is recorded (Figure 1.8). Then the capillary force can be expressed as

$$F_{capillary} = F_{max} - W = P \gamma = 2(l+b)\gamma$$
(1.5)

where W is the weight of the plate probe and 2(l+b) is the perimeter (P) of the probe. The term $F_{capillary}$ stands for the weight of the meniscus that is formed around

the perimeter of the Wilhelmy plate. If a finite contact angle forms between the plate and the liquid, then the surface tension can be calculated from

$$\gamma = \frac{F_{capillary}}{2(l+b)\cos\theta}$$
(1.6)

The plate is made of roughened platinum and is optimally wetted so that the contact angle is virtually 0°. This means that the term $\cos\theta$ has a value of approximately 1, so that only the measured force and the length of the plate need to be taken into consideration. Correction calculations are not necessary with the plate method.

Advantages of the plate method are mainly, unlike the ring method, no correction is required for measurement values obtained by the plate method. With the plate method, the densities of the liquids do not have to be known, as they have to be with the ring method. In an interfacial tension measurement, the surface is only touched and not pressed into/pulled out of the other phase. This avoids the phases becoming mixed. With the ring method, the surface or interface is renewed permanently due to the movement of the ring. If the ring is moving with high velocity, but also if solutions of large molecules or with high viscosities are used in the measurements, the maximum force is obtained when the diffusion equilibrium at the surface or interface is still not reached. The failure caused by this effect does not occur with the plate method. The plate method is a static measurement, i.e. the plate does not move after the surface or interface has been detected (Dettre and Johnson, 1966).

1.4 Contact Angle Theory

When a liquid does not completely spread on a substrate (usually a solid), a contact angle (θ) is formed, which is geometrically defined as the angle on the liquid side of the tangential line drawn through the three phase boundary where a liquid, gas and solid intersect, or two immiscible liquids and solid intersect.



Figure 1.9: Contact angles.

Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is the angle formed by the liquid at the three phase boundary where a liquid, gas (or a second immiscible liquid) and solid intersect (Figure 1.9). It is a direct measure of interactions taking place between the participating phases (gas/liquid/solid or liquid/liquid/solid). The contact angle is determined by drawing a tangent at the contact where the liquid and the solid intersect.



Figure 1.10: Young's equation.

The shape of the drop and the magnitude of the contact angle are controlled by three interaction forces of interfacial tension of each participating phase (gas, liquid and solid). The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often, the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young-Laplace equation, given in Figure 1.10. The contact angle plays the role of a boundary condition. In an ideal situation, the relation between these forces and the contact angle can be described by the Young's equation and is often referred to as Young's contact angle, which can be obtained by vector summation of the forces at equilibrium. However, often non-ideal conditions due environmental, roughness and chemical heterogeneity affects leads to deviations from this relationship. Many other theoretical approaches based on the Young's equation have therefore been developed to account for these non-ideal contributions. The non-ideal contact angles are referred to as apparent contact angles. The contact angle is not limited to a liquid/vapor interface; it is equally applicable to the interface of two liquids or two vapors.

The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid phase of the droplet (L), the solid phase of the substrate (S), and the gas/vapor phase of the ambient (V)

(which will be a mixture of ambient atmosphere and an equilibrium concentration of the liquid vapor). The *V* phase could also be another (immiscible) liquid phase (*L*₂). At equilibrium, the chemical potential in the three phases should be equal. It is convenient to frame the discussion in terms of the interfacial energies. We denote the solid/vapor interfacial energy as γ_S or γ_{SA} , the solid/liquid interfacial energy as γ_{SL} and the liquid/vapor energy (i.e. the surface tension) as simply γ_L , and we can write an equation that must be satisfied in equilibrium (known as the Young equation):

$$\gamma_{SA} = \gamma_{SL} + \gamma_L \cos \theta_e \tag{1.7}$$

where θ_e is the equilibrium contact angle. The Young equation assumes a perfectly flat surface, and in many cases, surface roughness and impurities cause a deviation in the equilibrium contact angle from the contact angle predicted by Young's equation. Even in a perfectly smooth surface a drop will assume a wide spectrum of contact angles between the highest (advancing) contact angle, θ_a , and the lowest (receding) contact angle, θ_r .

1.4.1 Wettability

Wettability or wetting is the actual process when a liquid spreads on (wets) a solid substrate. Wettability can be estimated by determining the contact angle or calculating the so-called spreading coefficient, *S*.

In the case of a liquid drop on a solid surface, if the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid) the droplet will completely spread out on the solid surface and the contact angle will be close to 0°. Less strongly hydrophilic solids will have a contact angle up to 90°. On many highly hydrophilic surfaces, water droplets will exhibit contact angles of 0° to 30°. If the solid surface is hydrophobic, the contact angle will be larger than 90°. If the angle θ is less than 90° the liquid is said to wet the solid. If it is greater than 90° it is said to be non-wetting. A zero water contact angle represents complete wetting (Figure 1.11).

The shape of a liquid front in contact with a solid substrate is determined by the interfacial forces of the participating phases as was shown for the contact angle. Wettability of a surface by a liquid is the actual process of spreading. One can qualitatively determine the wetting with the contact angles i.e. when the contact

angles are low this means good wetting, and when the contact angles are high, this means non-wetting conditions.



Figure 1.11: Partial and complete spreading of a liquid on a surface.

A quantitative measure of wetting is the spreading coefficient, *S*, which is the energy difference between the solid substrate with the contacting gas and liquid phases.

Spreading coefficient is shown in Figure 1.12 and can be expressed as



Figure 1.12: Partial and complete wetting conditions.

On highly hydrophobic surfaces, the surfaces have water contact angles as high as 150° or even nearly 180°. On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent. These surfaces are termed super hydrophobic (Figure 1.13) and can be obtained on fluorinated surfaces (Teflon-like coatings) that have been appropriately micro patterned. This is called the Lotus effect, as these new surfaces are based on lotus plants' surface (which has little protuberances) and would be super hydrophobic even to honey. The contact angle thus directly provides information on the interaction energy between the surface and the liquid.



Figure 1.13: Contact angles on different surfaces.

1.4.2 Contact Angle Measuring Methods

Contact angles can be measured either "in air" or "under water" conditions. Density of the dispersed fluid and continuous medium plays a key role under water contact angle measurements for the methods to be chosen. In addition, contact angles can be reported at equilibrium conditions as static contact angles and dynamic contact angles where drop shape is captured during a period.

1.4.2.1 Static Sessile Drop and Captive Bubble Method

Drop shape analysis is a convenient way to measure contact angles and thereby determine surface energy. The principal assumptions are the drop is symmetric about a central vertical axis: this means it is irrelevant, from which direction the drop is viewed. In addition, the drop is not in motion in the sense that viscosity or inertia is playing a role in determining its shape: this means that interfacial tension and gravity are the only forces shaping the drop. Calibration is straightforward in that only optical magnification is needed so that the contact angle can be measured with high accuracy.

The sessile drop method is applied by a contact angle goniometer using an optical subsystem to capture the profile of a pure liquid on a solid substrate. It is the contact angle measured of a sessile drop/captive bubble on a solid substrate when the three-phase line is not moving. The angle formed between the liquid/solid interface and the liquid/vapor interface is the contact angle. Older systems used a microscope optical system with a back light. Current generation systems employ high resolutions cameras and software to capture and analyze the contact angle.

Static contact angle is the contact angle when all participating phases i.e. gas (or liquid), liquid, solid, have reached their natural equilibrium positions and the three phase line is not moving anymore. The Static Contact Angle can be measured in a

sessile drop or captive bubble configuration. In the sessile drop case a liquid droplet is placed on a solid sample and the contact angle is then determined. In the captive bubble method, the solid sample is completely immersed in a liquid and an air bubble is brought in contact with the solid sample from below.

The sessile drop technique is a test performed to determine the chemical affinity that a liquid has to a solid. The test is usually done to examine either the physical properties of the liquid against different solid surfaces or the properties of a solid surface against different liquids.



Figure 1.14: "In air" and "under water" contact angles.

While performing sessile drop experiments, a drop of liquid is placed (or allowed to fall from a certain distance) onto a solid surface (Figure 1.14). When the liquid has settled (has become sessile) the drop will retain its surface tension and become ovate against the solid surface. The contact angle at which the oval of the drop contacts the surface determines the affinity between the two substances. That is, a flat drop indicates a high affinity, in which case the liquid is said to wet the substrate. A more rounded drop (by height) on top of the surface indicates lower affinity because the angle at which the drop is attached to the solid surface is more acute. In this case, the liquid is said not to wet the substrate.

This technique is very useful in determining the surface tension and density of different liquids. It is also useful to determine the effectiveness of waterproofing, for example, as water droplets will have higher affinity for untreated wood, and lower affinity for treated wood.

1.4.2.2 Dynamic Sessile Drop and Captive Bubble Method

The dynamic sessile drop is similar to the static sessile drop but requires the drop to be modified. A common type of dynamic sessile drop study determines the largest contact angle possible without increasing its solid/liquid interfacial area by adding volume dynamically. This maximum angle is the advancing angle, θ_a . Volume is

removed to produce the smallest possible angle, the receding angle, θ_r . Formation of advancing and receding contact angles are given in Figure 1.15. The difference between the advancing and receding angle is the contact angle hysteresis.



Figure 1.15: Advancing and receding contact angles.

Dynamic contact angles are the contact angles when the three-phase line is in controlled motion. The advancing angle is the contact angle when the three phase line is moving over and wetting the surface or pushing away the gas phase, while the receding angle is the contact angle when the three phase line is withdrawn over a pre-wetted surface or pushing away the liquid phase.

The production of sessile drops for advanced angles can be done by one of four strategies. First, allow a drop to fall onto the solid from the syringe tip. The drop should fall with a minimum of momentum (lowest possible height) to minimize the spreading and subsequent recoil after contact. Another method is to generate a pendant drop then raise the solid into contact drawing the drop off the syringe tip. With both these methods care should be taken to be consistent about the details of the transfer.

The third strategy is to lower the syringe tip near the solid so that the tip remains attached to the drop after contact with the solid. To create the advanced angle, drop is expanded with the embedded syringe tip. Smallest and cleanest tip available are used and execution area are moved (area enclosed by the blue rectangle) to neglect the section of the drop distorted by contact with the tip. The fourth strategy is to first make a normal on a solid and then tilt the stage. This will create an advanced angle on one side of the drop. For producing receding angles, the last two methods described above can be used. Use the embedded syringe tip method but remove fluid from the drop as opposed to adding fluid to it.

1.4.2.3 Dynamic Inclined Plate Contact Angle Measurements

Another ways to determine θ_a and θ_r on solids are by using a goniometer in which one is looking on a small liquid drop placed on the solid sample and measure the contact angles while the drop size is increased or decreased, or alternatively tilt the sample stage giving an inclination and put the drop in movement (Figure 1.16).





Drops can be made to have advanced edges by addition of liquid. Receded edges may be produced by allowing sufficient evaporation or by withdrawing liquid from the drop. Alternately, both advanced and receded edges are produced when the stage on which the solid is held is tilted to the point of incipient motion.

The difference between the advanced/receded and advancing/receding is that in the static case, motion is incipient and in the dynamic case, motion is actual. Dynamic contact angles can easily be assayed at various rates of speed. Often it is found that there exists a simple relationship between dynamic contact angles measured at low velocities with properly measured static angles.

1.4.2.4 Dynamic Wilhelmy Plate Method

It is a method for calculating average θ_a and θ_r on solids of uniform geometry. Both sides of the solid must have the same properties. Wetting force on the solid is measured as the solid is immersed in or withdrawn, like given in Figure 1.17, from a liquid of known surface tension. Unlike other methods, this method needs a tensiometer instrument.


Figure 1.17: Immersion and withdraw of a sample in Wilhelmy method.

The Dynamic Contact angles can be determined in several ways. Amongst these techniques, the best one is the Wilhelmy plate technique performed with a tensiometer where a solid sample is immersed and withdrawn into and out from a liquid while simultaneously measuring the force acting on the solid sample. Advancing and receding contact angles can then be determined from the obtained force curve. The main drawback of this technique is that the sample has to be symmetrical and has a regular shape (rod, cube, round rod, rectangle, wire etc.).

1.4.3 Contact Angle Hysteresis

Contact angle hysteresis is the difference between the measured advancing and receding contact angles.

The theory of contact angle hysteresis has a long history. In general, it was recognized long ago that the free energy of a system, which includes a solid, a liquid, and a fluid, has multiple minima if the solid surface is rough or heterogeneous. The minimum that has the lowest free energy is the global minimum, which corresponds to the stable equilibrium state. The other minima represent metastable equilibrium states. In between these minima, there must exist a local maxima, which represent energy barriers that need to overcome in order to move from one metastable state to another. The transition between metastable states, in the direction of the stable equilibrium state, depends on the availability of external energy. Most equilibrium theories of hysteresis have been based on these ideas. Non-equilibrium approaches have also been developed. However, in an analysis of a two-dimensional drop on a heterogeneous, smooth solid surface, the existence of multiple minima in the free energy is only a necessary condition for hysteresis, not a sufficient condition. For example, if the minima points were independent of the drop volume, no hysteresis would have been observed, despite the existence of multiple minima. The pioneering

thermodynamic theories of hysteresis explained why a range of metastable contact angles exists on non-ideal surfaces for a given drop volume. They did not explain why hysteresis is observed when the volume of a drop is changed, i.e. why contact angles are different when the volume of a drop is, for example, increased and then decreased. Thus, the mere existence of multiple minima does not necessarily lead to hysteresis. The sufficient condition is that the positions of the minima points must depend on the volume.

The contact angle hysteresis is simply calculated by subtracting the measured advancing (maximum) contact angle with the measured receding (minimum) contact angle i.e.:

$$H = \theta_a - \theta_r \tag{1.9}$$

One can thus say that the hysteresis is the range of stable apparent contact angles that can be measured for the system.

Contact angle hysteresis can be caused by roughness and chemical contamination or heterogeneity of a solid surface as well as deposition of solutes (surfactants, polymers) from the liquid onto the solid surface. If roughness is the primary cause, then the measured contact angles are meaningless in terms of Young's equation. On very rough surfaces, contact angles are different from those on chemically identical smooth surfaces, which do not reflect material properties of the surface; rather, they reflect morphological ones. In general, the experimentally observed apparent contact angle may or may not be equal to the Young contact angle. On ideal solid surfaces, there is no contact angle hysteresis and the experimentally observed contact angle is equal to Young contact angle. On smooth, but chemically heterogeneous solid surfaces, apparent contact angle is not necessarily equal to the thermodynamic equilibrium angle. Nevertheless, the experimental advancing contact angle can be expected to be a good approximation of Young contact angle. This has been illustrated using a model of heterogeneous (smooth) vertical strip surfaces. Therefore, care must be exercised to ensure that the experimental apparent contact angle, which is the advancing contact angle in order to be inserted into the Young equation. On rough solid surfaces, no such equality between advancing contact angle and Young contact angle exists. Thus, all contact angles on rough surfaces are meaningless in terms of Young's equation.

Contact angle hysteresis was suggested as a way to understand the underlying physical mechanism of the contact angle increase on a rough surface. Even if two solid surfaces have the same water contact angle, the water drop may slide easier on one than the other. If the actual area is all wetted by the liquid drop in Wenzel model, then contact angle hysteresis and, thus, the force required for drop motion are large and the drop sticks strongly to the surface (Wenzel, 1936). If the liquid drop sits partially on top of protrusions in Cassie-Baxter model, then contact angle hysteresis is small and the drop slips easily (Cassie and Baxter, 1944). A theory that quantitatively predicts a Wenzel type sticky surface and a Cassie-Baxter type slippery surface was reported. According to the theory, perturbations to the contact angle are amplified in the Wenzel regime and attenuated in Cassie-Baxter regime.

Several approaches to contact angle hysteresis and to the study of the effect of heterogeneities on the contact line have been developed. Neumann and Li (2002) were able to explain from an analysis of a heterogeneous surface model with two different types of horizontal strips with different widths why the advancing contact angles are more reproducible than the receding angles. These authors considered the case of a low-energy (high contact angle) solid surface with impurities of higher energy. The advancing contact angle is expected to represent the property of the predominant material of the surface in this case, while the receding contact angle is only a manifestation of the impurities of that solid surface. Joanny and Gennes (1984) have analyzed the origin of hysteresis in terms of pinning of the contact line on a defect on the surface. According to their analysis, there is an analogy between physically rough and chemically heterogeneous surfaces so that their conclusions can be applied to both types of surfaces. These authors concluded that the hysteresis created by a dilute assembly grows like the number of defects (or heterogeneous regions). Schwartz and Garoff (1985) concluded from an analysis using various shapes and arrangements of patches that hysteresis is found to be a strong function of the details of the arrangements of such patches, in addition to the dependence on the coverage fraction. In addition to roughness and heterogeneity, there are other causes of contact angle hysteresis. It is well known that hysteresis can be observed which results from time-dependent liquid/solid interactions. For example, the solid can swell in contact with a certain liquid or even interact by chemical interfacial reactions; it can also be partially dissolved. In the case of polymer surfaces, the

molecular reorientation in the surface region under the influence of the liquid phase is assumed to be a major cause of hysteresis. This reorientation or restructuring is thermodynamically favored: at the polymer/air interface, the polar groups are buried away from the air phase, thus causing a lower solid/vapor interfacial tension. In contact with a sessile water drop, the polar groups turn over to achieve a lower solid/liquid interfacial tension. Time-dependent changes in contact angles can also be observed. Since contact angle hysteresis is a very complex phenomena, a complete theory for such a process is not yet available because the existing models give only a partial explanation of the hysteresis. It should be stated that the precise scale and degree of non-uniformity in the case of rough and/or heterogeneous surfaces necessary to cause detectable effects in hysteresis are not yet clear. There still remain difficulties in relating the observed hysteresis to practical measures of surface roughness and inhomogeneities.

1.4.4 Uses of Contact Angle Data in Industry

The primary focus of contact angle studies is in assessing the wetting characteristics of solid/liquid interactions. Contact angle is commonly used as the most direct measure of wetting. Other experimental parameters may be derived directly from contact angle and surface tension results. These include:

Work of adhesion, given in Figure 1.18, is the work required separating the liquid and solid phases, or the negative free energy associated with the adhesion of the solid and liquid phases. It is used to express the strength of the interaction between the two phases. It is given by the Young-Dupre equation as:

$$W_a = \gamma_L \left(1 + \cos \theta \right) \tag{1.10}$$

Work of cohesion, given in Figure 1.18, is the work required to separate a liquid into two parts, it is a measure of the strength of molecular interactions within the liquid. It is given by:

$$W_c = 2\gamma_L \tag{1.11}$$



Figure 1.18: (a) Work of adhesion, (b) work of cohesion.

Work of spreading is the negative free energy associated with spreading liquid over solid surface. Also referred to as the spreading coefficient, S, see Equation (1.8) given as:

$$W_s = \gamma_L \left(1 + \cos \theta \right) \tag{1.12}$$

Wetting tension is the wetting force normalized for length. It represents the product of the cosine of the contact angle and the surface tension. It is most helpful in situations, such as in multi-component systems, where the surface tension at the interface may not equal equilibrium surface tension. It is also referred as the adhesion tension or the work of wetting. It is defined as:

$$\Gamma = F_w / P = \gamma_L \cos\theta \tag{1.13}$$

Measurement of contact angles and surface tensions provides a better understanding of the interactions between solids and liquids or liquids/liquids. These interactions play a key role in understanding adhesion, material wettability, biocompatibility, lubricity of solid surfaces, as well as the wetting, washability, spreading and adsorption of liquids. Contact angle and surface tension measurements provide the information needed for development and modification of liquids and solid surfaces using today's sophisticated surface engineering techniques. Almost any solid or liquid surface can be modified to fit an application.

Determination of contact angles plays an important role in the underwater studies. It would help to express the phenomenon of underwater restructuring of the polymer surfaces by calculating contact angle hysteresis.

1.5 Surface Free Energies of Solids in Air

Surface free energy is defined as the work required increasing the area of a substance by one unit area. The surface free energy of a solid is sometimes also referred as the *"surface tension"* of the solid substrate.

Measurements of surface tension yield data, which directly reflect thermodynamic characteristics of the liquid tested. Measurement of contact angles yield data, which reflect the thermodynamics of a liquid/solid interaction. To characterize the wetting behavior of a particular liquid/solid pair only reporting of the contact angle is needed. It is possible to characterize the wettability of a solid in a more general way. To characterize the thermodynamics of the solid surface itself more elaborate analysis is required. Various methods are used but the same basic principle applies for each. The solid is tested against a series of liquids and contact angles are measured. Calculations based on these measurements produce a parameter (critical surface tension or surface free energy), which quantifies the characteristics of the solid and mediates the properties of the solid substrate. The critical surface tension or the surface free energy obtained in this way can be regarded as the "surface tension" of the solid substrate, which is a characteristic property of the solid in the same way as the surface tension is for a liquid. Different approaches are used for determining the energy of solid substrates.

In order to determine the surface tension of solids based on this equation from contact angle measurements, an assumption is made about the interfacial tension between the solid and the liquid. There are various empirical models for this, each with their own strengths and weaknesses (Zisman's critical surface tension, state equation from Neumann et al., methods according to Fowkes (or Owens-Wendt) and according to van Oss-Good).

1.5.1 Calculation Methods of Surface Free Energies of Solids

1.5.1.1 Critical Surface Tension (Zisman) Method

When a drop of liquid on a solid surface does not spread but comes to some equilibrium state, it exhibits a finite contact angle toward the solid. Many authors have expressed this equilibrium by means of the Young equation.



Figure 1.19: A typical Zisman plot, adapted from Url-1.

A simple graphical representation method of estimating the surface energy of solids was developed by Zisman (1952a). Zisman proposed that a critical surface tension, γ_c , could be estimated by measuring the contact angle of a series of liquids with known surface tensions on the surface of interest. These contact angles are plotted as a function of the γ_L of the test liquid. Zisman noticed empirically that a plot of $cos\theta$ versus γ_L is often linear. The value for which $cos\theta$ extrapolates to 1 is termed the critical surface tension in other words, the critical surface tension is defined as the intercept of the horizontal line, $cos\theta=1$, with the extrapolated straight-line plot of $cos\theta$ against γ_L , as shown in Figure 1.19. This intersection is the point where the contact angle is 0°. A hypothetical test liquid having this γ_L would just spread over the substrate. Critical surface tension is often presented as the highest value of surface tension of a liquid that will completely wet the solid surface. This approach is most appropriate for low-energy surfaces that are being wetted by nonpolar liquids.

The critical surface tension of a material, γ_c , is a measure of the surface wettability and it is proportional to the surface free energy of the material. A liquid with a surface tension less than or equal to the critical surface tension of a particular material will wet that surface, i.e. the contact angle will be less than or equal to 90°.

1.5.1.2 Fowkes' Geometric Mean (Later Owens and Wendt) Method

By using the Fowkes (1964) method, the polar and disperse fractions of the surface free energy of a solid can be obtained. This method is based on a combination of the knowledge of Fowkes on the one hand and that of Owens and Wendt, as Fowkes initially determined only the disperse fraction and the latter were the first to determine both the components of the surface energy. The difference between the Fowkes method and the Owens and Wendt (1965) method is that, in the Fowkes

method the disperse and the polar fractions are determined in succession, i.e. in two steps, while in the Owens and Wendt method both components are calculated by using a single linear regression.

In this first step, the disperse fraction of the surface energy of the solid is calculated by making contact angle measurements with at least one purely disperse liquid. By combination of the surface tension equation of Fowkes for the disperse fraction of the interactions

$$\gamma_{SL} = \gamma_{S} + \gamma_{L} - 2(\gamma_{S}^{d} \gamma_{L}^{d})^{\frac{1}{2}}$$
(1.14)

By combination of the surface tension equation of Fowkes for the disperse fraction of the interactions (Figure 1.20) with the Young equation (1.7), the following equation for the contact angle is obtained after transposition:

$$\cos\theta_e = 2\left(\gamma_S^d\right)^{\frac{1}{2}} \left(\frac{\left(\gamma_L^d\right)^{\frac{1}{2}}}{\gamma_L}\right) - 1$$
(1.15)

And, based upon the general equation for a straight line, y = mx + b

 $\cos\theta$ is then plotted against the term γ_L^d/γ_L and $2(\gamma_S^d)^{\frac{1}{2}}$ can be determined from the slope m. The straight line must intercept the ordinate at the point defined as b=-1. As this point has been defined, it is possible to determine the disperse fraction from a single contact angle: however, a linear regression with several purely disperse liquids is more accurate. An assumption of $\gamma_L^d = \gamma_L$ is made for all non-polar liquids.



Figure 1.20: Determining the disperse fraction of surface energy according to Fowkes, adapted from Url-1.

In the second step, determining the polar fraction (Figure 1.21), by extending Equation (1.14) for polar fraction as

$$\gamma_{SL} = \gamma_{S} + \gamma_{L} - 2 \left\{ \left(\gamma_{S}^{d} \gamma_{L}^{d} \right)^{\frac{1}{2}} + \left(\gamma_{S}^{p} \gamma_{L}^{p} \right)^{\frac{1}{2}} \right\}$$
(1.16)

It is also assumed that the work of adhesion is obtained by adding together the polar and disperse fractions:

$$W_{SL} = W_{SL}^{d} + W_{SL}^{p}$$
(1.17)

Then as a third step, Young's equation (1.7) is added to the equation of Dupre (1.18).

$$W_{SL} = W_{SL}^{d} + W_{SL}^{p}$$
(1.18)

To obtain the following relationship for the work of adhesion:

$$W_{SL}^{p} = \gamma_1 (\cos \theta + 1) \tag{1.19}$$

Now all the components required for the calculation of the polar fraction of the surface energy have been assembled. A combination of Equations (1.16), (1.17) and (1.19) produces

$$W_{SL}^{p} = \gamma_{1} (\cos \theta + 1) - 2(\gamma_{S}^{d} \gamma_{L}^{d})^{\frac{1}{2}}$$
(1.20)

Based upon this relationship the contact angles of liquids with known polar and disperse fractions are measured and W_{SL}^{p} is calculated for each liquid. In this case a single liquid with polar and disperse fractions would be sufficient, although the results would again be less reliable.

As according to Equation (1.16), the polar fraction of the work of adhesion is defined by the geometric mean of the polar fractions of the particular surface tensions.

$$W_{SL}^{p} = 2 \left(\gamma_{S}^{p} \gamma_{L}^{p} \right)^{\frac{1}{2}}$$
(1.21)

Then, by plotting W_{SL}^p against $2(\gamma_S^p)^{\frac{1}{2}}$ and following this with a linear regression, the polar fraction of the surface energy of the solid can be determined from the slope. As in this case the ordinate intercept *b* is 0, the regression curve must pass through the origin (0;0).



Figure 1.21: Determining the polar fraction of surface energy according to Fowkes, adapted from Url-1.

In 1969, based on Fowkes equation, Owens and Wendt (1969) offered a new expression as the surface tension of each phase can be split up into a polar and a disperse fraction

$$\gamma_L = \gamma_L^p + \gamma_L^d \tag{1.22}$$

$$\gamma_S = \gamma_S^p + \gamma_S^d \tag{1.23}$$

The Fowkes method for calculating the surface energy has already been developed from this relationship. In contrast to the Fowkes method, in the Owens, Wendt, Rabel and Kaelble method, the calculation of the surface energy of the solid takes place in a single step.

Owens and Wendt took the equation for the surface tension in Equation (1.16) as their basis and combined it with the Young Equation (1.7).

The two authors solved the equation system by using the contact angles of two liquids with known disperse and polar fractions of the surface tension. Kaelble (1970a) and Kaelble and Cirlin (1971) solved the equation for combinations of two liquids and calculated the mean values of the resulting values for the surface energy. Rabel (Owens and Wendt, 1969) made it possible to calculate the polar and disperse fractions of the surface energy with the aid of a single linear regression from the contact angle data of various liquids (Figure 1.22). Rabel combined Equations (1.16) and (1.7) and adapted the resulting equation by transposition to the general equation for a straight line to fit y = mx + b,

The transposed equation is shown below:

$$\frac{\left(1+\cos\theta\right)\gamma_L}{2\left(\gamma_L^d\right)^{\frac{1}{2}}} = \left(\gamma_S^p\right)^{\frac{1}{2}} \left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{\frac{1}{2}} + \left(\gamma_S^d\right)^{\frac{1}{2}} + \left(\gamma_S^d\right)^{\frac{1}{2}}$$
(1.24)

In a linear regression of the plot of y against x, γ_S^p is obtained from the square of the slope of the curve m and γ_S^d from the square of the ordinate intercept b.



Figure 1.22: Determination of the disperse and polar fractions of the surface tension of a solid according to Rabel, adapted from Url-1.

1.5.1.3 Acid/Base (van Oss-Good) Method

Based on the Lifshitz theory of attraction between macroscopic bodies, van Oss, Good and Chaudhury developed a more advanced approach after 1985 to estimate the free energy of adhesion between two condensed phases (van Oss et al., 1988). They suggested that a solid surface consists of two terms: one the Lifshitz-van der Waals interactions, γ^{LW} , comprising dispersion, dipolar and induction interactions, and the other the acid/base interaction term, γ^{AB} comprising all the electron donoracceptor interaction, such as hydrogen bonding. They thought that the Lifshitz calculations yield γ^{LW} that is the consequence of all the electromagnetic interactions taken together, whether due to oscillating temporary dipoles γ^d permanent dipoles γ^p or induced dipoles γ^i . γ^{LW} also includes the interactions of pairs, triplets, quadruplets etc. of the molecules within each phase, in all the actual configurations that are taken on when they interact. Then, the corresponding components of work of adhesion are

$$-W_a = \Delta G_{SL}^{LW} + \Delta G_{SL}^{AB}$$
(1.25)

Combining rule for the γ^{LW} component is given as

$$\Delta G_{SL}^{LW} = \sqrt{\Delta G_S^{LW} \Delta G_L^{LW}}$$
(1.26)

The term γ_{SL}^{LW} can be written as

$$\gamma_{SL}^{LW} = \gamma_S^{LW} + \gamma_L^{LW} - 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}}$$
(1.27)

Van Oss and Good did not apply a geometric-mean combining rule to acid/base (*AB*) interactions. Since hydrogen bonds are a sub-set of acid/base interactions, and surfaces of a number of liquids possess only electron donor properties and have no electron acceptor properties, or the reverse is true, one may consider the asymmetry for these interactions. Thus, van Oss and Good adopted Small's combining rule for acid/base interactions, which is not a geometric mean:

$$-\Delta G_{SL}^{AB} = 2\left(\sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}\right)$$
(1.28)

where γ_i^+ and γ_i^- are Lewis acid and base parameters of surface tension, respectively. The term now γ_{SL}^{AB} can be expressed as

$$\gamma_{SL}^{AB} = 2 \left[\left(\gamma_{S}^{+} \gamma_{S}^{-} \right)^{\frac{1}{2}} + \left(\gamma_{L}^{+} \gamma_{L}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{S}^{+} \gamma_{L}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{S}^{-} \gamma_{L}^{+} \right)^{\frac{1}{2}} \right]$$
(1.29)

or

$$\gamma_{SL}^{AB} = 2 \left[\left(\left(\gamma_{S}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{L}^{-} \right)^{\frac{1}{2}} \right) \left(\left(\gamma_{S}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{L}^{-} \right)^{\frac{1}{2}} \right) \right]$$
(1.30)

If γ^{LW} interfacial energy is written in conjunction with Young-Dupre equation, yield is

$$-\Delta G_{SL}^{LW} = \gamma_S^{LW} + \gamma_L^{LW} - \gamma_{SL}^{LW}$$
(1.31)

by combining Equations (1.27) and (1.31)

$$-\Delta G_{SL}^{LW} = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}}$$
(1.32)

Total interfacial free energy can be obtained by combining Equations (1.25), (1.28) and (1.32)

$$-\Delta G_{SL} = 2 \left[\sqrt{\gamma_S^{LW} \gamma_L^{UW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \right]$$
(1.33)

Combining Equation (1.33) with Young-Dupre equation and by neglecting spreading pressure, gives the general contact angle equation as

$$(1 + \cos\theta)\gamma_{LV} = 2\left[\left(\gamma_{S}^{LW}\gamma_{L}^{LW}\right)^{\frac{1}{2}} + \left(\gamma_{S}^{-}\gamma_{L}^{+}\right)^{\frac{1}{2}} + \left(\gamma_{S}^{+}\gamma_{L}^{-}\right)^{\frac{1}{2}}\right]$$
(1.34)

Contact angles against at least three liquids with known values of γ^d , γ^+ and γ^- are measured. γ_{LV} is the same as γ_L in Equation (1.34). The values for each experiment are put into the Equation (1.34), where γ refers to surface tension (surface free energy), the subscripts *L* and *S* refer to liquid and solid, and the superscripts "*d*", "+" and "-" refers to dispersive, acid and base components. Then, three equations are formed with three unknowns and they can be solved for γ_S^d , γ_S^+ and γ_S^- . The total surface free energy of the solid is then given by:

$$\gamma_{S} = \gamma_{S}^{\ d} + \gamma_{S}^{\ AB} \tag{1.35}$$

where
$$\gamma_{S}^{AB} = 2(\gamma_{S}^{+}\gamma_{S}^{-})^{\frac{1}{2}}$$
 (1.36)

1.6 Past Literature on Two Immiscible Liquid Contact Angle Methods

The surface free energy of solids is a characteristic factor, which affects the surface properties such as adsorption, wetting, adhesion, etc. The surface free energies of polymers cannot be measured directly because of the elastic and viscous restraints of the bulk phase, which necessitates the use of indirect methods. As to low-energy solids, many authors have used indirect methods to determine the surface free energy (Kaelble, 1970 and 1971; Dann, 1970a and 1970b; Owens and Wendt, 1969; Wu, 1973). Owens and Wendt (1969) and Kloubek (1974) have calculated the polar surface free energies of polymers from the contact angle of various liquids by assuming polar interaction to be represented by the geometric mean of the polar components of the surface free energies. Zisman (1964) has plotted cosines of contact angles of several liquids against their surface free energies and introduced the concept of critical surface tension, about the meaning of which there is, however, no

general agreement. Several approximations are currently available to evaluate the surface free energies of polymers from contact angle data (Adamson, 1997). These semi-empirical approximations were derived from the works of Girifalco and Good (1957), Fowkes (1964), Owens and Wendt (1969), and Wu (1970) and resulted in large controversy in this field. The use of nonlinear programming methods did not completely solve the problem (Erbil, 1987; Erbil and Meric, 1988a and 1988b). The above approximations depend on the data obtained by measuring the contact angle of liquids on the polymer surface under its vapor atmosphere, which is also called the *"one-liquid method"*. Tamai et al. (1967) have extended this method to high-energy surfaces such as metals as well as to low-energy surfaces such as polymers by measurements of the contact angles of water drops in different hydrocarbons. This method is called the *"two-liquid method"*.

Later, Hamilton (1972 and 1974), El-Shimi and Goddard (1974), Tamai et al. (1977), Schultz et al. (1977a and 1977b), Matsunaga (1977), Bagnal and Green (1979), Matsunaga and Ikada (1981), Ratner et al. (1981), Schultz and Lavielle (1985) and Erbil (1989 and 1994) have made experiments and modeling work by using twoliquid method.

1.6.1 Tamai Approach

Tamai et al. (1967) introduced a work that aims to introduce an extension of the method based on similar assumptions to those of Fowkes. An experimental method of estimating molecular forces at the plane surface of solids was proposed. This method was based on the relation between interfacial and surface tensions due to Fowkes and on the Young-Dupre equation. Experimentally, contact angles were measured in a three-phase system of two immiscible liquids and a solid surface. Experimental studies have been carried out on hydrocarbon/water/solid systems. Solids such as iron, copper, cadmium, aluminum, polyethylene, poly(viny1 chloride), and poly(methyl methacrylate) has studied. Values were obtained for the dispersion force component of the surface tensions of the solids and for the interaction energy of the nondispersion force at the interface of the solid and water.

Tamai proposed that in the case where nondispersion forces such as electrostatic, metallic, hydrogen bonding and dipole image are present and interacting at the interface, one needs to consider another additional energy term to Fowkes approach

(Equation 1.14), I_{12} due to the stabilization by the nondispersion forces and by rewriting equation as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} - I_{12}$$
(1.37)

where it is assumed that all different forces act independently. In this development, the Young-Dupre relation between equilibrium contact angle θ on a plane solid must also be considered and Equation (1.7) can be rewritten as

$$\gamma_{SA} = \gamma_{SB} + \gamma_{AB} \cos \theta \tag{1.38}$$

where the subscript *S* refers to the solid, and *A* and *B* denote one-liquid phase and another liquid or gas (saturated vapor) phase, respectively.

If two immiscible liquids as phases A and B are employed, one can often measure the contact angle even when the solid is wettable either by liquids A and B. For this reason, the solid/liquid/liquid combination was used in the work. Using Equation (1.37), it can be written as

$$\gamma_{SA} = \gamma_{S} + \gamma_{A} - 2\left(\gamma_{S}^{d}\gamma_{A}^{d}\right)^{\frac{1}{2}} - I_{SA}$$
(1.39)

and

$$\gamma_{SB} = \gamma_S + \gamma_B - 2\left(\gamma_S^d \gamma_B^d\right)^{\frac{1}{2}} - I_{SB}$$
(1.40)

Substituting these relations into Equation (1.38), result is

$$\gamma_A - 2\left(\gamma_S^d \gamma_A^d\right)^{\frac{1}{2}} - I_{SA} = \gamma_B - 2\left(\gamma_S^d \gamma_B^d\right)^{\frac{1}{2}} - I_{SB} + \gamma_{AB}\cos\theta$$
(1.41)

Now a saturated hydrocarbon liquid and water were chosen as A and B. Fowkes has shown that the nature of the intermolecular force of a hydrocarbon liquid is purely dispersion; thus, γ_H^d can be replaced with γ_H (where H refers to the hydrocarbon). Fowkes has also shown that the liquid hydrocarbon is attracted very little, if at all, by forces other than the dispersion force when contacted with water and mercury. Using Equation (1.37), which does not contain the term I_{12} and the measured surface and interfacial tensions of each material, Fowkes obtained consistent values of γ^d for water and mercury from measurements with various hydrocarbons. This means that if one phase is hydrocarbon, the term I_{12} may be negligible. From these facts, for a hydrocarbon/water/solid two-liquid system a final equation is obtained from the simplified form of Equation (1.41), that is

$$\gamma_H - 2\left(\gamma_S^d \gamma_H\right)^{\frac{1}{2}} = \gamma_W - 2\left(\gamma_S^d \gamma_W^d\right)^{\frac{1}{2}} + \gamma_{HW} \cos\theta - I_{SW}$$
(1.42)

where *W* refers to water. In this equation, γ_H , γ_W , γ_{HW} and θ are measurable, and γ_W^d has been determined by Fowkes. However, two unknown terms, γ_S^d and I_{SW} , remain independent of the nature of the hydrocarbon liquid. Therefore, various forces can be measured using two different hydrocarbon liquids, two independent equations of Equation (1.42) in two unknowns can be obtained, and thereby γ_S^d and I_{SW} are determined.

Tamai et al. (1977) evaluated the dispersion force component of surface tension γ_s^d and the nondispersive interaction energy at the water/solid interface (or the nondispersive work of adhesion) I_{sw} for poly-(tetrafluoroethylene) (PTFE-Teflon), poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) by the analysis of the contact angles of water drops in hydrocarbon (the two-liquid contact angle method). The results were then compared with those obtained by the one-liquid contact angle method with 1-bromonaphthalene and methylene iodide as probe liquids, which was the method usually adopted. The values of γ_s^d from the two-liquid method, whereas their high sensitivity to error in the measurement of contact angles was taken into account. This discrepancy might be attributed to the neglect of the surface pressure π in the one-liquid method and the π values of the liquids used on the sample solids were calculated.

Tamai et al. have extended Fowkes method to high-energy surfaces such as metals, as well as to low-energy surfaces, by measurement of contact angles of water drops in two different hydrocarbons. However, the γ_s^d values obtained by Tamai seem to be considerably different from those of the one-liquid method, as pointed out by Panzer (1973). There might still be some possibility that this difference is due to the difference between samples such as the surface structure of polymers or the surface preparation method, etc. In this work, using the same samples of several organic polymer plates prepared by the same method, one-liquid method was compared to

two-liquid method for the evaluation of γ_s^d values and the nondispersive water/solid interaction energy I_{SW} .

Young-Dupre Equation (1.7) can be rewritten, for a drop of nonpolar liquid *L*, by adding π , which is the surface pressure of the liquid at the vapor/solid interface as,

$$\gamma_{S} - \pi_{L} = \gamma_{SL} + \gamma_{L} \cos\theta \tag{1.43}$$

From the geometrical mean assumption for the dispersive interaction at the solid/liquid interface, Fowkes Equation (1.14) can be written for above conditions.

Combining Equations (1.43) and (1.14),

$$\gamma_L (1 + \cos \theta) = 2 \left(\gamma_S^d \gamma_L^d \right)^{\frac{1}{2}} - \pi_L$$
(1.44)

By neglecting π_L and rearranging Equation (1.44), in the one-liquid method, the dispersion component of surface tension γ_s^d can be obtained as

$$\gamma_S^d = \gamma_L (1 + \cos\theta)^2 / 4 \tag{1.45}$$

The fundamental relation for the contact angle of water in hydrocarbon is given in Equation (1.42).

Subscripts *H* and *W* indicate nonpolar hydrocarbon and water, respectively. Since this equation contains two unknowns, γ_s^d and I_{SW} , two hydrocarbons H_1 and H_2 are employed to obtain two relations such as Equation (1.42), and the solutions for the two unknowns can be obtained as

$$\gamma_{S}^{d} = \frac{\left(\gamma_{H_{1}} - \gamma_{H_{2}}\right) - \left(\gamma_{H_{1}W}\cos\theta_{1} - \gamma_{H_{2}W}\cos\theta_{2}\right)}{2\left(\gamma_{H_{1}}^{1/2} - \gamma_{H_{2}}^{1/2}\right)}$$
(1.46)

$$I_{SW} = \frac{1}{\left(\gamma_{H_1}^{1/2} - \gamma_{H_2}^{1/2}\right)} \begin{cases} \left[\gamma_{H_2}^{1/2} - \left(\gamma_{W}^{d}\right)^{1/2}\right] \left[\gamma_{H_1} - \gamma_{W} - \gamma_{H_1W} \cos\theta_1\right] - \left[\gamma_{H_1}^{1/2} - \left(\gamma_{W}^{d}\right)^{1/2}\right] - \left[\gamma_{H_2} - \gamma_{W} - \gamma_{H_2W} \cos\theta_1\right] \end{cases}$$
(1.47)

Also, in the one-liquid method, I_{SW} can be calculated from contact angles of water as reported by Dann (1970b) using the equation

$$\gamma_W (1 + \cos \theta_W) = 2 \left(\gamma_S^d \gamma_W^d \right)^{\frac{1}{2}} + I_{SW} - \pi_W$$
(1.48)

Here also the surface pressure of water π_W must be neglected.

Schultz and co-workers (1977a) offered a method for measuring the dispersive part of the surface free energy, γ_s^d of a high-energy solid, and its interaction energy with water and n-alkanes, W_{SL} . It was based on the measurement of the contact angle of water on the solid under n-alkanes. Muscovite mica was chosen as a model high surface energy solid. The results obtained for γ_s^d and W_{SL} of mica are in good agreement with the results obtained by other techniques. The present method can be considered as applicable for other solids. For high surface energy solids, the wetting is generally complete and determination of surface energy from simple contact angle measurements becomes impossible. In this series of investigations, experiments were carried out to analyze the surface free energy components of a high-energy solid by employing a modified method giving a finite contact angle.

The approach was based on the method of Peper and Berch (1964), Tamai et al. (1967) and Hamilton (1972 and 1974). They measured the contact angle of liquid on solid under another liquid.

Assuming Young's equation to hold for a liquid (L_1) /liquid (L_2) /solid (S) system, an equation was obtained,

$$\gamma_{SL_2} = \gamma_{SL_1} + \gamma_{L_1L_2} \cos \theta_{SL_1}$$
(1.49)

where, γ_{SL_2} , $\gamma_{L_1L_2}$ and γ_{SL_1} represent the interfacial free energies of *S*-*L*₂, *L*₁-*L*₂, and *S*-*L*₁ interfaces, respectively. θ_{SL_1} is the contact angle of a droplet of liquid *L*₁ on solid *S* under liquid *L*₂.

According to Fowkes Equation (1.37), it might be written γ_{SL_1} and γ_{SL_2} as

$$\gamma_{SL_1} = \gamma_S + \gamma_{L_1} - 2\left(\gamma_S^d \gamma_{L_1}^d\right)^{1/2} - I_{SL_1}$$
(1.50)

$$\gamma_{SL_2} = \gamma_S + \gamma_{L_2} - 2\left(\gamma_S^d \gamma_{L_2}^d\right)^{\frac{1}{2}} - I_{SL_2}$$
(1.51)

where γ and γ^{d} are the surface free energy and its London dispersion force component, and I_{SL} is the nondispersive interaction which includes dipole/dipole interactions, dipole/induced dipole interactions, hydrogen bonds, π bonds, charge transfer interactions, etc. Substituting Equations (1.50) and (1.51) in Equation (1.49) yields:

$$\gamma_{L_1} - \gamma_{L_2} + \gamma_{L_1L_2} \cos \theta_{SL_1} = 2 \left(\gamma_S^d \right)^{\frac{1}{2}} \left[\left(\gamma_{L_1}^d \right)^{\frac{1}{2}} - \left(\gamma_{L_2}^d \right)^{\frac{1}{2}} \right] + \left(I_{SL_1} - I_{SL_2} \right)$$
(1.52)

In the case where L_1 is water (subscript W) and liquid L_2 is n-alkane (H), the term, I_{SL_2} may be neglected since the surface free energy of n-alkane consists of only the London dispersion energy. Therefore, by rewriting equation (1.52) as

$$\gamma_{W} - \gamma_{H} + \gamma_{HW} \cos \theta_{SW} = 2 \left(\gamma_{S}^{d} \right)^{\frac{1}{2}} \left[\left(\gamma_{W}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{H}^{d} \right)^{\frac{1}{2}} \right] + I_{SW}$$
(1.53)

If the angles for several n-alkanes are measured, the plot of $\gamma_W - \gamma_H$ + $\gamma_{HW} \cos \theta_{SW}$ against $\left[\left(\gamma_W^d \right)^{\frac{1}{2}} - \left(\gamma_H^d \right)^{\frac{1}{2}} \right]$ should give a straight line with intercept I_{SW} and slope 2 $\left(\gamma_S^d \right)^{\frac{1}{2}}$. This principle is based on the assumption that a droplet of water immediately displaces the alkane layer from the surface at contact.

Schultz et al. (1977b) also developed a method of determining the polar term of the adhesion energy of several liquids to a high-energy solid, I_{SW} , based on the measurement of the contact angle of water on a solid in a liquid medium other than hydrocarbons. The I_{SW} values for mica are found to be a linear function of the square root of the polar term of the surface free energies of liquids. This finding agrees with the suggestion that the polar term of the energy of adhesion may be represented by the geometric mean of the polar term of the surface free energy of a solid and a liquid. The results were compared with those obtained by a cleavage method and discussed in terms of each component of the surface free energy of mica. The present method was found to be useful for the determination of the polar part of the energy of adhesion of a high-energy solid to liquids, and its surface free energy. In this investigation, it was extended the method previously described in order to determine the polar adhesion energy of a high-energy solid to liquids, to examine the validity of the equation, which correlates polar surface free energy with the polar part of the adhesion energy, and to determine the polar surface free energy. The method is basically the same as that described previous method Schultz et al. (1977a), i.e., the measurement of the contact angle of liquid (L_1) on solid (S) under liquid (L_2) .

As rearranging Schultz's Equation (1.52), in the conditions of liquid L_1 is water (subscript W), and L_2 is a liquid other than hydrocarbons this time, yield is

$$I_{SL_2} = \gamma_{L_2} - \gamma_{WL_2} \cos \theta_{SW} - 2(\gamma_S^d)^{\frac{1}{2}} (\gamma_{L_2}^d)^{\frac{1}{2}} + I_{SW} + 2(\gamma_S^d)^{\frac{1}{2}} (\gamma_W^d)^{\frac{1}{2}} - \gamma_W$$
(1.54)

In the Equation (1.54), the values of γ_W , γ_W^d , γ_S^d and I_{SW} are available from Schultz et al., (1977a). Therefore, measurements of γ_{L_2} , γ_{WL_2} , θ_{SW} and $\gamma_{L_2}^d$ lead to a calculation of the polar interaction I_{SL_2} .

Matsunaga (1977) investigated on surface free energy analysis of polymers related to their surface composition. In his work, the dispersion force component of surface free energy, γ_S^d , and the nondispersive interaction free energy between solid and water, I_{SW} , were determined by the two-liquid contact angle method, i.e., by the measurement of contact angles of water drops on plain solids in hydrocarbon, for commercially available organic polymers such as nylons, halogenated vinyl polymers, polyesters, etc. A method to estimate the I_{SW} values from the knowledge of the polymer composition was also proposed, based on the assumption of the spherical monomer unit and the sum of interactions between functional groups and water molecules at the surface. Since I_{SW} values can give useful surface energy information on polar terms, it may be of value such adhesion phenomena if the I_{SW} values can be estimated from the knowledge of polymer position. In the calculations, Matsunaga obtained the same Equation (1.53) with Schultz et al. (1977a), in which the two unknowns γ_S^d and I_{SW} can be solved by measurement of contact angles in two different hydrocarbons.

Later, Matsunaga and Ikada (1981) investigated dispersive component of surface free energies of hydrophilic polymers like PMMA and PVA. The London dispersive component of surface free energy, γ_s^d , and the nondispersive interactions with polar liquids, I_{SW} , were determined for hydrophilic polymers *S*, that is cellulose, polyvinyl alcohol (PVA), and poly(methyl methacrylate) (PMMA). On applying the geometricmean relation $2(\gamma_s^d \gamma_W^d)^{\frac{1}{2}}$ to the dispersive interaction, I_{SW} the γ_s^d values were found to be 30, 29, and 37 erg/cm² for cellulose, PVA and PMMA, respectively. Each of them was completely independent of the nature of the testing liquids *W*, indicating that the geometric-mean equation is appropriate for representing the dispersive interaction. On the contrary, such a geometric-mean expression was shown to be inapplicable to the nondispersive interactions. It was suggested that Fowkes' approach, in which intermolecular forces are regarded to be dominated by dispersion force interactions and election donor/acceptor interactions, is more reasonable than the popular approach.

Matsunaga urged that Fowkes equation could not be used for hydrophilic polymers since a difficulty arises from hydrogen bonding which may take place at the interface if the testing liquid is capable of being hydrogen bonded. As Fowkes has pointed out, it is incorrect to treat the hydrogen bonding by the geometric-mean relationship. Matsunaga offered a graphical method by using Equation (1.42) where θ is the contact angle of a droplet of liquid W on solid S under liquid H and π_e is the surface spreading pressure. Here γ_H is assumed to have only the dispersive component such as saturated hydrocarbon $(\gamma_H = \gamma_H^d)$ while γ_W is assumed to have not only the dispersive but also the nondispersive component. Neglecting contact angles against a fixed liquid W under several n-alkanes, if $(\gamma_W - \gamma_H + \gamma_{HW} \cos \theta_{SW})$ against $[(\gamma_W^d)^{1/2} (\gamma_H)^{1/2}$] is plotted, it can be obtained that γ_S^d and I_{SW} values. This is because I_{SW} should have no relation with liquids H. If the contact angle is measured with the conventional one-liquid method, neither γ_S^d nor I_{SW} can be determined. In this work it was described that the determination of γ_S^d and I_{SW} for two representatives of nonionic hydrophilic polymer, cellulose, PVA, and a hydrophilic polymer, PMMA, by a graphical method with the help of Equation (1.42). Only a few studies have attempted to determine the surface free energies of hydrophilic polymers because of its complexity, though hydrophilic surfaces are no less important than hydrophobic surfaces.

In 1985, Schultz and Lavielle (1985) investigated surface properties of graft polyethylene in contact with water. In order to measure in situ the evolution of the surface energy of PEg, the following method of the two-liquid phase system was adopted (Schultz et al., 1977a). The PEg film (S) in a metallic holder is immersed in water (W). A drop of n-alkane (H) is introduced and placed on the underside of the solid (because of its lower density). The equilibrium state of the solid/liquid/liquid

system is described by the relationship in Equation (1.53). Polar part was expressed as below and entered into Equation (1.55).

$$I_{SW} = 2 \left(\gamma_{S}^{p} \ \gamma_{W}^{p} \right)^{\frac{1}{2}}$$
(1.55)

The yielding equation is given as,

$$\gamma_{H} - \gamma_{W} + \gamma_{HW} \cos \theta_{SW} = 2 \left(\gamma_{S}^{d} \right)^{\frac{1}{2}} \left[\left(\gamma_{H}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{d} \right)^{\frac{1}{2}} \right] - 2 \left(\gamma_{S}^{p} \gamma_{W}^{p} \right)^{\frac{1}{2}}$$
(1.56)

where γ is the surface energy and γ_s^d and γ_s^p are the dispersive and polar components of the surface energy, respectively.

By using a series of n-alkanes (from C₆ to C₁₂), a linear relationship is obtained by plotting the quantity $\gamma_H - \gamma_W + \gamma_{HW} \cos \theta_{SW}$ as a function of $\left[\left(\gamma_H^d \right)^{\frac{1}{2}} - \left(\gamma_W^d \right)^{\frac{1}{2}} \right]$. According to Equation (1.56), γ_S^d and γ_S^p are readily calculated from the slope and intercept at the origin of this line.

1.6.2 El-Shimi Approach

El-Shimi and Goddard (1974) compared experimental values of contact angles in various hydrocarbon liquid/water/solid systems with calculated values based on the Fowkes-Young and Wu-Young equations, in 1973. Satisfactory agreement is obtained with the Wu equation for Teflon and poly(methyl methacrylate) provided the receding angle in the hydrocarbon liquid is used. Both equations predict complete wetting of paraffin wax by the hydrocarbon liquids, as was observed. On the other hand, the contact angles observed on Nylon 11 and Bovine hoof keratin are much higher than predicted. These results are attributed to the ability of Nylon and keratin to hydrate under water so promoting aqueous phase/solid interaction at the expense of hydrocarbon/solid interaction. These surfaces possess a dual functionality hydrophobic in air, hydrophilic in water. In addition, keratin has the property that water will not readily displace oil from its surface. Apparently, surface keratin molecules adopt and retain a conformation most compatible with their immediate environment. The agreement between observed and calculated (Fowkes, Wu) angles for n-hexanol/water/solid systems was poor. This lack of agreement is attributed to adsorption of the alcohol on the solid. Good agreement was, however, obtained with values based solely on the Young equation, utilizing contact angles for the liquids in air, in the case of Teflon.

The preferential wetting of a given solid in contact with two mutually saturated immiscible liquids can be predicted based on the values of the contact angles of the individual liquids on the given solid in air, and application of Young's equation. For example, consider the case of a nonpolar liquid (O) and water (W) on a low-energy substrate (S), such that we have for the air/water/substrate system:

$$\gamma_{s} - \gamma_{sw} = \gamma_{w} \cos \theta_{w} \tag{1.57}$$

and for the air/oil/substrate system

$$\gamma_{S} - \gamma_{SO} = \gamma_{O} \cos \theta_{O}, \qquad (1.58)$$

and for the oil/water/substrate system

$$\gamma_{SW} - \gamma_{SO} = \gamma_{OW} \cos \theta_{OW} \tag{1.59}$$

where, γ_s is the solid surface tension and the other terms having their usual significance. (In this work, θ_{OW} was measured in the oil phase).

Substituting (1.57) and (1.58) in (1.59) gives the Bartell-Osterhof equation, Equation (1.60) (Bartell and Osterhof, 1927).

$$\gamma_{OW} \cos \theta_{OW} = \gamma_O \cos \theta_O - \gamma_W \cos \theta_W \tag{1.60}$$

Equation (1.60) allows contact angle prediction in systems containing two immiscible liquids and a solid. Since Young's equation is only valid in cases in which the contact angle is finite, Equation (1.60) would not be expected to hold in such cases where the contact angle θ equals zero in air as is commonly observed for many low-energy solids and nonpolar liquids (Bargeman, 1972). However, Equation (1.60) could be verified using Teflon substrates since all common nonpolar liquids exhibit a finite contact angle on it. A less direct approach to predict θ_{OW} in liquid/ liquid/solid systems, where $\theta = 0^{\circ}$ in air for one of the liquids, is based on evaluation of the forces effecting such processes as wetting and adhesion. Interaction across the interface between two condensed phases in contact has been described by an equation due to Fowkes (1962) which has been found successful if the interaction is solely due to London-van der Waals forces. The general form of Fowkes' Equation (1.37) in which the interaction across the interface is presented as the geometric mean of the dispersion components of the surface tension of each phase.

In the case of a solid/water system,

$$\gamma_{SW} = \gamma_S + \gamma_W - 2\left(\gamma_S^d \ \gamma_W^d\right)^{\frac{1}{2}}$$
(1.61)

and for a solid/oil system,

$$\gamma_{SO} = \gamma_S + \gamma_O - 2\left(\gamma_S^d \ \gamma_O^d\right)^{\frac{1}{2}}$$
(1.62)

Substituting (1.61) and (1.62) in (1.59) gives

$$\gamma_{OW} \cos \theta_{OW} = \gamma_W - 2 \left(\gamma_S^d \ \gamma_W^d \right)^{\frac{1}{2}} - \gamma_O + 2 \left(\gamma_S^d \ \gamma_O^d \right)^{\frac{1}{2}}$$
(1.63)

Where the γ_s^d terms are the dispersion component of the surface tensions. The γ_o^d value is usually taken as equal to γ_o for nonpolar liquids.

Equation (1.63) allows us to predict θ_{OW} from a knowledge of γ_S^d and γ_W^d .

1.6.3 Wu Approach

Another approach that accounts for contribution of forces other than dispersion forces is due to Wu (1971), according to which the polar interactions, like dispersion interactions, are expressed in reciprocal-mean form. The general form of Wu's equation to determine the energy of interaction between two phases, 1 and 2, resulting from dispersion and polar interactions is

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(1.64)

where γ^{P} is the polar component of the surface tension. For the water/solid system the interfacial energy is given by

$$\gamma_{SW} = \gamma_S + \gamma_W - \frac{4\gamma_S^d \gamma_W^d}{\gamma_S^d + \gamma_W^d} + \frac{4\gamma_S^P \gamma_W^P}{\gamma_S^P + \gamma_W^P}$$
(1.65)

Similarly for the oil/solid system

$$\gamma_{SO} = \gamma_S + \gamma_O - \frac{4\gamma_S^d \gamma_O^d}{\gamma_S^d + \gamma_O^d} + \frac{4\gamma_S^P \gamma_O^P}{\gamma_S^P + \gamma_O^P}$$
(1.66)

Substituting Equations (1.64) and (1.65) in Equation (1.59) gives

$$\gamma_{OW}\cos\theta_{ow} = \gamma_w - \frac{4\gamma_s^d\gamma_o^d}{\gamma_s^d + \gamma_w^d} - \frac{4\gamma_s^P\gamma_o^P}{\gamma_s^P + \gamma_w^P} - \gamma_o + \frac{4\gamma_s^d\gamma_o^d}{\gamma_s^d + \gamma_o^d} + \frac{4\gamma_s^P\gamma_o^P}{\gamma_s^P + \gamma_o^P}$$
(1.67)

Equation (1.67) allows us to predict contact angles in the oil/water/substrate system, taking into account the polar interactions as well as the more universal dispersion interactions. Again, information on the components of the solid surface free energy is available and it is assumed that for a nonpolar liquid $\gamma_O^d = \gamma_O$.

Substitution of appropriate values in Equations (1.63) and (1.67) thus allows prediction of θ_{OW} values based on two approaches. These values were then compared with experimental data.

1.6.4 Ratner Approach

Ratner et al. (1981) made the characterization of hydrophilic and hydrophobic polymer surfaces by using one-liquid and two-liquid methods. Contact angles on these polymeric surfaces were determined in air and under water. The critical surface tension γ^c of each polymeric surface in air was estimated by the Zisman method. Geometric mean and harmonic mean approximation methods were utilized to estimate the dispersion force contribution γ_s^d and the polar contribution γ_s^p to the total surface free energy, γ_s , from contact angle data in air. The geometric mean approximation was also used to estimate γ'_s^a and γ'_s^p from contact angles under water. The calculated values of γ_s^d , γ_s^p are strongly dependent on the pair of liquids chosen for the calculation regardless of the approximation adopted. The values of γ_s , calculated as the sum of γ_s^d and γ_s^p were found to be close to the γ'' values and were less dependent on the pair of liquids used. A comparison of the ratio γ_s^d/γ_s^p for the same surface in air and under water suggests that major polymer chain conformational changes occur, particularly with respect to the hydroxyl side chain, when such surfaces are immersed in water.

Several approximation methods are currently available to estimate the surface free energy, γ_s , of solids from contact angle data. Girifalco and Good (1957) have proposed that the work of adhesion might be proportional to the geometric mean of

the surface free energy of the solid and the surface tension of the liquid. Fowkes (1964) has put their proposal into a convenient form for hydrophobic surfaces where the dispersion energy contribution is predominant. For hydrophilic surfaces, Kaelble (1970) and Kaelble and Uy (1970) have extended the Girifalco-Good-Fowkes approach by adding a polar energy interaction term:

$$\gamma_L (1 + \cos \theta) = 2 \left(\gamma_S^d \gamma_L^d \right)^{\frac{1}{2}} + 2 \left(\gamma_S^p \gamma_L^p \right)^{\frac{1}{2}}$$
(1.68)

For the oil/water/solid system, the following equation can be derived from the Young-Dupre equation, when the Fowkes method is used for the interfacial free energies at the oil/water and the oil/solid interfaces and when the Kaelble's approximation is adopted for the interfacial free energy at the solid/water interface:

$$2\left\{ \left(\gamma_{WV}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{OV}^{d} \right)^{\frac{1}{2}} \right\} \left(\gamma_{S}^{d} \right)^{\frac{1}{2}} + 2\left(\gamma_{WV}^{p} \gamma_{S}^{p} \right)^{\frac{1}{2}} = \gamma_{WV} - \gamma_{OV} - \left(\gamma_{WV} + \gamma_{OV} - 2\left(\gamma_{OV}^{d} \gamma_{WV}^{d} \right)^{\frac{1}{2}} \right) \cos \theta$$
(1.69)

where subscripts (*W*) and (*O*) refer to oil and water, respectively. Here, superscript prime (') is used to distinguish the surface free energy in air (no prime) from that in water (prime). In Equation (1.69), only γ'_s^a and γ'_s^p are not accessible quantities. Therefore if contact angles of two different water-immiscible liquids on the solid surfaces are determined in water, one can estimate γ'_s^a and γ'_s^p .

1.6.5 Hamilton Approach

Hamilton (1972) offered a technique for the characterization of hydrophilic solid surfaces by using octane drops under water medium. Using the finding that the dispersion force contributions to the surface free energies of octane and water are equal, 21.8 dyn/cm, and that octane's surface free energy has no polar component, whereas water has a polar contribution of 50.2 dyn/cm, Hamilton offered a simple method to be developed to characterize the hydrophilic nature of solid surfaces. This technique involves measuring octane contact angles on solid surfaces under water. Nonhydrophilic solids unable to interact by polar forces exhibit a predicted 50° contact angle, whereas those able to interact by polar forces give values greater than 50°. The greater the contact angle, the stronger are the polar interactions. The

deviation of the contact angle from 50° can be used to evaluate, I_{SW} , defined as the interfacial stabilization energy from the nondispersion (polar) forces.

Octane and water have surface free energies of 21.8 and 72.0 dyn/cm, respectively, at 20°C. Fowkes (1964) has demonstrated that the surface free energy value for octane is due to dispersion forces only, but that the surface free energy value for water consists of two components, dispersion forces (21.8 dyn/cm) and polar forces (50.2 dyn/cm). Fowkes has also shown that the only forces, which contribute to the interfacial free energy between two liquids, are those forces, which exist in both liquids. Because the dispersion force contributions to the surface free energy values of octane and water are identical, octane underwater contact angles would be expected to have an identical value on those solid surfaces, which can only interact through dispersion forces, but have different (higher) values on those solid surfaces that have the ability to interact through polar forces as well.

Young's expression for the octane/water/solid contact angle can be expressed as

$$\cos\theta = (\gamma_{SW} - \gamma_{SO})/\gamma_{WO}$$
(1.70)

 γ_{WO} (water/octane interfacial free energy) is 48.3 and later 50.8 dyn/cm, determined experimentally. γ_{SO} and γ_{SW} , the interfacial free energies for the solid/octane/saturated water and solid/water/saturated octane interfaces, can be estimated by the method of Fowkes in Equation (1.37). Inserting Fowkes' expressions into Young's Equation (1.70) gives the following relationship:

$$\cos\theta = \left(\gamma'_W - \gamma_O - 2\sqrt{\gamma_S^d \gamma_W^d} + 2\sqrt{\gamma_S^d \gamma_O^d}\right) / \gamma_{OW}$$
(1.71)

 γ'_W is the surface tension of octane/saturated water (51.6 dyn/cm), and γ_o the surface tension of water/saturated octane (21.8 dyn/cm), γ_s^d and γ_W^d are the dispersion components of the free energies of the solid and water, respectively. Since γ_s^d and γ_W^d are both 21.8 dyn/cm, the two square root terms in Equation (1.37) cancel for a given solid, and the value of the contact angle becomes insensitive to variations in γ_s^d . The value of θ should, therefore, be equal, in eases where dispersion forces are the only forces present. On this basis, θ calculated from Equation (1.37) for the solid/octane/water system should be 50°. The incorporation

of the stabilization contribution from nondispersion, polar forces I_{sw} into Equation (1.37) gives:

$$\cos\theta = (\gamma_W - \gamma_O - I_{SW}) / \gamma_{OW}$$
(1.72)

This equation can be solved directly to obtain values for polar stabilization energy between water and the solid, I_{SW} . No attempt was made to differentiate I_{SW} further into hydrogen bonding and dipole-dipole contributions, and no polar terms are required for the octane/water and octane/solid interfacial free energies. This theory does not take into account the possibility of adsorption of water at the octane/solid interface, or of octane at the water/solid interface.

Later, Hamilton (1974) investigated polar force contributions to adhesive bonding. The dispersion force contributions to the surface free energies of octane and water are equal to 21.8 dyn/cm. Octane's surface free energy has no polar component, whereas water has a polar contribution of 50.2 dyn/cm. Therefore, the increase in the contact angle of octane on various polar polymer surfaces underwater is a quantitative measure of the interracial stabilization energy from polar forces. Octane contact angles were measured underwater on polyethylene, polytetrafluoroethylene, and polyethyleneglycolterephthalate surfaces before and after surface oxidation in a low temperature asher. The octane contact angles increased in each case as the surfaces became oxidized. Breaking forces on polymer surfaces was tested with a mechanical tester and found that breaking forces were well correlated with the octane contact angles.

When polymeric substances are brought into intimate contact, they should interact with sufficient strength that considerable force should be required to separate them. The attractive force between these polymeric substances would be approximately from 10^8 - 10^{10} dyn/cm². Forces of this order of magnitude are not found in studying polymer-polymer adhesion and, therefore, considerable time has been spent rationalizing the lower measured adhesion forces.

Bikerman (1970) explains low adhesive forces by postulating the existence of weak boundary layers. Huntsberger (1967) and many others feel that poor (limited) interfacial contact causes poor adhesive performance. Low values are also often related to the various destructive bond-breaking techniques used to measure adhesion, as these techniques tend to concentrate the applied stresses. A complete stress analysis is impossible to perform due to the unknown surface geometries.

Several authors as Hamilton, (1972), Tempel (1972) and Good (1967) have shown that polar and nonpolar forces should contribute to adhesive strengths. However, in most cases the introduction of polar groups into a surface and resultant increases in strength have been interpreted in terms of better wetting contact. It was shown in this paper that the increase in polar forces could be used to predict directly the resultant increases in measured joint strengths.

Using the geometric mean approximation for polar interactions employed by Dahlquist (1969), the following expression is obtained:

$$I_{SW} = \left(\gamma_S^p \ \gamma_W^p\right)^{1/2} \tag{1.73}$$

Since I_{SW} can be easily determined by Equation (1.72) above and γ_W^p for water has been shown to be 50.2 dyn/cm, then Equation (1.73) can be used to determine γ_S^p , the polar contribution to the surface free energies of solids.

Adhesive strengths equal to the predicted work of adhesion are rarely if ever encountered, due to such factors as stress concentration during joint breaking and limited interracial contact. Therefore, the calculated work of adhesion cannot be used to predict joint strength. However, with any given polymer, the increase in joint strength obtained by introducing polar groups or by increasing the number of polar groups can be predicted by determining the work of adhesion for each case and taking the ratio.

Hamilton (1972 and 1974) has proposed the use of octane contact angles under water to determine the polar character of solid surfaces, and has shown that such contact angles should be independent of surface free energy for surfaces with no polar character. This arises because the dispersive force contributions to the surface free energies of octane and water are fortuitously equal. Hamilton calculated a contact angle of 50° for nonpolar surfaces, and showed that any deviation from 50° could be correlated with the polar nature of the surface being studied.

Bagnal and Green (1979) believed that Hamilton's technique was a particularly useful and sensitive method for determining the polar nature of unknown surfaces, but they claimed that their work suggested that the contact angle with nonpolar surfaces should have been 0° rather than 50°. Hamilton's observed contact angle of 50° with the three nonpolar surfaces polytetrafluoroethylene, polyethylene, and polypropylene was due to a small polar character of the order of 1.0 to 1.5 dyn/cm rather than to any inherent property of nonpolar surfaces.

In particular, Hamilton used Equation (1.37) for the contact angle on nonpolar surfaces, where γ_W' is the surface tension of octane/saturated water, γ_O is the surface tension of water/saturated octane, γ_S^d , γ_W^d , and γ_O^d are the dispersive components of the surface free energies of the solid, water, and octane, respectively, and γ_{WO} is the water/octane interfacial tension. Since $\gamma_O^d = \gamma_W^d = 21.8 \text{ dyn/cm}$, Equation (1.37) reduces to Equation (1.40) which is independent of the nature of the solid surface.

$$\cos\theta = (\gamma'_W - \gamma_O) / \gamma_{OW}$$
(1.74)

According to Hamilton, γ'_W , γ_O and γ_{OW} values are 51.6, 21.8 and 48.3 dyn/cm respectively, so that $\theta = 50^{\circ}$. Any surface with polar character would then require an additional term I_{SW} to describe its polar interaction with water, as shown in Equation (1.72). I_{SW} will always increase θ , and Hamilton suggested that this increase should be correlated with I_{SW} , and hence with the polar nature of the surface under test.

 θ was recalculated from Equation (1.74) using Hamilton's figures, and the result was 51.9° for θ , rather than 50°. More importantly, however, they considered γ'_W to be rather low, and have recalculated it from Equation (1.75), the Fowkes expression for interfacial tension when only dispersive interactions are involved.

$$\gamma_{WO} = \gamma_W' + \gamma_O - 2(\gamma_W^d \gamma_O^d)^{1/2}$$
(1.75)

Using the more generally accepted value of 50.8 dyn/cm for γ_{WO} , γ'_W should be 72.6 dyn/cm, i.e., indistinguishable from that of pure water, and this confirmed by the ring detachment technique, using alumina-treated octane with triple-distilled water, and charcoal-treated deionized water. It is possible therefore, that the low value of 51.6 dyn/cm reported by Hamilton may have been caused by impurities in the samples used. Inserting these new values into Equation (1.75) the result was θ should be 0° for surfaces with only dispersive character.

To correlate deviations from 0° with the polar nature of any unknown surface, Equation (1.75) was used where the term I_{SW} in Equation (1.74) has been replaced by a geometric mean in which γ_s^p and γ_W^p are the polar components of the surface free energies of the solid and water, respectively, and γ_W^p is 50.8 dyn/cm.

$$\cos\theta = \left[\gamma_{W}^{\prime} - \gamma_{O} - 2\left(\gamma_{W}^{p} \gamma_{S}^{p}\right)^{\frac{1}{2}}\right] / \gamma_{WO}$$
(1.76)

The use of such a geometric mean for polar interfacial interactions has been supported in the work (Schultz et al., 1977b and Kaelble and Uy, 1970) and it was separately confirmed its general experimental validity for the contact angle in water technique using several polymer surfaces and a range of liquid drops.

From the new values above, Equation (1.76) can be solved for γ_s^p as a function of. It can be seen that an observed contact angle of 50° may be accounted for by a polar surface free energy component as low as 1.6 dyn/cm, and the surface properties of polytetrafluoroethylene and polyethylene, are consistent with this.

As a result, Bagnall and Green would suggest therefore that Hamilton's observed contact angle of 50° on polytetrafluoroethylene, polyethylene, and polypropylene might be due to the fortuitous choice of surfaces with a polar free energy component of 1.0 to 1.5 dyn/cm, rather than to any fundamental property of surfaces interacting by dispersive forces only.

1.7 Spreading Pressure

The equilibrium spreading pressure (also called surface pressure and film pressure) is defined as

$$\pi_e = \gamma_{\rm S} - \gamma_{\rm SA} \tag{1.77}$$

where $\gamma_{\rm S}$ is the surface free energy of the solid in vacuum, and $\gamma_{\rm SA}$ is that of the solid in equilibrium with the saturated vapor of the liquid. In a statistical mechanical treatment of π_e , the energy and entropy of transfer of molecules from the bulk liquid is considered to the adsorbed state. Thus π_e is a lowering of surface free energy, accompanying adsorption of the vapor on the solid surface. The determination of $\gamma_{\rm S}$ and $\gamma_{\rm SA}$ is not usually possible but the surface or spreading pressure, π_e , may be obtained indirectly by some methods.

The spreading pressure π_e , is the equilibrium film pressure of the adsorbed vapor of the liquid on the solid. It corresponds to the reduction of the surface free energy of the solid when in contact with the saturated vapor of the wetting liquid. Generally, π_e is assumed to be zero for low-energy surfaces such as polymers, so that,

 $\gamma_{\rm S} = \gamma_{\rm SA} \tag{1.78}$

In contrast, there have been several experimental studies which have shown large values for low-energy surfaces, and it was suggested that, to some extent, a spreading pressure might exist even if finite contact angles were observed. This is a very important value since it is related to the surface free energy of the solid . The unit of spreading pressure is one of the following units dyn/cm, mN/m, erg/cm^2 and mJ/m² which are equal to each other.

The effect of the spreading pressure on contact angle is important since spreading pressure does not only reduces the spreading effect of the solid surface on the drop by an energy π_e , but also reduces the resistance of the solid/liquid interface of the drop to being spread, by an equal energy of π_e .

Young-Dupre equations for all six cases (Figure 1.25) including spreading pressure values, are given in Equations (1.79) - (1.84).

 $\gamma_{SA} = \gamma_{SW} + \gamma_{WA} \cos \theta_1 - \pi_1 \tag{1.79}$

$$\gamma_{SW} = \gamma_{SA} + \gamma_{WA} \cos \theta_2 + \pi_2 \tag{1.80}$$

$$\gamma_{SA} = \gamma_{SO} + \gamma_{OA} \cos \theta_3 + \pi_3 \tag{1.81}$$

$$\gamma_{SO} = \gamma_{SA} + \gamma_{OA} \cos \theta_4 - \pi_4 \tag{1.82}$$

$$\gamma_{SW} = \gamma_{SO} + \gamma_{OW} \cos\theta_5 + \pi_5 \tag{1.83}$$

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW} \cos \theta_6 - \pi_6 \tag{1.84}$$



Figure 1.23: Interfacial free energies in a solid/vapor/liquid system, showing the effects of spreading pressure on the interfacial free energies.

The spreading pressure term, given in Figure 1.23, π_e , can be assumed to be zero only for the system, where high-energy liquids are brought in contact with lowenergy solids (Figure 1.24). The basic reason for this assumption is that all theoretical and experimental evidence predicts that adsorption of high-energy materials cannot reduce the surface energy of a low-energy material. For example, adsorbing water never reduces the surface tension of a liquid hydrocarbon. The fact that a given liquid has a contact angle greater than zero degree on a given low-energy solid asserts that the liquid possesses a higher energy and therefore π_e should be zero. This holds true only for the solids interacting by dispersion forces only. It does not apply for the high-energy solids such as metals, graphite; water does not wet these solids but it does absorb and produce appreciable π_e .



Figure 1.24: Contact angle of a sessile drop: a) neglecting the spreading pressure b) accounting for spreading pressure.

The spreading pressure may not be taken into account in some cases. This pressure gives the contribution to surface free energy of the adsorption of an external layer from the atmosphere and has to be calculated for surface free energy calculation correction if surface free energy is higher than 60 mJ/m² (van Oss, 1996).



Figure 1.25: Contact angle schematic including related vectors.

1.7.1 Methods to Calculate Spreading Pressure

1.7.1.1 BET Adsorption Isotherms

The spreading pressure is one of the terms of the Young equation. A normal case consists of a drop of water at a certain vapor pressure on a solid surface. In order that this system is in thermodynamic equilibrium that is stable in time with no loss or gain of water to the vapor phase, the equilibrium vapor pressure should be the same as that of the water of the drop. The value of the vapor pressure (P/P₀) of pure water of a drop is almost equal to 1 at 25° C since a drop of water of a radius of 105 cm. has only a P/P₀ value 1% greater than a flat surface of pure water as the Kelvin equation would indicate. The Young equation for the above-described system is therefore only valid at this single vapor pressure. This conclusion becomes obvious writing the Young equations for different values of vapor pressure:

$$\pi_e = -k_B T \int_{P_0}^{P} \tau d(\ln P)$$
(1.85)

where π_e is the spreading pressure, P is the vapor pressure, P₀ is the saturation vapor pressure, T is the temperature, and τ is the number of adsorbed molecules per unit area.

The spreading pressure may be obtained from either by a graphical integration, or by fitting the experimental isotherm to a polynomial of the form

$$\tau = a_1 p + a_2 p^2 + a_3 p^3 + \dots + a_n p^n$$
(1.86)

by a least-squares technique, followed by integration. A five or six-term polynomial was usually necessary for a very good fit.

To obtain the spreading pressure π_e , the amount adsorbed (x, mmol g/1) is plotted against ln P, and π_e is obtained by graphical integration according to the Gibbs equation, where R is the gas constant, T is the absolute temperature, and P is the pressure corresponding to the monolayer adsorption.



Figure 1.26: Adsorption isotherm of octane on PTFE-Teflon, by Whalen (1968).

According to graph in Figure 1.26, spreading pressure of octane on PTFE-Teflon powders was calculated as 0.343 mN/m by graphical integration method, which is in good agreement with other method's results.

1.7.1.2 Ellipsometry Determined Adsorption Isotherms

Ellipsometry involves the measurements of the effect of reflection on the state of polarization of light. The measurements can be interpreted to yield the optical constants of the reflecting material and, when this last is a filmcovered surface, the thickness of the film. The changes in the state of polarization of light upon reflection are represented by the changes in the amplitude and phase difference for beams polarized in the plane of incidence and perpendicular to it.

Adsorption isotherms can be recorded on flat, nonpowdered samples by ellipsometry, measuring the adsorbed layer thickness as a function of the vapor pressure as has previously been described by Adamson et al. (1964, 1974 and 1977).

Spreading pressures are subsequently calculated by direct graphical integration of the isotherm according to Equation (1.85).

There are limitations to the ellipsometric method. It applies to specularly reflecting flat and smooth surfaces. One may, however, measure film thicknesses ranging from 1 to 1000 A° to within a fraction of an angstrom. Thus, even submonolayer films may be observed, although the method is better suited to the multilayer region.

1.7.1.3 Inverse Gas Chromatography

A relatively new technique for studying the thermodynamic and interactive nature of solid surfaces is *"inverse gas chromatography"* (IGC). Here the solid is placed in a gas chromatographic column as the stationary solid phase. It may be as a film on the wall, coated on inert particles or as particulate or fibrous polymer. Probe gases of known as chemical nature arc introduced into the inert carrier gas stream and the retention time measured. Retention time is related to polymer probe interaction energy and the equilibria existing between adsorbed and gas phase molecules. The technique yields thermodynamic information, when used carefully, and can be used to establish adsorption isotherms.
1.7.2 Past Literature on Spreading Pressure

In 1940, Washburn and Keim (1940) reported a simple and sensitive method for determining the spreading pressure on water of any spontaneously spreading organic liquid compound. Their method, which is a logical extension of the "indicator" or "piston oil" technique of Cary and Rideal (1925) and Langmuir and Schaefer (1937) used a mono-molecular adsorbed film of a water-insoluble, nonvolatile, surface-active compound such as stearic acid, palmitic acid, or tristearin to function as a "piston film" on water for transmitting surface pressure. A small drop of the liquid the spreadability of which was being measured was placed in the middle of the area covered by the insoluble piston monolayer, where it formed a floating lens. As the liquid lens spread, the pressure it created was transmitted to the floating barrier of a Langmuir-Adam film balance. The film balance was adjusted by means of the floating and sliding barriers until the piston film allowed the spreading lens to become thin enough so that gravitational effects in the lens did not affect the film pressure. At that stage a slight displacement of the sliding barrier would expand or contract the thin lens without altering the film pressure indicated by the floating barrier. The observed constant pressure is defined as the "spreading pressure" on water of that liquid. Ellison and Zisman (1956) demonstrated that the piston monolayer method could be adapted to measuring the spreading pressure of compounds on organic liquid substrates. Important advantages of the piston monolayer method are: (a) only one drop of the organic liquid is required for each measurement; (b) the method is so rapid that it allows a reliable measurement to be made on compounds as volatile as benzene and hexane; and (c) measurements of sufficient accuracy can be made with a compact, rugged film balance. Since only a few minutes are needed for measurement of the spreading pressure, undesirable effects on spreading properties arising from oxidation or other chemical changes in the organic liquid are much decreased; this is an especial advantage in research on the spreading properties of unsaturated hydrocarbons or other oxidation-susceptible compounds. Washburn and co-workers (1940, 1942 and 1954) have pointed out that each of the pure volatile compounds investigated by them had a spreading pressure equal to the Harkins initial spreading coefficient. These compounds are: benzene, toluene,

ethylbenzene, the isomeric propylbenzenes and butyl-benzenes, 2,2,4trimethylpentane, isoamyl chloride, acetophenone, and diethyl carbonate. The equality of the spreading pressure and the initial spreading coefficient for each of four organic compounds spreading on a hydrocarbon liquid substrate was subsequently demonstrated by Ellison and Zisman (1956).

The spreading pressure of an adsorbed film on a low-energy solid on which the bulk liquid forms a nonzero contact angle, θ , has been a matter of controversy for years. Zisman and Fox (1950) concluded that π_e is probably negligible in most such systems. This was confirmed experimentally by Graham (1964 and 1965), Wade and Whalen (1968) and Whalen (1968 and 1971). Numerous authors have determined π_e by gas adsorption in systems where θ is zero; in every case, π_e was found to be large. For the n-alkanes on TFE-Teflon, it was reported that the trend of π_e , with chain length shows a discontinuity, which occurs at the same place in the series as the γ_c value of Fox and Zisman (1950). Adamson and Ling (1964) have suggested that the value of π_e may well be large in a system in which θ is greater than zero, provided the adsorbed layer has a high degree of structure. Adamson (1974) has reported 42 ergs/cm² for π_e of water on polyethylene; his experiments are in conflict with expectations based on earlier experimental work. These reports have led us to attempt a general prediction of the values of π_e and of the trend of π_e with carbon number in homologous series.

Good (1975) showed that with increasing carbon number, the predicted values of π_e , decrease strongly. For the lower alkanes than C₆, two-dimensional condensation occurs and a very important increase in π_e , for alkanes with low carbon number is observed. Indeed, one would expect a transition from Langmuir to multilayer adsorption below hexane. This is exactly what was found by Graham (1964 and 1965). Thus, it is no coincidence that in the n-alkane series on TFE-Teflon, the value of γ_c (Zisman 1952) is about 18 ergs/cm², which lies between the surface tensions of pentane and hexane. The values of π_e for the alkanes on Teflon TFE are lower than those reported in the literature. For example, Whalen (1968 and 1971) has found $\pi_e = 2.9 \text{ ergs/cm}^2$ for n-octane; compare this to Good's estimate of 2×10^{-2} on a molecularly flat fluorocarbon surface. On a Teflon surface, Good estimated $\pi_e = 0.15 \text{ ergs/cm}^2$ for n-octane. Further hypotheses of geometric complexity of the surface would lead to yet higher values of π_e and introduction of a small amount of heterogeneity in chemical composition would have an effect in the same direction. It is known that TFE-Teflon powder contains micropores and hydrophilic sites (Zettlemoyer, 1956). So the greater complexity required to account for the difference between predictions and the observed results is consistent with what is known about the surface. (The complex configurations hypothesized, however, would be on too small a scale to be observed directly with electron microscopy). Therefore, the experimental results can be considered as substantiating the prediction.

Ratner (1981) expressed that, a common assumption in contact angle analyses of surface properties is that the spreading pressure is negligible. This is not necessarily true for hydrophilic surfaces in air, especially those with both polar and nonpolar groups, in the presence of low-energy liquid drops.

Busscher (1983) investigated the effect of spreading pressure on surface free energy determinations by means of contact angle measurements. Contact angle measurements have been carried out on various solid substrates using water-propanol mixtures and 1-bromonaphthalene as wetting liquids. These substrates were polytetrafluorethylene, parafilm, polyethylene, polyurethane, polystyrene, poly(methyl methacrylate), fluorapafite, and hydroxyapatite. The dispersion and the polar components of the surface free energy, γ_{s}^{p} and γ_{s}^{d} have been calculated from the geometric mean equation, Two approaches have been considered: Neglecting the spreading pressure π_{e} and taking π_{e} into account (Dann, 1970). The results show that both approaches actually yield the same results for the surface free energy, γ_{s} , if a proper interpretation of the approaches is considered. Busscher used the Geometric mean approach in order to obtain the spreading pressure. First, the γ_s^d is determined by using a contact angle with an apolar liquid, and then the contact angle with a series of water-propanol mixtures is obtained.

Using ellipsometrically determined adsorption isotherms, Hu and Adamson (1977) calculated spreading pressures employing a Polanyi potential function. For the water-polyethylene system as well as for the propanol-polyethylene system 14 erg/cm² was

found. Unfortunately, few data is presented for polar liquids on polar substrates. The determination of adsorption isotherms and subsequent π_e values on polar surfaces for various liquids will be carried out in the near future. Comparing the data of Hu on PE with Busscher's results, one can see that Busscher's π_e values are smaller. This might be due to the fact that Hu introduced hydrophilic groups during sample higher adsorption. Busscher reported that an preparation resulting in а interpretation of $\gamma_{\rm S}$ values determined by neglecting π_e as $\gamma_{\rm SA}$ values gives consistent results with methods of calculations that take π_e into account. Various points in the analysis show that if water-propanol mixtures are employed for wetting experiments, π_e can (in a first approximation) be considered as constant. Surface free energies determined by contact angle measurements are in reasonable agreement with the few available surface free energies obtained by employing independent techniques and theories.

Later, Erbil (1989) combined the results obtained from both the one-liquid and the two-liquid methods (where the contact angle with one-liquid is measured in presence of another immiscible liquid and not air), in order to determine π_e values. He applied geometric mean approach to obtain the spreading pressure of water/polymer interactions. Erbil resulted in the effect of the spreading pressure, π_e , on the surface tension determination of polymers should not be neglected in the one-liquid method. For two liquid phases in contact with a solid in the two-liquid method, both spreading film pressures of the solutes arising from the mutual solubilities in each other are found to be negligible when compared with the spreading pressure of any liquid vapor in thermodynamic equilibrium in the one-liquid method. The results obtained from both the oneliquid and the two-liquid method can be combined in order to determine π_e values. The π_e values determined with this method are in agreement with which the values reported in the literature were determined from ellipsometrically measured adsorption isotherms.

In Erbil's work, π_e values for PTFE-Teflon found as 6.6 and 8.2 erg/cm² and compared with the values reported by Hu and Adamson (1977) determined from ellipsometrically measured adsorption isotherms as 8.8 erg/cm², very good

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agreement is obtained. Busscher et al. (1986) reported 9.0 erg/cm² for water/PTFE-Teflon and 26.0 erg/cm² for the water/PMMA interactions. The new value reported by Erbil for PMMA is 16.3 erg/cm², which is approximately 63% of the value reported by Busscher et al. Busscher et al. (1986) pointed out that many difficulties are encountered in transforming the measured ellipsometric parameter into the adsorbed layer thickness and the precision of such adsorption measurement is questionable; thus, it is reasonable that we cannot expect the same now values at this stage from the literature. However, the agreement of the values reported in this work with the independent adsorption results shows that the π_e values for the one-liquid method are sufficiently large that they cannot be neglected. The controversy regarding the application of the equation of state approach (Neumann, 1987), geometric-mean equation (Owens, 1969 and Kaelble, 1970) and harmonic-mean equation (Wu, 1970 and 1973) and the rejection of the use of contact angle data in the determination of the polymer surface tension due to the acid/base interaction concept (Fowkes, 1987) should be clarified after considering the π_e values determined from adsorption measurements or from this combined one, and the and Ling (1964) pointed two-liquid methods. Adamson out that thermodynamically, only the difference γ_S - $\gamma_{SL},$ has significance and that ${\gamma_S}^0$ - γ_{SL} , need not be viewed as the difference of independent quantities. The difference $\gamma_{\rm S}^0$ - $\gamma_{\rm SL}$, can be viewed as arising from the local interactions between the molecules in the solid/vapor and solid/liquid phases.

Some researchers have expressed objections to the reasoning behind the splitting up of the polymer surface tension into components (Bikerman, 1971 and Neumann, 1987). Later, Fowkes (1987) has completely rejected the use of contact angle data in polymer surface tension determination. Van Oss et al. (1987) proposed a methodology to calculate the acid/base interactions from contact angle data. However, it is a common fact that in all of these approaches, the spreading pressure, π_e , which is the equilibrium film pressure of the adsorbed vapor of the liquid on the solid, is assumed to be zero for low-energy surfaces. In contrast, there have been several experimental studies which have shown large π_e values for low-energy surfaces, and it was suggested that, to some extent, a spreading pressure might exist even if finite

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contact angles were observed (Melrose, 1964; Zettlemoyer, 1968; Tadros, 1974 and Hu and Adamson, 1977). Dann (1970) has taken π_e into account in the geometric-mean approach. Good (1975) proposed a theory for calculating the spreading pressure. Busscher et al. (1983, 1985 and 1986) examined the effect of π_e on the surface tension determination of polymers. Busscher and co-workers used water-n-propanol mixtures as the probe liquids. However, they made too many assumptions such as $\gamma_s^p=0$ for parafilm when $\pi_e = 0$, $y_L^p = 0$ for 1bromonaphthalene $\pi_e = 0$ for apolar liquids, and π_e was constant and did not depend on the composition of the water-n-propanol mixtures. Their method is useful for pointing out that similar values are obtained for π_e and $\gamma_s^0 - \gamma_{SV}$, when γ_{SV} is calculated by assuming that $\pi_e = 0$.

The equilibrium film pressure π_e causes a decrease of the surface energy of solids by substances which are adsorbed from the gaseous phase. The decrease of the surface free energy by adsorption phenomena is generally neglected due to a lack of experimental values of π_e . However, the striking dependence of the surface free energy of cellulosic fibers on the relative humidity of air (Goebel 1976) as well as the spreading pressure of alkanes PTFE-Teflon measured by Davis (1977) indicate that the influence of the adsorption on the surface free energy of polymers is considerable. Adamson et al. (1977 and 1983) demonstrated, by means of ellipsometry, that even at apolar polymers a significant adsorption of vapor of water and organic liquids takes place, which results in a decrease of the surface free energy. Hence, the values of the surface free energy of polymers determined by contact angle measurements are likely to be always smaller than the theoretical value. All technical processes which are interpreted by means of contact angle measurements are performed in a moist atmosphere. Thus, the surface free energies of the polymers involved in the process are also decreased by the adsorption of water vapor. Hence it is not surprising that experiments often showed a correlation between the surface free energy and the course of the technical process.

Erbil (1994) proposed a novel analysis to determine the spreading pressure, π_e , for water/polymer interactions from contact angle data by using van Oss et al.'s

interfacial Lifshitz-van der Waals and acid base interactions by combining the oneliquid and two-liquid contact angle methods in 1994 .In this analysis, first measurements of the contact angles of water drops on the polymer in different hydrocarbons in the two-liquid method are performed; then the contact angle determination of a water drop on the same polymer sample in the one-liquid method is carried out. The data obtained from the one-liquid method are evaluated by using the data obtained from the two-liquid method in order to calculate π_W . The precise contact angle data on polytetrafluoroethylene (PTFE-Teflon), poly(methyl methacrylate) (PMMA), and poly(vinychloride) (PVC) reported by Tamai et al. (1967) are used in the calculations and good agreement is obtained with the π_W , data obtained from independent adsorption measurements.

Most of the methods use either the Geometric mean approach or Lifshitz van der Waals acid/base approach. The equation of state approach applies to ideal solids, which does not absorb vapors essentially true for low-energy solids, e.g. Teflon, etc. However, deviation of some of the points from the γ_{LV} vs. $\gamma_{LV} \cos\theta$ curves gives a possibility to determine the spreading pressure.

The water spreading pressure on PTFE-Teflon is not equal to zero, it is 6.2 mJ/m^2 and is in good agreement with the published data from ellipsometric measurements and the results obtained from different calculation routes (Busscher, 1986; Erbil, 1989 and Adamson, 1977).

Water has a spreading pressure of 18.58 mJ/m^2 on PMMA which is in good agreement with values reported in references (Busscher, 1986 and Erbil, 1989). It is approximately 71% of the value reported by Busscher et al. (1986) from ellipsometrically measured adsorption isotherms.

In this study, Erbil has determined only π_W values for water/polymer interactions. However, it is also possible to calculate π_e values of hydrophobic liquids on polymers when the reverse two-liquid method (i.e. hydrocarbon drops formed by inverted needles in water, which is well known for characterizing hydrophilic polymers) is applied simultaneously with the one-liquid method in which hydrocarbon drops are used.

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Erbil concluded on two points. In the one-liquid method, π_e should not be neglected. The results obtained from both the one-liquid and the two-liquid methods can be combined to determine π_e values using Van Oss et al. methodology. The π_W values for water/polymer interaction obtained by this method are in agreement with the values reported in the literature which were determined from ellipsometrically measured adsorption isotherms.

Lee (1999) demonstrated the spreading pressure and interfacial film pressure to be profoundly relevant to interfacial tension, miscibility of liquids, and the Lewis acid/base approach. For immiscible liquid/solid and liquid/liquid systems, we prefer to employ Harkins' spreading model containing the equilibrium spreading pressure π_e . With the inclusion of π_e , one can also improve the Lewis acid–base approach for hydrogen-bonding, proposed by van Oss, Chaudhury, and Good. Lee established an acidity–basicity scale for the initial surface tension by taking π_e into account, and we further calculate interfacial tensions for liquid pairs containing formamide or dimethyl sulfoxide (DMSO) with dispersion components cited in Fowkes et al.'s publication.

Bangham and Razouk (1937a and 1937b) first observed the effect of vapor of the liquid adsorbed on the solid on surface energy, and they have indicated that the equilibrium spreading (or film) pressure π_e of the adsorbed layer on the solid surface tends to lower the equilibrium work of adhesion W_A of the solid. Bangham and Razouk pointed out the importance of not neglecting the adsorption of vapor on the surface of the solid phase in deriving the equilibrium relation concerning the contact angle.

For high surface energy liquids, e.g., mercury, the equilibrium spreading pressure has been shown by Harkins et al. (1942) and Xu et al. (1995) to be substantial. However, Good (1975) has claimed that π_e is probably negligible for pure liquids forming a nonzero contact angle on homogeneous, low surface energy solids. For simplicity, van Oss, Chaudhury and Good (1989, 1987 and 1991) also discounted the equilibrium spreading pressure, especially in their Lewis acid–base methodology.

Hirasaki (1993) has compiled a list of spreading coefficients and π_e 's for liquids on water, consisting of published data by Harkins (1952), Ottewill (1951), Shewmaker

et al. (1954) and Dettre and Johnson (1966). Hirasaki noted that the theoretical equilibrium spreading pressures on water for benzene, toluene, o-xylene, and chloroform are much lower than the corresponding experimental values. However, those differences could be narrowed by considering acid–base interactions. Shewmaker et al. (1954) also noticed that Harkins' spreading pressures were determined in the presence of the vapor of a liquid; therefore, Harkins' values were different from his. For example, his π_e for the benzene/water system as 9.0 dyn/cm² instead of 10.5 dyn/cm².

Xu (1995) estimated the spreading pressure of water π_W on mercury to be 32 mJ/m² from the interfacial tension in comparison with some experimental value of 25 mJ/m² obtained by other workers (Harkins, 1952). This is a typical immiscible liquid–liquid system to which the spreading model applies. There are other methods for determining π_e at the immiscible liquid–solid interface, such as vapor adsorption (Tadros, 1968) and ellipsometry (Busscher, 1986).

After Lee contemplated the vapor adsorption on PMMA to be substantial, he found many revealing results. There have been several reports claiming that the vapor of polar (Tamai 1967, Bellon-Fontaine 1990) as well as apolar liquids (Erbil, 1994 and Berg, 1995) can be readily adsorbed on PMMA. Furthermore, the adsorption was rather substantial, resulting in high π_e 's. Bellon-Fontaine and Cerf (1990) examined the adsorption of several liquids on four polymers, including PMMA. They indicated that their results had an experimental error of $\pm 12 \text{ mJ/m}^2$. The validity of their results may be in question, because of their use of mercury as the reference. In comparison with the data generated by other workers (Tamai, 1967; Busscher, 1986 and Bellon-Fontaine, 1990), their results do appear somewhat high, so Lee used the lower limit of their π_e 's for calculations. For example, the lower limit of π_W for PMMA is 23.0 mJ/m² which is comparable to the value of 26.0 mJ/m² obtained by Busscher et al. (1986) and 18.6 mJ/m² by Erbil (1994). The lower limit π_e values are 31.7 mJ/m² for formamide and 27.3 mJ/m² for glycerol. In addition, for ethylene glycol, Lee estimated π_e by plotting π_e versus γ_L of different liquids.

The water-propanol mixture surface tension parameters are obtained by contact angle measurement on paraffin wax surface $\gamma_8^d = 25.5 \text{ mJ/m}^2$ and $\gamma_8^p = 0$. Bellon-Fontaine

and Cerf (1990) also evaluated the spreading pressure using the fact that the work of adhesion, W_A , is a maximum value when there is no vapor adsorption on the solid surface. A plateau region is observed in the plot between the work of adhesion W_A and γ_{LV} for different liquids on the solid surface. The spreading pressure is determined from the difference between the plateau work of adhesion and the work of adhesion of the liquid.

It should be pointed out that most surface tensions or surface free energies for solids and polymers determined earlier without the inclusion of π_e are essentially γ_{SV} 's. Thus, if π_e 's are substantial, the initial surface tensions of solids and polymers should be higher than corresponding surface tension data obtained earlier in the presence of a vapor.

Lee has demonstrated that the Harkins' spreading model is applicable to immiscible liquid–solid interface and immiscible liquid–liquid interface. For the immiscible interface, we included the equilibrium spreading pressure π_e in some familiar interfacial tension formulations, which are applicable to liquid–solid as well as liquid–liquid interfaces. However, for the initially immiscible liquids, which become miscible later, he needed to propose an adsorption model. According to this adsorption model, the interfacial tension for the initially immiscible liquid–liquid interface varies between the initial and the equilibrium states, and surface tensions of two bulk liquids at a distance from the interface remain constant. The difference between the initial and equilibrium interfacial spreading coefficients equals the equilibrium interfacial film pressure, π_e , and that equals the difference between the interfacial tensions. It is noteworthy that the discrepancy is not caused by π_e as shown in Harkins' model.

Spreading pressure is the reduction of the solid surface energy due to the vapor adsorption. In general, the approaches assume this term negligible, which is true for low-energy solids in contact with high-energy liquids (Fowkes, 1964a and 1964b). The spreading pressure term is significant for high-energy surfaces when the lowenergy liquid spontaneously spreads and forms a very thin layer in order to reduce the total energy of the system. It has been made possible to quantify the spreading pressure on polymer surfaces but spreading pressure quantification due to water bacterial surface has not yet been reported.

1.7.3 Published Values of Spreading Pressures with Different Methods

1.7.3.1 Water Spreading Pressures

Tadros (1974) has ellipsometrically determined the adsorption isotherms and reported them for water on polyethylene for relative pressures up to close to the saturation pressure, P_0 , and for various temperatures. Contact angle data on polyethylene was observed at 89° and spreading pressure was computed as 14.4 erg/cm² by Gibbs method.

He believed that their results establish that π_e is not always negligible in highcontact-angle systems, that π_e can vary considerably among systems having about the same contact angle, and therefore this term should be included in even first-order semi empirical treatments of contact angle and spreading phenomena.

Adamson (1977), by using ellipsometrically determined adsorption isotherms, reported spreading pressure for water, n-octane and n-hexane on a polished polytetrafluoroethylene and polyethylene surface. These are nonwetting systems, and contact angles were also measured. The experimental π_e values, that is, the values calculated from the Gibbs area under the measured adsorption isotherms, are given as 8.8 and 14.0 ergs/cm² as water on PTFE-Teflon and PE respectively. Adamson also reported that hexane and octane values on PTFE-Teflon as 5.3 and 1.8 ergs/cm². Their water contact angle value on PTFE-Teflon was 98°, is 10 to 15° lower than frequently reported values. They did find the more usual value of 109° for the unpolished PTFE-Teflon and it may be either that there is a roughness effect or that flow-smoothing method introduced polar sites to the surface. Their data for n-hexane and n-octane give $\gamma_S{}^d$ values of 17.6 and 19.0 ergs/cm², respectively, if π_e is neglected. If π_e is not neglected, the values of 23.2 and 20.8 $ergs/cm^2$ are obtained. The average values of $\gamma_S{}^d$ a are 18.3 and 22.0 ergs/cm² according to whether π_e is or is not neglected; there is again a significant effect.

Spreading pressure values found in the literature were listed in Table 1.1, according to different methodologies.

Substrate	Spreading Pressure (π_1)	Researcher	Methodology	
	(mJ/m)			
PTFE-	8.8	Adamson, 1977	Ellipsometric	
Teflon	9.0	Busscher, 1986	Ellipsometric	
	6.2	Erbil, 1994	Contact Angle	
	6.6 and 8.2	Erbil, 1989	Contact Angle	
	0-10	Binks, 1995	n/a	
	11	Lee, 1999	n/a	
PMMA	26	Busscher, 1986	Ellipsometric	
	18.58	Erbil, 1994	Contact Angle	
	16.3	Erbil, 1989	Contact Angle	
	35	Bellon-Fontaine, 1990	n/a	
	35	Lee, 1999	n/a	
PP (PE)	14.0	Adamson, 1977	Ellipsometric	
	14.4	Tadros, 1974	Ellipsometric	
РС	33	Busscher, 1986	Ellipsometric	
	34	Meyer, 2001	IGC	
Glass	120	Whalen, 1961	BET Adsorption	
	141	Busscher, 1986	Ellipsometric	
	35	Chibowski, 1988	Ellipsometric	

Table 1.1: Published water spreading pressure values for substrates.

Busscher (1986) dealt with spreading pressures of water on polytetrafluoroethylene, polystyrene, poly(methyl methacrylate), polycarbonate and glass are determined from ellipsometrically measured adsorption isotherms by graphical integration, yielding for water 9, 37, 26, 33, and 141 erg/cm² on PTFE-Teflon, PMMA, PC and glass, respectively.

For glass, Chibowski (1988) reported spreading pressure of water film π_W , as 35 mJ/m² and spreading pressure of n-octane as 10 mJ/m². Water spreading pressure does not correlate well with the Busscher's results as he reported 141 mJ/m² for π_W . On the other hand, Busscher's value is in good agreement with Whalen's value as 120 erg/cm² obtained from BET water vapor adsorption calculations.

In Erbil (1989) method, following work was performed; first measurement of the contact angles of water drops on the polymer in different hydrocarbons in the two-liquid method was performed; then the contact angle determination of a water drop on the same polymer sample in the one-liquid method was carried out. The data obtained from the one-liquid method are evaluated by using the data obtained from the two-liquid method in order to calculate π_W .

Erbil, when π_W values for PTFE-Teflon found as 6.6 and 8.2 erg/cm² and compared with the values reported by Hu and Adamson (1977), determined from ellipsometrically measured adsorption isotherms as 8.8 erg/cm², very good agreement is obtained. Busscher et al. (1986) reported 9.0 erg/cm² for water/PTFE-Teflon and 26.0 erg/cm² for the water/PMMA interactions. The new value reported by Erbil for PMMA is 16.3 erg/cm², which is approximately 63% of the value reported by Busscher et al.

Erbil (1994) urged that water spreading pressure on PTFE-Teflon is not equal to zero, it is 6.2 mJ/m^2 and is in good agreement with the published data from ellipsometric measurements and the results obtained from different calculation routes (Busscher, 1986; Erbil, 1989 and Adamson, 1977).

Water has a spreading pressure of 18.58 mJ/m^2 on PMMA which is in good agreement with values reported in references (Busscher, 1986 and Adamson, 1977). It is approximately 71% of the value reported by Busscher et al. from ellipsometrically measured adsorption isotherms (Busscher 1986).

Binks (1995) investigated adsorption of semifluorinated alkanes at hydrocarbon/air surfaces. According to Binks, for SFA films at hydrocarbon/air surfaces, the maximum surface pressure is expected to be of the order of the difference in surface tension between hydrocarbon/air and fluorocarbon/air surfaces (typically 10.0 mN/m or so). This data is comparable with our substrate Teflon as both are having fluorinated molecular structure.

Lee (1999) reported spreading pressures of water on PMMA and PTFE-Teflon surfaces as 35.0 and 11.0 mJ/m², respectively.

1.7.3.2 Spreading Pressures of n-Alkanes

Spreading pressure values found in the literature were listed in Table 1.2, according to different methodologies.

Graham (1964) used polypropylene powder as adsorbent. Adsorption isotherms were obtained by using ethane as adsorbate. Film pressures, or changes in the surface free energy with adsorption, were calculated from the adsorption data for a coverage of one statistical monolayer by graphic integration of the Gibbs equation. The value obtained for ethane was 14.0 ergs/cm². The hydrocarbon polymers, of which polypropylene is one, are low-energy solids, but are more strongly bonded than the perfluorocarbon polymers.

Graham (1965) calculated film pressures or changes in the surface free energy with adsorption were calculated from the adsorption data for a quantity of adsorbate equivalent to one complete monolayer by graphic integration of the Gibbs equation as described by Harkins. He made experiments of adsorption of n-octane with spreading pressures for a complete monolayer. It does not spread on polytetrafluoroethylene and developed only 1.7 ergs/cm² with deposition of a quantity equivalent to monolayer.

Whalen (1967) measured immersion heats for Teflon 6 in a homologous series of hydrocarbons from hexane to hexadecane have been obtained in a joint calorimetric program. Thermodynamic interrelationships between energetic quantities derived from immersion heats of clear and film-covered surfaces and contact angle data have been examined. Temperature derivatives for spreading pressures and contact angles have been estimated for the systems studied. By using Gibbs spreading pressure equation related to heat of immersion, he concluded in spreading pressure terms are negligible for paraffin hydrocarbons of ten or more carbon atoms. Where significant adsorption occurs, the temperature derivative of the spreading pressure is negative and of the order of 0.01 erg/cm² deg⁻¹.

Substrate	Spreading Pressure (π_3)	Researcher	Methodology	
	(mJ/m)			
PTFE-	1.7 n-octane	Graham, 1965	BET Adsorption	
Teflon	0.7 n-octane	Davis, 1977	n/a	
	0.15 n-octane	Good, 1975	Contact Angle	
	0 for C ₁₀ C ₁₄ C ₁₆	Whalen, 1967	BET Adsorption	
	3.28 hexane, 2.95 n-octane	Whalen, 1968	BET Adsorption	
	5.3 hexane, 1.8 n-octane	Adamson, 1977	Ellipsometric	
PMMA	n/a	n/a	n/a	
PP (PE)	14 ethane	Graham, 1964	BET Adsorption	
	n/a	Tse and Adamson,	Ellipsometric	
		1979		
PC	n/a	n/a	n/a	
Glass	10 n-octane	Chibowski, 1998	Ellipsometric	

Table 1.2: Published spreading pressure values of alkanes.

Whalen (1968) later in 1968, investigated adsorption on low-energy surfaces. Hexane and octane adsorption on polytetrafluoroethylene were performed and Gravimetric isotherms at 25°C for hexane and octane on PTFE-Teflon were presented. Spreading pressure values have been resolved to a reasonable approximation for hexane and octane adsorption on polytetrafluoroethylene, supporting efforts to relate energetic measurements and contact angle values 3.28 and 2.95 ergs/cm² values were reported for hexane and octane, respectively, by Whalen.

Good (1975) made computations on surface pressure of n-octane on PTFE-Teflon and estimated π_e as 0.15 erg/cm²

Adamson (1977) reported that hexane and octane values on PTFE-Teflon as 5.3 and 1.8 ergs/cm^2 by using ellipsometry as spreading pressure determination method.

Davis (1977) reported that n-octane film pressure on PTFE-Teflon as 0.7 dyn/cm by using Good and Grifalco approach.

Tse and Adamson (1979) ellipsometrically determined the adsorption isotherms and reported for n-hexane on optically smooth polyethylene at 20°C. The contact

angle behavior of the corresponding liquid substrates on the same surface was also determined. n-hexane isotherms did not fit the characteristic isotherm well so that π_e could not be published.

Chibowski (1988) made ellipsometric experiments on determining film pressure of n-octane on glass surfaces and reported the spreading pressure of n-octane as 10.0 mJ/m^2 .

1.8 Scope of Thesis

The purpose of the study is investigating the sources of the discrepancies from the ideal conditions, when combining one-liquid and two-liquid contact angle data on the same polymer and glass substrates by using the same immiscible fluid couples. In this method, first, measurement of the contact angles of water and different oil drops on the polymer and glass surface in different hydrocarbons and water in the twoliquid method is performed; then the contact angle determination of a water or oil droplet on the same polymer and glass sample in the one-liquid method is carried out. The data obtained from the one-liquid method are evaluated by using the data obtained from the two-liquid method in order to calculate discrepancies from the ideal conditions. These discrepancies were explained according to the surface properties. In addition, these deviations were attributed to semi-empiric models. In the study, on FEP-Teflon, polypropylene (PP), poly(methyl methacrylate) (PMMA), polycarbonate (PC) and glass surfaces, one-liquid and two-liquid contact angle values were measured by using different liquids and immiscible fluid couples. Summation of both results was compared to examine deviations of difference from ideal condition, total of 180°, for the complementary cases.

2. EXPERIMENTAL

2.1 Materials

In this work, commercially available polymers were used. For this purpose, FEP-Teflon, Polypropylene (PP), Poly(methyl methacrylate) (PMMA), Polycarbonate (PC) and glass surfaces were used in the experiments. PP was obtained from IKEA. PC slides were supplied from BASF, Germany. PMMA as SANITALATE® Sanitary Acrylic Sheet was obtained from Polifen Kimya, Turkey and TEFLON® FEP-100 was obtained from DuPont Company, U.S.A. Glass slides as Plain Microscope Slides, SIS8902, were from Sigma-Aldrich. All the substrates were cut to 26x76 mm. microscope slide dimensions to be used in the experiments.

All substrates were cleaned with hexane to get rid of oils on the surface, following wiping with ethanol and then ended up rinsing with distilled water for about 5 min. The cleaned surface was wiped with Kimwipe sheets and then kept in a desiccator with phosphorus pentoxide until the experiments were accomplished. Polymers were in the form of plate sheets and their surface was satisfactorily flat.

1 ml. Hamilton syringes and needles were used in the experiments. Prior to use, both were flushed with hexane to get rid of the oils inside then washed trough distilled water. Different syringes and needles were used for different types of liquid groups to prevent cross contamination. Compatible and easily rinsable liquids were used in the same syringe, according to their carbon atom content, by starting at the lowest carbon content. Homologous series of alkanes were used in the same syringe while the series of alcohols were used in another. For water, a separate syringe was reserved. Two types of needles were used according to the type of the measurement. For contact angle under air measurement, standard needles were used, while for under water contact angle measurements, hooked (inverted) needles were used. For the surface free energy, liquid surface and interfacial tension measurements, standard and hooked needle were both used.

HPLC grade chemicals were used in the experiments. n-Heptane, n-octane, nnonane, n-decane, n-dodecane, n-hexadecane liquids were used in under air experiments as well as in under water contact angle experiments since they are immiscible against water. Chemicals were supplied from vendors Lab Scan, Ireland, Acros Organics, U.S.A., Merck, U.S.A., and JT Baker, U.S.A. All liquids were mutually saturated in a separatory funnel, overnight, and then poured into previously well-cleaned bottles with chromic acid.

The contact angles measured by using water, ethylene glycol, formamide, glycerol, paraffin, methylene iodide and 1-bromonaphtalane drops were used in the solid surface free energy calculations by using Zisman, Fowkes and acid/base equations, given in Sections 1.5.1.1, 1.5.1.2 and 1.5.1.3, respectively.

2.2 Instrumentation

2.2.1 Tensiometer

The measurement of surface/interfacial tension of liquids was performed by a tensiometer, which is based on force measurements of the interaction of a solid probe with the interface of a liquid or between two immiscible liquids. KSV Sigma 700 Tensiometer manufactured in Helsinki, Finland, was used during the experimental work (Figure 2.1).

The KSV Sigma 700 Tensiometer system is a modular high performance surface tension/contact angle meter. It expands from a basic all round tensiometer into a highly sophisticated precision measuring system for research and development applications. The KSV Sigma 700 Tensiometer system is a computer controlled tensiometer for the measurement of surface and interfacial tension. The instrument can also measure single force curve measurements with the du Noüy ring method, continuous surface tension measurements with the Wilhelmy plate method, critical micelle concentration, dynamic contact angles, powder and porous solid wettability, single fiber wettability, adsorption behavior of solids, surface free energies of solids, and density of liquids.



Figure 2.1: KSV Sigma 700 model multi purpose tensiometer.

In the experiments, a probe was hung on a balance and brought into contact with the liquid interface. The forces experienced by the balance as the probe interacts with the surface of the liquid were used to calculate surface/interfacial tension. The forces present in this situation depend on the following factors; size and shape of the probe, contact angle of the liquid/solid interaction and surface tension of the liquid. The size and shape of the probe are easily controlled.

For surface/interfacial tension measurements, the contact angle of the liquid towards the probe is controlled to be zero (complete wetting). This is achieved by using probes with high-energy surfaces. For example, probes made of a platinum/iridium alloy insure complete wetting and they can be very easily cleaned in a reliable way. The mathematical interpretation of the force measurements depends on the shape of the probe used. Two types of probes are commonly used for surface/interfacial tension measurements, the Wilhelmy plate and du Noüy ring.

2.2.2 Contact Angle Instrument

Contact angle is measured using a contact angle goniometer. Goniometers are imagebased instruments obtaining the capturing images of liquid droplets in air or air/oil bubbles in liquid for determining contact angles and surface/interfacial tensions of liquids.

In the experiments, KSV CAM 200 contact angle measuring instrument was used (Figure 2.2). This optic contact angle goniometer is a computer controlled and user programmable video-based instrument designed for the measurement of surface and interfacial tension, static and dynamic contact angles, as well as calculation of surface free energies of solids by using contact angle data. The instrument includes a firewire video camera, an adjustable sample stage, and a LED light source. The open design and modular construction allow the instrument to be adapted to a wide variety of applications.

A contact angle or a pendant drop experiment collects experimental data. A calibration must be made every time the focus has been altered, i.e. the zoom lens or aperture has been moved.



Figure 2.2: KSV CAM 200 contact angle measurement instrument at GYTE lab.

The software included with this instrument allows the data storage to the hard drive and can be retrieved and analyzed later. Data files can be exported to another data reduction software (i.e. Excel spreadsheet) than the one provided, if preferred.



Figure 2.3: A typical contact angle goniometer design.

The light source given in Figure 2.3, is LED based. The LED's are in a reflective sphere that integrates the light and directs it towards the sample. The light is monochromatic. These features help to assure a sharp image, even for moving objects, with minimal sample heating.

KSV CAM 200 can record up to 60 photo frames per second (fps) by using an interface firewire camera. The resolution of the camera is 512×480 pixels. A firewire cable runs from the body of the instrument to the camera and another attaches the CAM 200 to a computer.

The objective lens provided with the camera is telecentric with a 55 mm focus length. A monochromatic filter is provided for mounting on the front of the lens. The magnification of the image seen on the screen during measurement is changed by releasing the camera zoom lock and pulling out or pressing in the camera lens zoom. It is advisable to have the lens zoom extended as far as possible to magnify the image and thus provide a better quality result.



Figure 2.4: KSV CAM 200 physical features, adapted from KSV Instruments.

KSV CAM 200 is equipped with many screws for the adjustment of the position of the sample stage and the syringe. In Figure 2.4, parts numbered between 1-6 are for this purpose. These screws are used to position the sample and syringe so that their images appear at the appropriate positions and baseline can be easily determined when recording images. Items numbered between 7-10 are for syringe adjustment for liquid dispensing. Figure 2.4 shows only manual dispensing system, while the instrument is also having an automatic single liquid dispenser, which is not shown on the illustration.

Analysis of the shape of a sessile drop of test liquid, or an air bubble in liquid placed on a solid, is the basis for optical contact angle/surface tension measurement or goniometry. The basic elements of a measuring device include a light source, sample stage, liquid/air bubble dispensing device, lens, and image capture. Contact angle can be assessed directly by measuring the angle formed between the solid and the tangent to the drop surface.

2.3 Procedure

2.3.1 Liquid Surface and Interfacial Tension Measurements by Drop Profile Instrument

The equilibrium surface tension of liquids was measured with two different methods: Du Noüy ring and drop shape analysis method. The temperature was recorded during the measurement as 24–25°C. The value of density plays a key role in the pendant and raising drop method, also heavy and light phases must be determined correctly in the experimental setup screen. Otherwise, wrong calculations are employed and the results may be useless.

Contact angle measuring instrument can employ pendant and raising drop method (given in Figures 1.3 and 1.4), while determining surface and interfacial tensions of liquids and two immiscible liquids. A pendant drop experiment is very similar to a contact angle experiment in procedure. A surface tension measurement involves a liquid drop and a gas whereas an interfacial tension measurement involves two phases.

For the surface tension measurements, by using KSV WinCAM software main menu, a new pendant drop experiment was started, the values were filled in the experimental setup screen, and then needle adjustments were done. Capture rate of frames were adjusted to 60 fps, which is maximum for the highest sensitivity, and then it was tried to get the image of the drop, just before the drop fell down, while drop size was increased by the manual syringe. Then curve-fitting section could fit an algorithm to the desired captured image to obtain the surface tension value of the liquid.

For the interfacial tension measurements, the same procedure was applied, except for hooked needle was used and *"Flip Image Vertically"* button was engaged. This way, when the heavier phase liquid drop was trying to be formed in a denser liquid, since the shape of the drop was upside down. Flipping image function allowed the software to process images as the measurements looked like as if they were standard pendant drop measurements in air.

For the capture frame rates, although the camera is capable of maximum capturing 60 fps, sometimes this introduced inadequate resolution to determine the image when the drop just released the needle. Then software's trigger option could help to start

recording as soon as drop become a predetermined volume and it could also save time and hard disk space.



Figure 2.5: Surface tension of "water in air" by pendant drop method, $\gamma_{WA} = 72.48 \text{ mN/m.}$



Figure 2.6: Interfacial tension of "n-heptane in water" by raising drop method, $\gamma_{OW} = 51.32 \text{ mN/m}.$

Figures 2.5 and 2.6 show surface and interfacial tension experimental data, obtained by contact angle goniometer system.

2.3.2 Liquid Surface and Interfacial Tension Measurements by Tensiometer

The ring method was used both for surface tensions (liquid/air) and for determination of the interfacial tensions (water/oil, water/air and oil/air). Experiments were also performed, where the atmosphere above the liquid was saturated with its own vapor. These experiments were based on measurements of the force of interaction of the ring with the surface or the interface of two liquids. The ring was submerged below the interface and was then raised. The platinum ring was thoroughly cleaned and flame-treated before each measurement.

The glassware was cleaned with hexane then rinsed with acetone and distilled water flush was done at the end. Glassware was fully dried. Pure liquid was poured from the bottle and immediately put into sample holder of tensiometer to prevent any dust getting into it. The lid of the instrument was closed. Du Noüy ring was also cleaned the same way it was done to glassware, but additionally it was burnt by open flame at high temperatures by caring not to excess the contact time of maximum 5 seconds to the flame. The ring was hanged onto balance and software was carried out the measurements automatically. Alike in the contact angle measurements, selecting of heavy and light phase and densities in the software library is very important to get the correct answer. For surface tension measurements, heavy phase was selected as the probe liquid and light phase was selected as air, for the liquid/air interface.

For the interfacial tension measurements by means of tensiometer, after cleaning of the ring and glassware, this time the heavier phase was poured then the light phase was placed on top of it. The ring was placed just in the heavy liquid but above the interface. Tensiometer carries out the measurement automatically and finds the maximum force before the lamella breaks. It is reported as interfacial tension between two immiscible liquids.

In fact, surface tension is a part of interfacial tension. In Figure 1.6, if air is used instead of top phase, interfacial tension becomes surface tension. Surface tension also includes two phases, one of them is air.

2.3.3 Contact Angle Measurements on Solids

There are some tricks to follow when performing contact angle measurements. As in all surface chemistry applications, cleanliness is essential for reproducible results. All liquids should be pure and uncontaminated. Any plastic or glassware that comes into contact with liquids should be scrupulously rinsed to remove any traces of surfactants used in cleaning. In order for the results to be reproducible, the solids that are tested must have a consistent history of events or exposures, which might affect the surface.

The lighting system for the KSV CAM 200 provides ideal illumination for sharp image capture. The brightness of the image may be adjusted with the lens aperture. The image need not be a bright one to get good results, indeed in most bright lighting situations, the highlights present on the drop may detract from the ability to model the curve profile accurately.

The quality of the image profile and curve fitting is enhanced if the image of the drop fills a larger part of the screen. Whenever possible magnification is set so that the image of the drop is as large as possible.

Ideal drop size varies with different applications but generally, larger drops are desirable. Line tension effects may cause small drops to exhibit higher contact angles. Earlier literature, which used circular fitting on the drop, warned against using large drops, which display gravitational distortion. When fitting with the Young-Laplace equation, this is no longer a consideration. Drops of 5-7 ml. are reasonable. The most important factor is the consistent use of the same volume.

One of the major factors limiting the reproducibility of contact angle measurements is the accurate assignment of a baseline for the image analyzed. Two methods are commonly employed. One is to make the surface of the solid horizontal with respect to the camera. The solid thus appears as a sharp-edged, flat object with no three dimensional aspect. The image does not show the surface of the solid receding above the front edge of the sample. The drop is placed near the front edge of the sample and the sharp front edge on the image is used as the baseline. The other approach is to align the camera so that it is pointing slightly downwards towards the sample (less than 5°). The more distant surface of the sample is seen receding above the front of the sample. In this case, the reflection of the drop onto the solid surface may be observed. The baseline is assigned at the point where the curve of the drop and its reflection meet.

2.3.3.1 One-Liquid Contact Angle Measurements

The syringe was cleaned, and then the investigated liquid was placed into it and attached to the syringe clamp. The solid sample were prepared and placed on the sample stage. From the KSV WinCAM software main menu and a new contact angle experiment was started. The relevant data was filled in on the "*Experimental Setup*" screen. When needed, it is easy to add users, liquids, or solids to the database. It was done by clicking on "*Edit Database*" and then continued to image recording.

The sample stage was lifted or lowered until the solid was visible on the bottom part of the screen. The syringe was lowered or raised until it was just visible at the top of the screen. An appropriate drop from the syringe was dispensed. A recording mode was selected, one possible setting is having *"Fast + Normal"* and the *"Fast Frame Interval"* at about 200 ms. with number of frames at 10 and the normal frame interval at 1 s. with number of frames at 20. Manual dispenser syringe was lowered to leave the liquid drop onto substrate and record button was pressed to capture images then *"Done"* button was pressed.

In the "*Curve Fitting*" window, the recorded images could be viewed. If necessary to find an image with a drop shape visible, captured images could be cycled forwards if the needle or anything else distorted the first images. "*To End*" button was selected from the "*Fitting Options*" box, by making sure that, "*Use Auto Baseline*" was selected and "*Execute*" button was pressed. The software would then process all of the images from the viewed one onwards, and the results along with the images were then stored on the computer.

The red line represented the baseline, and it should have connected the widest points of the curve profile and its reflection to each other. It was checked visually all the time, and if needed *"Use Auto Baseline"* function of the software could be used. Blue box (the execution area) was placed around the entire drop profile similarly; *"Execute"* button was pressed to start curve-fitting process. Then *"Close"* button was pressed to continue to data analysis.

One-liquid contact angle measurement images on FEP-Teflon surface, were given in Figures 2.7 and 2.8, for "water in air" and "oil in air cases", respectively.



Figure 2.7: "Water in air" on FEP-Teflon, $\theta_e = 111^\circ$, (case 1 of Figure 1.25).



Figure 2.8: "n-Octane in air" on FEP-Teflon, $\theta_e = 29^\circ$, (case 3 of Figure 1.25).

2.3.3.2 Two-Liquid Contact Angle Measurements

This time substrate was placed into a custom manufactured quartz cuvette having 160 ml. capacity, specially made by LPO Company, U.K. (Figures 2.9 and 2.10). Quartz has high transmittance value and optimum for video imaging experiments. In addition, another PMMA cuvette, manufactured locally, was used for the small amounts of continuous phase usage in the cuvette, when the liquid is precious and fewer volumes are available in the laboratory.



Figure 2.9: Homemade cuvette for two-liquid experiments.



Figure 2.10: Homemade cuvette above sample stage of KSV CAM 200.

The cell was filled with continuous liquid phase and a drop of dispensed fluid was formed in the continuous phase. Substrates were hold in the cuvette by means of two magnets inserted into both edges of the substrate. Substrate must be horizontally parallel to cuvette bottom. This was obtained either by playing with the magnets at the edges and or by playing with the knobs of the sample stage of the instrument. The initial alignment check of the sample stage was performed by water balance. Then contrast and sharpness adjustments were applied by pressing "*Adjust*" button. Lighter droplets were formed in the medium liquid, which was heavier respectively. After waiting approximately 5 seconds for drops to settle down on the substrate,

images were captured. The images recorded were flipped automatically by the software and then analyzed for contact angle calculations.



Figure 2.11: "Air under water" on PP, $\theta_e = 100^\circ$, (case 2 of Figure 1.25).



Figure 2.12: "Air under n-octane" on PP, $\theta_e = 171^\circ$, (case 4 of Figure 1.25).



Figure 2.13: "n-Octane under water" on PP, $\theta_e = 50^\circ$, (case 5 of Figure 1.25).



Figure 2.14: "Water under n-octane" on PP, $\theta_e = 146^\circ$, (case 6 of Figure 1.25). Some images and results by KSV WinCAM drop shape analysis software for twoliquid experiments on PP substrate are given in Figures 2.11-2.14.

2.3.3.3 Advancing and Receding Contact Angle Measurements

While measuring advancing and receding contact angles, the syringe was lowered as close as close to the substrate, without touching it. Prior experiments were tried to determine how much liquid should be dispensed to achieve noticeable advancing and receding points in the graphs. Graphs were plotted by the software as drop size or time against mean contact angle. Since different substrates gave different sessile drop contact angle values, the droplet volume needed to obtain a good graph changed for every substrate and liquid for both measurements.

In the advancing contact angle measurements, i.e., for a substrate, 8 μ l. of liquid was dispensed and capture resolution was adjusted by playing with capturing duration and capture interval as frame per second. Adjusting captured image frame per second value and captured image amount gave the capture duration which dispensing flow rate also must be adjusted accordingly. Manual dispenser type of 1 ml. Hamilton syringe was used during experiments. Trigger function was enabled to start capturing between desired drop volumes and to get rid of unwanted drop volumes to save time and hard disk space. For an example of 8 μ l. dispensing volume, capturing was adjusted to start after 5 μ l. drop size obtained. Droplet size was increased between 5 and 8 μ l. during measurement.

Receding contact angle measurements were accomplished just after forming the drop for advancing contact angle experiments. For the above example, after forming 8 μ l. drop, the needle was not moved and sucking operation manually operated while capturing already started. Capturing carried out until the drop slips due to its boundaries were receding. Expected drop size during capturing would be between 8 and 3 μ l., while it was intended to suck out of around 5 μ l. volumes. After sucking 5 μ l., if it was carried on sucking, the software would not curve fit for the unusual drop shape, which determined by experience.

Both for the one-liquid and two-liquid experiments, the same procedure by KSV WinCAM software was executed to process captured advancing and receding contact angle images.

Figures 2.15 and 2.16 show advancing and receding contact angle graphs of contact angle mean value, plotted against time, on PP surface, in the cases "water in air" and "oil under water".



Figure 2.15: Advancing "water in air" contact angle result of PP, $\theta_a = 110^\circ$.



Figure 2.16: Receding "oil under water" contact angle result of PP, $\theta_r = 106^{\circ}$.

3. RESULTS

3.1 Surface and Interfacial Tension Measurement Results

Surface tension values of n-heptane, n-octane, n-nonane, n-decane, n-dodecane, n-hexadecane, water, ethylene glycol, formamide, glycerol, paraffin oil, 1bromonaphthalene and methylene iodide are given in Tables 3.1 and 3.2. The values were measured by both du Noüy tensiometry and drop shape analysis methods. The results were compared to the literature values and found in good agreement with them. Equation (1.1) given in Section 1.3.1 was used for drop shape analysis method covering both pendant drop and captive bubble methods. Equations (1.3) and (1.4), given in Section 1.3.2, were used for du Noüy ring tensiometry method. Surface tension results by the image shape analysis and ring tensiometry methods were obtained by using KSV CAM 200 contact angle instrument and KSV Sigma 700 tensiometer, respectively. Results were obtained according to the procedures described in Sections 2.3.1 and 2.3.2.

Oil	Du Noüy Ring	Pendant Drop	Literature	
	(mN/m)	(mN/m)	(mN/m)	
n-heptane	20.06	20.32	20.05 (Goebel, 1997)	
n-octane	21.45	21.52	21.55 ^(Goebel, 1997)	
n-nonane	22.60	22.66	22.70 ^(Goebel, 1997)	
n-decane	23.55	23.81	23.70 ^(Goebel, 1997)	
n-dodecane	25.20	25.63	25.30 (Goebel, 1997)	
n-hexadecane	27.37	27.38	27.20 (Goebel, 1997)	

Table	3.1: Surf	ace tension v	alues of	forganic	liquids	s mutual	ly saturated	with	water.
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It was observed that pendant drop shape analysis method by video goniometry gave better results than the ring tensiometry results for the determination of the liquid surface tension values, when they are compared with the literature values. Afterwards, pendant drop shape analysis results were used in the future calculations.

Liquid	Du Noüy Ring (mN/m)	Pendant Drop (mN/m)	Literature (mN/m)
water	71.78	72.48	72.14 (Jasper, 1972)
ethylene glycol	47.59	47.79	47.54 (Jasper, 1972)
formamide	58.16	58.21	57.02 (Jasper, 1972)
glycerol	n/a	64.46	63.40
paraffin oil	n/a	30.80	28.90 (Good, 1993)
1-bromonaphthalene	n/a	44.42	44.60 ^(Wu, 1982)
methlyene iodide	n/a	50.90	50.80 ^(Wu, 1982)

Table 3.2: Surface tension values of other pure liquids.

Table 3.3: Interfacial tension values of water/organic liquid layer between two immiscible mutually saturated solutions.

Oil	Du Noüy Ring	Raising Drop	Literature	
	(mN/m)	(mN/m)	(mN/m)	
n-heptane	46.88	51.32	51.90 (Goebel, 1997)	
n-octane	47.43	51.48	52.50 (Goebel, 1997)	
n-nonane	46.72	51.24	52.40 (Goebel, 1997)	
n-decane	47.85	52.58	53.20 (Goebel, 1997)	
n-dodecane	46.20	53.10	53.70 (Goebel, 1997)	
n-hexadecane	42.55	54.95	55.20 ^(Goebel, 1997)	

Interfacial tension results measured by both techniques are reported in Table 3.3. Interfacial tension measurements were performed by using raising drop method for n-alkanes, by means of the goniometer. The results were obtained as explained in Section 2.3.1 by using Equation (1.1), given in Section 1.3.1. Equations (1.3) and (1.4), given in Section 1.3.2 were used for the du Noüy ring tensiometer method to calculate the interfacial tension. Du Noüy ring tensiometer method was applied according to the procedures as given in Section 2.3.2. It was observed that drop shape analysis methods resulted in more accurate results which are comparable with the literature, as given in Table 3.3, than the ones measured with ring tensiometry and it was decided that drop shape analysis results were used in the future calculations.
3.2 Results of Contact Angle Measurements

3.2.1 One-Liquid Contact Angle in Air Results

3.2.1.1 One-Liquid Static Equilibrium Contact Angle in Air Results

Equilibrium one-liquid in air (case 1 and 3) contact angle results, referring to θ_1 and θ_3 in Figure 1.25, are given in Table 3.4 and Table 3.5, respectively. Measurements were done according to the procedure described in the experimental Section 2.3.3.1 by using KSV CAM 200 contact angle measurement instrument. Standard deviations of the results were found within $\pm 1^\circ$, which are in accordance with the literature.

Liquid	FEP-Teflon	PP	PMMA	PC	Glass
water	111	101	76	91	22
n-heptane	24	spr.	spr.	spr.	spr.
n-octane	29	spr.	spr.	spr.	spr.
n-nonane	35	spr.	spr.	spr.	spr.
n-decane	39	spr.	spr.	spr.	spr.
n-dodecane	44	spr.	spr.	spr.	spr.
n-hexadecane	48	spr.	spr.	spr.	spr.

Table 3.4: One-liquid equilibrium contact angle results of polymer and glass surfaces in air (θ_1 and θ_3 of Figure 1.25 and all results are within $\pm 1^\circ$).

In Table 3.4, abbreviation "*spr*." stands for "*spreading*", meaning that liquid dispensed on the substrate almost completely spreads on the surface; by giving less than 10° mean contact angle value.

Table 3.5: One-liquid equilibrium contact angle results of polymer and glass surfaces in air (all results are within $\pm 1^{\circ}$).

Liquid	FEP-Teflon	PP	PMMA	PC	Glass
ethylene glycol	92	67	55	63	52
formamide	99	84	56	69	58
methylene iodide	83	54	36	45	49
glycerol	104	92	71	80	83
paraffin oil	62	23	25	20	21
1-bromonaphthalene	76	49	31	12	48

3.2.1.2 One-Liquid Dynamic Contact Angle in Air Results

Dynamic one-liquid in air (case 1 and 3) contact angle measurements are given in Table 3.6 and Table 3.7. Measurements were done according to the procedure described in the experimental Section 2.3.3.3 by means of KSV CAM 200 contact angle measurement instrument.

Liquid	FEP-Teflon	PP	PMMA	PC	Glass
water	114	110	82	93	25
n-heptane	18	spr.	spr.	spr.	spr.
n-octane	20	spr.	spr.	spr.	spr.
n-nonane	22	spr.	spr.	spr.	spr.
n-decane	31	spr.	spr.	spr.	spr.
n-dodecane	36	spr.	spr.	spr.	spr.
n-hexadecane	41	spr.	spr.	spr.	spr.

Table 3.6: One-liquid advancing contact angle results of polymer and glass surfaces in air (θ_1 and θ_3 of Figure 1.25).

Table 3.7: One-liquid receding contact angle results of polymer and glass surfaces in air (θ_1 and θ_3 of Figure 1.25).

Liquid	FEP-Teflon	PP	PMMA	PC	Glass
water	99	80	61	56	14
n-heptane	31	spr.	spr.	spr.	spr.
n-octane	36	spr.	spr.	spr.	spr.
n-nonane	38	spr.	spr.	spr.	spr.
n-decane	46	spr.	spr.	spr.	spr.
n-dodecane	49	spr.	spr.	spr.	spr.
n-hexadecane	54	spr.	spr.	spr.	spr.

3.2.2 Two-Liquid Contact Angle Results

3.2.2.1 Two-Liquid Static Equilibrium Contact Angle Results

All measurements were done according to the procedure described in Section 2.3.3.2 by using KSV CAM 200 contact angle measurement instrument. Two-liquid contact angle results, "air bubble under water" (case 2) results are reported in Table 3.8, while air bubbles were formed on the substrate in the oil phase (case 4) are given in Table 3.9.

Table 3.8: Two-liquid equilibrium contact angle results, "air bubble under water" by using inverted needle (θ_2 of Fig.1.25 and all results are within $\pm 3^{\circ}$).

Fluid	FEP-Teflon	PP	PMMA	PC	Glass
air bubble under water	78	100	124	136	150

Table 3.9: Two-liquid equilibrium contact angle results of the same samples determined by "air bubble under oil" by using inverted needle $(\theta_4 \text{ of Figure 1.25 and all results are within <math>\pm 3^\circ)$.

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	168	173	159	167	171
n-octane	165	171	162	170	170
n-nonane	165	170	165	170	168
n-decane	162	171	161	172	169
n-dodecane	160	169	162	171	168
n-hexadecane	158	167	161	170	169

Table 3.10 included "oil under water" (case 5) results, where oil droplets in continuous medium water were formed and their measured contact angles. When oil was used as the medium in the cuvette and water drops were formed on the substrate (case 6), the following results were obtained as given in Table 3.11.

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	45	52	92	83	114
n-octane	44	50	92	81	112
n-nonane	42	51	89	82	110
n-decane	41	49	85	78	117
n-dodecane	40	50	93	77	115
n-hexadecane	38	49	92	80	111

Table 3.10:	Two-liquid	equilibrium	contact	angle	results,	"oil	under	water"	by
	using inverte	ed needle (θ_5	of Fig. 1	.25 and	d all resu	ılts ar	e withi	$n \pm 3^{\circ}$).	

Table 3.11: Two-liquid equilibrium contact angle results, "water drop under oil" by using normal needle (θ_6 of Figure 1.25 and all results are within $\pm 3^\circ$).

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	174	144	118	140	98
n-octane	173	146	119	138	105
n-nonane	170	149	121	140	103
n-decane	168	149	124	141	102
n-dodecane	166	150	122	139	101
n-hexadecane	163	151	122	140	100

3.2.2.2 Two-Liquid Dynamic Contact Angle Results

Advancing and receding contact angle values were measured for two-liquid setup, according to experimental procedure described in Section 2.3.3.2 and Section 2.3.3.3 by using KSV CAM 200 contact angle measurement instrument. Advancing contact angle results are reported in Tables 3.12-3.15.

Two-liquid advancing contact angle "air bubble under water" (case 2) results are reported in Table 3.12, while air bubbles were formed on the substrate in the oil phase (case 4) are given in Table 3.13.

Table 3.12: Two-liquid advancing contact angle results, "air bubble under
water" by using inverted needle (θ_2 of Figure 1.25).

	FEP-Teflon	PP	PMMA	PC	Glass
air under water	109	112	127	151	152

Table 3.13: Two-liquid advancing contact angle results of the same samples determined for "air bubble under oil" case, by using inverted needle (θ_4 of Figure 1.25).

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	169	174	162	170	175
n-octane	167	173	164	171	172
n-nonane	166	172	168	171	169
n-decane	163	172	164	173	171
n-dodecane	164	171	164	172	170
n-hexadecane	161	170	163	171	170

Table 3.14 included "oil under water" (case 5) results, where oil droplets in continuous medium water were formed and their measured contact angles. When oil was used as the medium in the cuvette and water drops were formed on the substrate (case 6), the following results were obtained as given in Table 3.15.

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	53	70	94	86	130
n-octane	52	72	96	84	129
n-nonane	57	69	91	84	126
n-decane	54	67	89	83	135
n-dodecane	49	68	95	82	137
n-hexadecane	51	70	94	84	139

Table 3.14: Two-liquid advancing contact angle results, "oil under water" by using inverted needle (θ_5 of Figure 1.25).

Table 3.15: Two-liquid advancing contact angle results, "water drop under oil" by using normal needle (θ_6 of Figure 1.25).

Oil	FEP-Teflon	РР	PMMA	PC	Glass
n-heptane	174	160	132	142	110
n-octane	174	163	135	141	111
n-nonane	171	163	136	143	111
n-decane	170	160	137	145	110
n-dodecane	169	161	130	146	112
n-hexadecane	166	163	134	147	116

Receding contact angle results are reported in Tables 3.16-3.19. Two-liquid receding contact angle "air bubble under water" (case 2) results are reported in Table 3.16, while air bubbles were formed on the substrate in the oil phase (case 4) are given in Table 3.17.

Table 3.16: Two-liquid receding contact angle results, "air bubble under water" by using inverted needle (θ_2 of Figure 1.25).

Fluid	FEP-Teflon	PP	PMMA	PC	Glass
air under water	74	76	116	93	121

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	147	149	152	144	154
n-octane	146	148	158	146	152
n-nonane	140	147	162	148	145
n-decane	137	152	157	147	142
n-dodecane	138	148	154	146	142
n-hexadecane	136	148	155	150	144

Table 3.17: Two-liquid receding contact angle results of the same samples determined by "air bubble under oil" by using inverted needle (θ_4 of Figure 1.25).

Table 3.18 included "oil under water" (case 5) results, where oil droplets in continuous medium water were formed and their measured contact angles. When oil was used as the medium in the cuvette and water drops were formed on the substrate (case 6), the following results were obtained as given in Table 3.19.

Table 3.18: Two-liquid receding contact angle results, "oil under water" by using
inverted needle (θ_5 of Figure 1.25).

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	19	28	67	38	81
n-octane	21	25	70	34	78
n-nonane	23	23	62	32	80
n-decane	26	22	61	32	88
n-dodecane	24	24	63	26	92
n-hexadecane	22	23	62	26	93

Table 3.19: Two-liquid receding contact angle results, "water drop under oil" by using normal needle (θ_6 of Figure 1.25).

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	121	119	72	70	59
n-octane	124	126	70	72	62
n-nonane	125	113	62	76	68
n-decane	126	112	61	78	69
n-dodecane	126	110	63	81	72
n-hexadecane	124	108	62	83	74

3.2.3 General Comments on Contact Angle Results According to the Substrate Types

All advancing contact angle (θ_a) values were found to be larger than the equilibrium static contact angle (θ_e) values for the one-liquid measurements. The receding contact angles (θ_r) were measured less than the equilibrium contact angle values as expected.

Equilibrium contact angle values in air for cases 1 and 3 were in the range of ± 1 (reported in Tables 3.4 and 3.5) and two-liquid results for cases 2, 4, 5 and 6 were within ± 3 (reported in Tables 3.8-3.11). Experimental results were in close agreement with those reported in the literature.

For the interpretation of one-liquid contact angles, in "water in air" experiments (case 1); substrates are listed in order as FEP-Teflon, PP, PC, PMMA and glass in terms of hydrophobicity. However, hydrocarbon drops spreaded on all the surfaces in "oil in air" experiments (case 3) except for FEP-Teflon. This can be explained by the surface free energy phenomena and the Zisman critical surface tension model (Section 1.5.1.1): FEP-Teflon exhibited 18.5 mN/m critical surface tension value calculated by the Zisman method. According to the Zisman theory, when a droplet placed on to a solid surface, if the surface tension of the liquid is higher than the critical surface tension of solid, the droplet gives a finite contact angle value on the surface, otherwise the droplet provides a perfect wetting. Liquids used "oil in air" experiments gave surface tension values between 20.32-27.38 mN/m, as shown in Table 3.1. Since these surface tension values are higher than FEP-Teflon's critical surface tension value determined by the Zisman method, then all oil droplets showed finite contact angle values on this surface. On the contrary, the remaining surfaces which have higher critical surface tension values than FEP-Teflon showed zero contact angle with all the hydrocarbon liquids having smaller than the substrate surface tension (n-hexadecane surface tension value is 27.38 mN/m). This resulted in complete spreading on these surfaces. In these experiments, as the C unit of homologous series hydrocarbons were increasing, a noticeable increase in the contact angle in air values on FEP-Teflon surface was also observed. This was due to selfcohesion of the hydrocarbon molecules. These results are given in Table 3.4.

Ethylene glycol, formamide, methylene iodide, 1-bromonaphthalene, glycerol and paraffin oil contact angle in air experiments were also performed to be used in surface free energy calculations of solids, given in Section 3.3. They are reported in Table 3.5.

Case 2, as being the complementary case of case 1, indicated opposite order of hydrophobicity of solids, compared to case 1.

In two-liquid experiments of "air bubble under oil" case (case 4), when the surface is immersed into oil, oil film is formed. If the immersed solid loves the oil, i.e., it forms a very low or zero contact angles for "oil in air" (case 3) measurements, in this case, formed air bubble droplet is unable to push the oil film on the surface horizontally. Due to this, as the C unit of hydrocarbon droplets increases, except FEP-Teflon, all other surfaces gave almost constant results of contact angle values $(170\pm3^\circ, 162\pm3^\circ, 170\pm3^\circ$ and $169\pm1^\circ$) for PP, PMMA, PC and glass, respectively. FEP-Teflon measurements presented finite contact angle values with "oil in air" results, as shown in Table 3.4. For FEP-Teflon, in "air bubble under oil" case (case 4), as the C unit of hydrocarbon droplets increases, air bubble contact angle values were observed to be decreasing. On the other hand, by getting almost the same results on all substrates immersed in oil, it was understood that air droplet was so weak to get rid of oil film on the surface and air droplets were formed on oil film. All results are given in Tables 3.9, 3.13 and 3.17.

In two-liquid experiments, when the surface is immersed in water (case 2 and 5), a water film formation on the surface is expected. If the immersed surface loves water, i.e., gives lower water contact angle values in air, formed water film is expected to be strong and hard to be removed by droplet from the surface. Water contact angles of surfaces can be ranked as from high contact angle to low contact angles, as FEP-Teflon, PP, PC, PMMA and glass in case 1. The most hydrophobic surface, namely FEP-Teflon, has more tendency to push water film on its surface, compared to other substrates. As a result, oil droplets on case 5 were formed on substrate, not on the water film. This way, effect of the C unit changes of used hydrocarbons to measured contact angle values was observed clearly. Parallel outcome was also obtained in spreading pressure model described in Section 4.2.2.4, in Tables 4.14-4.18, where spreading pressure values for water film in "oil under water" experiments (case 5) are given. As the hydrophobicity of surfaces decreases, spreading pressure of water

film (π_5) is also increasing, meaning stronger water film pressure value. If the changes of contact angle value according to hydrocarbon C unit is investigated, one can see that as long as surface loves water, it did not leave the water film on its surface and oil droplets formed on this water film, and the contact angles do not change according to the C unit of hydrocarbon, since oil droplet is formed on water film, rather than substrate surface. Contact angle values of surfaces PC and PMMA loves water more compared to other surfaces, are not affected in the changes of the C unit in homologous alkane series. On the other hand, FEP-Teflon and PP surfaces give higher water contact angle values in air, and they do not like water and it was observed that oil droplet contact angles are inversely proportional to hydrocarbon droplet C unit increase in homologous series, which is given in Tables 3.10, 3.14 and 3.18.

In the "water under oil" (case 6) two liquid experiments, oil film is expected to form on the substrate surface, since it is immersed into oil medium. Parallel to the explanation in case 4, the formed water droplet, will push the oil film more easily, compared to air bubble droplet in case 4. Since FEP-Teflon does not like oil, oil film cannot adhere to FEP-Teflon surface, due to this fact, "water droplet under oil" contact angles are inversely proportional to the C unit increase in hydrocarbons. As the C unit increases, water contact angles under oil decrease. Other surfaces indicate almost no changes in water contact angles under oil, according to change in the C unit of hydrocarbon, since they like oils more, compared to FEP-Teflon, which can be evaluated in Tables 3.11, 3.15 and 3.19.

3.3 Results of Surface Free Energy Calculations in Air

Surface free energy calculations were done based on the one-liquid contact angle data in air given in Table 3.4 and Table 3.5. Surface tension values of solids were calculated according to three different methods, namely: Zisman, Fowkes and acid/base methods.

3.3.1 Results of Zisman Method



Figure 3.1: Zisman plot of FEP-Teflon.



Figure 3.2: Zisman plot of PP.



Figure 3.3: Zisman plot of PMMA.



Figure 3.4: Zisman plot of PC.

Zisman plots were obtained as explained in Section 1.5.1.1. Figures 3.1-3.5 show Zisman plots which were drawn by using one-liquid contact angle data. Data from different liquids was combined to get a straight line. Regression coefficient values were also calculated and all values were found close to 1.000 except for glass surface.



Figure 3.5: Zisman plot of glass.

Table 3.20: Results of Zisman method.

	Zisman, γ_c	Literature, γ_c
	(mJ/m^2)	(mJ/m^2)
FEP-Teflon	15.3	17.5 ^(Good, 1970)
РР	29.5	31.0 ^(Fowkes, 1964) 30.1 ^(Deshmukh, 2008)
PMMA	39.7	39.0 ^(Fowkes, 1964)
PC	42.6	n/a
Glass	n/a	n/a

Since the experimental contact data was highly precise and the data varied within $\pm 1^{\circ}$ for the one-liquid equilibrium contact angle results, it was found that the critical surface tension results determined by the above plots agree well with the literature values as given in Table 3.20.

Glass surface critical surface tension was not evaluated by the Zisman method since this method cannot be applied to high-energy solids like glass, in theory. All other substrates gave the meaningful results by the Zisman method, since they are considered as low-energy surfaces. Zisman method relies on the intersection of $y=cos\theta=1$, according to trend in the fitted straight line, and it is not considered to be a precise method since a wrong data can change the trend of the straight line and so intersection to y=1 point. Despite this nature of the method, after omitting some data, lines were fitted very well.

3.3.2 Results of Fowkes Method

Equation (1.24) given in Section 1.5.1.2 was used to calculate γ_s^d and γ_s^p values for each surface by using contact angle values of water/methylene iodide and water/1-bromonaphthalene couples. Mean values of γ_s^d and γ_s^p were calculated for two couples and listed in Table 3.21 and Table 3.22.

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γ_S^d Values	Fowkes	Fowkes	Mean
(mJ/m^2)	(W-Methylene Iodide)	(W-1-Bromonaph.)	γ_S^d Values
FEP-Teflon	15.6	14.5	15.1
РР	32.6	26.4	29.5
PMMA	37.1	28.4	32.8
PC	35.9	37.4	36.7
Glass	20.7	14.0	17.3

Table 3.21: Surface free energy calculations according to Fowkes method, γ_S^d values.

Table 3.22: Surface free energy	calculations according to	Fowkes method, γ_s^p values.
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γ_S^p Values	Fowkes	Fowkes	Mean
(mJ/m^2)	(W-Methylene Iodide)	(W-1-Bromonaph.)	γ_S^p Values
FEP-Teflon	0.5	0.6	0.6
PP	0.2	0.6	0.4
PMMA	5.5	8.1	6.8
PC	1.2	1.0	1.1
Glass	46.8	54.4	50.6

Table 3.23: Mean γ_S^{total} values by Fowkes method.

	γ_S^{total}	Literature γ_S^{total}
	(mJ/m^2)	(mJ/m^2)
FEP-Teflon	15.6	21.0 ^(Dann, 1970a)
PP	29.9	30.4 ^(Deshmukh, 2008)
PMMA	39.5	41.0 ^(Dann, 1970a)
PC	37.8	n/a
Glass	67.9	n/a

Different polar-apolar couples were used for Fowkes calculations. In calculations, water/methylene iodide couple is used. The results are in good agreement with the literature results, as given in Table 3.23.

3.3.3 Results of Acid/Base Method

Acid/Base Equations (1.34), (1.35) and (1.36) given in Section 1.5.1.3, were calculated against both water/formamide and water/ethylene glycol couples. The mean values are reported at Table 3.24.

Table 3.24: Surface free energy calculations according to acid/base method, mean $\frac{L^{W}}{S}$ values.

Substrate	$\frac{\text{Mean } \gamma_S^{LW} \text{ Values}}{(\text{mJ/m}^2)}$
FEP-Teflon	16.7
РР	31.5
PMMA	40.3
PC	40.7
Glass	33.2

Table 3.25: Surface free energy calculations according to acid/base method, γ^{-} and γ^{+} values.

Substrate	γ¯	γ^+
FEP-Teflon	0.0	0.0
РР	0.2	0.1
PMMA	9.7	0.6
PC	2.0	0.0
Glass	76.3	0.0

Table 3.26: Mean γ_S^{LW} and γ_S^{AB} and γ^{total} values by acid/base method.

Substrate	γ_S^{LW} Values	γ_S^{AB} Values	γ_S^{total} Values
	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
FEP-Teflon	16.7	0.0	16.7
РР	31.5	0.2	31.7
PMMA	40.3	5.0	45.3
PC	40.7	0.0	40.7
Glass	33.2	0.0	33.2

 γ_{S}^{AB} values were obtained by using Equation (1.36) and γ_{S}^{total} values were calculated by means of Equation (1.35).

3.3.4 Evaluation of Surface Free Energy Experimental Results

IAll experimental results reported in Table 3.27 were found to be close to each other and to the results reported in the literature.

Polycarbonate values differed than the literature values, this difference would be related to the difference between polycarbonate types used in the publications.

Because of the fact that different types of glass slides are commercially available, surface tension of glass slides varies in a wide range as reported in the literature.

γs	Zisman	Fowkes	Acid/Base	Literature
(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
FEP-Teflon	15.3	15.6	16.7	17.5 ^(Good, 1970)
РР	29.5	29.9	31.7	32.0 ^(Wu, 1982)
PMMA	39.7	39.5	45.3	42.0 (Hamilton, 1972)
PC	42.6	37.8	40.7	42.0 ^(Safrin, 1966) 38.0 ^(Chen et al., 2006)
Glass	n/a	67.9	33.2	43.1-73.3 ^(Url-2)

Table 3.27: Surface free energy summary of all three methods and literature values.

4. DISCUSSION

4.1 General Problems

While measuring surface and interfacial tension values, both drop profile and du Noüy ring methods were used. Both results were compared to the ones found in the literature and it was found that drop profile method gave results that are more reliable. This may be due to the contamination of impurities within the vessel in the ring method, and it was thought that the cleanliness of syringe and needle in the drop profile method is much better when compared to cleanliness of vessels and du Noüy ring. In addition, du Noüy ring method includes correction and we cannot assume zero contact angles between ring and liquid, this adds a noticeable amount of error.

Two-liquid contact angle method is much more sensitive to errors compared to oneliquid method, because of the thin liquid film formation on the substrate. Thus, the results achieved in two-liquid method were giving higher errors compared to oneliquid method.

Surface free energy calculations done by Zisman, Fowkes and acid/base methods cannot be used to characterize polymers under water situations. Two-liquid data cannot be used in the calculations of surface free energy. This is because polymer under water would behave differently compared to in air conditions, due to polymer restructuring on the surface. There are also practical problems, i.e. it is impossible to measure "1-bromonaphthalene under water" contact angle values, in water/oil two-liquid experiments. For surface free energy calculation trials in the two-liquid measurements, Zisman method would be a good starting point. Two-liquid advancing and receding measurements are done for the first time in literature.

Surface free energy calculations with one-liquid data indicate us a basic surface free energy value of the polymer. This will be used as a guide in the two-liquid determinations. If there is no restructuring on the polymer and no polarization of the molecules on the surface, so that the surface is the same as before when it is immersed into any liquid, that means that surface free energies would match the ones calculated by one-liquid contact angle data.

4.2 Model Development

4.2.1 Trials for Past Models

4.2.1.1 Trials Using Tamai (1967), (1977) and Matsunaga (1981) Approach

There are many studies citing Tamai equations however, this approach was generally found to be unsuccessful and confusing because of large differences in dispersive component of surface free energy.

Experimental results, given in Tables 3.4-3.7, were tried by using Equation (1.42) derived by Tamai et al. (1967) given in Section 1.6.1.

Surface and interfacial tension values of immiscible pairs were taken from Tables 3.1-3.3. Contact angle values were taken from Table 3.11. Results are listed in Table 4.1.

Substrate	γ_S^d calculated	γ_S^d Tamai Result	I_{SW} calculated	ISW Tamai Result
	(mJ/m^2)	(mJ/m^2)	(ergs/cm ²)	(ergs/cm ²)
FEP-Teflon	20.0	n/a	0.0	n/a
PP (PE)	90.0	42.0	7.7	1.3
PMMA	140.0	69.0	24.8	25.5
PC	53.0	n/a	10.8	n/a
Glass	96.0	n/a	40.3	n/a

Table 4.1: Calculated and literature values of γ_S^d and I_{SW} by Tamai method.

In the calculations, Equation (1.42) was solved by using two pairs of hydrocarbon experiments. The hydrocarbon surface tension values, which are very close to each other, were not selected as pairs in the calculations since they gave nonsense results. This is the defect of Equation (1.42) derived by Tamai et al. For this reason, in the choosing of couples for calculations, couples giving less than 2 mN/m surface tension differences were omitted while calculating the mean values.

In Table 4.1, for PMMA substrate, calculated γ_S^d value is different from the one obtained by Tamai et al., while I_{SW} value agrees well with Tamai finding. PE

substrate can be evaluated in comparison to our PP results, because of the similar chemical structure. For PP and PE, γ_S^d and I_{SW} values are very close to Tamai results. This is also confirmed as matching 35 and 23 dyn/cm value of Fowkes' γ_S^d and I_{SW} results, respectively. In addition, other I_{SW} values agree well with the findings of Tamai.

Tamai et al. (1977) model was applied to our experimental data by using proposed Equations (1.46) and (1.47) in the literature, given in Section 1.6.1. Here again, n-heptane/n-octane, n-octane/n-nonane and n-decane/n-nonane pairs were not taken into consideration since their respective surface tension values are very close and they yielded to obtain wrong results.

Tamai tested his approach with PTFE-Teflon and PMMA. Our PMMA γ_s^d result is found to be far from Tamai's calculation, which is yielding 75.1 erg/cm². On the contrary, I_{SW} value is found to be same with Tamai result. For PTFE-Teflon samples, I_{SW} result is also the same, while this time, γ_s^d result is very close to Tamai.

Surface and interfacial tension values of immiscible pairs were taken from Tables 3.1-3.3. Calculated results and data are given in Table 4.2.

	PMN	Í A	P	С	PI		FEP-T	feflon	Gla	ISS
Couples	γs^d	I_{SW}	γs^d	I_{SW}	γs^d	ISW	γs^d	I_{SW}	γs^d	I_{SW}
water in H/water in N	63.6	35.5	20.4	11.4	88.2	7.7	20.0	0.0	89.9	40.9
water in H/water in D	121.2	34.5	45.9	10.7	89.7	7.6	20.7	0.0	91.5	40.9
water in O/water in D	159.8	35.2	28.9	10.1	94.6	6.8	19.2	0.0	50.4	39.9
water in H/water in O	64.4	35.5	87.4	9.9	80.9	7.7	23.5	0.0	198.7	39.5
water in O/water in N	62.8	35.5	0.5	10.4	96.5	7.7	16.6	0.0	20.2	40.0
water in D/water in N	303.8	37.2	133.8	12.7	92.8	7.7	22.2	0.0	94.9	41.0

Table 4.2: Calculated and literature values of γ_S^d and I_{SW} according to Tamai.

Matsunaga (1981) approach is based on Tamai et al. (1967) and reports results in a graphical method. Our experimental results were tried by using Equation (1.42), offered by Tamai et al. Surface and interfacial tension values of immiscible pairs were taken from Tables 3.1-3.3. Contact angle values were taken from Table 3.11.

In Figures 4.1-4.5, plots are represented together with Table 4.3 containing final results.



Figure 4.1: Matsunaga model, graph for FEP-Teflon.



Figure 4.2: Matsunaga model, graph for PP.



Figure 4.3: Matsunaga model, graph for PMMA.

The only comparable result with the Matsunaga findings is the PMMA result; Matsunaga reported that γ_S^d and I_{SW} values are 37 dyn/cm and 24 ergs/cm², respectively. Our data match only for I_{SW} values while giving different result for γ_S^d .



Figure 4.4: Matsunaga model, graph for PC.



Figure 4.5: Matsunaga model, graph for glass.

Substrate	γ_S^d calculated	I_{SW} calculated
	(mJ/m^2)	(ergs/cm ²)
PMMA	402	25
PC	32	11
PP	44	0
FEP-Teflon	34	0
Glass	258	37

Table 4.3: Results obtained by Matsunaga approach.

4.2.1.2 Trials Using Schultz et al. (1977a) and (1985) Approach

Our experimental results, which were given in Tables 3.4-3.7, were tried by using Equation (1.53) derived by Schultz et al. (1977a).

Surface and interfacial tension values of immiscible pairs were taken from Tables 3.1-3.3. Contact angle values were taken from Table 3.11.

Results are listed in Table 4.4.



Figure 4.6: Schultz graph for FEP-Teflon.



Figure 4.7: Schultz graph for PP.



Figure 4.8: Schultz graph for PMMA.

As can be seen in the graphs (Figures 4.6-4.10), for all surfaces, regression coefficient values of the plots gave satisfactory good results meaning agreement between measured data was acceptable.



Figure 4.9: Schultz graph for PC.



Figure 4.10: Schultz graph for glass.

Substrate	γ_S^d calculated	I_{SW} calculated
	(mJ/m^2)	(ergs/cm ²)
PMMA	113.8	35.0
PC	36.5	10.7
PP	90.3	7.6
FEP-Teflon	20.3	0.0
Glass	82.8	40.6

Table 4.4: Calculated and literature values of γ_S^{d} and I_{SW} .

According to Schultz approach, our data yielded logical results for PC and PP, on the other hand, giving higher results for glass, PTFE-Teflon and PMMA by means of Equation (1.53). This model is applied for mica, a high-energy surface, by Schultz, and then it would be expected from this model to perform good results for glass slides. High dispersive surface tension result of glass surface would be correlated to unreliable results during measurements.

Our experimental results, which were given in Tables 3.1-3.3 and Table 3.10, were tried by using Equation (1.56) derived by Schultz et al. (1985) given in Section 1.6.1.



Figure 4.11: Schultz and Lavielle graph for FEP-Teflon.



Figure 4.12: Schultz and Lavielle graph for PP.



Figure 4.13: Schultz and Lavielle graph for PMMA.

Results obtained by Equation (1.56) given in Section 1.6.1 by Schultz (1985) were reported in Table 4.5, together with the plots in the Figures 4.11-4.15.



Figure 4.14: Schultz and Lavielle graph for PC.



Figure 4.15: Schultz and Lavielle graph for glass.

Substrate	γ_S^d calculated	I _{SW} calculated
	(mJ/m^2)	(ergs/cm ²)
FEP-Teflon	21.51	0.0
РР	19.49	0.0
PMMA	19.67	0.0
PC	24.58	0.0
Glass	24.19	0.0

Table 4.5: Results of Schultz approach.

Schultz approach results were compared to Fowkes γ_S^d values, given in Table 3.21, and observed that only FEP-Teflon and glass results are close to each other.

Schultz approach did not give satisfactory results with our data. Except for FEP-Teflon, PP and PC, regression coefficient values were low, which is an indicator of represented plot and the calculations are not reliable. Schultz results would be meaningful for only FEP-Teflon, by giving close results to Fowkes method. Regression coefficient was also very close to 1,000.

Tamai et al., by developing extensions or modifications to the equations by considering the nondispersion, merely added a polar term equations, but obtained γ_S^d values for several solids which differed considerably from those obtained by one-liquid methods as in Fowkes and Panzer's method. These large differences suggest that Tamai's approach is ineffective.

Tamai-Schultz approach was failed to correlate the two-liquid contact angle data with one-liquid contact angle data, which was discussed in Section 4.2.1. I_{SW} values were useless this approach to describe the polarity of surfaces. Besides, for low-energy surfaces, the spreading pressure was neglected this might be affected the results.

4.2.2 New Models

4.2.2.1 Difference from the Total of 180° Contact Angle Approach

It was expected that the one-liquid measurement results and inverted two-liquid measurement results would complement each other to 180° when Young-Dupre equation is considered. However, this is not the case for experimental results and the

differences of the total of "water in air" and "air under water" contact angles from 180° are listed in Table 4.6.

 Table 4.6: "Water in air/air under water" contact angle differences.

	FEP-Teflon	PP	PMMA	PC	Glass
Water/Air System	9	21	20	47	8

The differences from the total of "oil under water" and "water under oil" contact angles from the 180° are reported in Table 4.7, by using the values taken from Tables 3.5-3.8.

 Table 4.7: "Oil under water/water under oil" contact angle differences from the total of 180°.

Oil	FEP-Teflon	PP	PMMA	PC	Glass
n-heptane	39	16	30	43	32
n-octane	37	16	31	39	37
n-nonane	32	20	30	42	33
n-decane	29	18	29	39	39
n-dodecane	26	20	35	36	36
n-hexadecane	21	20	34	40	31

In Tables 4.6 and 4.7, it is obvious that there are discrepancies from the total of 180°. In Table 4.7, when the C unit of hydrocarbons is increasing, for FEP-Teflon, differences from the total of 180° are decreasing while for the remaining surfaces, this decrease was not observed, as contact angle value changes remain constant. This is due to FEP-Teflon behavior is different from other surfaces as giving finite contact angle values in air when compared with others, FEP-Teflon is the most hydrophobic surface by giving high water contact and also exhibiting a finite oil contact angle on its surface. As a result, FEP-Teflon wants to push both air or water film formed on its surface, then droplets can be formed on surface other than formed film, this leads in to the C unit changing of oils effect can be observed as contact angle changes. On the other hand, glass surface by being the most hydrophilic against water, would not want to leave water film formed on its surface and oil droplets will be formed on water film. FEP-Teflon values are decreasing between 39-21°, as others remain as for PP 18±2°, PMMA 32±2°, PC 40±3° and for glass 35±4°. These behaviors can be explained by the spreading pressure model, which will be given in Section 4.2.2.4. π_5/π_6 ratios are calculated to compare the different substrate behavior. This ratio is around 2 for PP and PC and, 3 for PMMA and glass, while it is almost equal for 10 for FEP-Teflon surface. π_5 and π_6 spreading pressure values are rather closer to each other except for FEP-Teflon surface.

Contact angle value discrepancies would be expressed according to substrate properties, also surface free energies of substrates. According to Young-Dupre equation given in Equation (1.7) in Section 1.4, if the surface were ideal, for the complementar cases, total contact angles would be 180° for both cases. As the surfaces starts to behave non-ideal type, the differences from the sum of 180° contact angle will increase. It is known that solids with lower surface free energies are accepted to behave close to ideal conditions, like FEP-Teflon. In our case, as the surface free energies of solids increase, in Table 4.6, it was observed that discrepancies from the total of 180° increase, except glass, which can be related to experimental errors. The same trend would be observed in Table 4.7, if some experimental errors omitted.

4.2.2.2 Cosine of Difference from the Total of 180° Contact Angle Approach

 $\cos[180-(\theta_6+\theta_5)]$ value multiplied by interfacial tension of oil/water can be represented as a vector. "Water under oil" and "oil under water" two-liquid contact angle values are taken from Tables 3.10 and 3.11 and results are reported in Table 4.8.

Oil	FEP-Teflon	РР	PMMA	РС	Glass
n-heptane	39.88	49.33	44.44	37.53	43.52
n-octane	41.11	49.49	44.13	40.01	41.11
n-nonane	43.45	48.15	44.38	38.08	42.97
n-decane	45.99	50.01	45.99	40.86	40.86
n-dodecane	47.73	49.90	43.50	42.96	42.96
n-hexadecane	50.93	51.26	45.22	41.79	46.76
mean values	44.85	49.69	44.61	40.20	43.03

Table 4.8: Calculated $\gamma_{OW} \cos[180 - (\theta_6 + \theta_5)]$ values.

Mean value of $\gamma_{OW} \cos[180 \cdot (\theta_6 + \theta_5)]$ for all homologous series hydrocarbon results was reported in Table 4.8. This value was varying as 44.95±4.75, by showing that as the surface free energies of solids were changing, this vector value was not changed.

No high regression coefficient observed when plotted against $\gamma_{OA} \cos[180 \cdot (\theta_6 + \theta_5)]$ versus surface free energy values. $\gamma_{OA} \cos[180 \cdot (\theta_6 + \theta_5)]$ values are reported in Table 4.9. Mean value was calculated as 20.22 ± 2.11 . $\gamma_{OW} \cos[180 \cdot (\theta_6 + \theta_5)]$ and, γ_{OA} $\cos[180-(\theta_6+\theta_5)]$ data were plotted against surface free energies of solids and these data did not give enough agreement with each other, by giving regression coefficients of 0.132 and 0.149.

Oil	FEP-Teflon	РР	PMMA	PC	Glass
n-heptane	15.79	19.53	17.60	14.86	17.23
n-octane	17.19	20.69	18.45	16.72	17.19
n-nonane	19.22	21.29	19.62	16.84	19.00
n-decane	20.82	22.64	20.82	18.50	18.50
n-dodecane	23.04	24.08	20.99	20.74	20.74
n-hexadecane	25.56	25.73	22.70	20.97	23.47
mean values	20.27	22.33	20.03	18.11	19.36

Table 4.9: Calculated $\gamma_{OW} \cos[180 \cdot (\theta_6 + \theta_5)]$ values.

Table 4.10: Calculated $\gamma_{WA} \cos[180 - (\theta_2 + \theta_1)]$ values.

Substrate	$\gamma_{WA} \cos[180 - (\theta_2 + \theta_1)]$
FEP-Teflon	71.59
PP	67.67
PMMA	68.11
PC	49.43
Glass	71.77

Plotting $\gamma_{WA} \cos[180 \cdot (\theta_2 + \theta_1)]$ values against surface free energies indicated that "water in air" and "air under water" cases, would fit in a linear graph, by giving regression coefficient very close to zero. Again, no effect of surface free energy differences on this vector was observed. All vectoral approaches did not give successful results for complementary cases, to explain contact angle differences from the total of 180°.

This calculated vector results gave almost constant values for all substrates since the cosine of calculated values $[180-(\theta_6+\theta_5)]$ and $[180-(\theta_2+\theta_1)]$ almost were not changing. This was the weakness of the offered model.

4.2.2.3 Complementary Hysteresis Model

 $(\cos\theta_2 - \cos\theta_1)$ shows the difference between the complementary angles of 1 & 2 cases and $(\cos\theta_6 - \cos\theta_5)$ shows the difference between the complementary angles of 5 & 6 cases. When mean of these values are multiplied with the interfacial tension γ_{OW} $(\cos\theta_6 - \cos\theta_5)$ and γ_{WA} $(\cos\theta_2 - \cos\theta_1)$, then we obtain a new parameter, which is named "Complementary Hysteresis" which can be plotted with a surface property. In

order to carry out this task, γ_{OW} ($\cos\theta_6$ - $\cos\theta_5$) and γ_{WA} ($\cos\theta_2$ - $\cos\theta_1$) values were tabulated for each surface and given in Tables 4.11 and 4.12. Results are plotted versus surface free energies of substrates. Surface free energy values were taken from Table 3.26, calculated by using acid/base method. Glass surface free energy value was taken from Fowkes's method, reported in Table 3.23.

Substrate	SFE (mN/m)	$\gamma_{WA} (\cos \theta_2 - \cos \theta_1)$
FEP-Teflon	16.7	- 41.04
PP	31.7	-1.24
PMMA	45.3	58.06
PC	40.7	50.87
Glass	67.9	129.97

Table 4.11: Complementary hysteresis results for "water in air/air under water" couples.

Table 4.12: Complementary hysteresis results for "oil under water/water under oil" couples.

Substrate	SFE (mN/m)	$\gamma_{\rm OW} \left(\cos \theta_6 - \cos \theta_5 \right)$
FEP-Teflon	16.7	-90.41
PP	31.7	-77.92
PMMA	45.3	-26.52
PC	40.7	-48.89
Glass	67.9	10.17



Figure 4.16: γ_{WA} ($\cos\theta_2$ - $\cos\theta_1$) values against surface free energies of solids.





As seen in Figures 4.16 and 4.17, both plots showed linearity for the sets of substrates and this approach can be used to explain surface free energy differences between one-liquid and two-liquid conditions.

This model is highly related to surface free energies and complementary contact angle results. Model shows a material property by giving high regression coefficient for all surfaces used in the work. Model can help determine two-liquid contact angle value for surfaces, if one-liquid contact angle value is measured. By only measuring "water in air" one liquid contact angles, substrate's behavior when immersed into water (two-liquid method) can be estimated by using this model. To do this, one needs to calculate surface free energies of solids by using "liquid in air" contact angle results of different liquids. As similar, if "oil under water" contact angle value of a sample is already known, "water under oil" contact angle value can be determined by using wetting hysteresis model. This model may be tested for other surfaces as well.

In Figure 4.16, for the cases 1 and 2, as the surface free energies of solids are increasing, complementary hysteresis values are increasing. On the contrary, in cases 5 and 6, in Figure 4.17, the trend is similar to one in case 1 and 2, however, low-energy surfaces indicate high complementary hysteresis values. This may be caused

by the water film effect. For the cases 1 and 2, a surface with surface free energy value of 28.9 mN/m indicates zero complementary hysteresis value, while a surface having 62.3 mN/m of free energy gives zero complementary hysteresis for cases 5 and 6. For cases 1 and 2, complementary hysteresis values order can be reported that "PP < FEP-Teflon < PC < PMMA < glass", while this order is "glass < PMMA < PC < PP < FEP-Teflon" for cases 5 and 6.

4.2.2.4 Spreading Pressure Model

The spreading pressure values of the water films have been expected to be equal $(\pi_2=\pi_5)$ as an assumption, for the cases "air under water" and "oil under water", since the substrates are dipped into same continuous media as water in both cases. A water thin film was assumed to cover the substrate media, as long as it is immersed into water, before the droplets are formed on the substrates. Then both air and oil droplets were formed on these thin water films, rather than substrate. This fact will increase the measured contact angle deviating from the ideal situation. Similarly, the spreading pressure values of the oil film on the substrates are expected to be very close to each other ($\pi_4=\pi_6$) for the cases 4 and 6, where oil is used as the continuous media. This approach was tested by using all one-liquid and two-liquid contact angle data.

Contact angle values are measured different from ideal conditions, in presence of the spreading pressure vectors. This is because full contact with droplet and surface is not provided by the effect of film formed on the surface. A method was offered to calculate each spreading pressure values for each case. 6 cases, given in Figure 4.18, were tested by using Equations (1.79)-(1.85) in Section 1.7 and spreading pressures were calculated for formed films in each case, except for case 3, where liquids spread on surfaces and spreading pressures are assumed to be zero. Some interfacial tension values, not known for some solids, were taken from liquids showing similar behavior with these solids. For each case, independent values were used to calculate spreading pressure and not any data was used obtained from other case.



Figure 4.18: Contact angle cases with Young-Dupre equations including spreading pressures.

Calculation of spreading pressure values for FEP-Teflon was described in the following paragraphs. In calculation of all the π values, surface free energy of FEP-Teflon, γ_{SA} , was taken as 16.7 mN/m from acid/base calculations, given in Table 3.26. Surface and interfacial tensions of liquids used in experiments were taken from Tables 3.1-3.3, given in Section 3.1. One and two-liquid equilibrium contact angle values were taken from Tables 3.4 and Tables 3.8-3.11.

Spreading pressure of "water film in air", for case 1 (given in Figure 4.18), π_1 , was calculated by using Equation (1.79) given in Section 1.7. γ_{SA} value calculated by using acid/base equation, was very close to the value of perfluorodecalin surface tension, given in literature by Chaudhury (1992) and tetrafluoroethylene-
perfluoro(propylvinylether) copolymer surface tension reported by Reardon and Zisman (1973) as 18.2 mN/m and 17.7-18.7 mN/m, respectively. After searching surface free energy of solid, γ_{SA} and interfacial tension, γ_{SW} values in the literature, it was assumed that the liquid perfluorodecalin properties could be used as γ_{SW} data in these calculations, by showing similar surface behavior with FEP-Teflon because of the presence of CF₃ groups on both material surfaces. Interfacial tension of perfluorodecalin against water, reported by Su (2005) as 52 mN/m, was used in the calculations as γ_{SW} value of FEP-Teflon. Spreading pressure of water film in air, π_1 was calculated as 9.3 mN/m. This value of π_1 , was in good agreement with published values (Erbil, 1994 and 1989 and Binks, 1995). Spreading pressure of water film for "air bubble under water" case (case 2 in Figure 4.18), π_2 was computed as 20.2 mN/m, by using Equation (1.80).

In FEP-Teflon/water/air system (cases 1 and 2), spreading pressure values are not equal to each other in both "water in air" and "air under water" systems. Contact angle value, which correspondences to 111° in "water in air" system, would be higher as 118° in the absence of the spreading pressure vector. As a result, presence of π_1 , decreases contact angle value in "water in air" system. Unlike this behavior, presence of spreading pressure π_2 for "air under water" system increased contact angle degree from 62° to 78°. These calculations supported that spreading pressure affects contact angle value measurements.

 γ_{SO} values are required as an input in Young-Dupre Equations (1.81)-(1.85) for cases 3-6. These values were taken as in agreement with the work done by Neuman (1971). Neuman reported γ_{SO} value of n-hexadecane/PTFE-Teflon system between 0.8 and 0.9 mN/m. Values for the other oils/FEP-Teflon systems were calculated according to their carbon unit and by considering as the carbon unit decreases, γ_{SO} values should be decreasing accordingly. This was because of the self-cohesion of oils. γ_{SO} was taken as 0.9 mN/m for n-hexadecane as starting point, other γ_{SO} values were calculated according to their carbon atom unit, proportional to n-hexadecane's carbon unit, which is 16. For example, n-octane γ_{SO} value was calculated as follows: (0.9/16)*8= 0.45 mN/m. These values are listed in Table 4.13.

Oil	$\gamma_{SO} (mN/m)$
n-heptane	0.39
n-octane	0.45
n-nonane	0.51
n-decane	0.56
n-dodecane	0.68
n-hexadecane	0.90

Table 4.13: Interfacial tension values of solid/oil for FEP-Teflon.

After applying Young-Dupre Equation (1.81), in case 3 (given in Figure 4.18), π_3 values were found to be very close to zero value and can be approximated to zero. Literature values by Graham (1965), Davis (1977), Whalen (1967 and 1968) and Adamson (1977) agree well with our results. Since oil spreads on most solids other than FEP-Teflon, then no calculations were made for case 3.

In case 4 (given in Figure 4.18), "air bubble under oil" situation was investigated. π_4 values were calculated according to Equation (1.82), resulting negative values. This indicates that the spreading pressure vector would be in the inverse direction, compared to other substrates. An increasing trend was also observed from 3.6 to 9.6 mN/m for π_4 values, as the C unit of hydrocarbons increases.

After testing Young-Dupre equation for "oil under water" system (case 5, given in Figure 4.18), by using Equation (1.83), it can be easily seen that a numerical spreading pressure value must be assigned. By using Equation (1.83), these values (π_5) were found between 15.3 and 8.1 as decreasing for FEP-Teflon/oil/water system, when the C unit of hydrocarbons were increasing. On the other hand, in case 6 (given in Figure 4.18), by means of Equation (1.85), π_6 values, were found to be very close to zero value including some negative values which may be approximated to zero. This zero values indicate that water drop can easily push the oil film on the surface laterally and the drops are in direct contact with the substrate surfaces. This outcome is parallel to the result of contact angle hysteresis model for FEP-Teflon, given in Section 4.2.2.5.

Calculated spreading pressure values for cases 4, 5 and 6 are reported in Table 4.14 for FEP-Teflon.

Oil	$\pi_4 ({ m mN/m})$	π_5 (mN/m)	π_6 (mN/m)
n-heptane	-3.6	15.3	0.6
n-octane	-4.5	14.5	0.5
n-nonane	-5.7	13.4	1.0
n-decane	-6.5	11.8	0.0
n-dodecane	-8.1	10.6	-0.2
n-hexadecane	-9.6	8.1	-1.1

Table 4.14: Calculated spreading pressure values by using homologous hydrocarbon series for FEP-Teflon.

Calculation of spreading pressure values for PP was described in the following paragraphs. In calculation of all the π values, surface free energy of PP, γ_{SA} , was taken as 31.7 mN/m from acid/base calculations, given in Table 3.26. Surface and interfacial tensions of liquids used in experiments were taken from Tables 3.1-3.3, given in Section 3.1. One and two-liquid equilibrium contact angle values were taken from Tables 3.4 and Tables 3.8-3.11.

Spreading pressure of water film in air (case 1 in Figure 4.18), π_1 , was calculated by using Equation (1.79) given in Section 1.7. γ_{SA} value calculated by using acid/base equation was very close to the value of a long chain hydrocarbon, n-hexadecane surface tension, as 27.38 mN/m, given in Table 3.3. After searching γ_{SA} and γ_{SW} values in the literature, it was assumed that the liquid n-hexadecane properties could be used as γ_{SW} data in calculations, by showing similar surface behavior with PP. Interfacial tension of n-hexadecane against water, was measured as 54.95 mN/m, and was used in the calculations as γ_{SW} value of PP. According to Young-Dupre equation, spreading pressure of water film in air, π_1 was calculated as 9.4 mN/m. This value of π_1 , was in good agreement with published values (Adamson, 1977 and Tadros, 1974). Spreading pressure of water film for "air bubble under water" case (case 2 in Figure 4.18), π_2 , was computed as 35.8 mN/m, by using Equation (1.80).

All γ_{SO} values, required as an input in Young-Dupre Equations (1.81)-(1.85), were taken as zero, since the fact that polypropylene like n-hexadecane hydrocarbon is naturally miscible with any oil.

Since oil spreads on most PP in case 3 (given in Figure 4.18), then no calculations were made for this case.

In case 4 (given in Figure 4.18), "air bubble under oil" situation was investigated. π_4 values were calculated according to Equation (1.82). A decreasing trend from 11.5 to 5.0 mN/m was observed for π_4 values, as the C unit of hydrocarbons increases, due to self-cohesion of hydrocarbons used.

After testing Young-Dupre equation for "oil under water" system (case 5, given in Figure 4.18), by using Equation (1.83), it can be easily seen that a numerical spreading pressure value must be assigned. These values (π_5) were found between 23.4 and 19.2 as decreasing for PP/oil/water system, when the C unit of hydrocarbons were increasing. On the other hand, in case 6 (given in Figure 4.18), by using Equation (1.85), π_6 values were found to be between 13.4 and 7.2 as decreasing for PP/oil/water system, when the C unit of hydrocarbons were increases are related to self-cohesion of hydrocarbons.

Calculated spreading pressure values for cases 4, 5 and 6 are reported in Table 4.15 for PP.

Oil	π_4 (mN/m)	π_5 (mN/m)	π_6 (mN/m)
n-heptane	11.5	23.4	13.4
n-octane	10.5	21.9	12.3
n-nonane	9.5	22.7	11.0
n-decane	8.3	20.5	9.9
n-dodecane	6.6	20.8	9.0
n-hexadecane	5.0	19.2	7.2

Table 4.15: Calculated spreading pressure values by using homologous hydrocarbon series for PP.

Calculation of spreading pressure values for PMMA was described in the following paragraphs. In calculation of all the π values, surface free energy of PMMA, γ_{SA} , was taken as 45.3 mN/m from acid/base calculations, given in Table 3.26. This value is in agreement with PMMA polymer melts value as 41.1 mN/m, reported by Wu (1970). Surface and interfacial tensions of liquids used in experiments were taken from Tables 3.1-3.3, given in Section 3.1. One and two-liquid equilibrium contact angle values were taken from Tables 3.4 and Tables 3.8-3.11.

Spreading pressure of water film in air (case 1 in Figure 4.18), π_1 , was calculated by using Equation (1.79) given in Section 1.7. γ_{SW} value of PMMA was taken as 38.0 mN/m. According to Young-Dupre equations, spreading pressure of water film in air,

 π_1 was calculated as 10.2 mN/m. This value of π_1 , was lower than published values by Erbil (1989 and 1994), Busscher (1986), Bellon-Fontaine (1990) and Lee (1999). Spreading pressure of water film for "air bubble under water" case (case 2 in Figure 4.18), π_2 , was computed by using Equation (1.80), as 33.2 mN/m.

All γ_{SO} values, required as an input in Young-Dupre Equations (1.81)-(1.85) were taken as zero, since laboratory experiments in our work showed that liquid MMA (methlymethacrylate monomer) is miscible with any homologous alkanes used in the experimental work.

Since oil spreads on most PMMA in case 3 (given in Figure 4.18), then no calculations were made for this case.

In case 4 (given in Figure 4.18), "air bubble under oil" situation was investigated. π_4 values were calculated according to Equation (1.82). A decreasing trend from 26.3 to 19.4 mN/m was observed for π_4 values, as the C unit of hydrocarbons increases, due to self-cohesion of hydrocarbons used.

After testing Young-Dupre equation for "oil under water" system (case 5 given in Figure 4.18), by using Equation (1.83), it can be easily seen that a numerical spreading pressure value must be assigned. These π_5 values were found as almost constant for all oil types; giving 39.5 ± 2.4 mN/m value (Result for n-decane was considered as an outlier and omitted in mean value calculation). On the other hand, in case 6 (given in Figure 4.18), by using Equation (1.85), π_6 values were found to be between 13.9 and 9.1 mN/m as decreasing for PMMA/oil/water system, when the C unit of hydrocarbons were increasing. This decrease is related to self-cohesion of hydrocarbons.

Calculated spreading pressure values for cases 4, 5 and 6 are reported in Table 4.16 for PMMA.

Oil	$\pi_4 ({ m mN/m})$	π_5 (mN/m)	π_6 (mN/m)
n-heptane	26.3	39.8	13.9
n-octane	24.8	39.8	13.0
n-nonane	23.4	37.1	11.6
n-decane	22.8	33.4	8.6
n-dodecane	20.9	40.8	9.9
n-hexadecane	19.4	39.9	9.1

Table 4.16: Calculated spreading pressure values by using homologous hydrocarbon series for PMMA.

Calculation of spreading pressure values for PC was described in the following paragraphs. In calculation of all the π values, surface free energy of PC, γ_{SA} , was taken as 40.7 mN/m from acid/base calculations, given in Table 3.26. Surface and interfacial tensions of liquids used in experiments were taken from Tables 3.1-3.3, given in Section 3.1. One and two-liquid equilibrium contact angle values were taken from Tables 3.4 and Tables 3.8-3.11.

Spreading pressure of water film in air (case 1 in Figure 4.18), π_1 , was calculated by using Equation (1.79) given in Section 1.7. γ_{SW} value of PC was taken as 71.1 mN/m. According to Young-Dupre equations, spreading pressure of water film in air, π_1 was calculated as 29.1 mN/m. Spreading pressure of water film in "water in air" experiments π_1 , was in good agreement with published values by Busscher (1986) and Meyer (2001). Spreading pressure of water film for "air bubble under water" case (case 2, given in Figure 4.18), π_2 was computed by using Equation (1.80), as 82.5 mN/m.

All γ_{SO} values, required as an input in Young-Dupre Equations (1.81)-(1.85) were taken as zero.

Since oil spreads on most PC in case 3 (given in Figure 4.18), then no calculations were made for this case.

In case 4 (given in Figure 4.18), "air bubble under oil" situation was investigated. π_4 values were calculated according to Equation (1.82). A decreasing trend ranging between 20.9 and 13.7 mN/m was observed for π_4 values, as the C unit of hydrocarbons increases, due to self-cohesion of hydrocarbons used.

After testing Young-Dupre equation for "oil under water" system (case 5 in Figure 4.18), by using Equation (1.83), it can be easily seen that a numerical spreading

pressure value must be assigned. These values (π_5) were found as almost constant for all oil types, giving an average of 62.1±3.0 mN/m value. In case 6 (given in Figure 4.18), by using Equation (1.85), π_6 values were found also as almost constant for all oil types, giving an average of 31.2±1.9 mN/m.

Calculated spreading pressure values for cases 4, 5 and 6 are reported in Table 4.17 for PC.

Oil	$\pi_4 ({ m mN/m})$	π_5 (mN/m)	$\pi_6 (mN/m)$
n-heptane	20.9	64.8	31.8
n-octane	19.5	63.0	32.8
n-nonane	18.4	64.0	31.8
n-decane	17.1	60.2	30.2
n-dodecane	15.4	59.2	31.0
n-hexadecane	13.7	61.6	29.3

Table 4.17: Calculated spreading pressure values by using homologous hydrocarbon series for PC.

Calculation of spreading pressure values for glass was described in the following paragraphs. In calculation of all the π values, surface free energy of glass, γ_{SA} , was taken as 67.9 mN/m from Fowkes calculations in Table 3.23. Surface and interfacial tensions of liquids used in experiments were taken from Tables 3.1-3.3, given in Section 3.1. One and two-liquid equilibrium contact angle values were taken from Tables 3.4 and Tables 3.8-3.11.

Spreading pressure of water film in air (case 1 in Figure 4.18), π_1 , was calculated by using Equation (1.79) given in Section 1.7. γ_{SW} value of glass was taken as 52.0 mN/m. According to Young-Dupre equations, spreading pressure of water film in air, π_1 was calculated as 51.3 mN/m. This value of π_1 , was founded close to published value obtained by ellipsometric measurements by Chibowski (1988), however, rather far away from Whalen (1961) and Busscher (1986). Spreading pressure of water film for "air bubble under water" case (case 2 given in Figure 4.18), π_2 was computed as 46.9 mN/m by using Equation (1.80).

All γ_{SO} values, required as an input in Young-Dupre Equations (1.81)-(1.85) were taken as 22.0 mN/m, as constant.

Since oil spreads on most glass in case 3 (given in Figure 4.18), then no calculations were made for this case.

In case 4 (given in Figure 4.18), "air bubble under oil" situation was investigated. π_4 values were calculated according to Equation (1.82). A decreasing trend ranging between 25.8 and 19.0 mN/m was observed for π_4 values, as the C unit of hydrocarbons increases, due to self-cohesion of hydrocarbons used.

After testing Young-Dupre equation for "oil under water" system (case 5 in Figure 4.18), by using Equation (1.83), it can be easily seen that a numerical spreading pressure value must be assigned. Values of π_5 , were found as almost constant for all oil types, giving an average of 50.6±3.1 mN/m value. In case 6 (given in Figure 4.18), by using Equation (1.85), π_6 values were found also as almost constant for all oil types, giving an average of 19.6±2.9 mN/m.

Calculated spreading pressure values for cases 4, 5 and 6 are reported in Table 4.18 for glass.

Oil	$\pi_4 ({ m mN/m})$	π_5 (mN/m)	π_6 (mN/m)
n-heptane	25.8	50.9	22.9
n-octane	24.7	49.3	16.7
n-nonane	23.7	47.5	18.5
n-decane	22.5	53.9	19.1
n-dodecane	20.8	52.4	19.9
n-hexadecane	19.0	49.5	20.5

Table 4.18: Calculated spreading pressure values by using homologous hydrocarbon series for glass.

General comments are given in the following paragraphs. In case 2, spreading pressure value of water film is relevant to hydrophobicity of the surfaces. FEP-Teflon, as having the highest water contact angle value in air amongst all surfaces tested, by being most dislike against water, has given the lowest spreading pressure value (π_2). Inverse proportional can be observed in this situation. For the case 4, PMMA is the most oil liking surface and FEP-Teflon is the least. As a result, FEP-Teflon, by being the least oil-loving surface, has given bigger oil contact angles in air, and as contact angle increases, π_4 value is increases.

Expected approach, which is, $\pi_4 = \pi_6$ is found to be invalid. For the spreading pressure π_6 , FEP-Teflon does not love water much, when considering if air droplet or water droplet can affect oil films formed on the substrate. Water droplet on FEP-

Teflon will push oil film more, compared to air bubble droplet. This results in $\pi_4 < \pi_6$ and supported by experimental results



Figure 4.19: Spreading pressure values against SFE of solids for cases 1, 2 and 4. In Figure 4.19, for the cases "water in air", "air under water" and "air under oil", as the surface free energies of solids are increasing, spreading pressure values are becoming higher.



Figure 4.20: Spreading pressure values against surface free energy of solids for "oil under water" and "water under oil" cases.

Figure 4.20 shows that, in cases 5 and 6, rather low regression coefficients were obtained compared to other cases, although, a similar trend like in other cases was observed. Low regression coefficients may be related to experimental errors.

It is evident that as the surface free energies of materials are getting higher, "water wettability" is improved, and then adhesion properties of water films were also improved (cases 1, 2 and 5). This behavior was the same in terms of "oil wettability" and "oil wettability" is also improved, as the surface tension of solids are getting higher, in cases where oil films formed (cases 4 and 6).

4.2.2.5 One and Two-Liquid Contact Angle Hysteresis Models

Contact angle hysteresis results were calculated from the Equation (1.9), given in Section 1.4.3. All results are given in Tables 4.19-4.23.

Substrate	$\theta_1 CAH$
FEP-Teflon	15
РР	30
PMMA	21
PC	37
Glass	28

Table 4.19: Contact angle hysteresis values of "water in air" results.

Table 4.20: Contact angle hysteresis values of "air under water" results.

Substrate	$\theta_2 CAH$
FEP-Teflon	35
РР	36
PMMA	11
PC	58
Glass	31

Table 4.21: Contact angle hysteresis values of "air under oil" results.

$\theta_4 \text{ CAH}$	Н	0	N	D	DD	HD	mean
TEFLON-FEP	22	21	26	26	26	25	24.3
PP	25	25	25	20	23	22	23.3
PMMA	10	6	6	7	10	8	7.8
PC	26	25	23	26	26	21	24.5
Glass	21	20	24	29	28	26	24.7

$\theta_5 \text{ CAH}$	Н	0	Ν	D	DD	HD	mean
TEFLON-FEP	34	31	34	28	25	29	30.2
РР	42	47	46	45	44	47	45.2
PMMA	27	26	29	28	32	32	29.0
PC	48	50	52	51	56	58	52.5
Glass	49	51	46	47	45	46	47.3

Table 4.22: Contact angle hysteresis values of "oil under water" results.

 Table 4.23: Contact angle hysteresis values of "water under oil" results.

$\theta_6 \text{ CAH}$	Н	0	Ν	D	DD	HD	mean
TEFLON-FEP	53	50	46	44	43	42	46.3
PP	41	37	50	48	51	55	47.0
PMMA	60	65	74	76	67	72	69.0
PC	72	69	67	67	65	64	67.3
Glass	51	49	43	41	40	42	44.3





plotted against surface free energy values and graphs are given in Figure 4.21 and 4.22.

In one-liquid contact angle hysteresis theory, as the surface free energies of solids decrease, solid are becoming ideal, as a result, contact angle hysteresis is decreased. Our results given in Table 4.19 and Figure 4.21 supported this theory.

Contact angle hysteresis calculations in two-liquid evaluations gave low regression coefficient and in "air under oil" and "air under water" cases, results did not show similar trends compared to one-liquid results. As the surface free energies of materials were increasing, contact angle hysteresis values were constant. They were reported as 20.9±13.9° and 34.2±23.2° for "air under oil" (case 4) and "air under water" (case 2) cases, respectively. That would be caused from in both cases, air bubble droplets were unable to push liquid films formed on the substrate surfaces, and surface free energy changes of different surfaces did not affect dynamic contact angle values as a parameter, since droplets were placed on the liquid films rather than surfaces.



Figure 4.22: Oil/water/substrate system two-liquid contact angle contact angle hysteresis plots.

In the cases 5 and 6, "water under oil" (case 6) case showed a similar contact angle hysteresis trend (given in Figure 4.22) as one-liquid experimental results. That means water droplet had enough energy to push oil film laterally in all surfaces and water droplet was formed on the real substrate surface. On the other hand, in case 5, water film could not be pushed laterally by oil droplet and this droplet was formed on water film, since no contact angle hysteresis changes were observed as the surface free energies of substrates were increasing.

5. CONCLUSION AND FURTHER SUGGESTIONS

In this study, one-liquid and two-liquid contact angle values were determined by using different hydrocarbon and air bubble droplets on FEP-Teflon, PP, PMMA, PC and glass surfaces.

One of the most important conclusions was that "*Tamai-Schultz Approach*" failed to correlate the two-liquid contact angle data with one-liquid contact angle data. I_{SW} values were not helpful for this approach to describe the polarity of surfaces.

Large contact angle value discrepancies were found with the variation of surface free energies of substrates in the "*Difference from the Total of 180° Contact Angle Approach*" for the complementary cases. It was observed that discrepancies from the total 180° increased as the surface free energies of solids increased. The same behavior was observed in "oil under water/water under oil" as well.

 $\gamma_{WA} \cos[180-(\theta_2+\theta_1)]$ and $\gamma_{OW} \cos[180-(\theta_6+\theta_5)]$ values were provided by "*Cosine of Difference from the Total of 180° Contact Angle Approach*". The relationship between these values and surface free energy of solids were found to be linear having regression coefficient very close to zero for both complementary cases. These vectoral approach failed to give successful results to explain contact angle differences from the total of 180°, which underscored the need to use model that take surface free energy into account.

For this purpose, "*Complementary Hysteresis Model*", expressed as γ_{WA} ($\cos\theta_2$ - $\cos\theta_1$) and γ_{OW} ($\cos\theta_6$ - $\cos\theta_5$), which is highly related to surface free energy and complementary contact angle results, was employed. This model successfully showed the strong relationship of a material property by giving high regression coefficient for all surfaces used in this work. This model can help to determine two-liquid contact angle value for surfaces, if one-liquid contact angle value is measured. For the cases 1 and 2, the complementary hysteresis values became increasingly linear as the surface free energy of solids increases. For cases 5 and 6, same linear behavior was observed, however, low-energy surfaces indicated high complementary

hysteresis values. This may be caused by the water film effect. For cases 1 and 2, complementary hysteresis value order can be reported as "PP < FEP-Teflon < PC < PMMA <glass", while this order in cases 5 and 6 is "glass < PMMA < PC < PP < FEP-Teflon".

To explain the contact angle differences from total 180° in complementary cases, a second approach, named "Spreading Pressure Model" was used. By applying the model, it was confirmed that the contact angle values measured in presence of the spreading pressure vectors, differed from the values measured in ideal conditions. This was because, film formation prevented full contact with droplet and surface. This reason motivated the need to modify the Young-Dupre Equations by adding spreading pressure values for each case in this study. These values were calculated for each case and reported. The expected approaches $\pi_4 = \pi_6$ and $\pi_2 = \pi_5$ were found to be invalid, when the substrates were immersed into same continuous medium. Spreading pressure values for each complementary case were also found to be different from each other. Spreading pressure value changes were investigated according to surface free energy of substrates. For cases 1, 2 and 5, "water wettability" of the materials was improved as the surface free energy of materials increased. In addition, the adhesion properties of water films were also improved. This behavior was the same in terms of "oil wettability" in cases 4 and 6 where oil films were formed. As the surface tension of solids increased, "oil wettability" of the materials was improved.

"Contact Angle Hysteresis Model" was applied for all cases. Advancing and receding contact angle values were measured in two-liquid setup for the first time in the literature. Two behaviors were observed during the experiments conducted by using surfaces having different surface free energies: One of them was the increase in contact angle hysteresis; the other was observing almost constant contact angle hysteresis values for increasing surface free energies of the solids. According to the one-liquid contact angle hysteresis theory, the solids became ideal as their surface free energies decreased and this decrease affected their contact angle hysteresis in same trend. The results obtained from one-liquid experiments in this work supported this theory. Different behaviors were observed in two-liquid experiment results corresponding to the cases. For the "air bubble under water" and "air bubble under oil" cases, where air bubble droplets were mentioned, it was noticed that as the

surface free energy of surfaces increased, contact angle hysteresis values were not showing an increase trend. This was explained by the air bubble droplets where they were unable to push liquid films formed on the substrate surfaces. Surface free energy changes of different surfaces did not affect dynamic contact angle values as a parameter, since droplets were placed on the liquid films rather than surfaces. Differently, in "water under oil" case, a similar contact angle hysteresis trend to oneliquid (in air) experimental results was observed. That was because water droplet had enough energy to push oil film laterally in all surfaces and water droplet was formed on the real substrate surface. On the contrary, in "water in oil" case, water film could not be pushed laterally by oil droplet and this droplet was formed on water film, since no contact angle hysteresis changes were observed as surface free energy of substrates increased.

For the future work, rough surfaces can be investigated besides flat surfaces for the successful models. Different substrates having different polar groups can also be tested for extracting contact angle hysteresis information by means of dynamic contact angle measurements.

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