

AN ABSTRACT OF THE THESIS OF

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Title: Temperature Effects on Surface Energetic Parameters
Evaluated at Solid/Liquid Interfaces.

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Measurable surface parameters which may be related to the response evoked upon contact with biofluids have been suggested to provide direction for characterization, prediction, and ultimate control of biofluid behavior at interfaces. With respect to fouling of heat exchange equipment by biofluids, such properties may be useful for the development of models which include a surface-related term. However, their dependence on temperature has not been adequately studied. Surface energetic parameters for a variety of contact surfaces were recorded at temperatures from 7 to 80°C using contact angle analysis with a modified sessile drop technique. A linear dependence in surface energetic properties with temperature was observed. The observed temperature effect suggests a need for account of this influence in development of models describing biofluid-contact surface interactions outside of the ambient range.

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Evaluated at Solid/Liquid Interfaces

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TEMPERATURE EFFECTS ON SURFACE ENERGETIC PARAMETERS EVALUATED AT SOLID/LIQUID INTERFACES

1. INTRODUCTION

1.1 Background

The determination of the surface properties of a solid is of interest in fields such as adhesion and adsorption of biofluid components where forces at an interface are present. In the control of biological fouling of heat exchange surfaces, such determination would be useful for prediction of the interactions which take place between biofluids and their contact surfaces. Research in many fields, particularly previous studies related to the biofouling of heat exchange surfaces (McGuire and Swartzel, 1989; Depalma et al., 1978; Meyer et al., 1988) have demonstrated that materials placed into contact with biological fluids spontaneously adsorb films onto their surfaces, and these first adsorbed films may strongly affect all subsequent events such as further denaturation, spore adhesion and microbial growth. Clearly, control of such events requires an understanding of the original solid surface energy properties which likely govern the formation and persistence of biofilms.

Many studies related to the interfacial behavior of non-food biofluids (e.g., lake, river and seawater) at heat exchange surfaces have focused on developing a useful empirical correlation between a solid's critical surface tension (related to the surface energy of the

solid) and its propensity for biofouling. Using a more theoretical approach, McGuire (1989) has published a relationship that can be used to predict the rate of irreversible protein adsorption from whole milk flowing through a tubular heat exchanger. With respect to the surface influence on irreversible adsorption, this model is useful for comparing potential deposition rates which might be experienced by different candidate processing or packaging materials for use in food contact. Unambiguous surface characterization is required for use of this model or similar expressions which may include a surface-related term. Knowledge of the solid surface energy, γ_s , aids evaluation of the potential surface influence on food constituent interfacial interactions.

The total solid surface energy, γ_s , can be expressed as the sum of polar (γ_s^p) and dispersive (γ_s^d) contributions, where $\gamma_s = \gamma_s^p + \gamma_s^d$. With reference to the effects of temperature on the solid surface properties, γ_s and γ_s^p may be dependent on temperature. To more clearly elucidate biomolecular behavior at interfaces as it relates to such phenomena as fouling of heat exchange surfaces, a quantitative relationship between solid surface energetic parameters and temperature is needed.

Contact angle measurements are the basis for methods that describe surface energetics and thermodynamics. Contact angle data have been used extensively to evaluate solid surface properties related to surface energy. Unfortunately, no reliable data have been reported that relate surface energetic properties of materials to

temperature; contact angle measurements reported were made at or near ambient temperature. Additionally, materials are often characterized under conditions which are not representative of an aqueous biological environment. Consequently, in some cases, there may be little correlation observed with respect to their tendency to interact with constituents in biological fluids.

A modified sessile drop technique to measure contact angles, suited for materials exposed to biological fluid as it employs a series of aqueous solutions as diagnostic liquids on water-equilibrated surfaces, was adopted in this work. The method has been successfully used for the characterization of surfaces contacting a biological environment (McGuire and Kirtley, 1989a,b).

1.2 Objectives

The objective of this research was to study the effect of temperature on surface energetic parameters evaluated at the solid/liquid interface. Such properties have previously been shown to be strongly related to the extent of interaction which occurs between biofluid constituents and the materials they describe. The author is aware of no previous studies which incorporate the effects of temperature on the solid surface energy, γ_S and the polar contribution to the surface energy of the solid, γ_S^P .

2. LITERATURE REVIEW

2.1 Solid Surface Chemistry

Contact angle measurements are the basis for one of the most powerful but simple and inexpensive techniques for the evaluation of solid surface energetics. The derivation of these techniques and their development are discussed in most surface chemistry texts (Aveyard and Haydon, 1973; Hiemenz, 1986). The contact angle, θ , formed when a drop of liquid contacts a solid surface is shown in Fig. 2-1. θ is determined by the three interfacial forces represented by γ_L , γ_S , and γ_{LS} . The subscripts L and S refer to the liquid-vapor and solid-vapor interfaces, respectively and LS refers to the liquid-solid interface. Young's equation (a force balance) for a drop of liquid at equilibrium on a flat surface is

$$\gamma_S = \gamma_{LS} + \gamma_L \cos \theta \quad (1)$$

where γ refers to surface (or interfacial) tension.

The Dupre' equation (an energy balance) defines the work of adhesion, W_a , required to separate the liquid from the solid,

$$W_a = \gamma_S + \gamma_L - \gamma_{LS} \quad (2)$$

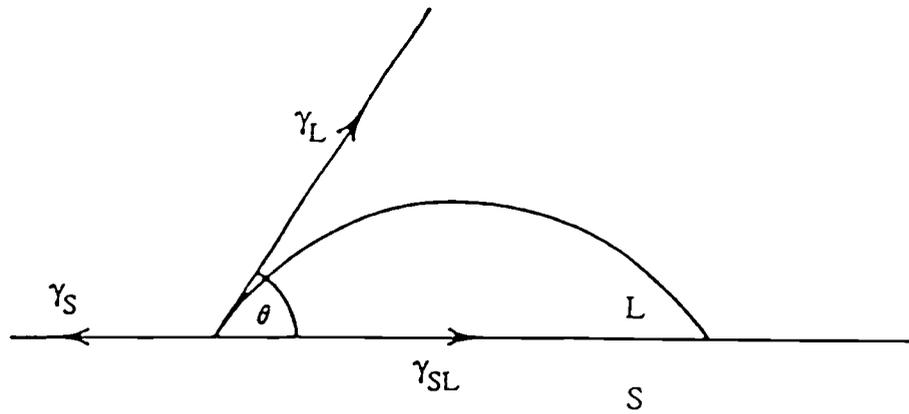


Fig. 2-1. A Drop of Liquid, L, Resting on the Surface of Solid, S

Since the quantity γ_{LS} is experimentally inaccessible, the Young and Dupre' equations are combined to yield the following relationship for the work of adhesion between the solid and the liquid,

$$W_a = \gamma_L(1 + \cos \theta) \quad (3)$$

Rigorously, equation (3) is applicable only to a system at equilibrium. Consequently, the liquid must be saturated with the solid, and the vapor and solid surface must be at adsorption equilibrium. This is not often the case, hence, values of θ for a given system may vary widely. Several methods are available for the determination of θ . The choice of method for measuring contact angles depends quite directly on the gross geometry of the system. The most commonly used method to identify differences in surface constitution for materials used in biofluid contact is a sessile drop technique. This is a so-called advancing angle technique since the line of solid-liquid contact occurs on a dry surface, i.e., the liquid advances along the surface of a solid with which it has not previously been equilibrated. Alternatively, the line of solid-liquid contact may occur at a position on the solid that was previously immersed in the test liquid, i.e., the liquid recedes or is pulled back across that part of the surface with which it has reached equilibrium. Obtained this way, θ is referred to as the receding contact angle. Two major criteria must be satisfied for experimental determination of γ_S by contact angle methods. Most importantly, the system defined by drop and solid surface must be in equilibrium. Secondly, if targeted for biofluid contact, the surface must be characterized while in

equilibrium with water. These conditions are met if aqueous solutions are chosen as diagnostic liquids, and if contact angles are measured on water-equilibrated surfaces. Such is the case with respect to receding angle experiments performed with aqueous solutions. However, receding angle experiments require greater volumes of each diagnostic liquid and generally require more expensive equipment. Additionally, more simple sessile drop techniques and associated equipment are currently used in the context of quality control at sites of packaging manufacture where polymeric coatings are applied to paper. Therefore, it has been suggested that sessile drop techniques not be abandoned but modified to incorporate the above mentioned criteria. This may be accomplished if contact angles are recorded in a controlled environment of water-saturated air (McGuire and Kirtley, 1989a).

Substantial inaccuracies will result in the measured contact angle if surface roughness, adsorption of impurities or water, or possible molecular re-orientation of the solid surface in the presence of the water exist. Roughness of a surface has the effect of making the value of the contact angle further from 90° ; if the smooth material yields an angle greater than 90° , roughness increases this angle still further, but if θ is less than 90° , roughness decreases the angle (Hiemenz, 1986).

The uses of contact angle data are of two kinds. First, as is well known, the contact angle yields information which may directly govern important processes such as adsorption, adhesion, and

wetting. Second, the contact angle may be used to characterize the solid surface itself. Thus, contact angle data may be used to deduce a fundamental property, γ_S , of a solid surface. γ_S , as obtained from contact angle studies, is one-half the free energy of cohesion, G^c , of the solid with respect to the plane that constitutes the surface.

$$\gamma_S = G^c/2 = (\partial G/\partial A)_{T,P,n} \quad (4)$$

where G is Gibbs free energy and A is surface area. T , P , and n refer, respectively, to absolute temperature, pressure, and number of moles of the various components, which are constant. The terms "surface free energy" and "surface tension" are both used in literature for γ_S . There are mechanical reasons for preferring the former. As a quantitative measure of surface properties, γ_S is related to an important qualitative criterion for classifying solids. Thus, solids may be characterized as "high-energy" or "low-energy" on the basis of whether or not liquids with relatively high surface tension, such as water, spread with zero contact angle on the solid. Hard solids are generally high-energy solids; however, the surface energy characterization is not uniquely related to mechanical properties (Good, 1979).

In one method of analysis, the contact angle is determined for a series of pure liquids in contact with a solid test surface. The cosines of the contact angle are then plotted against the liquid-vapor surface tension of the corresponding liquid. Zisman (1964) developed this most widely used method of contact angle analysis and found

empirically that, for a given surface, a rectilinear fit of the data is most often obtained. The intercept at the $\cos \theta = 1$ axis is recorded as the critical surface tension of the solid. However, since the data points fall within a rectilinear band, different values of the critical surface tension may be determined for one material. In addition, as suggested by Andrade (1985), the method can be highly misleading when examining the properties of solids in aqueous environments. This is especially true for hydrophilic surfaces, as water rarely falls within the band of data determined with other test liquids commonly used. This is in part due to water penetration into the surface (facilitated by its small molecular volume) and in part due to surface restructuring under water to a more energetically favorable state.

In less commonly used receding contact angle experiments, reasonable correlations have been achieved between surface energetics of polymers and both protein adsorption and cell adhesion (Young, 1982). This is likely due to surface characterization having been performed on water-equilibrated surfaces, i.e., the surfaces were characterized in a state they would experience if contacted with an aqueous (biofluid) system. Receding angle data recorded with liquids other than water, however, are representative of the solid equilibrated with that liquid and do not represent surface properties at the solid-water interface.

Toward a more quantitative treatment of contact angle data, Fowkes (1964) introduced the London dispersion force contribution

to the surface free energy, γ_L^d . Liquid surface tension may then be expressed as

$$\gamma_L = \gamma_L^p + \gamma_L^d \quad (5)$$

and solid surface energy as

$$\gamma_S = \gamma_S^p + \gamma_S^d \quad (6)$$

where superscripts p and d refer to polar and dispersive force components, respectively. At the interface between any liquid and another in which the intermolecular attraction is entirely due to London dispersion forces, the only appreciable interfacial interactions to which these liquids are subject are the London dispersion forces. The polar contribution to surface tension represents the sum of all forces which may be referred to as nondispersive (e.g., hydrogen bonding, electrostatic and dipole-dipole interactions). If only dispersive interactions are present at the liquid-liquid interface, Fowkes (1964) suggested that the effect of interfacial attraction on the tension in the interface can be predicted by the geometric mean of the dispersion force components of the surface tension of two liquids 1 and 2 as $(\gamma_1^d \gamma_2^d)^{1/2}$. Then, $\gamma_1 - (\gamma_1^d \gamma_2^d)^{1/2}$ is the tension in the interfacial region of liquid 1. Similarly, the tension in the interfacial region of liquid 2 is $\gamma_2 - (\gamma_1^d \gamma_2^d)^{1/2}$. The interfacial tension is the sum of the tensions in both regions and is given by

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (7)$$

By analogy with the Dupre' equation, the energy required per unit area to separate the liquid-liquid interface is expressed as

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (8)$$

Fowkes (1972) emphasized that W_a may also be divided into dispersive and polar components,

$$W_a = W_a^d + W_a^p \quad (9)$$

then the dispersive contribution to the work of adhesion is

$$W_a^d = 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (10)$$

With respect to solid-liquid contact, Kaelble (1970) applied these concepts to liquid contact with low energy solids and developed a method for determining the dispersive and polar components of γ_S from contact angle data. Given a pure liquid, L, whose γ_L , γ_L^p , and γ_L^d are known, if θ is the contact angle between the liquid and some solid, S, the interaction can be described in terms of the reversible work of adhesion (per unit area), W_a , as

$$W_a = \gamma_L(1 + \cos \theta) = W_a^d + W_a^p = 2(\gamma_L^d \gamma_S^d)^{1/2} + 2(\gamma_L^p \gamma_S^p)^{1/2} \quad (11)$$

Contact angle data from two liquids, therefore, provides two equations containing the unknowns, γ_S^d and γ_S^p . For each set of n pure liquids on a given surface, n equations can be written where any and all pairs of equations can be solved simultaneously for γ_S^d and γ_S^p . Finally, the mean force contributions are determined by averaging the results (Kaelble, 1970; Nyilas et al., 1977; McGuire and Swartzel, 1987). Problems associated with respect to interpretation of the data stem from the fact that there is no theoretical basis for equating W_a^p to the geometric mean of the polar components of solid and liquid surface tension as done in evaluation of W_a^d (Fowkes, 1972). Therefore, equation (11) should be rewritten as

$$W_a = \gamma_L(1 + \cos \theta) = 2(\gamma_L^d \gamma_S^d)^{1/2} + W_a^p \quad (12)$$

Certainly, the influence of polar interactions is present in many biofluid-contact surface interactions. The value of the polar contribution to the work of adhesion depends upon the polar character of both the solid and the the liquid which are in contact, i.e.,

$$W_a^p = f(\gamma_S^p, \gamma_L^p) \quad (13)$$

However, there is no way to calculate γ_S^p directly, and the functional representation of equation (13) is not known. Elucidation of the dependence of W_a^p on γ_L^p has contributed to elucidation of the functional representation of equation (13) and has lead to calculation of a property related to γ_S .

2.2 Evaluation of Surface Chemical Parameters

2.2.1 Diagnostic Liquid Characterization and Evaluation of γ_S^d

Evaluation of both the dispersive and polar component of diagnostic liquid surface tension is essential to determine the dispersive contribution to the surface free energy, γ_S^d . In a given solid-liquid contact, if the surface tension of either the solid or the liquid has only a dispersive component (i.e., γ_S^p or $\gamma_L^p = 0$), then the interaction between the two is entirely due to dispersive forces (Fowkes, 1964; 1972). For this case, equation (12) may be written

$$W_a = \gamma_L(1 + \cos \theta) = 2(\gamma_L^d \gamma_S^d)^{1/2} = W_a^d \quad (14)$$

i.e., the work of adhesion is totally due to dispersive (nonpolar) interactions. Rearranging,

$$\gamma_L^d = \gamma_L^2(1 + \cos \theta)^2 / 4\gamma_S^d \quad (15)$$

γ_L and θ are readily measurable. Consequently, given a solid surface of known γ_S^d with which no polar interactions may take place, the dispersive component of liquid surface tension, γ_L^d , may be found with a single contact angle measurement. Paraffin wax is such a solid, for which $\gamma_S = \gamma_S^d$. Obviously, evaluation of γ_S^d requires knowledge of γ_L^d . Fortunately, many liquids exist (particularly hydrocarbons) whose surface tension is totally due to dispersive

forces. For these liquids, $\gamma_L = \gamma_L^d$, where γ_L may be measured by conventional methods.

A different rearrangement of equation (12) yields

$$\cos \theta = [2(\gamma_S^d)^{1/2}(\gamma_L^d)^{1/2} / \gamma_L] - 1 \quad (16)$$

Choosing a series of nonpolar liquids, for any solid a plot of $\cos \theta$ vs. $(\gamma_L^d)^{1/2} / \gamma_L$ ($= 1/\gamma_L^{1/2}$) should be a straight line with slope $2(\gamma_S^d)^{1/2}$ intercepting the ordinate at -1. If such a plot is constructed for a totally nonpolar solid (Teflon or paraffin wax) for which only dispersive forces interact, polar diagnostic liquids of choice may be characterized with use of equation (15) because we now know γ_S^d .

2.2.2 Evaluation of Surface Properties

With polar diagnostic liquids of known γ_L , γ_L^d , and γ_L^p , and with methodology for evaluation of γ_S^d , elucidation of the mathematical identity of W_a^p is possible. With reference to equation (12),

$$W_a^p = \gamma_L(1 + \cos \theta) - 2(\gamma_L^d \gamma_S^d)^{1/2} \quad (17)$$

Equation (17) can be used to evaluate W_a^p for each polar diagnostic liquid put in contact with a given material. Since γ_L^p of each polar diagnostic liquid is known, plots of W_a^p vs. γ_L^p can be constructed for any one material. Consequently, the relationship between W_a^p and γ_L^p , suggested to be unique for each material due

solely to differences in γ_S^P , may be determined. For a variety of metals and polymers, it has been observed that the relationship between W_a^P and γ_L^P is linear and totally dependent upon γ_S^P (Dann, 1970; McGuire and Kirtley, 1988a,b), i.e.,

$$W_a^P = k\gamma_L^P + b = f(\gamma_S^P, \gamma_L^P) \quad (18)$$

where the slope, k , has been observed to decrease with decreasing polar character of the solid, and the negative values of the intercept, b , have been suggested to be a measure of π_s , the reduction in surface energy of the solid resulting from adsorption of vapor from the diagnostic liquid (Dann, 1970). High energy surfaces such as metals, metal oxides, and glass bind enough molecules to make π_s significant. On the other hand, π_s is negligible for a solid which possesses a low energy surface (Hiemenz, 1986). Most solid organic compounds, including organic polymers, have low-energy surfaces. We need not be concerned with whether or not π_s is negligible, except as regards the question of maintaining saturated vapor in contact with the solid. However, for interpretation in terms of γ_S values, the π_s value is of some importance (Good, 1979).

Neumann et al. (1974) described an equation of state approach to the determination of surface energy of low energy solids using contact angle data. It involves solution of the following semi-empirical equation:

$$\cos \theta_Y = \{(2\alpha\gamma_S - 2\beta)(\gamma_S\gamma_L)^{1/2} + \gamma_L\} / \{\gamma_L[2\alpha(\gamma_S\gamma_L)^{1/2} - 1]\} \quad (19)$$

where the θ_Y are referred to as Young contact angles, designated as the contact angles formed on any smooth, heterogeneous solid surface whose value may be expected to be uniquely determined by the low energy portions of the solid surface. The parameters α and β are approximately equal to 0.00775 and 1.00, respectively, and describe the linear dependence of Good's interaction parameter, ϕ (Good and Girifalco, 1960), with respect to γ_{SL} on a solid surface, i.e.,

$$\phi = -\alpha\gamma_{SL} + \beta \quad (20)$$

where ϕ is defined as follows:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\phi(\gamma_S\gamma_L)^{1/2} \quad (21)$$

The method of testing as to whether experimental values of θ correspond to values of θ_Y is to measure the contact angle for a number of liquids on a single solid and calculate γ_S in each case using equation (19). If the value of γ_S so obtained is independent of the liquid used, the contact angles are said to closely approximate Young angles.

With respect to surface characterization of materials targeted for biofluid contact (aqueous contact), limitations associated with equation (19) can be serious. The solid surfaces considered in development of this method were all of relatively low surface energy, i.e., below 30 ergs/cm². Additionally, deviations from constancy of γ_S as estimated by this method have been observed to

be most serious with high energy diagnostic liquids such as water (Good, 1979). This is unfortunate with regard to biofluid contact materials, since the phenomenon of surface restructuring in aqueous environments makes it imperative that they be characterized while in equilibrium with water. Nevertheless, Absolom et al. (1988) used the method of equation (19) to evaluate γ_S for several high energy as well as low energy surfaces. Using only water as a diagnostic liquid, they sought to relate endothelialization of solid surfaces to surface energy. Although they observed a potentially useful correlation, calculated values of γ_S appeared extraordinarily low. Indeed, values of γ_S^d evaluated for several materials by well established methods (Fowkes, 1964; Kaelble, 1970) are significantly greater than corresponding values calculated by Absolom et al. with use of equation (19).

2.3 Use of Surface Chemical Parameters

It is now possible to write equations relating W_a^p to γ_L^p and γ_S^p , but until accurate values of γ_S^p are attained by some other method, the validity of such equations cannot be described. Undoubtedly, W_a^p is a function of both γ_L^p and γ_S^p , and the following equation is therefore valid:

$$\gamma_S^p = f(k, b) \quad (22)$$

It is probable that the functional relationship of equation (22) is not simple. At the very least, however, γ_S^d , k , and b are

unambiguously calculable and may now be related to the biological response evoked upon material surface contact with biofluid. Such relationships would prove useful in attempts to characterize, predict and ultimately control biofluid behavior at interfaces.

Certainly, biofluids exhibit strong polar character and the potential for contact surface interactions with constituents of a biofluid will be dependent to some extent on the polar character of the solid surface. Use of the parameter k alone would be unsatisfactory as it provides no insight with respect to differences in nonpolar materials. Rather, construction of a composite surface energy related to k , b , and γ_S^d presently appears to be a logical application of these methods. One such development (McGuire and Kirtley, 1989b) proceeds as follows.

The value of γ_S for a film-covered surface is lower than that γ_S^\dagger for the solid-vacuum interface by an amount π_s , the surface pressure of the adsorbed film, i.e.,

$$\gamma_S = \gamma_S^\dagger - \pi_s \quad (23)$$

Consequently, W_a in the previous equations refers to the work required to part unit area of solid and liquid, the final solid surface having on it the equilibrium adsorbed film (due to adsorption of diagnostic liquid). Since the parameter b has been suggested to provide an index of the amount by which the "true" surface energy is reduced, by analogy with equation (23), we can write

$$\gamma_S^\dagger = (\gamma_S + \pi_s) \approx \gamma_S^* = (\gamma_S - b) \quad (24)$$

where γ_S^* is a composite surface energy, analogous to the thermodynamic property, γ_S^\dagger . According to equation (6), then, an expression for γ_S^P enables calculation of γ_S^* .

Toward this end, the polar component of the energy required to separate water from the surface of a material, $W_{a^P_{\text{water}}}$, was recorded as it provides an index of relative hydrophobicity or hydrophilicity of a surface (McGuire and Kirtley, 1989b). Qualitatively, one might expect the relative magnitude of k among surfaces to be similar to corresponding relative magnitude of $W_{a^P_{\text{water}}}$ (McGuire and Kirtley, 1989b).

From purely dimensional considerations, McGuire and Kirtley (1989b) suggest that

$$\gamma_S^P \approx kW_{a^P_{\text{water}}} \quad (25)$$

It must be stressed that equations (24) and (25) are useful only to the extent that they identify differences in surface energetics among biofluid contact materials, and not for elucidation of absolute properties of such materials. It follows that a composite surface energy may be written:

$$\gamma_S^\dagger = (\gamma_S^P + \gamma_S^d + \pi_s) \approx \gamma_S^* = (kW_{a^P_{\text{water}}} + \gamma_S^d - b) \quad (26)$$

Qualitatively, preliminary results of the relationship between γ_S^* and both the post-adsorptive and equilibrium behavior of β -lactoglobulin (McGuire and Kirtley, 1989b) are very similar to those observed by Baier (1980) with respect to the relationship between cell adhesion and the critical surface tension of the solid, γ_C and Meyer et al. (1988) with respect to the relationship between biofouling of heat exchange surfaces in power plant and γ_C . Also, observations of McGuire and Swartzel (1987, 1989) with respect to the relationship between dairy protein adhesion and γ_S evaluated by Kaeble's method (Kaeble, 1970) and Absolom et al. (1988) with respect to the relationship between endothelial cell adhesion and γ_S evaluated by an equation of state approach (Neumann et al., 1974) are similar to those of McGuire and Kirtley (1989b). The major difference is that the present method is more suited for materials exposed to biofluid as it employs a series of aqueous solutions as diagnostic liquids on water-equilibrated surfaces (McGuire and Kirtley, 1989b). Additionally, the results (i.e., k and b) are simply and unambiguously determined for real engineering materials.

Intermolecular interactions such as adsorption have been described as polar and nonpolar, following the principle that polar groups bond to polar surfaces and that nonpolar groups develop hydrophobic bonds to nonpolar surfaces. Fowkes (1985) suggests, however, that some polar interactions are actually Lewis acid-base interactions, in which two polar groups may interact only when one is acidic and the other basic. Acknowledging the complexity of biofluids, the constituents of which exhibit acidic sites, basic sites,

and sites of different relative acidities and basicities, it is suggested that general polar interactions will always be present if the solid surface exhibits any degree of polar character (McGuire and Kirtley, 1989b).

Much has been done with influence of temperature on the liquid surface tension. As the temperature is raised, the surface tension of a liquid in equilibrium with its own vapor decreases and becomes zero at the critical point (Adamson, 1967; Reid et al., 1977). The near linearity has stimulated many suggestions as to algebraic forms that give exact linearity. An old and well-known relationship, attributed to Eotvos (1886), is

$$\gamma_L v^{2/3} = k(T_c - T) \quad (27)$$

where v is molar volume, T_c , the critical temperature, and the empirical constant k is essentially the same for most liquids and has a value of about 2.1 ergs/degree. A second well-known relation originated by van der Waals and refined by Guggenheim (1945) is

$$\gamma_L = \gamma_{L0}(1 - T/T_c)^n \quad (28)$$

where γ_{L0} represents the surface tension of the liquid extrapolated to $T = 0$ K. n is 11/9 for many organic liquids but may be closer to unity for metals (Grosse, 1962).

No literature exists on the temperature dependence of the solid surface energy. However, by analogy with the above mentioned linear decrease in γ_L with rising temperature, the solid surface energetic parameters, γ_S and γ_S^P , may be dependent on temperature to some extent due to increases in vibrational motions of the solid surface with increasing temperature corresponding to thermal motions of the liquid.

3. THEORY

It is well known that surface tension decreases linearly with increasing temperature (Adamson, 1967). If the temperature is $T(K)$, then simply

$$\gamma_L = C_1 - C_2T \quad (29)$$

where C_1 and C_2 are positive constants.

The liquid surface tension may be divided into dispersive and polar contributions,

$$\gamma_L = C_1 - C_2T = \gamma_L^p + \gamma_L^d \quad (30)$$

Dispersive (nonpolar) forces exist in all types of matter and always give an attractive force between adjacent atoms or molecules no matter how dissimilar their chemical natures may be. The forces depend on electrical properties of the volume elements involved and the distance between them, and are independent of temperature (Fowkes, 1964). On the other hand, polar forces are suggested to include all nondispersive forces such as Lewis acid-base interactions.

The polar components of the total liquid surface tension, which can be expressed as the difference between total liquid surface tension and dispersive force contributions which are kept constant, may decrease with temperature due to the general temperature

reliance on the liquid surface tension. Consequently, temperature may affect the work of adhesion, W_a , required to separate the liquid from the solid. Increase in the thermal motions of the liquid surface is the cause of decrease in its surface tension, and therefore W_a and W_a^P appear to be decreased. It is suggested that the decrease in the adhesive field of force with rising temperature is much less in solids than in liquids, and may be principally or wholly due to translatory motions (Adam, 1964).

At a given temperature, the previously introduced composite surface energy, γ_S^* may be constructed to describe surface energetics of a particular material. It is suggested that the properties k and $W_{a^P_{\text{water}}}$ should decrease with increasing temperature, and the dispersive contribution to the solid surface energy can be considered constant. Consequently, if the temperature effect on b , suggested to be a measure of the surface pressure of the adsorbed film, could be determined experimentally or theoretically, it becomes possible to identify whether values of γ_S^* are influenced by temperature changes.

The spreading pressure, π_s , related to the surface concentration, Γ , can be written as follows (Aveyard and Haydon, 1973) when the saturated vapor obeys the ideal gas law:

$$\pi_s = RT \int_0^{P_0} (\Gamma/P) dP \quad (31)$$

where P_0 is the pressure of the saturated vapor, R the gas constant, and T the absolute temperature. Since the surface concentration is linearly dependent on the number of molecules contained in the adsorbed film, it may be decreasing with increasing temperature. On the contrary, the saturated vapor pressure must increase with increasing temperature, i.e., the upper limit P_0 augments with rising temperature for the integral of the above expression. Therefore, the integral term may increase or decrease with respect to the relative behavior of Γ and P_0 with varying temperature. Considering that the surface concentration is a function of solid surface chemistry, and its chemistry may change with temperature, it is difficult to predict a definite temperature dependence on π_s . Consequently, from equation (31), if surface chemistry of a material is much less affected by temperature than the product of R and T , π_s (related to the negative value of b) might be observed to increase with rising temperature. Conversely, if surface chemistry is dramatically influenced by temperature, this may not be observed.

4. EXPERIMENTAL

4.1 Materials

Reagents used (Sigma Chemical Co., St. Louis, MO - acid dichromate cleaning solution; Aldrich Chemical Co., Inc., Milwaukee, WI - seven different hydrocarbons, benzene, and acetone; EM Science, Cherry Hill, NJ - anhydrous ethanol) were of the highest purity available.

Polymeric materials (Universal Plastics Co., Portland, OR) used included ultra-high molecular weight (UHMW) polyethylene, high density polyethylene (HDPE), polypropylene, polytetrafluoroethylene (PTFE), nylon, and a food grade acetal. Also, two metals (Alaskan Copper and Brass Co., Portland, OR), no. 304 stainless steel and copper, and a glass slide were used. Each material was machined into two rectangular plates (0.2 cm thick x 1.5 cm wide x 2.5 cm long) in order to easily fit into the environmental chamber.

Polar diagnostic liquids used included eleven different water-ethanol mixtures (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 volume% EtOH). Water used in making up the aqueous mixtures was deionized and distilled through greaseless equipment having Teflon joint sleeves. The polar series of liquids were used on solids of sufficiently low energy (PTFE, HDPE, UHMW, and polypropylene) such that relatively little polar attraction could be expected across the solid/liquid interface, and higher energy solids (stainless steel,

copper, acetal, glass slide, and nylon) in order to determine surface energetic parameters at solid/liquid interfaces.

Nonpolar diagnostic liquids (hydrocarbons) used included nonane, decane, dodecane, dicyclohexyl, hexadecane, 1-bromonaphthalene, and diiodomethane.

4.2 Apparatus

All contact angle data were obtained with a sessile drop contact angle goniometer shown in Fig. 4-1 (Rame-Hart, Inc., Mountain Lakes, NJ, NRL Model 100-00) equipped with an environmental chamber which protects from contamination due to dust and oil in the atmosphere, and makes it possible to have the atmosphere around the drop saturated with the vapor of the liquid. This instrument consists of a light source, which illuminates a stage on which the liquid drop/solid system rests, and a telescope. Fig. 4-2 illustrates a drop of liquid viewed through the telescope; cross hairs in the telescope and a 360° scale around the eyepiece enable rapid, accurate measurement of the contact angle. The contact angle is read directly from the measuring reticule at the six o'clock position. A 30° contact angle measurement of a liquid drop is demonstrated in Fig. 4-2.

Contact angle measurements were made for advancing angles and averages were taken of readings from both sides of each drop at six different temperatures: 7, 15, 30, 40, 60, and 80°C. A brief

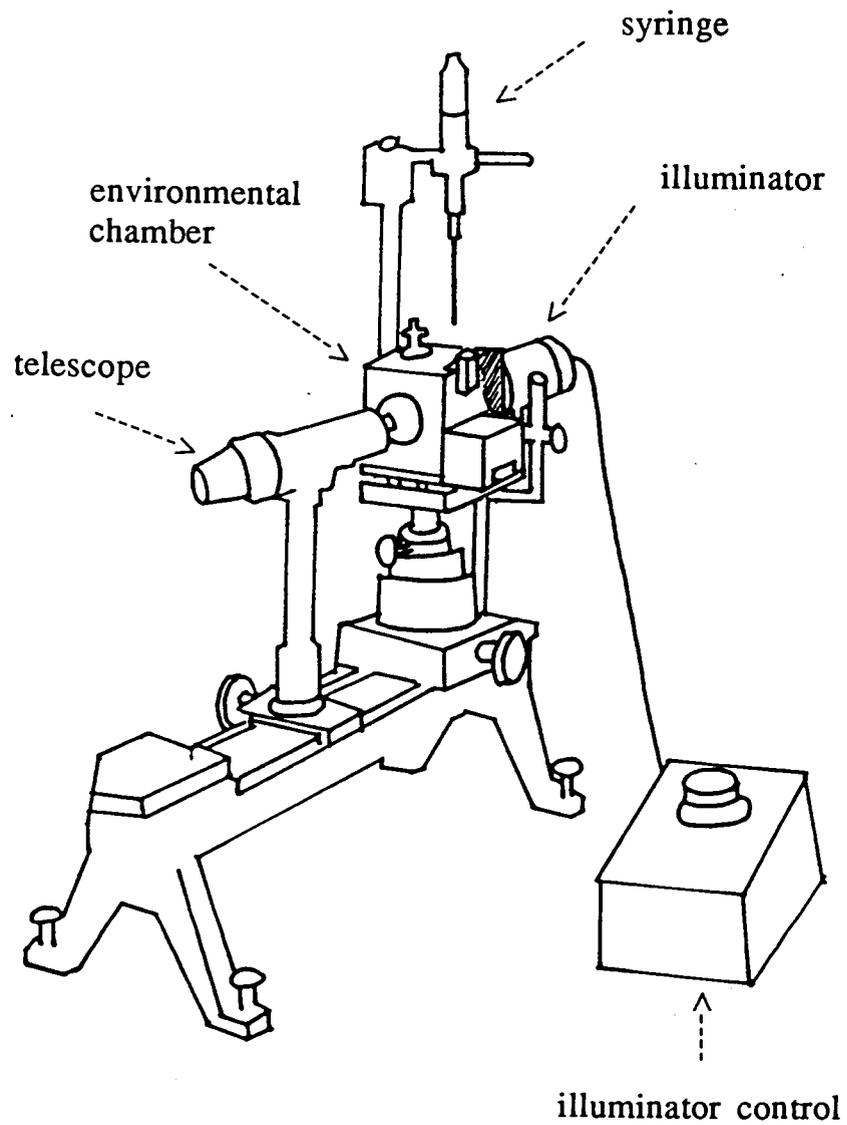


Fig. 4-1. NRL Contact Angle Goniometer Equipped with an Environmental Chamber

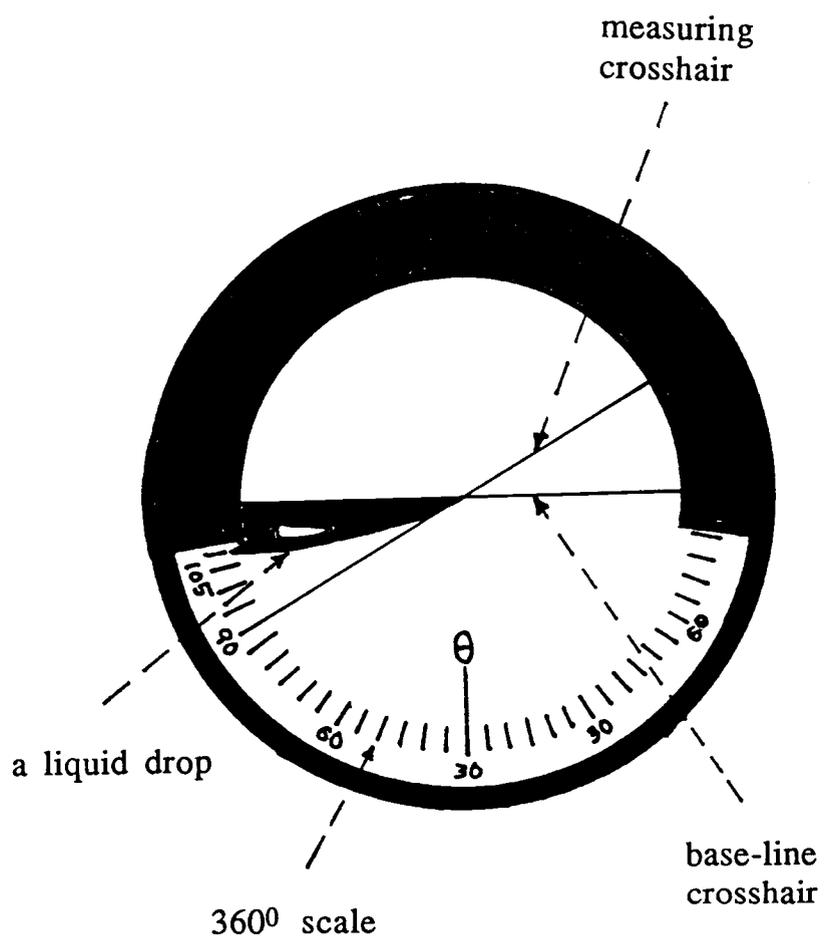


Fig. 4-2. A Drop of Liquid Viewed through the Telescope

temperature control schematic is shown in Fig. 4-3. Temperature control at 15°C was achieved by circulation of ice water through the environmental chamber with a diaphragm pump (Neptune Chemical Co., Lansdale, PA, N-feeder series, PD diaphragm pump); whereas, 7°C control was obtained with an iced, NaCl solution used as coolant. The remaining temperatures were produced by internal electric heaters with which the chamber is equipped and were regulated with a separate temperature controller (Love Controls Co., Wheeling, IL, Model 151-786). Temperatures were controlled to within $\pm 1^\circ\text{C}$.

Liquid surface tensions were measured by the ring method with a DuNouy tensiometer (CSC Scientific Co., Fairfax, VA, Model 70535). This method allows short time (15 to 30 seconds) of measurement. Other advantages of the ring method include elimination of mathematical calculations, high precision measurement, and reduction in the quantity of test liquid required. For liquid surface tension measurements, the wire ring is dipped until totally wetted. During the measurement, the withdrawal of the ring causes a film of liquid to be pulled up. It is then raised until the film ruptures along the breaking line as shown in Fig. 4-4. The force required to pull the ring out of the surface is measured. The dispersive and polar components of liquid surface tension (γ_L^d and γ_L^p) were evaluated by methods detailed earlier (Dann, 1970; McGuire and Kirtley, 1988a). Measurements of all polar diagnostic liquid surface tensions were performed at four different temperatures (5, 15, 27, and 45°C) to make interpolation and extrapolation of diagnostic liquid surface

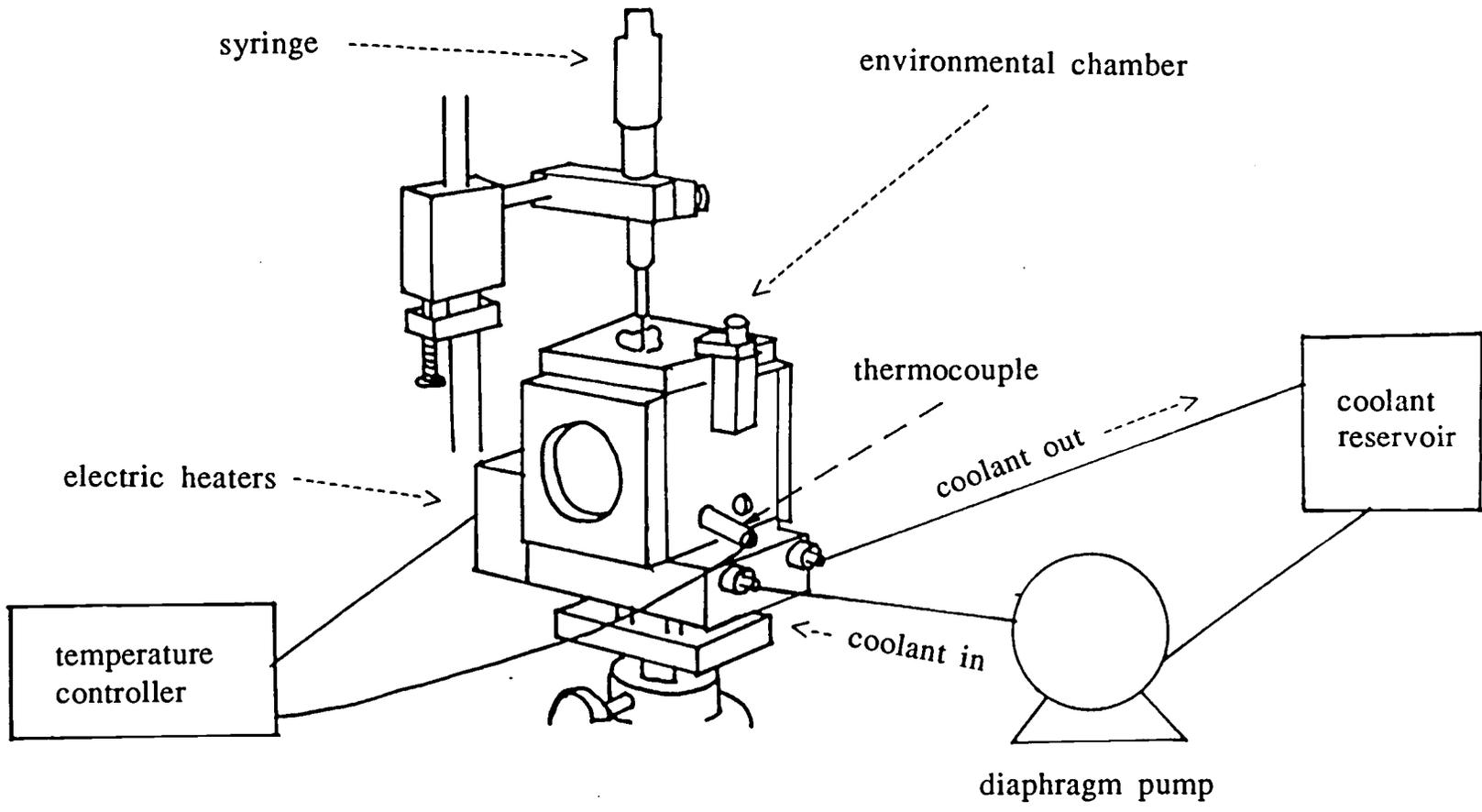


Fig. 4-3. Temperature Control Schematic for the Environmental Chamber

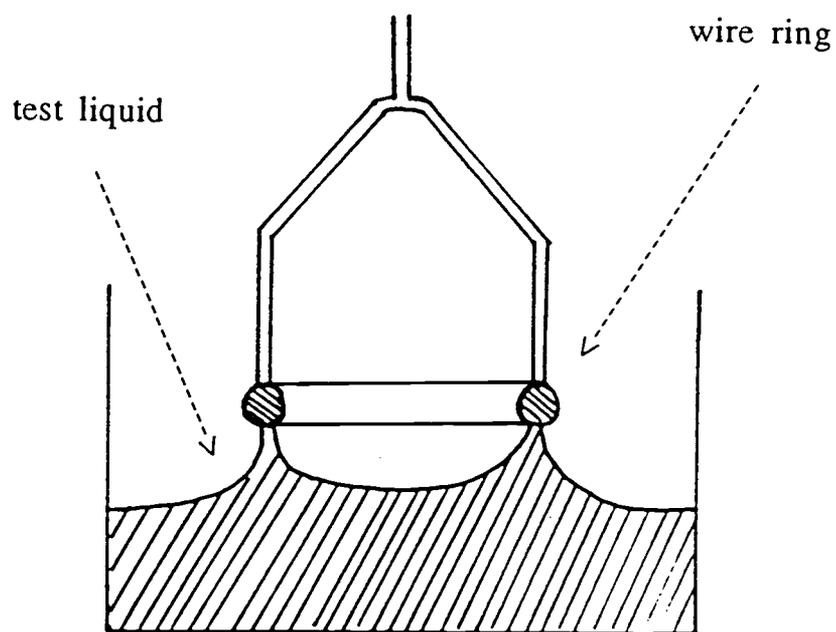


Fig. 4-4. Condition of Surface Film at Breaking Point

tensions for whole range of experimental temperature. Surface tensions were reproducible to within ± 0.1 dynes/cm.

4.3 Procedure

The closed sample chamber incorporates the stainless steel needle of the associated syringe assembly which allows the continuous addition or withdrawal of diagnostic liquid from the sessile drop. Water-saturated conditions were assured by the presence of one medium size cotton ball with warm water. Before a volume ($5 \mu\text{l}$) of diagnostic liquid was placed on the solid test surface producing a drop of diameter equal to approximately 2.5 mm, liquid temperature (temperature differences between diagnostic liquids and test solid surfaces were $\pm 3^{\circ}\text{C}$) was obtained by moving $5 \mu\text{l}$ of liquid up and down through the metal needle of syringe. This system was considered as a thermal solid-liquid equilibrium state. The surface of each metal and the glass slide reached equilibrium in less than one minute; polymeric material surfaces required 10 times longer. The values of contact angle were reproducible to within $\pm 2^{\circ}$.

Surfaces were prepared in the following manner prior to each contact angle measurement with each diagnostic liquid. The surfaces of each material with the exception of nylon and acetal were cleaned with acid dichromate cleaning solution. Subsequently, nine different surfaces were cleaned with acetone, followed by thorough rinsing in deionized, distilled water and drying in air. The work was not done

in a "white room"; reproducibly clean as opposed to optically clean surfaces were sufficient.

5. RESULTS AND DISCUSSIONS

5.1 Diagnostic Liquid Evaluation

Surface tensions of nonpolar hydrocarbon liquids evaluated by the ring method at 303 K are listed in Table 5-1. From equation (16), a liquid series of pure hydrocarbons having only dispersion energies were used for the evaluation of the dispersive component of each material's solid surface energy. Table 5-2 shows nonpolar contribution to solid surface energy for each material at 303 K. Dispersive forces of polar diagnostic liquids were evaluated by equation (15) and all surface tension components of polar diagnostic liquids were evaluated at each temperature. Values of γ_L , γ_L^d , and γ_L^p of ethanol solutions at 303 K are presented in Table 5-3. Contact angle data evaluated with the aqueous series of ethanol solutions were recorded at each temperature. These data were used as follows. For each material, W_a^p was calculated with equation (17) and plotted against γ_L^p at each temperature. A linear fit to the data was obtained in all cases. The slope k and the intercept b were recorded. Additionally, the value of the polar component of the work of adhesion between the solid surface and water ($W_{a^p_{water}}$) was recorded at each temperature. The surface energetic parameters k , b , and γ_S^d are unique for each material at each temperature. A composite surface energy, γ_S^* , composed of these parameters were evaluated with equation (26) for each material tested at each temperature.

TABLE 5-1

Surface Tension of Nonpolar Liquids at 303 K

Diagnostic liquid	$\gamma_L (= \gamma_L^d)$ (dynes/cm)
nonane	22.78
decane	23.86
dodecane	25.20
dicyclohexyl	25.62
hexadecane	27.36
1-bromonaphthalene	44.41
diiodomethane	52.24

Table 5-2

Nonpolar Contribution to Solid Surface Energy
for Each Material at 303 K

Material	γ_s^d (ergs/cm ²)
PTFE	22.58
HDPE	31.83
Polypropylene	30.69
UHMW	32.40
Stainless Steel	32.44
Nylon	33.25
Copper	32.47
Glass Slide	27.54
Acetal	46.36

TABLE 5-3

Surface Tension Components of Polar Diagnostic Liquids at 303 K

Vol.% of EtOH	γ_L (dynes/cm)	γ_L^d (dynes/cm)	γ_L^p (dynes/cm)
0	71.09	21.43	49.66
10	51.12	13.42	37.70
20	40.93	11.29	29.64
30	35.98	17.93	18.05
40	32.93	19.23	13.70
50	30.02	21.90	8.12
60	28.24	20.59	7.65
70	27.14	20.01	7.13
80	25.49	19.04	6.45
90	24.42	19.40	5.45
100	22.77	18.28	4.49

5.2 The Influence of Temperature on γ_L^P

The total surface tension of the series of polar liquids (ethanol-water) was measured by the ring method with a tensiometer at four different temperatures. Interpolations and extrapolations of liquid surface tensions (γ_L) for six different experimental temperatures were made. Fig. 5-1 illustrates the temperature effect on liquid surface tension. Fig. 5-2 shows the temperature dependence of the polar component of liquid surface tension (γ_L^P). Both figures demonstrate that both γ_L and γ_L^P of the diagnostic liquids linearly decrease with rising temperature. It should be made clear that γ_L^P is a function of temperature. This relationship may be more useful than $\gamma_L = f(T)$ to describe temperature effects on surface energetic properties.

5.3 The Relationship between W_a^P and γ_L^P

By use of equation (17), the polar component of the work of adhesion between a solid and liquid (W_a^P), required for evaluation of surface energetic properties, was calculated for each diagnostic liquid put in contact with a given material. Plots of W_a^P vs. γ_L^P were constructed for all materials tested at each temperature. See Fig. 5-3 for PTFE, HDPE, and Nylon surfaces at 303 K. The linear relationship between W_a^P and γ_L^P demonstrates that for solid surfaces with polar character, as the polar component of liquid surface tension increases, the polar component of W_a increases. Additionally, as the polar component of the solid increases, the slope, k , of the W_a^P vs. γ_L^P

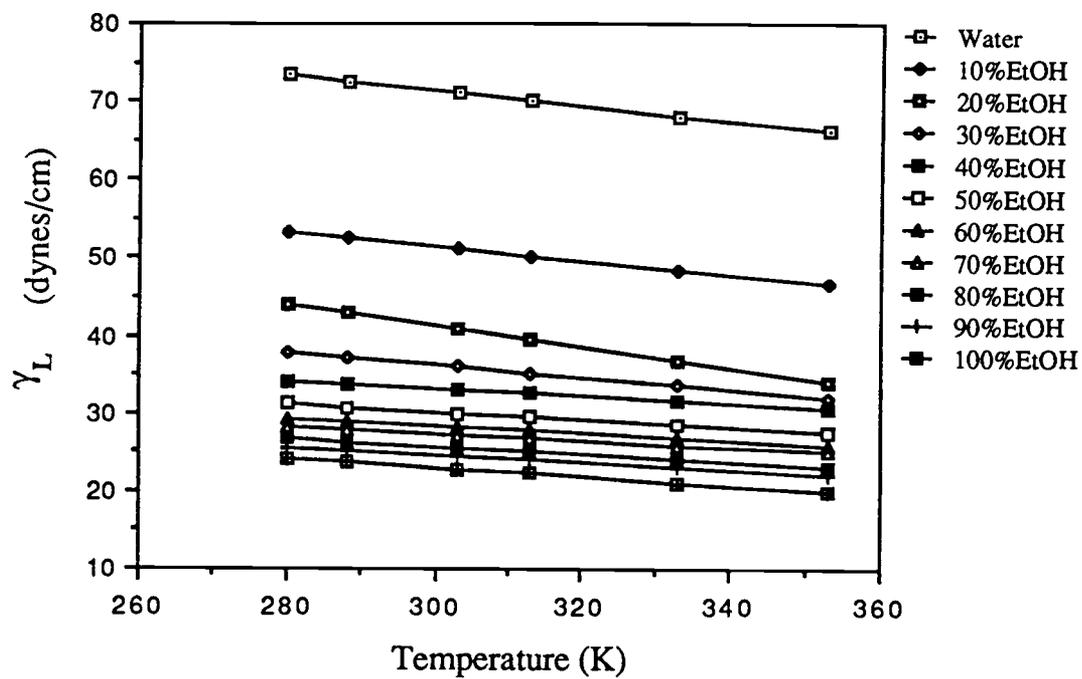


Fig. 5-1 Effect of Temperature on Liquid Surface Tension

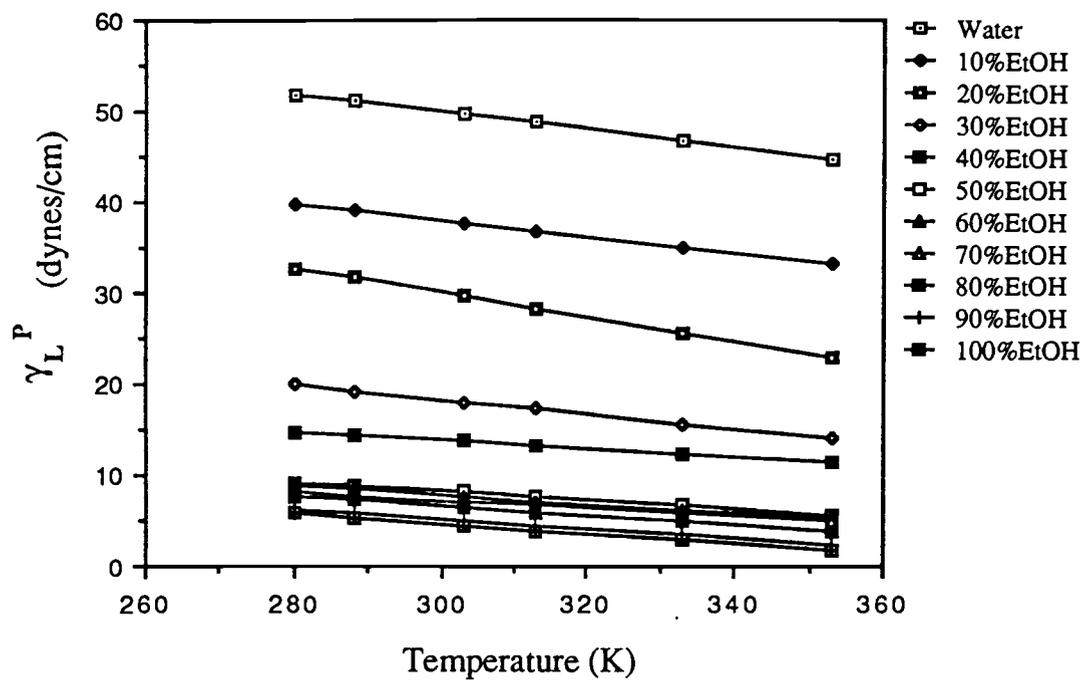


Fig. 5-2 Effect of Temperature on the Polar Component of Liquid Surface Tension

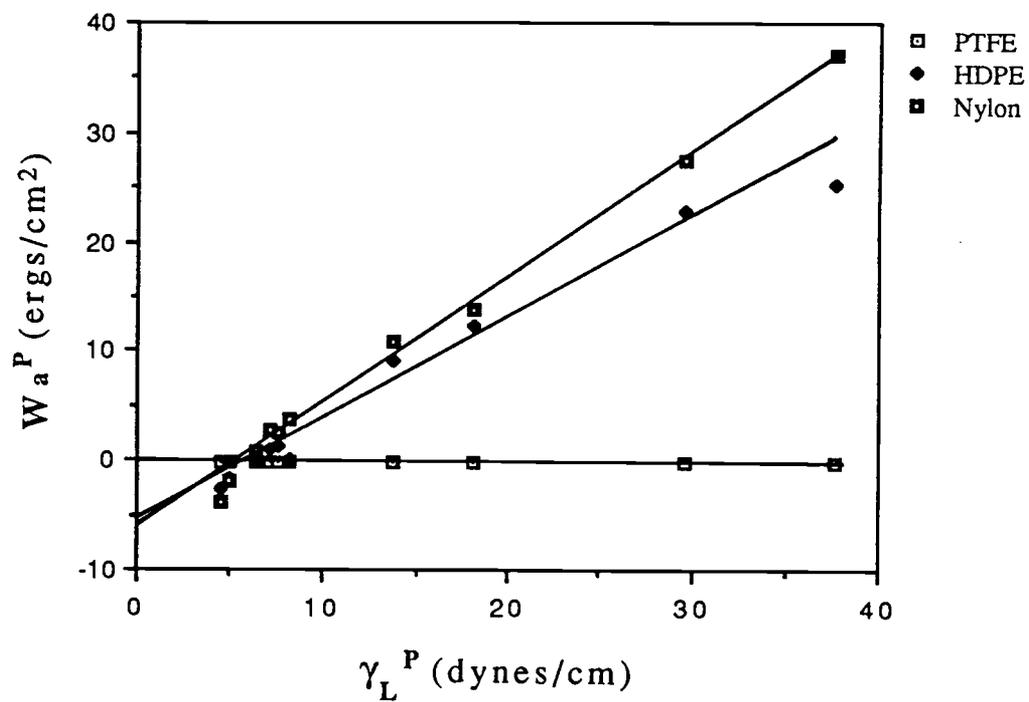


Fig. 5-3 The Linear Relationship between W_a^P and γ_L^P for Selected Solid Surfaces at 303 K

curve increases. Similar trends have been observed for the rest of materials tested: all with differing values of the slope, k , as shown in Table 5-4. Such a relationship between W_a^P and γ_L^P was predicted earlier by Dann (1970).

5.4 The Relationship between W_a^P and Temperature

For each material, the polar component of the energy required to separate water from its surface (W_a^P), as determined with the following equation

$$W_a^P = k(\gamma_L^P) + b \quad (30)$$

was evaluated at each temperature. As described earlier, W_a^P provides an index of relative surface hydrophobicity or hydrophilicity. Similar to the behavior of the slope k , values of W_a^P shown in Fig. 5-4 decrease with decreasing polar character of the solid at any temperature:

$$W_a^P, \text{copper} > W_a^P, \text{S.S.} > W_a^P, \text{HDPE} > W_a^P, \text{PTFE}$$

In addition, Fig. 5-4 illustrates that the polar components of the work of adhesion between selected solid surfaces (PTFE, HDPE, S.S., and Copper) and water (W_a^P) decrease with rising temperature in a linear fashion. W_a^P is a function of not only the polar character of the solid surface but also the polar character of the water surface. Both polar character of the liquid and solid decrease with rising

TABLE 5-4

Slope k of the W_a^p vs. γ_L^p Curve for Each Material at 303 K

Material	k
PTFE	0.00
HDPE	0.88
Polypropylene	0.89
UHMW	0.91
Acetal	0.97
Stainless Steel	1.00
Nylon	1.10
Copper	1.18
Glass Slide	1.76

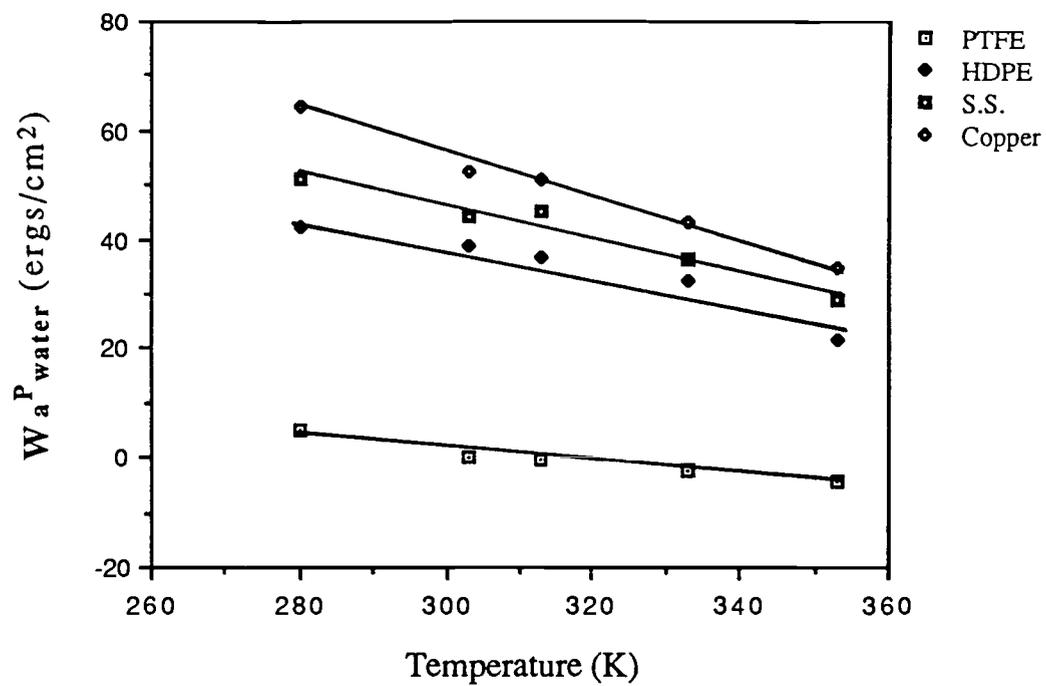


Fig. 5-4 Effect of Temperature on the Polar Component of the Energy Required to Separate Water from Solid Surface

temperature due to increased thermal motions of molecular groups at the liquid surface and translatory motions of atomic or molecular groups at the solid surface (Adam, 1964). Therefore, for a given material, $W_{a^P_{water}}$ decreases with increasing temperature. Also, Fig. 5-4 shows that the magnitude of the slopes of $W_{a^P_{water}}$ as a function of absolute temperature gradually increases with increasing polar character of the solid, where the value of k gives an indication of the polar character. This suggests that the extent of all polar interactions between the material surface and the diagnostic liquid surface strongly depends on temperature. For example, values of $W_{a^P_{water}}$ for copper decrease more sharply with temperature than those of stainless steel and HDPE. Whereas, for the surfaces of PTFE, values of $W_{a^P_{water}}$ remain relatively unchanged with varying temperature; probably, because the PTFE surfaces have much less polar character than any other materials tested.

5.5 Temperature Influences on k and b Related to Solid Surface Chemistry

As indicated previously (McGuire and Kirtley, 1989a,b), the magnitude of k agrees with the expected polar contribution of each solid surface. Since one might expect the relative magnitude of k among surfaces to be similar to corresponding relative magnitudes of $W_{a^P_{water}}$, k might be expected to have the same temperature dependence as $W_{a^P_{water}}$ with respect to the same sample surfaces (PTFE, HDPE, S.S., and Copper). Indeed, Fig. 5-5 demonstrates that values of k decrease linearly with temperature. However, slopes of k

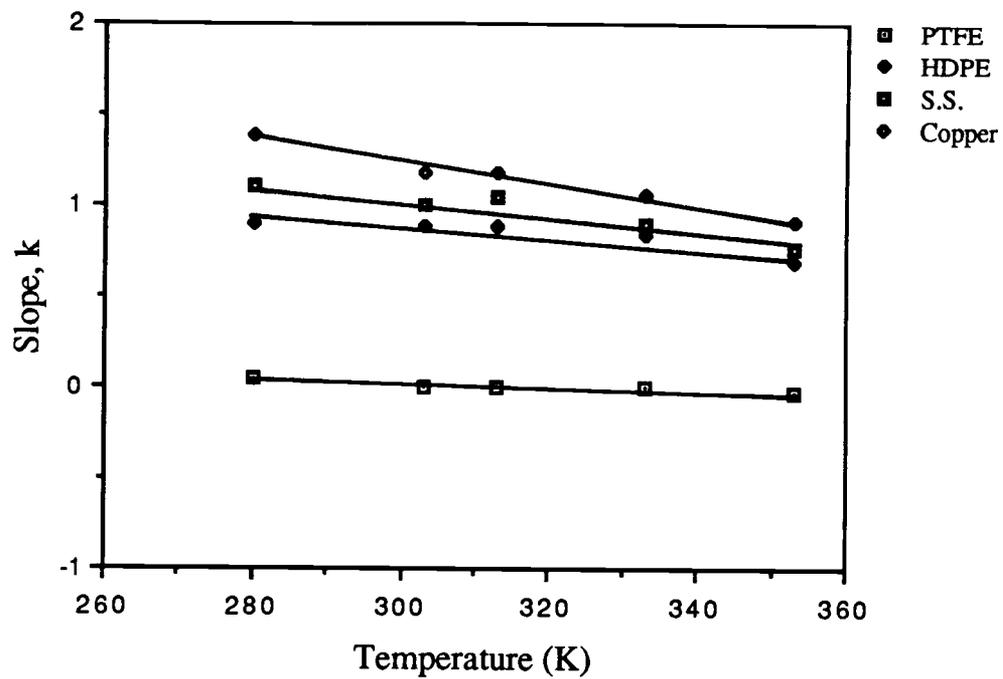


Fig. 5-5 Effect of Temperature on the Slope, k, of W_a^P vs. γ_L^P

vs. $T(K)$ are not as steep as slopes of $W_a^{P_{\text{water}}}$ vs. $T(K)$. This can be partially explained by recognizing that the slope k depends only on the polar character of the material. A decrease in the adhesive field of force with rising temperature is much less in solids due to their relative immobility, and slopes of k vs. $T(K)$ may be lower than those of $W_a^{P_{\text{water}}}$ vs. $T(K)$. Unlike polar materials, it should be noted that the values of k for the nonpolar surfaces of PTFE at each temperature were invariably less than or almost equal to zero. Therefore, the slope of such a line is suggested to have no physical significance with temperature.

The negative values of the intercept b have been suggested to be a measure of π_s , the reduction in surface energy of the solid resulting from adsorption of vapor from the diagnostic liquid (Dann, 1970). The value of the integral in equation (31) may increase or decrease with temperature depending upon the relative behavior of the surface concentration, Γ , and the upper limit of the integral, P_0 . Γ decreases with increasing temperature whereas P_0 , the saturated vapor pressure, must increase. It is therefore difficult to decide the temperature influence of π_s without the pertinent adsorption data.

Values of the surface energetic parameter b evaluated at each temperature are presented in Table 5-5. The magnitude of b of low energy surfaces such as PTFE, HDPE, polypropylene, and UHMW increases with increasing temperature. On the other hand, those of higher energy surfaces like stainless steel, nylon, and copper do not change uniformly with temperature. In addition, Table 5-5 shows

TABLE 5-5

b (ergs/cm²) for Each Material at Six Different Temperatures

Temp.(K)	PTFE	HDPE	Polypro	UHMW
280	2.81	-3.79	-3.79	-4.76
288	1.00	-4.72	-4.86	-5.82
303	0.00	-5.37	-6.38	-6.48
313	-0.55	-6.00	-6.11	-6.93
333	-2.73	-6.89	-6.29	-7.54
353	-3.35	-9.22	-9.35	-8.97

Temp.(K)	S.S.	Nylon	Copper	Glass Slide
280	-5.87	-6.11	-7.08	-6.25
288	-3.98	-5.65	-5.98	-5.98
303	-5.22	-6.13	-6.18	-6.12
313	-5.54	-6.06	-6.57	-6.31
333	-5.30	-5.11	-6.37	-6.27
353	-5.33	-7.61	-6.18	-9.89

that values of b recorded for low energy surfaces are greater than or similar to those of high energy surfaces. These errors may come from difficulties encountered in attempting to maintain saturated vapor in contact with higher energy solids, particularly at high temperatures. However, relative to the high energy surfaces, the mobility of low energy surfaces enables them to more easily adopt an energetically favorable state in contact with liquid. One might therefore expect an apparent π_s to be greater for a low energy surface. Increased temperature enhances this effect. Nevertheless, it is difficult to make a definite conclusion with certainty.

5.6 Temperature Effect on Composite Surface Energy

At a given temperature, a composite surface energy which is composed of the parameters k , b , $W_{a^P_{water}}$, and γ_S^d , unique for each material at each temperature can be constructed to describe surface energetics of a particular material by use of equation (26). The property γ_S^d is independent of temperature; however, properties related to the polar component of surface energy (γ_S^P) are not independent of temperature as just shown. The properties k and $W_{a^P_{water}}$ were observed to decrease linearly with temperature as shown in Fig. 5-4 and Fig. 5-5. The decrease in the adhesive field of force with rising temperature is more apparent in the product of k and $W_{a^P_{water}}$ than in the intercept b . Thus, it is depicted in Fig. 5-6 that values of γ_S^* linearly decrease with increasing temperature.

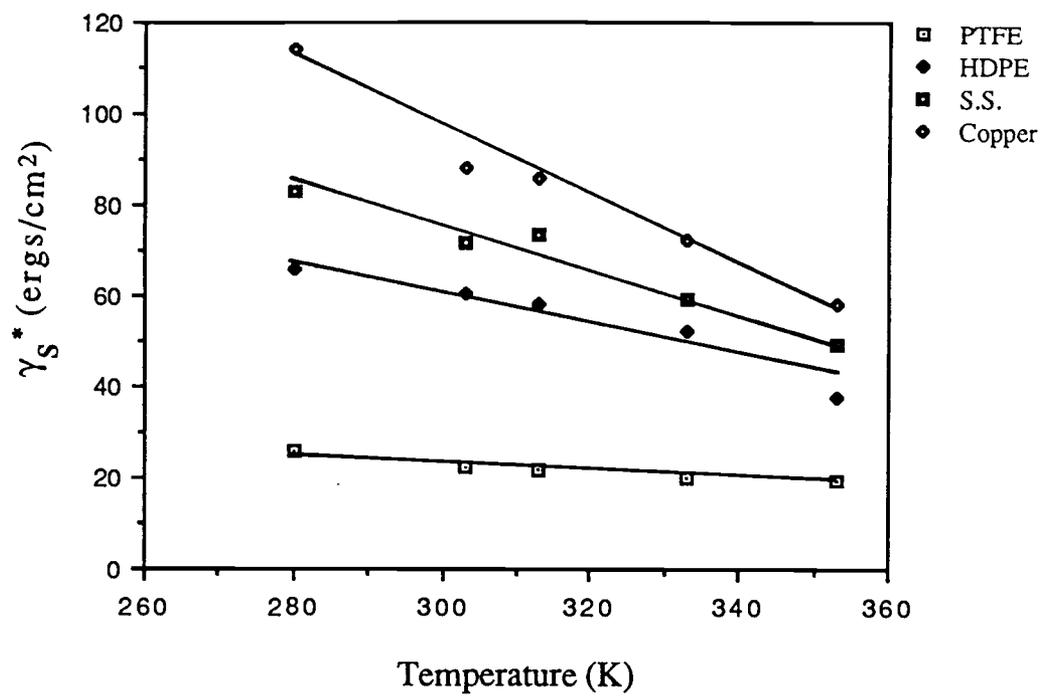


Fig. 5-6 Effect of Temperature on Composite Surface Energy

6. CONCLUSIONS

The surface energetic parameters k , γ_S^* , and $W_{a^P_{\text{water}}}$ decrease linearly with temperature. The polar component of liquid surface tension, γ_L^P , has been observed to be a function of temperature. A linear relationship between W_{a^P} and γ_L^P predicted earlier by Dann (1970) has been observed; moreover, this relationship was observed not to vary with temperature. It has been demonstrated that $W_{a^P_{\text{water}}}$, like the slope k , decreases with decreasing polar character of the solid at a given temperature. Slopes of $W_{a^P_{\text{water}}}$ vs. $T(K)$ are steeper than those of k vs. $T(K)$ because $W_{a^P_{\text{water}}}$ is influenced by two polar components: the surface of water and the solid surface. The decrease in magnitude of the product of k and $W_{a^P_{\text{water}}}$ with increasing temperature is greater than that observed with the intercept b . Consequently, γ_S^* linearly decreases with increasing temperature.

The negative values of the intercept b , suggested to be a measure of π_s by Dann (1970) have been observed to increase with rising temperature for low energy surfaces like PTFE, HDPE, polypropylene, and UHMW, but not to change uniformly for higher energy surfaces including stainless steel, nylon, and copper. It has also been shown that values of π_s of low energy surfaces are greater than or at least similar to those of higher energy surfaces. Nonetheless, it is difficult to make an authentic conclusion.

This study to incorporate effects of temperature into solid surface energy demonstrates that surface energetic properties do indeed change with temperature. This information should provide direction in development of models for both prediction and control of interfacial behavior of biofluid components. However, the results described here are not enough to rigorously understand the relationship between γ_s^* and T(K), thus, additional studies with more accurate experimental systems - with respect to temperature control and contact angle measurement - are warranted.

7. RECOMMENDATIONS

Evaluation of π_s , which is of importance in the interpretation of the temperature dependence of γ_s , has been shown to be difficult. This is especially true for high energy solids such as stainless steel, nylon, and copper. These difficulties may have resulted from establishment of incomplete water-equilibrated surfaces.

One possible alternative approach to combat this problem is to use receding contact angle techniques performed with aqueous solutions. If it is possible to prepare a flat plate of the solid a few centimeters in length, as for example with glass and certain metals, and if a sufficient volume of liquid is available, the tilting plate method, a receding angle technique, can be employed (Aveyard and Haydon, 1973). The plate is held with a clamp, which can be appropriately adjusted, and dipped into the liquid. The angle of the plate is arranged so that there is no curvature on the surface of the liquid in contact with one side of the plate. The angle of the plate from the horizontal which is equal to θ is then determined. This tilting plate method is subject to further refinements which may contribute to the subject of future work. Moreover, the study of temperature effects on solid surface properties with other aqueous diagnostic liquid series should contribute to the subject of future experiments.

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APPENDICES

Appendix A

Nomenclature

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
b	Intercept of W_a^P vs. γ_L^P curve	[erg/cm ²]
k	Slope of W_a^P vs. γ_L^P curve	
P	Pressure	[atm]
P_0	Pressure of the saturated vapor	[atm]
R	Gas constant	[J/mole K]
T	Absolute temperature	[K]
W_a	Work of adhesion between solid and liquid	[erg/cm ²]
W_a^d	Dispersive contribution to W_a between solid and liquid	[erg/cm ²]
W_a^P	Polar contribution to W_a between solid and liquid	[erg/cm ²]
$W_a^P{}_{\text{water}}$	Polar component of the energy required to separate water from solid surface	[erg/cm ²]
Γ	Surface concentration	[mole/cm ²]
γ_{LS}	Liquid-solid interface energy	[erg/cm ²]
γ_L	Liquid surface tension	[dyne/cm]
γ_L^d	Dispersive force contribution to liquid surface tension	[dyne/cm]
γ_L^P	Polar force contribution to liquid surface tension	[dyne/cm]
γ_S	Solid surface energy for a film-covered surface	[erg/cm ²]

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
γ_S^d	Dispersive contribution to γ_S for a film-covered surface	[erg/cm ²]
γ_S^p	Polar contribution to γ_S for a film-covered surface	[erg/cm ²]
γ_S^\dagger	Solid surface energy for a solid-vacuum interface	[erg/cm ²]
γ_S^*	Composite surface energy	[erg/cm ²]
θ	Contact angle	[degree]
π_s	Surface pressure of the adsorbed film	[erg/cm ²]

Appendix B

Arrhenius Model of the slope, k , as a Function of Temperature

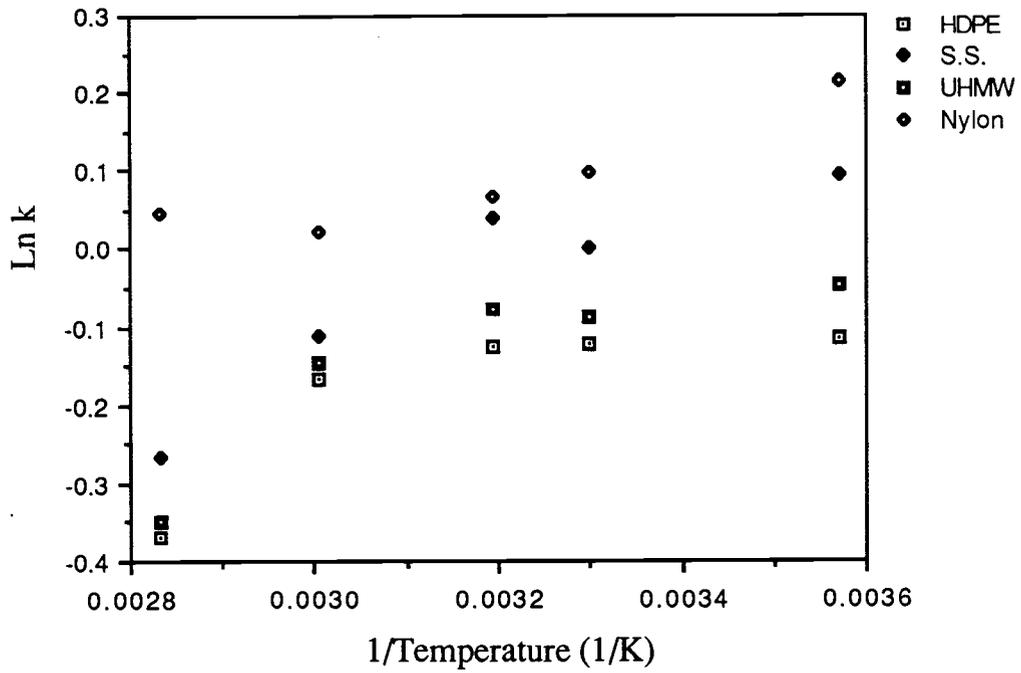


Fig. A-1 Ln k vs. 1/T

An Arrhenius model for k though not expected, might be useful. Fig. A-1 verifies that k 's dependence on temperature does not follow an Arrhenius type dependence.

Appendix C

Sample Calculation of γ_S^* and $W_{a^p_{\text{water}}}$ for Copper at 303 K

1. By use of equations (15) and (16), a series of drops of nonpolar diagnostic liquids on copper yields γ_S^d , and a solid of known γ_S^d (paraffin wax) can be used to evaluate γ_L^d and γ_L^p of polar diagnostic liquids of known γ_L .

γ_S^d of copper = 32.47 (ergs/cm²) (Appendix E)

values of γ_L , γ_L^d , and γ_L^p at 303K are tabled in Appendix D.

2. Measure contact angles (θ) of diagnostic liquids (ethanol/water solutions) on copper.

3. Now, we know the liquid surface properties (γ_L , γ_L^d , and γ_L^p) and γ_S^d . We could plot W_a^p (using by equation (17)) vs. γ_L^p ($\gamma_L - \gamma_L^d$). The relationship between W_a^p and γ_L^p is linear. From linear regression, slope $k = 1.1823$, y intercept $b = -6.1859$ (Appendix E and F).

4. Evaluate γ_S^* and W_a^p water (Appendix E).

$$\begin{aligned} W_a^p \text{water} &= k(\gamma_L^p \text{water}) + b \\ &= (1.1823)(49.66) + (-6.1859) \\ &= 52.5271 \text{ (ergs/cm}^2\text{)} \end{aligned}$$

$$\begin{aligned} \gamma_S^* &= (kW_a^p \text{water} + b + \gamma_S^d) \\ &= (1.1823)(52.5271) + (-6.1859) + 32.47 \\ &= 88.39 \text{ (ergs/cm}^2\text{)} \end{aligned}$$

Appendix D

Data of γ_L , γ_L^d , and γ_L^p at Each Test Temperature

γ_L , γ_L^d , and γ_L^p at 280 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	73.34	21.43	51.91
10%EtOH	53.17	13.42	39.75
20%EtOH	44.08	11.29	32.79
30%EtOH	37.80	17.93	19.87
40%EtOH	33.95	19.23	14.72
50%EtOH	31.14	21.90	9.24
60%EtOH	29.38	20.59	8.79
70%EtOH	28.15	20.01	8.14
80%EtOH	26.67	19.04	7.63
90%EtOH	25.59	19.40	6.19
100%EtOH	24.06	18.28	5.78

 γ_L , γ_L^d , and γ_L^p at 288 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	72.56	21.43	51.13
10%EtOH	52.45	13.42	39.03
20%EtOH	42.99	11.29	31.70
30%EtOH	37.17	17.93	19.24
40%EtOH	33.60	19.23	14.37
50%EtOH	30.75	21.90	8.85
60%EtOH	28.98	20.59	8.39
70%EtOH	27.80	20.01	7.79
80%EtOH	26.26	19.04	7.22
90%EtOH	25.19	19.40	5.79
100%EtOH	23.61	18.28	5.33

γ_L , γ_L^d , and γ_L^p at 303 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	71.09	21.43	49.66
10%EtOH	51.12	13.42	37.70
20%EtOH	40.93	11.29	29.64
30%EtOH	35.98	17.93	18.05
40%EtOH	32.93	19.23	13.70
50%EtOH	30.02	21.90	8.12
60%EtOH	28.24	20.59	7.65
70%EtOH	27.14	20.01	7.13
80%EtOH	25.49	19.04	6.45
90%EtOH	24.42	19.40	5.02
100%EtOH	22.77	18.28	4.49

 γ_L , γ_L^d , and γ_L^p at 313 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	70.11	21.43	48.68
10%EtOH	50.23	13.42	36.81
30%EtOH	35.19	17.93	17.26
40%EtOH	32.49	19.23	13.26
50%EtOH	29.53	21.90	7.63
60%EtOH	27.75	20.59	7.16
70%EtOH	26.70	20.01	6.69
80%EtOH	24.98	19.04	5.94
90%EtOH	23.91	19.40	4.51
100%EtOH	22.21	18.28	3.93

γ_L , γ_L^d , and γ_L^p at 333 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	68.15	21.43	46.72
10%EtOH	48.45	13.42	35.03
20%EtOH	36.83	11.29	25.54
30%EtOH	33.60	17.93	15.67
40%EtOH	31.60	19.23	12.37
50%EtOH	28.55	21.90	6.65
60%EtOH	26.76	20.59	6.17
70%EtOH	25.83	20.01	5.82
80%EtOH	23.96	19.04	4.92
90%EtOH	22.88	19.40	3.48
100%EtOH	21.09	18.28	2.81

 γ_L , γ_L^d , and γ_L^p at 353 K

Liquids	γ_L	γ_L^d	γ_L^p
Water	66.19	21.43	44.76
10%EtOH	46.68	13.42	33.26
20%EtOH	34.09	11.29	22.80
30%EtOH	32.01	17.93	14.08
40%EtOH	30.71	19.23	11.48
50%EtOH	27.58	21.90	5.68
60%EtOH	25.77	20.59	5.18
70%EtOH	24.95	20.01	4.94
80%EtOH	22.93	19.04	3.89
90%EtOH	21.86	19.40	2.46
100%EtOH	19.97	18.28	1.69

Appendix E

Summary of Surface Parameters at Each Test Temperature

Summary at 280 K

Materials	k	b	$W a^P_{\text{water}}$	γ_S^d	γ_S^P	γ_S^*
PTFE	0.04	2.81	5.06	22.58	3.03	25.61
HDPE	0.88	-3.79	42.39	31.83	33.93	65.76
Polypro	0.85	-3.79	40.56	30.69	30.88	61.57
UHMW	0.95	-4.76	44.70	32.40	37.84	70.24
S.S.	1.09	-5.87	51.15	32.44	50.32	82.76
Nylon	1.23	-6.11	58.16	33.25	65.91	99.16
Copper	1.37	-7.08	64.52	32.47	81.94	114.41
Glass Slide	1.68	-6.25	81.29	27.54	130.85	158.39
Acetal	0.97	-14.26	36.20	46.36	20.93	67.29

Summary at 288 K

Materials	k	b	$W a^P_{\text{water}}$	γ_S^d	γ_S^P	γ_S^*
PTFE	0.00	1.00	1.26	22.58	1.01	23.59
HDPE	0.80	-4.72	36.21	31.83	24.27	56.10
Polypro	0.73	-4.86	32.87	30.69	19.41	50.10
UHMW	0.85	-5.82	37.83	32.40	26.49	58.89
S.S.	0.84	-3.98	39.05	32.44	28.88	61.32
Nylon	1.06	-5.65	48.75	33.25	46.22	79.47
Copper	1.18	-5.98	54.78	32.47	59.14	91.61
Glass Slide	1.65	-5.98	78.40	27.54	123.43	150.97
Acetal	0.88	-14.20	31.04	46.36	13.27	59.63

Summary at 303 K

Materials	k	b	$W a^p_{\text{water}}$	γ_S^d	γ_S^p	γ_S^*
PTFE	0.00	0.00	0.00	22.58	0.00	22.58
HDPE	0.88	-5.37	38.59	31.83	28.80	60.63
Polypro	0.89	-6.38	37.83	30.69	27.30	57.99
UHMW	0.91	-6.48	38.99	32.40	29.22	61.62
S.S.	1.00	-5.22	44.45	32.44	39.25	71.69
Nylon	1.10	-6.13	48.58	33.25	47.41	80.66
Copper	1.18	-6.18	52.52	32.47	55.92	88.39
Glass Slide	1.76	-6.12	81.53	27.54	137.80	165.34
Acetal	0.87	-14.62	28.98	46.36	10.83	57.19

Summary at 313 K

Materials	k	b	$W a^p_{\text{water}}$	γ_S^d	γ_S^p	γ_S^*
PTFE	-0.00	-0.55	-0.62	22.58	-0.56	22.02
HDPE	0.88	-6.00	36.87	31.83	26.48	58.31
Polypro	0.86	-6.11	35.82	30.69	24.74	55.43
UHMW	0.92	-6.93	38.08	32.40	28.28	60.68
S.S.	1.03	-5.54	45.05	32.44	41.28	73.72
Nylon	1.06	-6.06	45.96	33.25	43.07	76.32
Copper	1.18	-6.57	50.88	32.47	53.49	85.96
Glass Slide	1.76	-6.31	79.78	27.54	134.82	162.36
Acetal	0.83	-14.70	26.06	46.36	7.12	53.48

Summary at 333 K

Materials	k	b	$W_{a^P_{water}}$	γ_S^d	γ_S^P	γ_S^*
PTFE	0.00	-2.73	-2.46	22.58	-2.75	19.83
HDPE	0.84	-6.89	32.59	31.83	20.66	52.49
Polypro	0.74	-6.29	28.70	30.69	15.21	45.90
UHMW	0.86	-7.54	32.79	32.40	20.77	53.17
S.S.	0.89	-5.30	36.41	32.44	27.21	59.65
Nylon	1.02	-5.11	42.65	33.25	38.51	71.76
Copper	1.06	-6.37	43.35	32.47	39.76	72.23
Glass Slide	1.74	-6.27	75.41	27.54	125.58	153.12
Acetal	0.85	-15.54	24.21	46.36	5.07	51.43

Summary at 353 K

Materials	k	b	$W_{a^P_{water}}$	γ_S^d	γ_S^P	γ_S^*
PTFE	-0.02	-3.35	-4.41	22.58	-3.25	19.33
HDPE	0.69	-9.22	21.74	31.83	5.82	37.65
Polypro	0.64	-9.35	19.73	30.69	3.47	34.16
UHMW	0.70	-8.97	22.58	32.40	6.95	39.35
S.S.	0.76	-5.33	28.78	32.44	16.70	49.14
Nylon	1.04	-7.61	39.22	33.25	33.43	66.68
Copper	0.91	-6.18	34.85	32.47	25.77	58.24
Glass Slide	1.84	-9.89	72.87	27.54	124.86	152.40
Acetal	0.86	-17.35	21.35	46.36	1.11	47.47

Appendix F

Contact Angle Data of Each Material at Each Test Temperature

PTFE ($\gamma_S^d = 22.58$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	111.9	73.34	21.43	51.91	1.99
10%EtOH	102.8	53.17	13.42	39.75	6.57
20%EtOH	98.2	44.08	11.29	32.79	5.86
30%EtOH	77.0	37.80	17.93	19.87	6.06
40%EtOH	69.9	33.95	19.23	14.72	3.94
50%EtOH	62.2	31.14	21.90	9.24	1.18
60%EtOH	55.5	29.38	20.59	8.79	2.89
70%EtOH	53.2	28.15	20.01	8.14	2.50
80%EtOH	46.2	26.67	19.04	7.63	3.66
90%EtOH	44.3	25.59	19.40	6.19	2.04
100%EtOH	35.1	24.06	18.28	5.78	3.11

$$k = 0.04$$

$$b = 2.81$$

$$r^2 = 0.38$$

$$W_{a^p_{\text{water}}} = 5.06$$

HDPE ($\gamma_S^d = 31.83$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	72.2	73.34	21.43	51.91	43.52
10%EtOH	69.1	53.17	13.42	39.75	30.80
20%EtOH	63.6	44.08	11.29	32.79	25.76
30%EtOH	49.9	37.80	17.93	19.87	14.36
40%EtOH	40.8	33.95	19.23	14.72	10.16
50%EtOH	33.8	31.14	21.90	9.24	4.21
60%EtOH	29.0	29.38	20.59	8.79	3.87
70%EtOH	19.9	28.15	20.01	8.14	4.14
80%EtOH	13.5	26.67	19.04	7.63	3.36
90%EtOH	0.0	25.59	19.40	6.19	1.48
100%EtOH	0.0	24.06	18.28	5.78	-0.12

$$k = 0.88$$

$$b = -3.79$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 42.39$$

Polypro ($\gamma_S^d = 30.69$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	73.1	73.34	21.43	51.91	43.36
10%EtOH	71.9	53.17	13.42	39.75	29.10
20%EtOH	65.2	44.08	11.29	32.79	25.34
30%EtOH	52.8	37.80	17.93	19.87	13.73
40%EtOH	46.2	33.95	19.23	14.72	8.86
50%EtOH	38.3	31.14	21.90	9.24	3.72
60%EtOH	35.3	29.38	20.59	8.79	3.08
70%EtOH	29.0	28.15	20.01	8.14	3.20
80%EtOH	21.0	26.67	19.04	7.63	3.22
90%EtOH	13.5	25.59	19.40	6.19	1.67
100%EtOH	0.0	24.06	18.28	5.78	0.74

$$k = 0.85$$

$$b = -3.79$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 40.56$$

UHMW ($\gamma_S^d = 32.40$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	75.9	73.34	21.43	51.91	38.50
10%EtOH	65.9	53.17	13.42	39.75	33.17
20%EtOH	62.9	44.08	11.29	32.79	25.90
30%EtOH	48.1	37.80	17.93	19.87	14.83
40%EtOH	41.3	33.95	19.23	14.72	9.53
50%EtOH	33.9	31.14	21.90	9.24	3.71
60%EtOH	28.7	29.38	20.59	8.79	3.49
70%EtOH	19.1	28.15	20.01	8.14	3.82
80%EtOH	12.1	26.67	19.04	7.63	3.07
90%EtOH	0.0	25.59	19.40	6.19	1.03
100%EtOH	0.0	24.06	18.28	5.78	-0.55

$$k = 0.95$$

$$b = -4.76$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 44.70$$

S.S. ($\gamma_S^d = 32.44$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	65.9	73.34	21.43	51.91	50.55
10%EtOH	58.0	53.17	13.42	39.75	39.61
20%EtOH	59.9	44.08	11.29	32.79	27.91
30%EtOH	45.9	37.80	17.93	19.87	15.87
40%EtOH	40.7	33.95	19.23	14.72	9.73
50%EtOH	30.9	31.14	21.90	9.24	4.55
60%EtOH	28.3	29.38	20.59	8.79	3.55
70%EtOH	15.9	28.15	20.01	8.14	4.26
80%EtOH	9.4	26.67	19.04	7.63	3.27
90%EtOH	0.0	25.59	19.40	6.19	1.00
100%EtOH	0.0	24.06	18.28	5.78	-0.58

$$k = 1.09$$

$$b = -5.87$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 51.15$$

Nylon ($\gamma_S^d = 33.25$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	58.7	73.34	21.43	51.91	58.05
10%EtOH	52.5	53.17	13.42	39.75	43.29
20%EtOH	49.1	44.08	11.29	32.79	34.19
30%EtOH	41.4	37.80	17.93	19.87	17.32
40%EtOH	27.1	33.95	19.23	14.72	13.60
50%EtOH	15.5	31.14	21.90	9.24	7.17
60%EtOH	11.7	29.38	20.59	8.79	5.81
70%EtOH	0.0	28.15	20.01	8.14	4.71
80%EtOH	0.0	26.67	19.04	7.63	3.01
90%EtOH	0.0	25.59	19.40	6.19	0.38
100%EtOH	0.0	24.06	18.28	5.78	-1.18

$$k = 1.23$$

$$b = -6.11$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 58.16$$

Copper ($\gamma_S^d = 32.47$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	52.5	73.34	21.43	51.91	65.22
10%EtOH	45.0	53.17	13.42	39.75	49.01
20%EtOH	44.5	44.08	11.29	32.79	37.22
30%EtOH	41.1	37.80	17.93	19.87	18.02
40%EtOH	28.6	33.95	19.23	14.72	13.78
50%EtOH	21.1	31.14	21.90	9.24	6.85
60%EtOH	16.3	29.38	20.59	8.79	5.86
70%EtOH	0.0	28.15	20.01	8.14	5.32
80%EtOH	0.0	26.67	19.04	7.63	3.61
90%EtOH	0.0	25.59	19.40	6.19	0.98
100%EtOH	0.0	24.06	18.28	5.78	-0.60

$$k = 1.37$$

$$b = -7.08$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 64.52$$

Glass ($\gamma_S^d = 27.54$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	26.6	73.34	21.43	51.91	90.32
10%EtOH	40.0	53.17	13.42	39.75	55.45
20%EtOH	41.5	44.08	11.29	32.79	41.82
30%EtOH	37.9	37.80	17.93	19.87	23.18
40%EtOH	27.9	33.95	19.23	14.72	17.92
50%EtOH	17.8	31.14	21.90	9.24	11.67
60%EtOH	0.0	29.38	20.59	8.79	11.13
70%EtOH	0.0	28.15	20.01	8.14	9.35
80%EtOH	0.0	26.67	19.04	7.63	7.54
90%EtOH	0.0	25.59	19.40	6.19	4.95
100%EtOH	0.0	24.06	18.28	5.78	3.24

$$k = 1.68$$

$$b = -6.25$$

$$r^2 = 0.99$$

$$W_a^p_{\text{water}} = 81.29$$

Acetal ($\gamma_S^d = 46.36$) at 280 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	67.3	73.34	21.43	51.91	38.60
10%EtOH	70.3	53.17	13.42	39.75	21.20
20%EtOH	63.2	44.08	11.29	32.79	18.19
30%EtOH	51.5	37.80	17.93	19.87	3.66
40%EtOH	34.3	33.95	19.23	14.72	2.28
50%EtOH	26.6	31.14	21.90	9.24	-4.74
60%EtOH	21.7	29.38	20.59	8.79	-5.11
70%EtOH	13.4	28.15	20.01	8.14	-5.38
80%EtOH	11.4	26.67	19.04	7.63	-6.60
90%EtOH	0.0	25.59	19.40	6.19	-8.79
100%EtOH	0.0	24.06	18.28	5.78	-10.10

$$k = 0.97$$

$$b = -14.26$$

$$r^2 = 0.99$$

$$W_a^p_{\text{water}} = 36.20$$

PTFE ($\gamma_S^d = 22.58$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	112.1	72.56	21.43	51.13	1.26
10%EtOH	108.2	52.45	13.42	39.03	1.25
20%EtOH	102.9	42.99	11.29	31.70	1.45
30%EtOH	83.7	37.17	17.93	19.24	1.00
40%EtOH	75.7	33.60	19.23	14.37	0.22
50%EtOH	62.8	30.75	21.90	8.85	0.33
60%EtOH	59.3	28.98	20.59	8.39	0.65
70%EtOH	54.1	27.80	20.01	7.79	1.58
80%EtOH	48.8	26.26	19.04	7.22	2.08
90%EtOH	45.9	25.19	19.40	5.79	0.86
100%EtOH	38.9	23.61	18.28	5.33	1.35

$$k = 0.00$$

$$b = 1.00$$

$$r^2 = 0.14$$

$$W_a^p_{\text{water}} = 1.26$$

HDPE ($\gamma_S^d = 31.83$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	91.2	72.56	21.43	51.13	18.80
10%EtOH	73.1	52.45	13.42	39.03	26.36
20%EtOH	68.4	42.99	11.29	31.70	20.90
30%EtOH	55.9	37.17	17.93	19.24	10.22
40%EtOH	45.4	33.60	19.23	14.37	7.71
50%EtOH	40.8	30.75	21.90	8.85	1.22
60%EtOH	37.2	28.98	20.59	8.39	0.86
70%EtOH	25.4	27.80	20.01	7.79	2.43
80%EtOH	17.4	26.26	19.04	7.22	2.08
90%EtOH	11.1	25.19	19.40	5.79	0.20
100%EtOH	0.0	23.61	18.28	5.33	-1.02

$$k = 0.80$$

$$b = -4.72$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 36.21$$

Polypro ($\gamma_S^d = 30.69$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	95.3	72.56	21.43	51.13	14.56
10%EtOH	76.9	52.45	13.42	39.03	23.74
20%EtOH	71.2	42.99	11.29	31.70	19.61
30%EtOH	62.4	37.17	17.93	19.24	7.47
40%EtOH	50.6	33.60	19.23	14.37	6.34
50%EtOH	42.1	30.75	21.90	8.85	1.71
60%EtOH	39.7	28.98	20.59	8.39	1.00
70%EtOH	36.5	27.80	20.01	7.79	0.58
80%EtOH	31.0	26.26	19.04	7.22	0.42
90%EtOH	20.5	25.19	19.40	5.79	-0.01
100%EtOH	9.9	23.61	18.28	5.33	-0.50

$$k = 0.73$$

$$b = -4.86$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 32.87$$

UHMW ($\gamma_S^d = 32.40$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	95.9	72.56	21.43	51.13	12.40
10%EtOH	71.3	52.45	13.42	39.03	27.56
20%EtOH	66.8	42.99	11.29	31.70	21.67
30%EtOH	54.8	37.17	17.93	19.24	10.39
40%EtOH	50.2	33.60	19.23	14.37	5.18
50%EtOH	38.2	30.75	21.90	8.85	1.64
60%EtOH	36.0	28.98	20.59	8.39	0.76
70%EtOH	27.6	27.80	20.01	7.79	1.51
80%EtOH	21.4	26.26	19.04	7.22	1.03
90%EtOH	13.3	25.19	19.40	5.79	-0.43
100%EtOH	0.0	23.61	18.28	5.33	-1.45

$$k = 0.85$$

$$b = -5.82$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 37.83$$

S.S. ($\gamma_S^d = 32.44$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	77.7	72.56	21.43	51.13	35.28
10%EtOH	70.2	52.45	13.42	39.03	28.48
20%EtOH	66.5	42.99	11.29	31.70	21.85
30%EtOH	48.5	37.17	17.93	19.24	13.56
40%EtOH	39.3	33.60	19.23	14.37	9.64
50%EtOH	30.9	30.75	21.90	8.85	3.82
60%EtOH	28.9	28.98	20.59	8.39	2.66
70%EtOH	16.8	27.80	20.01	7.79	3.45
80%EtOH	11.9	26.26	19.04	7.22	2.25
90%EtOH	0.0	25.19	19.40	5.79	0.20
100%EtOH	0.0	23.61	18.28	5.33	-1.48

$$k = 0.84$$

$$b = -3.98$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 39.05$$

Nylon ($\gamma_S^d = 33.25$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	65.9	72.56	21.43	51.13	48.80
10%EtOH	61.2	52.45	13.42	39.03	35.47
20%EtOH	56.4	42.99	11.29	31.70	28.03
30%EtOH	45.9	37.17	17.93	19.24	14.20
40%EtOH	32.7	33.60	19.23	14.37	11.30
50%EtOH	27.0	30.75	21.90	8.85	4.17
60%EtOH	21.2	28.98	20.59	8.39	3.66
70%EtOH	0.0	27.80	20.01	7.79	4.01
80%EtOH	0.0	26.26	19.04	7.22	2.19
90%EtOH	0.0	25.19	19.40	5.79	-0.41
100%EtOH	0.0	23.61	18.28	5.33	-2.08

$$k = 1.06$$

$$b = -5.65$$

$$r^2 = 1.00$$

$$W_{a^p \text{water}} = 48.75$$

Copper ($\gamma_S^d = 32.47$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	65.3	72.56	21.43	51.13	50.12
10%EtOH	57.5	52.45	13.42	39.03	38.88
20%EtOH	47.3	42.99	11.29	31.70	33.85
30%EtOH	43.8	37.17	17.93	19.24	15.74
40%EtOH	33.9	33.60	19.23	14.37	11.51
50%EtOH	26.1	30.75	21.90	8.85	5.03
60%EtOH	19.3	28.98	20.59	8.39	4.61
70%EtOH	0.0	27.80	20.01	7.79	4.62
80%EtOH	0.0	26.26	19.04	7.22	2.79
90%EtOH	0.0	25.19	19.40	5.79	0.18
100%EtOH	0.0	23.61	18.28	5.33	-1.50

$$k = 1.18$$

$$b = -5.98$$

$$r^2 = 1.00$$

$$W_{a^p \text{water}} = 54.78$$

Glass ($\gamma_S^d = 27.54$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	31.6	72.56	21.43	51.13	85.77
10%EtOH	39.6	52.45	13.42	39.03	54.41
20%EtOH	41.1	42.99	11.29	31.70	40.11
30%EtOH	37.4	37.17	17.93	19.24	22.25
40%EtOH	30.7	33.60	19.23	14.37	16.46
50%EtOH	16.5	30.75	21.90	8.85	11.11
60%EtOH	0.0	28.98	20.59	8.39	10.33
70%EtOH	0.0	27.80	20.01	7.79	8.65
80%EtOH	0.0	26.26	19.04	7.22	6.72
90%EtOH	0.0	25.19	19.40	5.79	4.15
100%EtOH	0.0	23.61	18.28	5.33	2.34

$$k = 1.65$$

$$b = -5.98$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 78.40$$

Acetal ($\gamma_S^d = 46.36$) at 288 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	76.8	72.56	21.43	51.13	26.08
10%EtOH	63.8	52.45	13.42	39.03	25.72
20%EtOH	64.2	42.99	11.29	31.70	15.94
30%EtOH	55.2	37.17	17.93	19.24	0.72
40%EtOH	35.9	33.60	19.23	14.37	1.10
50%EtOH	30.6	30.75	21.90	8.85	-6.50
60%EtOH	34.7	28.98	20.59	8.39	-8.98
70%EtOH	14.9	27.80	20.01	7.79	-6.24
80%EtOH	12.4	26.26	19.04	7.22	-7.51
90%EtOH	0.0	25.19	19.40	5.79	-9.59
100%EtOH	0.0	23.61	18.28	5.33	-11.00

$$k = 0.88$$

$$b = -14.20$$

$$r^2 = 0.98$$

$$W_{a^p_{\text{water}}} = 31.04$$

PTFE ($\gamma_S^d = 22.58$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	112.4	71.09	21.43	49.66	0.00
10%EtOH	108.6	51.12	13.42	37.70	-0.00
20%EtOH	102.7	40.93	11.29	29.64	-0.00
30%EtOH	83.2	35.98	17.93	18.05	-0.00
40%EtOH	74.6	32.93	19.23	13.70	-0.00
50%EtOH	61.2	30.02	21.90	8.12	0.00
60%EtOH	58.2	28.24	20.59	7.65	-0.00
70%EtOH	55.5	27.14	20.01	7.13	-0.00
80%EtOH	51.2	25.49	19.04	6.45	-0.00
90%EtOH	44.4	24.42	19.40	5.02	0.00
100%EtOH	38.3	22.77	18.28	4.49	0.00

$$k = 0.00$$

$$b = 0.00$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 0.00$$

HDPE ($\gamma_S^d = 31.83$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	95.2	71.09	21.43	49.66	12.41
10%EtOH	72.3	51.12	13.42	37.70	25.32
20%EtOH	61.1	40.93	11.29	29.64	22.79
30%EtOH	48.0	35.98	17.93	18.05	12.27
40%EtOH	38.6	32.93	19.23	13.70	9.18
50%EtOH	38.0	30.02	21.90	8.12	0.87
60%EtOH	30.4	28.24	20.59	7.65	1.39
70%EtOH	26.2	27.14	20.01	7.13	1.01
80%EtOH	21.4	25.49	19.04	6.45	-0.01
90%EtOH	15.3	24.42	19.40	5.02	-1.72
100%EtOH	0.0	22.77	18.28	4.49	-2.70

$$k = 0.88$$

$$b = -5.37$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 38.59$$

Polypro ($\gamma_S^d = 30.69$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^P	W_{a^P}
Water	96.0	71.09	21.43	49.66	12.36
10%EtOH	75.2	51.12	13.42	37.70	23.58
20%EtOH	61.3	40.93	11.29	29.64	23.35
30%EtOH	52.1	35.98	17.93	18.05	11.16
40%EtOH	43.5	32.93	19.23	13.70	8.22
50%EtOH	41.9	30.02	21.90	8.12	0.51
60%EtOH	40.3	28.24	20.59	7.65	-0.49
70%EtOH	35.4	27.14	20.01	7.13	-0.29
80%EtOH	33.1	25.49	19.04	6.45	-1.50
90%EtOH	28.1	24.42	19.40	5.02	-2.83
100%EtOH	16.0	22.77	18.28	4.49	-2.71

$$k = 0.89$$

$$b = -6.38$$

$$r^2 = 0.98$$

$$W_{a^P_{\text{water}}} = 37.83$$

UHMW ($\gamma_S^d = 32.40$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^P	W_{a^P}
Water	90.2	71.09	21.43	49.66	18.14
10%EtOH	71.6	51.12	13.42	37.70	25.55
20%EtOH	62.1	40.93	11.29	29.64	21.83
30%EtOH	44.0	35.98	17.93	18.05	13.65
40%EtOH	42.2	32.93	19.23	13.70	7.40
50%EtOH	40.1	30.02	21.90	8.12	-0.29
60%EtOH	35.4	28.24	20.59	7.65	-0.39
70%EtOH	27.6	27.14	20.01	7.13	0.26
80%EtOH	25.0	25.49	19.04	6.45	-1.08
90%EtOH	16.4	24.42	19.40	5.02	-2.29
100%EtOH	0.0	22.77	18.28	4.49	-3.13

$$k = 0.91$$

$$b = -6.48$$

$$r^2 = 0.99$$

$$W_{a^P_{\text{water}}} = 38.99$$

S.S. ($\gamma_S^d = 32.44$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	77.7	71.09	21.43	49.66	33.50
10%EtOH	67.4	51.12	13.42	37.70	29.03
20%EtOH	52.0	40.93	11.29	29.64	27.85
30%EtOH	44.0	35.98	17.93	18.05	13.62
40%EtOH	35.0	32.93	19.23	13.70	9.95
50%EtOH	24.9	30.02	21.90	8.12	3.94
60%EtOH	22.3	28.24	20.59	7.65	2.67
70%EtOH	15.7	27.14	20.01	7.13	2.31
80%EtOH	10.3	25.49	19.04	6.45	0.86
90%EtOH	0.0	24.42	19.40	5.02	-1.33
100%EtOH	0.0	22.77	18.28	4.49	-3.16

$$k = 1.00$$

$$b = -5.22$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 44.45$$

Nylon ($\gamma_S^d = 33.25$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	66.2	71.09	21.43	49.66	46.39
10%EtOH	56.5	51.12	13.42	37.70	37.08
20%EtOH	51.9	40.93	11.29	29.64	27.43
30%EtOH	42.5	35.98	17.93	18.05	13.67
40%EtOH	30.4	32.93	19.23	13.70	10.76
50%EtOH	22.9	30.02	21.90	8.12	3.70
60%EtOH	19.2	28.24	20.59	7.65	2.57
70%EtOH	0.0	27.14	20.01	7.13	2.69
80%EtOH	0.0	25.49	19.04	6.45	0.65
90%EtOH	0.0	24.42	19.40	5.02	-1.95
100%EtOH	0.0	22.77	18.28	4.49	-3.76

$$k = 1.10$$

$$b = -6.13$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 48.58$$

Copper ($\gamma_S^d = 32.47$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	70.2	71.09	21.43	49.66	42.41
10%EtOH	54.2	51.12	13.42	37.70	39.27
20%EtOH	45.3	40.93	11.29	29.64	31.42
30%EtOH	41.6	35.98	17.93	18.05	14.62
40%EtOH	31.0	32.93	19.23	13.70	11.18
50%EtOH	22.5	30.02	21.90	8.12	4.42
60%EtOH	17.2	28.24	20.59	7.65	3.50
70%EtOH	0.0	27.14	20.01	7.13	3.30
80%EtOH	0.0	25.49	19.04	6.45	1.25
90%EtOH	0.0	24.42	19.40	5.02	-1.35
100%EtOH	0.0	22.77	18.28	4.49	-3.18

$$k = 1.18$$

$$b = -6.18$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 52.52$$

Glass ($\gamma_S^d = 27.54$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	29.0	71.09	21.43	49.66	84.67
10%EtOH	26.2	51.12	13.42	37.70	58.53
20%EtOH	24.3	40.93	11.29	29.64	42.96
30%EtOH	22.1	35.98	17.93	18.05	24.87
40%EtOH	18.5	32.93	19.23	13.70	18.13
50%EtOH	14.3	30.02	21.90	8.12	9.99
60%EtOH	0.0	28.24	20.59	7.65	8.85
70%EtOH	0.0	27.14	20.01	7.13	7.33
80%EtOH	0.0	25.49	19.04	6.45	5.18
90%EtOH	0.0	24.42	19.40	5.02	2.61
100%EtOH	0.0	22.77	18.28	4.49	0.66

$$k = 1.76$$

$$b = -6.12$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 81.53$$

Acetal ($\gamma_S^d = 46.36$) at 303 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	75.8	71.09	21.43	49.66	25.48
10%EtOH	68.5	51.12	13.42	37.70	19.96
20%EtOH	60.2	40.93	11.29	29.64	15.51
30%EtOH	50.9	35.98	17.93	18.05	1.00
40%EtOH	40.0	32.93	19.23	13.70	-1.56
50%EtOH	31.0	30.02	21.90	8.12	-7.97
60%EtOH	27.9	28.24	20.59	7.65	-8.59
70%EtOH	13.3	27.14	20.01	7.13	-7.36
80%EtOH	9.6	25.49	19.04	6.45	-8.79
90%EtOH	0.0	24.42	19.40	5.02	-11.13
100%EtOH	0.0	22.77	18.28	4.49	-12.68

$$k = 0.87$$

$$b = -14.62$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 28.98$$

PTFE ($\gamma_S^d = 22.58$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	112.6	70.11	21.43	48.68	-0.82
10%EtOH	107.9	50.23	13.42	36.81	-0.02
20%EtOH	102.4	39.56	11.29	28.27	-0.86
30%EtOH	83.4	35.19	17.93	17.26	-1.00
40%EtOH	73.9	32.49	19.23	13.26	-0.17
50%EtOH	62.8	29.53	21.90	7.63	-1.44
60%EtOH	58.7	27.75	20.59	7.16	-0.95
70%EtOH	55.5	26.70	20.01	6.69	-0.68
80%EtOH	46.0	24.98	19.04	5.94	0.86
90%EtOH	43.7	23.91	19.40	4.51	-0.66
100%EtOH	36.7	22.21	18.28	3.93	-0.61

$$k = -0.00$$

$$b = -0.55$$

$$r^2 = 0.03$$

$$W_{a^p_{\text{water}}} = -0.62$$

HDPE ($\gamma_S^d = 31.83$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	95.2	70.11	21.43	48.68	11.52
10%EtOH	72.1	50.23	13.42	36.81	24.33
20%EtOH	60.8	39.56	11.29	28.27	20.94
30%EtOH	51.1	35.19	17.93	17.26	9.50
40%EtOH	41.7	32.49	19.23	13.26	7.26
50%EtOH	36.3	29.53	21.90	7.63	0.52
60%EtOH	31.5	27.75	20.59	7.16	0.21
70%EtOH	24.7	26.70	20.01	6.69	0.48
80%EtOH	21.4	24.98	19.04	5.94	-0.99
90%EtOH	15.2	23.91	19.40	4.51	-2.71
100%EtOH	0.0	22.21	18.28	3.93	-3.82

$$k = 0.88$$

$$b = -6.00$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 36.87$$

Polypro ($\gamma_S^d = 30.69$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	97.1	70.11	21.43	48.68	10.15
10%EtOH	75.0	50.23	13.42	36.81	22.64
20%EtOH	61.0	39.56	11.29	28.27	21.51
30%EtOH	53.2	35.19	17.93	17.26	9.35
40%EtOH	43.9	32.49	19.23	13.26	7.31
50%EtOH	41.9	29.53	21.90	7.63	-0.34
60%EtOH	38.5	27.75	20.59	7.16	-0.80
70%EtOH	35.1	26.70	20.01	6.69	-1.01
80%EtOH	31.5	24.98	19.04	5.94	-2.06
90%EtOH	12.5	23.91	19.40	4.51	-1.54
100%EtOH	0.0	22.21	18.28	3.93	-2.95

$$k = 0.86$$

$$b = -6.11$$

$$r^2 = 0.98$$

$$W_{a^p_{\text{water}}} = 35.82$$

UHMW ($\gamma_S^d = 32.40$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	92.3	70.11	21.43	48.68	14.59
10%EtOH	71.6	50.23	13.42	36.81	24.38
20%EtOH	58.7	39.56	11.29	28.27	21.86
30%EtOH	50.1	35.19	17.93	17.26	9.55
40%EtOH	39.1	32.49	19.23	13.26	7.78
50%EtOH	38.5	29.53	21.90	7.63	-0.63
60%EtOH	34.2	27.75	20.59	7.16	-0.95
70%EtOH	26.2	26.70	20.01	6.69	-0.26
80%EtOH	24.3	24.98	19.04	5.94	-1.92
90%EtOH	16.4	23.91	19.40	4.51	-3.29
100%EtOH	0.0	22.21	18.28	3.93	-4.25

$$k = 0.92$$

$$b = -6.93$$

$$r^2 = 0.99$$

$$W_a^p_{\text{water}} = 38.08$$

S.S. ($\gamma_S^d = 32.44$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	80.7	70.11	21.43	48.68	28.70
10%EtOH	66.9	50.23	13.42	36.81	28.20
20%EtOH	47.9	39.56	11.29	28.27	27.80
30%EtOH	38.2	35.19	17.93	17.26	14.60
40%EtOH	31.1	32.49	19.23	13.26	10.35
50%EtOH	21.9	29.53	21.90	7.63	3.62
60%EtOH	22.3	27.75	20.59	7.16	1.73
70%EtOH	14.7	26.70	20.01	6.69	1.57
80%EtOH	9.7	24.98	19.04	5.94	-0.10
90%EtOH	0.0	23.91	19.40	4.51	-2.35
100%EtOH	0.0	22.21	18.28	3.93	-4.28

$$k = 1.03$$

$$b = -5.54$$

$$r^2 = 0.98$$

$$W_a^p_{\text{water}} = 45.05$$

Nylon ($\gamma_S^d = 33.25$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	67.6	70.11	21.43	48.68	43.43
10%EtOH	58.0	50.23	13.42	36.81	34.60
20%EtOH	51.1	39.56	11.29	28.27	25.65
30%EtOH	42.5	35.19	17.93	17.26	12.30
40%EtOH	25.1	32.49	19.23	13.26	11.33
50%EtOH	20.7	29.53	21.90	7.63	3.18
60%EtOH	18.6	27.75	20.59	7.16	1.72
70%EtOH	0.0	26.70	20.01	6.69	1.81
80%EtOH	0.0	24.98	19.04	5.94	-0.36
90%EtOH	0.0	23.91	19.40	4.51	-2.97
100%EtOH	0.0	22.21	18.28	3.93	-4.88

$$k = 1.06$$

$$b = -6.06$$

$$r^2 = 0.99$$

$$W_a^p_{\text{water}} = 45.96$$

Copper ($\gamma_S^d = 32.47$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_a^p
Water	76.7	70.11	21.43	48.68	33.48
10%EtOH	57.2	50.23	13.42	36.81	35.69
20%EtOH	48.3	39.56	11.29	28.27	27.58
30%EtOH	40.3	35.19	17.93	17.26	13.77
40%EtOH	31.0	32.49	19.23	13.26	10.36
50%EtOH	21.9	29.53	21.90	7.63	3.59
60%EtOH	17.9	27.75	20.59	7.16	2.44
70%EtOH	0.0	26.70	20.01	6.69	2.42
80%EtOH	0.0	24.98	19.04	5.94	0.23
90%EtOH	0.0	23.91	19.40	4.51	-2.37
100%EtOH	0.0	22.21	18.28	3.93	-4.30

$$k = 1.18$$

$$b = -6.57$$

$$r^2 = 1.00$$

$$W_a^p_{\text{water}} = 50.88$$

Glass ($\gamma_S^d = 27.54$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	28.5	70.11	21.43	48.68	83.13
10%EtOH	26.2	50.23	13.42	36.81	56.85
20%EtOH	25.1	39.56	11.29	28.27	40.11
30%EtOH	22.6	35.19	17.93	17.26	23.23
40%EtOH	19.2	32.49	19.23	13.26	17.14
50%EtOH	13.9	29.53	21.90	7.63	9.07
60%EtOH	0.0	27.75	20.59	7.16	7.87
70%EtOH	0.0	26.70	20.01	6.69	6.45
80%EtOH	0.0	24.98	19.04	5.94	4.16
90%EtOH	0.0	23.91	19.40	4.51	1.59
100%EtOH	0.0	22.21	18.28	3.93	-0.45

$$k = 1.76$$

$$b = -6.31$$

$$r^2 = 1.00$$

$$W_{a^p \text{water}} = 79.78$$

Acetal ($\gamma_S^d = 46.36$) at 313 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	78.0	70.11	21.43	48.68	21.64
10%EtOH	68.8	50.23	13.42	36.81	18.50
20%EtOH	60.0	39.56	11.29	28.27	13.58
30%EtOH	51.5	35.19	17.93	17.26	-0.56
40%EtOH	39.7	32.49	19.23	13.26	-2.22
50%EtOH	29.0	29.53	21.90	7.63	-8.36
60%EtOH	29.4	27.75	20.59	7.16	-9.86
70%EtOH	13.0	26.70	20.01	6.69	-8.19
80%EtOH	0.0	24.98	19.04	5.94	-9.46
90%EtOH	0.0	23.91	19.40	4.51	-12.15
100%EtOH	0.0	22.21	18.28	3.93	-13.80

$$k = 0.83$$

$$b = -14.70$$

$$r^2 = 0.98$$

$$W_{a^p \text{water}} = 26.06$$

PTFE ($\gamma_S^d = 22.58$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	113.3	68.15	21.43	46.72	-2.80
10%EtOH	108.4	48.45	13.42	35.03	-1.65
20%EtOH	102.9	36.83	11.29	25.54	-3.32
30%EtOH	83.7	33.60	17.93	15.67	-2.9
40%EtOH	74.6	31.60	19.23	12.37	-1.68
50%EtOH	63.6	28.55	21.90	6.65	-3.23
60%EtOH	59.1	26.76	20.59	6.17	-2.62
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.00 \\
 b &= -2.73 \\
 r^2 &= 0.13 \\
 W_{a^p}^{\text{water}} &= -2.46
 \end{aligned}$$

HDPE ($\gamma_S^d = 31.83$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	95.9	68.15	21.43	46.72	8.91
10%EtOH	71.6	48.45	13.42	35.03	22.40
20%EtOH	64.4	36.83	11.29	25.54	14.83
30%EtOH	52.6	33.60	17.93	15.67	6.22
40%EtOH	44.2	31.60	19.23	12.37	4.77
50%EtOH	38.6	28.55	21.90	6.65	-1.94
60%EtOH	32.8	26.76	20.59	6.17	-1.94
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.84 \\
 b &= -6.89 \\
 r^2 &= 1.00 \\
 W_{a^p}^{\text{water}} &= 32.59
 \end{aligned}$$

Polypro ($\gamma_S^d = 30.69$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	97.1	68.15	21.43	46.72	8.43
10%EtOH	77.2	48.45	13.42	35.03	18.59
20%EtOH	66.6	36.83	11.29	25.54	14.22
30%EtOH	55.3	33.60	17.93	15.67	5.81
40%EtOH	47.3	31.60	19.23	12.37	4.44
50%EtOH	42.6	28.55	21.90	6.65	-2.28
60%EtOH	38.5	26.76	20.59	6.17	-2.57
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.74 \\
 b &= -6.29 \\
 r^2 &= 0.99 \\
 W_{a^p_{\text{water}}} &= 28.70
 \end{aligned}$$

UHMW ($\gamma_S^d = 32.40$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	90.5	68.15	21.43	46.72	14.85
10%EtOH	71.7	48.45	13.42	35.03	21.95
20%EtOH	63.6	36.83	11.29	25.54	14.95
30%EtOH	51.7	33.60	17.93	15.67	6.21
40%EtOH	42.7	31.60	19.23	12.37	4.90
50%EtOH	39.6	28.55	21.90	6.65	-2.72
60%EtOH	35.1	26.76	20.59	6.17	-3.00
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.86 \\
 b &= -7.54 \\
 r^2 &= 0.99 \\
 W_{a^p_{\text{water}}} &= 32.79
 \end{aligned}$$

S.S. ($\gamma_S^d = 32.44$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	77.9	68.15	21.43	46.72	29.70
10%EtOH	67.6	48.45	13.42	35.03	25.18
20%EtOH	58.2	36.83	11.29	25.54	17.96
30%EtOH	44.9	33.60	17.93	15.67	9.16
40%EtOH	35.8	31.60	19.23	12.37	7.27
50%EtOH	28.4	28.55	21.90	6.65	0.35
60%EtOH	27.5	26.76	20.59	6.17	-1.19
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.89$$

$$b = -5.30$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 36.41$$

Nylon ($\gamma_S^d = 33.25$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	66.9	68.15	21.43	46.72	41.50
10%EtOH	57.8	48.45	13.42	35.03	32.02
20%EtOH	51.0	36.83	11.29	25.54	21.25
30%EtOH	41.3	33.60	17.93	15.67	10.00
40%EtOH	25.2	31.60	19.23	12.37	9.61
50%EtOH	20.3	28.55	21.90	6.65	1.35
60%EtOH	17.6	26.76	20.59	6.17	-0.06
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 1.02$$

$$b = -5.11$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 42.65$$

Copper ($\gamma_S^d = 32.47$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	74.8	68.15	21.43	46.72	33.26
10%EtOH	59.8	48.45	13.42	35.03	31.07
20%EtOH	54.0	36.83	11.29	25.54	20.18
30%EtOH	42.3	33.60	17.93	15.67	10.19
40%EtOH	32.9	31.60	19.23	12.37	8.15
50%EtOH	27.2	28.55	21.90	6.65	0.61
60%EtOH	24.0	26.76	20.59	6.17	-0.50
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 1.06$$

$$b = -6.37$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 43.35$$

Glass ($\gamma_S^d = 27.54$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	29.9	68.15	21.43	46.72	78.64
10%EtOH	27.3	48.45	13.42	35.03	53.05
20%EtOH	25.1	36.83	11.29	25.54	34.91
30%EtOH	22.8	33.60	17.93	15.67	20.13
40%EtOH	19.8	31.60	19.23	12.37	15.30
50%EtOH	14.0	28.55	21.90	6.65	7.13
60%EtOH	0.0	26.76	20.59	6.17	5.89
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 1.74$$

$$b = -6.27$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 75.41$$

Acetal ($\gamma_S^d = 46.36$) at 333 K

Liquids	θ	γ_L	γ_L^d	γ_L^P	W_{a^P}
Water	76.5	68.15	21.43	46.72	21.01
10%EtOH	67.9	48.45	13.42	35.03	16.79
20%EtOH	60.8	36.83	11.29	25.54	9.04
30%EtOH	51.2	33.60	17.93	15.67	-3.00
40%EtOH	38.8	31.60	19.23	12.37	-3.48
50%EtOH	29.9	28.55	21.90	6.65	-10.42
60%EtOH	33.3	26.76	20.59	6.17	-12.66
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.85$$

$$b = -15.54$$

$$r^2 = 0.98$$

$$W_{a^P_{\text{water}}} = 24.21$$

PTFE ($\gamma_S^d = 22.58$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^P	W_{a^P}
Water	113.7	66.19	21.43	44.76	-4.40
10%EtOH	108.7	46.68	13.42	33.26	-3.10
20%EtOH	103.1	34.09	11.29	22.80	-5.56
30%EtOH	84.6	32.01	17.93	14.08	-5.21
40%EtOH	72.0	30.71	19.23	11.48	-1.47
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = -0.02$$

$$b = -3.35$$

$$r^2 = 0.19$$

$$W_{a^P_{\text{water}}} = -4.41$$

HDPE ($\gamma_s^d = 31.83$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	95.6	66.19	21.43	44.76	7.49
10%EtOH	79.3	46.68	13.42	33.26	14.01
20%EtOH	72.5	34.09	11.29	22.80	6.42
30%EtOH	62.2	32.01	17.93	14.08	-0.84
40%EtOH	52.4	30.71	19.23	11.48	-0.03
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.69 \\
 b &= -9.22 \\
 r^2 &= 0.99 \\
 W_{a^p_{\text{water}}} &= 21.74
 \end{aligned}$$

Polypro ($\gamma_s^d = 30.69$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	105.2	66.19	21.43	44.76	-2.45
10%EtOH	82.3	46.68	13.42	33.26	12.34
20%EtOH	75.0	34.09	11.29	22.80	5.68
30%EtOH	66.1	32.01	17.93	14.08	-1.93
40%EtOH	55.5	30.71	19.23	11.48	-0.48
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$\begin{aligned}
 k &= 0.64 \\
 b &= -9.35 \\
 r^2 &= 0.98 \\
 W_{a^p_{\text{water}}} &= 19.73
 \end{aligned}$$

UHMW ($\gamma_S^d = 32.40$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	92.4	66.19	21.43	44.76	10.71
10%EtOH	78.3	46.68	13.42	33.26	14.44
20%EtOH	70.0	34.09	11.29	22.80	7.49
30%EtOH	60.6	32.01	17.93	14.08	-0.48
40%EtOH	50.8	30.71	19.23	11.48	0.19
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.70$$

$$b = -8.97$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 22.58$$

S.S. ($\gamma_S^d = 32.44$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	78.8	66.19	21.43	44.76	26.31
10%EtOH	68.9	46.68	13.42	33.26	21.75
20%EtOH	66.9	34.09	11.29	22.80	9.18
30%EtOH	49.4	32.01	17.93	14.08	4.60
40%EtOH	36.0	30.71	19.23	11.48	5.60
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.76$$

$$b = -5.33$$

$$r^2 = 0.95$$

$$W_{a^p_{\text{water}}} = 28.78$$

Nylon ($\gamma_S^d = 33.25$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	66.2	66.19	21.43	44.76	39.51
10%EtOH	59.8	46.68	13.42	33.26	27.91
20%EtOH	56.2	34.09	11.29	22.80	14.30
30%EtOH	44.9	32.01	17.93	14.08	5.85
40%EtOH	30.5	30.71	19.23	11.48	6.59
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 1.04$$

$$b = -7.61$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 39.22$$

Copper ($\gamma_S^d = 32.47$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	73.9	66.19	21.43	44.76	31.78
10%EtOH	63.3	46.68	13.42	33.26	25.90
20%EtOH	62.1	34.09	11.29	22.80	11.74
30%EtOH	45.3	32.01	17.93	14.08	6.26
40%EtOH	34.1	30.71	19.23	11.48	6.16
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.91$$

$$b = -6.18$$

$$r^2 = 0.97$$

$$W_{a^p_{\text{water}}} = 34.85$$

Glass ($\gamma_S^d = 27.54$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	29.4	66.19	21.43	44.76	75.26
10%EtOH	28.2	46.68	13.42	33.26	49.37
20%EtOH	26.3	34.09	11.29	22.80	29.38
30%EtOH	24.0	32.01	17.93	14.08	16.80
40%EtOH	20.8	30.71	19.23	11.48	13.39
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 1.84$$

$$b = -9.89$$

$$r^2 = 1.00$$

$$W_{a^p_{\text{water}}} = 72.87$$

Acetal ($\gamma_S^d = 46.36$) at 353 K

Liquids	θ	γ_L	γ_L^d	γ_L^p	W_{a^p}
Water	75.1	66.19	21.43	44.76	20.17
10%EtOH	70.3	46.68	13.42	33.26	12.52
20%EtOH	62.3	34.09	11.29	22.80	4.18
30%EtOH	55.2	32.01	17.93	14.08	-7.38
40%EtOH	44.2	30.71	19.23	11.48	-6.98
50%EtOH					
60%EtOH					
70%EtOH					
80%EtOH					
90%EtOH					
100%EtOH					

$$k = 0.86$$

$$b = -17.35$$

$$r^2 = 0.99$$

$$W_{a^p_{\text{water}}} = 21.35$$

Appendix G

Error Analysis of Contact Angle Data

Considering variations in the values of θ of $\pm 2^\circ$ and liquid surface tension of ± 0.1 dynes/cm, the values of γ_L^d , γ_L^p , γ_S^d , and W_a^p may be as follows. By use of equations (15), (16), (17), and (5),

$$\gamma_S^d = \pm 0.2 \text{ dynes/cm}$$

$$\gamma_L^d \text{ (for polar diagnostic liquids)} = \pm 4 \text{ dynes/cm}$$

$$\gamma_L^p = \pm 4 \text{ dynes/cm}$$

$$W_a^p = \pm 5 \text{ dynes/cm}$$

Table A-1 shows standard errors in polar surface properties of tested materials at 303 K. These errors for each material are nearly unchanged with respect to temperature. Finally, from equation (26), the deviations of γ_S^* caused by experimental errors may be within about ± 10 to 20%.

TABLE A-1

Standard Errors of Polar Surface Properties of Each Material at 303 K

Material	k	std. error in k	b	std. error in b
	(dimensionless)		(ergs/cm ²)	
PTFE	0.00	-	0.00	-
HDPE	0.88	0.05	-5.37	0.38
Polypro	0.89	0.05	-6.38	0.80
UHMW	0.91	0.05	-6.48	0.29
S.S.	1.00	0.04	-5.22	0.71
Nylon	1.10	0.05	-6.13	0.83
Copper	1.18	0.03	-6.18	0.40
Glass	1.76	0.03	-6.12	1.10
Acetal	0.87	0.04	-14.62	0.48