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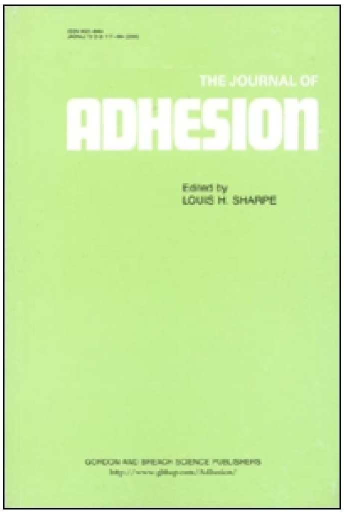

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Lee, Lieng-Huang(1998) 'Adhesion and Surface-Hydrogen-Bond Components for Polymers and Biomaterials', The Journal of Adhesion, 67: 1, 1 — 18

To link to this Article: DOI: 10.1080/00218469808011096

URL: http://dx.doi.org/10.1080/00218469808011096

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J. Adhesion, 1998, Vol. 67, pp. 1–18
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Adhesion and Surface-Hydrogen-Bond Components for Polymers and Biomaterials*

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(Received 11 October 1996; In final form 2 January 1997)

In this paper, we briefly discuss several ways to determine the work of adhesion and the requirements for achieving maximum adhesion and spontaneous spreading. Specifically, we will concentrate on the methodology developed by van Oss, Chaudhury and Good [5–7] for the determination of the work of adhesion and interfacial tension. Recently, Good [4] has redefined the surface interaction components γ^+ and γ^- as hydrogen bond acidic and basic parameters. We have related the surface-hydrogen-bond components γ^+ and γ^- to the Taft and Kamlet's [28, 29] linear solvation energy relationship (LSER) solvatochromic α and β parameters. We [8, 9] have found that, for water at ambient temperature, α [hydrogen-bond-donating (HBD) ability] and β [hydrogen-bond-accepting (HBA) ability] are not equal, and the ratio for the normalized α and β is 1.8. This new ratio is assumed to be equal to that of γ^+ & γ^- for water at 20°C. On the basis of the new ratio, we will present our recalculated surface-hydrogen-bond components for several polymers and biomaterials. This change in the ratio did not affect the total surface tension or the sign of the interfacial tension. The net improvement is in the lowering of the γ^- values. These data may be useful for predicting the adhesion between an adhesive and an adherend.

Keywords: Acid-base; biomaterials; hydrogen bonding; interfacial tension; linear free energy; polymer; solvation energy; spreading; surface tension; work of adhesion

1. INTRODUCTION

Adhesion between dissimilar and similar materials is governed by intermolecular and intramolecular forces through molecular bonding [1, 2].

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*Presented at the Symposium on *Fundamentals of Adhesion and Interfaces* at the Fall Meeting of the American Chemical Society in Orlando, Florida, USA, August 25–28, 1996.

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The well-known contributions of van der Waals (vdW) forces to adhesion [3] will not be elaborated. In this paper, we briefly discuss several methods to determine the work of adhesion and the requirements for achieving maximum adhesion and spreading. Specifically, we shall point out the importance of surface-hydrogen-bond components, as recently redefined by Good [4]. From these components, the work of adhesion and the interfacial tension have been derived by van Oss, Chaudhury and Good (VCG) [5–7]. We shall present our newly calculated surface-hydrogen-bond component data for several polymers and biomaterials on the basis of our new finding [8, 9] derived from the linear solvation free energy relationship (LSER) parameters.

2. ADHESION AND WETTING

2.1. Work of Adhesion

The thermodynamic reversible work of adhesion, $\mathbf{W}_A$, which is the negative of the Helmholz (or Gibbs) free energy change per unit area of interface of the hypothetical interaction between two phases across a plane boundary without change in area, is defined by the Dupré equation [10]

$$\mathbf{W}_A = -\Delta\mathbf{G}_{ij} = \gamma_i + \gamma_j - \gamma_{ij} \tag{1}$$

where $\Delta\mathbf{G}_{ij}$ (or $\Delta\mathbf{F}_{ij}$) is the free energy change when 1 cm^2 of the interface between phases **i** and **j** is created out of 1 cm^2 of free surface of phase **i** and 1 cm^2 of free surface of phase **j**; γ_i is the specific surface free energy (or surface tension) of phase **i**; γ_j is that of phase **j** in the presence of vapor of **i**, and γ_{ij} is that (or interfacial tension) of the interface between these two phases. Thus, to achieve the maximum work of adhesion, it is necessary to attain zero or negative interfacial tension, with two highest surface tensions of opposing phases. The maximum thermodynamic work of adhesion is the first surface-chemical criterion for forming a strong adhesive bond. There are other criteria beside the thermodynamic work of adhesion, such as deformation or viscoelastic factors, which are beyond the scope of this paper.

2.2. Equilibrium Spreading Pressure

Bangham and Razouk [11] first observed the effect of vapor of the liquid adsorbed on the solid on surface tension, and they indicated that the equilibrium spreading (or film) pressure, π_e, of the adsorbed layer on the solid surface tended to decrease the work of adhesion of the solid, $\mathbf{W}_{AO}$, in the absence of the vapor and

$$\pi_e = \mathbf{W}_{AO} - \mathbf{W}_A \tag{2}$$

where $\mathbf{W}_A$ is the work of adhesion in the presence of the vapor. Good [12] claimed that π_e was probably negligible for pure liquids forming a non-zero contact angle on homogeneous, low surface energy solids. There have been other claims that this may not be the case (see Sec. 3.2 in Ref. 15). Since this paper deals with low surface energy polymers and biomaterials, for simplicity we shall not consider π_e in the following discussion. However, for high surface energy materials, *e.g.* mercury [13], the spreading pressure cannot be ignored.

2.3. Equilibrium Spreading Coefficient

The interrelationship of surface tensions also affects wetting and spreading of a liquid on another liquid or a solid [14, 15]. Marangoni's law [16] states that spreading occurs if the surface tension of the underlying liquid surpasses the sum of the tensions of the liquid of the drop and of the interface of two liquids. Later, the equilibrium spreading coefficient was defined by Harkins [17] for the spreading of the liquid on a solid adsorbed by the vapor of the liquid:

$$\mathbf{S}_e = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} \tag{3}$$

Where $\mathbf{S}_e$ is the equilibrium spreading coefficient; γ is the surface tension; and the subscripts **l**, **v** and **s** represent liquid, vapor and solid. It is important to note that a liquid tends to spread on a solid when $\mathbf{S}_e$ is positive. Thus, for achieving spontaneous spreading, the sum of surface tension of the liquid and the interfacial tension (preferably zero or negative) should be smaller than that of the solid. The second surface-chemical criterion for good adhesion is that the adhesive should properly spread and wet the adherend. For assessing this criterion, the spreading coefficient is a covenient indicator to predict whether an adhesive can properly spread on an adherend.

3. COMPONENTS OF THE WORK OF ADHESION

There are at least three approaches for the determination of the work of adhesion. The Fowkes' method involves surface energies which can be determined by contant angle and other measurements, such as inverse gas chromatography, calorimetry, spectroscopy, etc. [18, 19a, 19b], while the VCG method is solely based on the contact angle technique. The third method is based on contact mechanics. Since each method has its own merit, we shall briefly describe them as follows:

3.1. Fowkes' Method

Fowkes [18] proposed to split the work of adhesion into two components, $\mathbf{W}_A^d$, due to dispersion, and $\mathbf{W}_A^{AB}$, due to the acid-base interaction (including hydrogen-bonding):

$$\mathbf{W}_A = \mathbf{W}_A^d + \mathbf{W}_A^{AB}(\textbf{Fowkes}) \tag{4}$$

According to Fowkes, the dispersion component can be derived from the geometric mean approach; thus,

$$\mathbf{W}_A^d = 2(\gamma_i^d \gamma_j^d)^{1/2} \tag{5}$$

However, as early as 1981, Fowkes [19a] cautioned that the acid-base component can not be derived by the same geometric mean method. Unfortunately, there have been different incorrect versions of geometric or harmonic means of polar components or hydrogen bonding components frequently used in the literature even to this day!

Based upon Drago's concept of the acid-base interaction [20], Fowkes derived the acid-base component of $\mathbf{W}_A$ through the enthalpy of the interaction, ΔH^{AB}. Thus,

$$\mathbf{W}_A^{AB} = -f n^{AB} \Delta H^{AB} \tag{6}$$

where *f* is a factor for converting the enthalpy to free energy and $\mathbf{n}^{AB}$ is the population of the acid-base interaction sites on the surface. Vrbanac and Berg [21] found that *f* was generally smaller than unity. On the basis of Drago's four-parameter approach, the enthalpy can be expressed as

$$\Delta H^{AB} = E_A E_B + C_A C_B \tag{7}$$

where $\mathbf{E}_A$ and $\mathbf{E}_B$ are susceptibilities of the acid (**A**) and base (**B**), respectively, to undergo the electrostatic interaction, while $\mathbf{C}_A$ and $\mathbf{C}_B$ are those to undergo covalent interactions. The four parameters of 31 acids and 43 bases were given by Drago [20]. Thus, $\mathbf{W}_A^{AB}$ can be readily calculated if *f* and $\mathbf{n}^{AB}$ are obtained by other means. For example, $\mathbf{W}_A^{AB}$ for the interaction of between dimethyl sulfoxide (base) and polyvinyl chloride (acid) [19b] was found to be 5.7 mJ m^{-2}. For this and other halogented polymers, the interactions presumably are not due to hydrogen bonding, but due to Lewis acid-base interaction. Thus, the Fowkes' method still remains a valid approach to determine the general Lewis acid-base component of the work of adhesion.

The Fowkes' method has further been verified by Hüttinger *et al.* [22], especially for Brønsted acids and bases. The acid-base component of the work of adhesion can be determined by the use of an aqueous acidic or basic solution as the test liquid in the pH range from 1 to 14. By this procedure, well-defined complexes between the surface functional group at the solid surface and the aqueous solutions of varying pH values can be found.

3.2. van Oss-Chaudhury-Good's (VCG) Method

Originally, the VCG method [5–7] was not based on hydrogen bonding, which is a subclass of the Lewis acid-base interactions. Upon Good's recent revision [4], it is now properly based on hydrogen bonding. Thus, unlike the Fowkes' approach, the total work of adhesion, W_A, is composed of the following two different components:

$$W_A = W_A^{LW} + W_A^{AB}(VCG) \tag{8}$$

where the Lifshitz-van der Waals component, $\mathbf{W}_A^{LW}$, includes contributions of the dispersion, **d**, induction, **i**, and polar, **p**, interactions, and the acid-base component represents that of hydrogen-bonding, **h**, only. van Oss, Chaudhury and Good [4] have assumed that in a condensed phase the polar and induction interactions are generally negligible. Thus,

$$\mathbf{W}_A^{AB}\ (\mathbf{VCG}) = \mathbf{W}_A^{h} \tag{9}$$

The calculation of the VCG work of adhesion between a liquid and a solid will be described later.

3.3. Johnson-Kendall-Roberts' Approach

Unlike the Fowkes' and the VCG methods, the third method is based solely on contact mechanics. On the basis of the equilibrium theory of adhesion, Johnson, Kendall and Roberts [23] introduced a convenient way to determine the work of adhesion between two elastic solids or films. This approach turns out to be a rather ingenious way for the determination of surface energy, interfacial energy or the work of adhesion between elastic particles [24]. When the contact radius, **a**, of a particle with a radius of, **R**, is determined, the work of adhesion in Eq. (10) can be obtained under an applied force, **P**:

$$\mathbf{a}^3 = \mathbf{R/K}\{\mathbf{P} + 3\pi\mathbf{W}_A\mathbf{R} + [6\pi\mathbf{W}_A\mathbf{RP} + (3\pi\mathbf{W}_A\mathbf{R})^2]^{0.5}\} \tag{10}$$

Where: $\mathbf{W}_A$ = work of adhesion = $2\gamma_S$ for the same material, or $\mathbf{W}_A = \gamma_1 + \gamma_2 - \gamma_{12}$, for two dissimilar materials. γ_S is the surface free energy of a solid and γ_{12} is the interfacial free energy.

At zero external load, $\mathbf{P} = 0$, and $\mathbf{a}^3 = 6\pi\mathbf{W}_A\mathbf{R}^2/\mathbf{K}$. The separation of the materials will just occur when the pull-off force, which is independent of the elastic modulus, becomes

$$\mathbf{Ps} = -\frac{3}{2}\pi\mathbf{W}_A\mathbf{R} \tag{11}$$

At separation, $\mathbf{a}_s = 0.64\ \mathbf{a}_0$ ($\mathbf{a}_0$ = initial contact radius).

Chaudhury and Whitesides [25], and Merrill *et al.* [26] have used the contact mechanics approach to determine the work of adhesion for silicone rubber and other polymers with a surface force apparatus, and the results compared fovorably with those obtained with contact angle methods. Recently, Thomas *et al.* [27] further applied the JKR approach to determine $\mathbf{W_A}$ between two self-assembled monolayer (SAM) films. Using interfacial force microscopy, they determined interfacial energies under three conditions: 1. between two van der Waals films (**CH_3** *vs* **CH_3**); 2. between two hydrogen-bonding films (**NH_2** *vs* **NH_2** and **COOH** *vs* **COOH**); and 3. between a pair of acid-basic films (**COOH** and **NH_2**). Their findings are as follows: First, the interfacial bond energies qualitatively scaled with van der Waals, hydrogen-bonding and acid-base interactions, respectively. Second, the work of adhesion is the highest between two dissimilar acid-base films. Third, the interfacial energy (or tension) is negative for the third case. However, it is not known whether the interaction for the dissimilar acid-base films is partially accompanied by hydrogen-bonding. In general, these results are in agreement with the thermodynamic criteria for the maximum work of adhesion. Thus, the JKR approach appears to provide an important bridge between mechanics and surface chemistry.

4. VAN OSS-CHAUDHURY-GOOD'S METHOD

In this section, we shall discuss the VCG method more fully. Specifically, we shall describe that method for the determination of the work of adhesion and the interfacial tension.

4.1. Surface-Hydrogen-Bond Components

The asymmetric hydrogen bond part of a dipolar system [4] has been divided into two separate components: a hydrogen-bonding acidic parameter, γ^+, and a hydrogen-bonding basic parameter, γ^-. In other words, γ^+ is identical to the contribution of the proton donor (or Brønsted acid), whereas γ^- that of the proton acceptor (or Brønsted base). Indeed, this revised definition is narrower than the original one based on surface Lewis acid-base components [4–7]. However, for clarity we prefer to name:

γ^+, the surface-hydrogen-bond-donating (**SHBD**) component, and
γ^-, the surface-hydrogen-bond-accepting (**SHBA**) component.

4.2. Work of Adhesion

In the VCG approach, the intrinsic asymmetry (or complementarity) of the two molecules can be taken into account when one is determining the hydrogen bonding interaction. The geometric mean rule is then applicable to the hydrogen-bond component of the maximum work of adhesion, $\mathbf{W}_{ij}^{AB}$, or the change in the negative free energy of interaction, ΔG_{ij}^{AB}, between the **i** and the **j** phases. Thus,

$$\mathbf{W}_{ij}^{AB} = -\Delta \mathbf{G}_{ij}^{AB} = 2[(\gamma_i^+ \gamma_j^-)^{1/2} + (\gamma_i^- \gamma_j^+)^{1/2}] \tag{12}$$

Then, according to Eq. (8), the maximum work of adhesion or the negative free energy of interaction for a polar system involving both Lifshitz-van der Waals and hydrogen bonding interactions is

$$\mathbf{W}_{ij} = -\Delta \mathbf{G}_{ij} = 2[(\gamma_i^{LW} \gamma_j^{LW})^{1/2} + (\gamma_i^- \gamma_j^+)^{1/2} + (\gamma_i^+ \gamma_j^-)^{1/2}] \tag{13}$$

Finally, for a polar system involving both vdW and hydrogen bonding interactions, the Young-Good-Girifalco-Fowkes equation for the work of adhesion can be expressed as

$$\gamma_{lv}(1 + \cos\theta_e) = 2[\gamma_i^{LW} \gamma_j^{LW})^{1/2} + (\gamma_i^+ \gamma_j^-)^{1/2} + (\gamma_i^- \gamma_j^+)^{1/2}] \tag{14}$$

4.3. Interfacial Tension

Since $\mathbf{W}_{ij}^{AB}$ can also be derived from the Dupré equation [10]

$$\mathbf{W}_{ij}^{AB} = \gamma_i^{AB} + \gamma_j^{AB} - \gamma_{ij}^{AB} \tag{15}$$

the interfacial tension, γ_{ij}^{AB}, due to hydrogen bonding is then expressed as:

$$\gamma_{ij}^{AB} = 2[(\gamma_i^+ \gamma_i^-)^{1/2} + (\gamma_j^+ \gamma_j^-)^{1/2} - (\gamma_i^+ \gamma_j^-)^{1/2} - (\gamma_i^- \gamma_j^+)^{1/2}] \tag{16}$$

Then, the total interfacial tension becomes

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} = [(\gamma_i^{LW})^{1/2} - (\gamma_j^{LW})^{1/2}]^2$$

$$+ 2[(\gamma_i^+ \gamma_i^-)^{1/2} + (\gamma_j^+ \gamma_j^-)^{1/2} - (\gamma_i^+ \gamma_j^-)^{1/2} - (\gamma_i^- \gamma_j^+)^{1/2}] \qquad (17)$$

The experimental procedure in determining different surface tension components has been described by Good *et al.* [7]. In fact, there are two methods for making the determination. In view of Eq. (14), the first method requires three polar liquids for calculating γ_i^{LW}, γ_i^+ and γ_j^-. The second method requires one apolar liquid for finding γ_i^{LW} and two other polar liquids to solve Eq. (14). In addition, because of the lack of one more equation, Good *et al.* also had to assume, presumably by the same convention of pH values, the surface-hydrogen-bond components for water at 20°C to be equal, or $\gamma_i^+ = \gamma_j^- = 25.5$ mJ m^{-2}.

5. SOLVATOCHROMIC PARAMETERS

For obtaining an appropriate ratio for these surface-hydrogen-bond components, we [8] found a relationship between γ_i^+ and γ_j^- and solvatochromic α and β parameters. In 1976, Taft and Kamlet [28,29] proposed a linear free energy relationship (LFER) [or linear solvation energy relationship (LSER)] to describe the value of the solvent-dependent physicochemical property **(XYZ)** (*e.g.* log K, log k, *etc.*) of the solute in a given solvent as:

$$\mathbf{XYZ} = (\mathbf{XYZ})_0 + \boldsymbol{a}\alpha + \boldsymbol{b}\beta + \boldsymbol{s}\Pi^* + \boldsymbol{m}\delta_H^2 + \cdots, \qquad (18)$$

where $(\mathbf{XYZ})_0$, $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{s}$ and $\boldsymbol{m}$ are solvent-independent coefficients characteristic of the system under study and indicative of its susceptibility to the solvent properties, *e.g.* α, β and Π^* as UV/vis spectroscopically-derived parameters [28,29]. Separately, α is an empirical, quantitative measure of the hydrogen-bond-donating (HBD) ability of a bulk solvent toward a solute [30]. β is an empirical, quantitative measure of the hydrogen-bond-accepting (HBA) or electron-pair-donating (EDP) ability of a bulk solvent toward a solute for a hydrogen bond or a Lewis coordination bond. On the other hand, Π* measures the exoergic effects (the effects involving a negative Gibbs free energy change) of solute-solvent, dipole-dipole, **p**, and dipole-induced dipole, **i**, interactions.

In other words, Π* measures the ability of a solvent to stabilize a neighboring charge or dipole by virtue of nonspecific interactions. In this manner, Π* is affected by a combination of dipolarity and polarizability of a solvent. Finally, δ_H^2 is the squared Hildebrand solubility parameter [31] of a solvent equivalent to the cavity term, which measures the work required to produce a cavity of unique volume in the solvent.

6. RESULTS AND DISCUSSION

It is important to note that Taft and Kamlet's approach to the acid-base interaction is not contradictory to, but is parallel to Drago's method which is linked to the Fowkes' work. Both methods have claimed success for describing the acid-base interactions. Our finding [8,9] of linking the VCG method to Taft and Kamlet's approach further establishes the VCG method to be equivalent to Fowkes' methodology in dealing with different aspects of the acid-base interaction. This may explain why the VCG approach does not have to involve Drago's four parameters. Originally, this was one of the criticisms raised by Fowkes [19b] against the VCG approach.

The above brief description of LSER parameters reveals a close relationship between surface-hydrogen-bond components and the solvatochromic α and β parameters. Thus, γ^+ resembles the HBD parameter, α, and γ^- the HBA parameter, β. A list of solvatochromic parameters for 170 liquids was given by Marcus [32]. We [8] found that for water the α and β parameters were not equal. For the convenience of parallel comparison, we then normalized all three scales (α, β and Π*) between 0 and 1. Recently, this normalization technique has also been applied by Taft *et al.* [33]. In addition, we assumed the ratio of α and β (normalized) of 1.8 for water to be equal to that of γ^+ and γ^- for water at 20°C. Solvatochromic parameters for several liquids customarily used for contact angle measurements are shown in Table I. Surface-hydrogen-bond-components for several probe liquids

TABLE I LSER Solvatochromic Parameters of Liquids (Values in parentheses are normalized between 0 and 1)

Liquid	α	(α)	β	(β)	$(\alpha\beta)$	(α/β)	Π^*	(Π^*)
Cyclohexane	0	0	0	0	0	–	0	0
Diiodomethane	0	0	0	0	0	–	0.65	0.54
Benzene	0	0	0.1	0.07	0	–	0.59	0.49
2-Cyanopyridine	0	0	0.29	0.2	0	–	1.2	1
Ethyl acetate	0	0	0.42	0.29	0	–	0.55	0.46
Tetrahydrofuran	0	0	0.55	0.38	0	–	0.58	0.48
Dimethyl sulfoxide	0	0	0.76	0.53	0	–	1	0.83
Acetone	0.08	0.04	0.43	0.3	0.01	0.13	0.71	0.58
1,2-Diaminoethane	0.13	0.07	1.43	1	0.07	0.07	0.47	0.39
Chloroform	0.2	0.1	0.1	0.07	0.01	1.43	0.58	0.48
Formamide	0.71	0.36	0.48	0.34	0.12	1.1	0.97	0.81
Ethylene glycol	0.9	0.46	0.52	0.36	0.17	1.3	0.92	0.77
Acetic acid	1.12	0.57	0.45	0.32	0.18	1.8	0.62	0.52
Water	1.17	0.6	0.47	0.33	0.22	1.8	1.09	0.91
Glycerol	1.21	0.62	0.51	0.36	0.22	1.7	0.62	0.52
Phenol	1.65	0.84	0.3	0.21	0.18	4.7	0.68	0.57
Hexafluoro-2-propanol	1.96	1	0	0	0	–	0.65	0.54

*The original data on the solvatochromic parameters (no specified temperature, presumably at ambient temperature) were compiled by Y. Marcus, *Chem. Soc. Revs.* 409 (1993).

[34] based on the original ratio for water of unity are shown in Table II. Then, based on the new ratio of 1.8 for water, we calculated surface-hydrogen-bond components for these liquids (Tab. III).

According to our calculation, the surface-hydrogen-bond-donating component (SHBD), γ^+, for water at 20°C should be 34.2 mJ m^{-2}, and the surface-hydrogen-bond-accepting component (SHBA), γ^-, 19 mJ m^{-2}. As expected, in general, by using the new reference for water, the values of γ^+ of these liquids increase substantially, while those of γ^- decrease. On the other hand, despite the change in the ratio of $\gamma^+$and γ^- the products γ^{AB} due to hydrogen bonding are unaffected. As a result, total surface tensions are essentially unchanged.

We selected some of the published advancing contact angle data on polymers [35–40] determined with an apolar liquid and a pair of polar liquids consisting of water and glycerol. Using the new reference for water at 20°C with γ^+ of 34.2 mJ m^{-2} and γ^- of 19 mJ m^{-2}, we recalculated surface tension components for many polymers [8]. We have verified [9] some of these data with existing surface tensions determined directly. Examples of other polymers, not mentioned

TABLE II Surface Tension Components for Probe Liquids in mJ m^{-2} at 20°C*. (Reference values for Water: $\gamma^+ = \gamma^- = 25.5$ mJ m^{-2})

Liquid	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Dimethyl sulfoxide	44	36	8	0.5	32
α-Bromonaphthalene	44.4	43.5	≈ 0	0	0
Ethylene Glycol	48	29	19	1.92	47
Diiodomethane	50.8	50.8	≈ 0	0	0
Formamide	58	39	19	2.28	39.6
Glycerol	64	34	30	3.92	57.4
Water	72.8	21.8	51	25.5	25.5

*Ref. 34.

TABLE III Surface Tension Components for Probe Liquids in mJ m^{-2} at 20°C. (Reference values for Water: $\gamma^+ = 34.2$ mJ m^{-2}; $\gamma^- = 19$ mJ m^{-2})

Liquid	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Dimethyl sulfoxide	44	36	8	0.7	23.8
α-Bromonaphthalene	44.4	43.5	≈ 0	0	0
Ethylene Glycol	48	29	19	2.6	34.8
Diiodomethane	50.8	50.8	≈ 0	0	0
Formamide	58	39	19	3.1	29.1
Glycerol	64	34	30	5.3	42.5
Water	72.8	21.8	51	34.2	19

Note: For the conversion, the ratios for $\gamma+(H_2O)/\gamma+(Gly)$, $\gamma+(H_2O)/\gamma+(For)$, $\gamma+(H_2O)/\gamma+(EG)$, and $\gamma+(H_2O)/\gamma+(DMSO)$ were kept at 6.5, 11, 13, and 51, respectively.

previously in Ref. [9], using the ratio of unity for water are illustrated in Table IV. These data are compared with those using the ratio of 1.8 in Table V. We would like to point out that even after we used the new ratio for water as the reference, polyvinyl chloride with an γ^+ of 0.1 is still not acidic in the Lewis sense. This simply demonstrates that the VCG method, based solely on hydrogen bonding, is not expected to differentiate Lewis acids from Lewis bases.

One of the problems of the VCG method is that it predicts different surface hydrogen-bond parameters for solids when different pairs of probe liquids (*e.g.* water and formamide) are used, presumably due to different interactions. We assume that the use of the new ratio for water, when it is one of the pair of the probe, should improve the data but does not prevent the problem caused by the other liquid. This is

TABLE IV Surface Tension Components for Polymers in mJ m^{-2} at 20°C. (Reference values for Water: $\gamma^+ = \gamma^- = 25.5$ mJ m^{-2})

Polymer	γ	γ^{LW}	γ^{AB}	γ^+	γ^-	*Ref.*
Cellulose acetate	38	35	0	0	32.3	35, 36
Poly(sucrose), Ficoll 400	41.4	41.4	0	0	57.9	35
Ethylene glycol-co-propylene glycol, MW 2000	47.5	42	5.5	0.13	58.8	35
Poly(methyl methacrylate)	43.2	43.2	0	0	22.4	36
Agarose (polygalactopyranoside)	41	41	0	0	26.9	36
Poly(vinyl chloride)	43.8	43	0.8	0.04	3.5	37
Cellulose nitrate	45	45	0	0	16	40
Poly(oxyethylene), PEG-6000	43	43	0	0	64	6
Dextran T-150 (poly-α-(1–6)glucose)	42	42	0	0	55	6, 35
Ethylene glycol-co-propylene glycol, MW 1000	47.9	40.9	7	0.22	55.6	35
Cellulose	49.2	44	5.2	0.28	24.3	35
Poly(vinyl pyrrolidone)	43.4	43.4	0	0	29.9	38
Poly(oxytetramethylene glycol), MW 2000	44	41.4	2.6	0.06	27.6	35
Dextran-T-70 (poly-α-(1–6) glucose)	55.5	41.8	13.7	1	47.2	38

TABLE V Surface Tension Components for Polymers in mJ m^{-2} at 20°C. (Reference values for water: $\gamma^+ = 34.2$ mJ m^{-2}; $\gamma^- = 19$ mJ m^{-2})

Polymer	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Cellulose acetate	38	38	0	0	25
Poly(sucrose), Ficoll 400	41.4	41.4	0	0	46.7
Ethylene glycol-co-propylene glycol, MW 2000	42	42	0	0	50.2
Poly(methyl methacrylate)	43.2	43.2	0	0	8.8
Agarose (polygalactopyranoside)	43.9	41	2.9	0.12	17.9
Poly(vinyl chloride)	44	43	1	0.1	2.4
Cellulose nitrate	45.2	44.7	0.53	0.01	10.7
Poly(oxyethylene), PEG-6000	46.7	43.5	3.2	0.06	43.5
Dextran T-150 (poly-α-(1–6)glucose)	47.1	42	5.1	1	42.9
Ethylene glycol-co-propylene glycol, MW 1000	48.2	40.9	7.3	0.32	41.8
Cellulose	48.3	44	4.3	0.2	21.3
Poly(vinyl pyrrolidone)	48.5	43.4	5.1	0.42	15.3
Poly(oxytetramethylene glycol), MW 2000	49.2	41.4	7.8	0.83	18.1
Dextran-T-70 (poly-α-(1–6) glucose)	55.2	41.8	13.4	1.3	35.7

the reason that all contact angle data of polymers and biomaterials except sucrose used for the calculations in this paper are based on the water-gycerol pair.

For biomaterials, surface tension components have been compiled by van Oss [35]. The data with the original ratio of unity for water are shown in Table VI and the recalculated surface tension components for biomaterials based on the new ratio for water are given in Table VII. Most of biomaterials are surface-hydrogen-bond-accepting.

TABLE VI Surface Tension Components for Biomaterials in mJ m^{-2} at 20°C. (Reference values for water: $\gamma^{+} = \gamma^{-} = 25.5$ mJ m^{-2})

Biomaterial	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	*Ref.*
Cholesterol	35.7	33.9	1.8	0.5	1.6	39
Ribosomal RNA, dry (yeast)	35.9	35.9	0	0	73.6	35, 38
Gelatin, dry	37.6	37.6	0	0	18.5	35
Human fibrinogen, hydrated	41.3	37.4	3.9	0.1	38.4	35
Bovin fibrin, dry	44	40.2	3.8	0.3	12	35
Human fibrinogen, dry	40.6	40.6	0	0	54.9	35
Zein, (corn protein), dry	42.8	41.1	1.7	0.04	18.4	35, 36
Sucrose (by sol'y)	41.6	41.6	0	0	36.1	35
Human serum albumin (HSA), dry, pH 7	41.4	41	0.4	0.002	20	35, 40
Human low density lipoprotein, dry	41.1	35.4	5.66	0.26	30.8	35
Lysozyme, dry (egg white)	48.8	41.2	2.6	0.07	23.4	35
Human immunoglobulin-G (IgG), dry, pH 7	45.2	42	3.2	0.3	8.7	35, 40
DNA, dry (calf thymus)	47.1	40.1	7	0.62	18.8	35, 40
Collagen, dry	48.9	42	6.9	0.57	21.1	35
Human serum albumin, 72% hydrated, (two-layers of hydration), pH 7	62.5	26.8	35.7	6.3	50.6	35, 38
Lysozyme, hydrated (egg white)	≈72.2	31.5	≈40.7	≈4.5	≈56.2	35
DNA, hydrated (calf thymus)	63.1	≈36.8	26.3	3.9	44.4	35, 40
Ribosomal RNA, hydrated (yeast)	62.9	32	30.9	4.9	48.7	35, 40

TABLE VII Surface Tension Components for Biomaterials in mJ m^{-2} at 20°C. (Reference values for water: $\gamma^{+} = 34.2$ mJ m^{-2}; $\gamma^{-} = 19$ mJ m^{-2})

Polymer	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Cholesterol	35.5	33.9	1.6	0.5	1.3
Ribosomal RNA, dry (yeast)	35.9	35.9	0	0	87
Gelatin, dry	37.6	37.6	0	0	13.9
Human fibrinogen, hydrated	37.6	37.6	0	0	54
Bovin fibrin, dry	40.2	40.2	0	0	16.3
Human fibrinogen, dry	40.6	40.6	0	0	44
Zein, corn protein, dry	41.1	41.1	0	0	15.9
Sucrose (by sol'y)	41.6	41.6	0	0	26.9
Human serum albumin (HSA), dry, pH 7	42	41	1	0.02	14.5
Human low density lipoprotein, dry	42.4	35.5	6.9	0.5	22.5
Lysozyme, dry (egg white)	43.2	41.2	2	0.1	18.1
Human immunoglobulin-G (IgG), dry, pH 7	44.2	42	2.2	0.2	7.6
DNA, dry (calf thymus)	47.2	40.2	7	0.8	14.9
Collagen, dry	48.7	42	6.7	0.7	16.3
Human serum albumin, 72% hydrated, (two-layers of hydration), pH 7	62	26.8	35.2	7.9	39.3
Lysozyme, hydrated (egg white)	62	31	31.4	6.6	37.2
DNA, hydrated (calf thymus)	63	36	26.5	5.3	33.1
Ribosomal RNA, hydrated (yeast)	65	32	33.1	6.3	43.4

In general, as expected, using the new ratio surface-hydrogen-bond-accepting, γ^-, parameters are much lower than those calculated with the original ratio of unity. However, unfortunately, for most of these materials there are no existing measured surface tension data which can be used for the verification.

In Table VIII, we have applied our recalculated values for the surface-hydrogen-bond components to the calculation of interfacial tensions which are compared with the original data using the ratio of unity for water. Some values may be somewhat different, but there are definitely no changes in signs. It is noteworthy that, for several compatible and soluble systems except those containing formamide, interfacial tensions are indeed negative. Thus, for the case of solvent-solute interaction, negative interfacial tension appears to favor dissolution.

In fact, a negative interfacial tension for polar materials can only be obtained with the VCG approach as shown in Eq. (17), but not with the incorrect geometric or harmonic mean expressions frequently used in the literature, because the incorrect approaches contain a sum of all squared terms, derived from various components, that yield no nega-

TABLE VIII Interfacial Tensions of Polymers and Biomaterials in mJ m^{-2} at 20°C

Polymer and Biomaterial	*Interfacial Tension ($mJ\ m^{-2}$)*		*Solubility at (20°C)*	*Ref.*
	γ^+/γ^- *(1,recalcd.)*	*(1.8)*		
Sucrose/water	−6.5	−6.5	+ +	6
Sucrose/formamide	+2.4	+2.9	+ +	6
Dextran T-150/water	−20.6	−25.9	+	6
Dextran T-70/water	−11.5	−12.2	+	38
Dextran T-150/formamide	−3.4	−9.7	Swelling	6
Agarose/water	+1.6	+4.6	Forming gels	6
Agarose/formamide	+3.3	+3.3	+ +	6
Gelatin/water	+9.7	+9.4	Insol. at r. t.	38
PEG-6000/water	−25.1	−21.2	+ +	38
Zein/water	+10.4	+7.4	−	6
Zein/formamide	+5.2	+5	+ +	6
Human serum albumin, (dry)/water	+8.7	+9.3	−	38
Human serum albumin, (33% Hydrated)/water	−10	−31.4	+	38
PMMA/water	+16.6	+16.9	−	6

Note: +···Soluble; + +···Spontaneously soluble; −···Insoluble.

tive numbers. The existence of a negative interfacial tension between two dissimilar acid-base materials has recently been verified independently by Thomas *et al.* [27] with the use of the JKR approach for determining the work of adhesion. This may be the first time that a negative interfacial tension has been found to be present for the maximum adhesion between two elastic films. As discussed previously, a negative interfacial tension is preferred for achieving not only the maximum work of adhesion but also spontaneous spreading of a liquid (or an adhesive) on a solid (or an adherend).

7. CONCLUSIONS

From the relationship between LSER solvatochromic parameters and surface-hydrogen-bond-accepting and -donating (or SHBA and SHBD) components, we found a new ratio for γ^+ and γ^- of 1.8 for water at 20°C. The change of that ratio for water from 1.0 to 1.8 did lower considerably the γ^- values for liquids, polymers and biomaterials without affecting the surface tensions or the signs of interfacial tension. Our work appears to be a significant improvement in obtaining appropriate values for the interfacial tension and the work of adhesion involving these polymers and biomaterials. The calculated surface tension component data given in this paper should be useful for further prediction of solubility or the adhesion between an adhesive and an adherend. For both cases, a negative interfacial tension is preferred. Furthermore, the VCG method is comparable to Fowkes' approach provided that the acid-base interaction as defined by VCG is limited to hydrogen bonding. However, the Fowkes' method is not tied to the contact angle measurement as in the case of the VCG method. Our work shows that the VCG method is somewhat linked to Taft and Kamlet's acid-base concept that is substantially different from Drago's approach which, in turn, is directly linked to Fowkes' method. This may explain why the VCG method does not require the four parameters proposed by Drago.

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