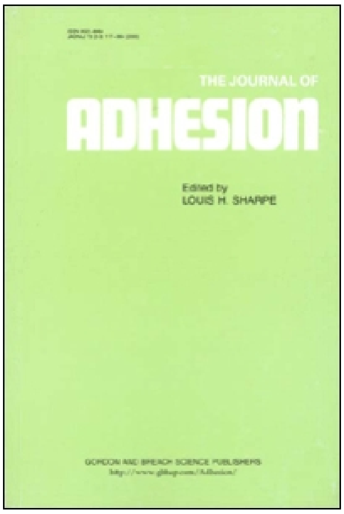

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The Unified Lewis Acid-Base Approach to Adhesion and Solvation at the Liquid-Polymer Interface

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We present our unified Lewis acid-base approach to adhesion and solvation at the liquid-polymer interface. This approach is to complement the original methodologies proposed by Fowkes and by van Oss, Chaudhury and Good (VCG). Intermolecular interactions are primarily dominated by dispersion, d, hydrogen bonding, h, and secondarily affected by orientation, o, and induction, i. Generally, the polarization component, p, represents both i and o interactions. Fowkes suggested that the acid-base component, γ^{ab}, of the surface tension should consist of both h and p interactions. However, VCG proposed that the acid-base components, γ^{ab}, result solely from hydrogen bonding, γ^{h}, that is equivalent to $2(\gamma^{+}\gamma^{-})^{1/2}$, where γ^{+} and γ^{-} are the two hydrogen bonding parameters. VCG defined γ^{LW} as the Lifshitz-van der Waals component consisting of d, o and i contributions, thus, surface tension, γ, equals $\gamma^{ab}(\text{VCG})+\gamma^{LW}$. Both Fowkes and VCG assumed that the polar interactions for a liquid on a low energy surface are negligible.

Now, we assume otherwise, and we treat the specific acid-base interaction to be hydrogen bonding. In addition, we also take into account the nonspecific polarization, p, interaction in terms of the equilibrium spreading pressure, π_e, resulting from the adsorption of a liquid vapor on the polymer surface. Thus, our unified approach uses the dispersion component, γ^{d}, of Fowkes, the hydrogen bonding, h, of VCG and the polarization, p, in terms of π_e. The difference between the initial (theoretical) and equilibrium (experimental) surface tensions is π_e, and others have observed that π_e on some polymers is substantial. The determination of several initial surface tensions of polymers by considering the effect of polarization is discussed.

In the Appendix, we shall illustrate that this polar component, π_e, is equivalent to the LESR polarity-dipolarity parameter, Π^*, (represented by the same symbol but in different context) for the solvatochromic treatment. Furthermore, the surface tension components, γ^{d}, γ^{+}, γ^{-} and π_e, are now somewhat comparable with the four parameters in the original Taft-Kamlet relationship, δ, α, B, and Π^*. Thus, our proposed

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unified approach may finally help elucidate the long-debated Lewis acid – base theories pertaining to adhesion and solvation of polymers.

Keywords: Adhesion; Associated liquid; Dipole; Dispersion; Hydrogen-bonding; Induction; Interface; Lewis acid – base interaction; Orientation; Polarization; Polymer; Solvation; Spreading pressure; Surface energy; Surface tension; Work of adhesion

1. INTRODUCTION

We present our unified Lewis acid – base approach to adhesion and solvation at the liquid-polymer interface in complementing the original methodologies proposed by Fowkes [1] and by van Oss, Chaudhury and Good (VCG) [2, 3]. As the basis for our unified approach [4 – 6], molecular interactions [7, 8] consist of dispersion, d, hydrogen bonding, h, orientation, o, and induction, i. Generally, the polarization component, p, represents both o and i interactions. Fowkes originally suggested that the Lewis acid – base component, γ^{ab}, of the surface tension consists of both h and p interactions. However, VCG proposed that the acid – base components, γ^{ab}, are equal to γ^{h}, that is $2(\gamma^{+}\gamma^{-})^{1/2}$, where γ^{+} and γ^{-} are the two hydrogen-bonding parameters. They defined γ^{LW} to be the Lifshitz-van der Waals component including d, o, and i contribution; hence, surface tension, γ, equals γ^{ab} (VCG)$+\gamma^{LW}$. Both Fowkes and VCG assumed that the polar interactions of a liquid on a low energy surface are negligible.

In this paper, we also treat hydrogen bonding as the major subset of Lewis acid – base interactions but, in addition, we consider the polar component in terms of the equilibrium spreading pressure, π_e, resulting from the adsorption of a liquid vapor on the solid (*e.g.*, polymer) surface. The effect of polarization on the acid – base (Fowkes) component or the hydrogen bonding (VCG) component is also discussed.

2. THEORETICAL BACKGROUND

2.1. Acid – Base Interactions

Originally, Lewis acid – base interaction [9] was narrowly defined as the interaction between an acid and a base involving the transfer of an electron pair. Later, this definition was broadened to include hydrogen bonding. In this paper, we deal mainly with hydrogen bonding, which involves both electrostatic and covalent bonding between a hydrogen atom and an electronegative atom, *e.g.*, O, S, N, or F. Hydrogen bonding is mainly electrostatic (ionic) in nature. For example, the weak hydrogen bond between water molecules is principally formed by the coulombic attraction between a positively-charged hydrogen atom (or proton) and a negatively-charged oxygen atom. Thus, it resembles, but is not identical to, the Brønsted acid–base interaction which involves the separate transfer of a proton (H^+). In a hydrogen bond, the proton is not separated but forms a bridge between two oxygen atoms. In fact, the hydrogen atom with depleted outer electrons appears to be donating itself to the neighboring oxygen atom having unpaired electrons.

Pauling [10] originally postulated the hydrogen bond to be partially covalent (nonionic). It is not until 1999 that Issac *et al.* [11] used a direct X-ray measurement to prove that the hydrogen bond in ice is indeed approximately 10% covalent. In this regard, hydrogen bonding may also be described partially as one of the Lewis acid–base interactions which are characterized by forming an adduct or a complex. However, it is still not in the narrow sense of Lewis acid–base interaction involving the transfer of unpaired electrons.

In describing hydrogen bonding as an acid–base interaction, we prefer the Taft-Kamlet LESR approach [12, 13] by assigning the acid as the functional group having an ability to donate a hydrogen atom, and the base as that having the ability to accept a hydrogen atom. In 1996, we [14, 15] found a correlation between the Taft-Kamlet approach and the acid–base methodology for surface interactions developed by van Oss, Chaudhury and Good [2, 3]. This finding has given VCG's work a sound theoretical backing. We shall mention more in the Appendix about the missing surface parameter in the previous study.

2.2. Intermolecular Interaction Energies

The short-range acid–base interaction energies at the molecular level [7, 8] consist of electrostatic, charge transfer, polarization, electron exchange, and the mixing term of higher orders. The first three terms are attractive energies and the last two are repulsive energies. Among the attractive energies [16], there are several van der Waals energy components: London dispersion, d, Keesom's dipole–dipole orientation interaction, o, and Debye's dipole-induced dipole induction interaction, i. Since Debye's interaction is in general smaller than Kessom's interaction, generally the polarization component, p, represents both o and i interactions.

Dispersion occurs whenever two neutral (apolar) similar (or dissimilar) atoms or molecules are in proximity, whether or not other interactions are also present. London dispersion energy, E_d, between two attracting spherical molecules is estimated to be a function of the polarizability, α, ionization potential, I, and inversely proportional to the sixth power of the interatomic distance, r.

$$E_d = -3/2[I_1 I_2/(I_1 + I_2)](\alpha_1\alpha_2/r^6) \tag{1}$$

Thus, as the interatomic distance increases, the dispersion energy decreases. At a distance beyond 100 Å, a retardation force sets in to change the distance dependence to r^{-7}. The magnitude of dispersion energy is about 2 kJ mol^{-1}. It is the second strongest intermolecular energy between apolar molecules after hydrogen bonding.

Keesom's dipole–dipole interaction energy, E_o, between two polar molecules with permenant dipoles is a measure of orientation, and it is a function of dipole moments, μ, and inversely proportional to κ (Boltzmann constant), the absolute temperature, T, and the sixth power of the distance, r:

$$E_o = -(2\mu_1^2\mu_2^2)/(3\kappa T r^6) \tag{2}$$

Debye's dipole-induced dipole interaction energy, E_i (i, induction), for a pair of polarizable molecules is somewhat weaker than Keesom's energy. It is a function of the product of dipole moment and polarizability, α, but independent of temperature. It is also inversely proportional to r^6:

$$E_i = -(\alpha_1\mu_2^2 + \alpha_2\mu_1^2)/r^6 \tag{3}$$

For liquids, the dipole moment is the chief factor in estimating both the Keesom's and Debye's energies. Since on a polar solid surface there are only functional groups with considerably smaller partial dipole moments [17], Keesom and Debye interactions between a liquid and a solid are generally smaller than those between two liquids.

Hydrogen bonding energy is the second important intermolecular energy which is stronger than van der Waals' energies. Inter-hydrogen bonds are generally stronger than intra-hydrogen bonds. Depending on the electronegative atoms involved [18], bond strengths in terms of enthalpies are between -7 and $-165\,\mathrm{kJ\,mol^{-1}}$. For the O—H bond in ice, the bond strength has recently been determined [11] to be $-28\,\mathrm{kJ\,mol^{-1}}$ and the bond length to be 1.75 Å, which is longer than a sigma bond of 1.0 Å. Hydrogen bonding, which is specific, can also occur concurrently with the nonspecific polarization at the interface. Thus, our approach to the overall acid–base interaction in the presence of hydrogen bonding is to include the effect of polarization, if it is substantial. Though polarization energy generally has been postulated to be negligible in most condensed matter [2, 3, 16], in the case of vapor adsorption on low surface energy material, sometimes it is not negligible.

Hydrogen bond interaction is also a relatively strong type of dipole–dipole interaction, o. Liquids like water and formamide are called associated liquids [16]. Thus, the energies of their initial state can differ substantially from those in equilibrium with other liquids or solids at the interface. Some of the initial associated bonds in the bulk liquid have to be cleaved before they start to form new intermolecular hydrogen bonds at the interface. This may explain why in some instances the initial and equilibrium hydrogen bonding energies are different.

2.3. Work of Adhesion and Surface Tension Components

In view of the additivity of intermolecular energies, Fowkes [1] proposed that various components of the work of adhesion, W_A, should be additive. In the beginning, he clearly perceived that there should be at least three independent components for W_A, and they are dispersion, d, hydrogen bonding, h, and polarization, p.

Thus, the total work of adhesion is expressed as:

$$W_A = W_A^d + W_A^h + W_A^p \tag{4}$$

Similarly, the total surface tension is:

$$\gamma = \gamma^{d} + \gamma^{h} + \gamma^{p} \tag{5}$$

Later, Fowkes [19] assumed that the polarization in the condensed phases was negligible and decided to combine the component p with the hydrogen bond component h into the acid–base component, ab. Thus,

$$W_A = W_A^{d} + W_A^{ab} \tag{6}$$

and

$$\gamma = \gamma^{d} + \gamma^{ab} \tag{7}$$

In the VCG methodology, the Lifshitz-van der Waals component, γ^{LW}, is defined as the sum of three components:

$$\gamma^{LW} = \gamma^{d} + \gamma^{i} + \gamma^{o} \tag{8}$$

Thus, γ^{LW} is no longer the apolar dispersion component, γ^{d}, originally defined by Fowkes. At the same time, they [2, 3] defined the acid–base component as the hydrogen bonding component which can be calculated as follows:

$$\gamma^{ab} = \gamma_{sv}^{h} = 2(\gamma^{+}\gamma^{-})^{1/2} \tag{9}$$

where γ^{+} is the surface acidic or hydrogen-bond-donating parameter, and γ^{-} is the surface basic or hydrogen-bond-accepting parameter.

2.4. Initial and Equilibrium Surface Free Energies

Bangham and Razouk [20] first observed the effect of the vapor of a liquid adsorbed on the solid on surface free energy (or surface tension), and they have indicated that the equilibrium spreading (or film) pressure, π_e, of the adsorbed layer on the solid surface tends to lower the surface free energy. Equilibrium spreading pressures, π_e's on polymers have been observed by others to be substantial, and the difference between the initial (theoretical) and equilibrium (experimental) surface tensions is π_e. If the vapor adsorption is substantial, the expression for the initial surface tension, γ_s, for a clean solid [4] should be

$$\gamma_s = \gamma_{sv} + \pi_e \tag{10}$$

where γ_{sv} is the equilibrium surface tension obtained in the presence of the vapor of a liquid.

According to Fowkes' approach, the equilibrium surface tension is

$$\gamma_{sv} = \gamma_{sv}^{d} + \gamma_{sv}^{ab} \tag{11}$$

and the initial surface tension becomes:

$$\gamma_s = \gamma_s^{d} + \gamma_s^{ab} = \gamma_s^{d} + \gamma_{sv}^{ab} + \pi_e \tag{12}$$

The dispersion component [16], γ_{sv}^{d}, is not affected by polarization resulting from adsorption, because this component is related to an apolar interaction. Thus, γ_{sv}^{d} is identical to the initial value, γ_s^{d}. As a result, γ_s^{ab} is not equal to γ_{sv}^{ab}, or the initial acid-base component is larger than the equilibrium value. This is partially owing to the cleavage of the associated bonds in the liquid medium and partly due to polarization as expressed in π_e. We shall continue to discuss this topic further in one of the following sections.

For the VCG approach, the equilibrium surface tension of a solid, affected by the adsorption, should consist of two terms, *i.e.*,

$$\gamma_{sv} = \gamma_{sv}^{LW} + \gamma_{sv}^{h} \tag{13}$$

If the adsorption is substantial, the initial surface tension becomes

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{h} = \gamma_{sv}^{LW} + 2(\gamma_{sv}^{+}\gamma_{sv}^{-})^{1/2} + \pi_e \tag{14}$$

According to VCG's definition, γ_s^{LW}, unlike γ_s^{d}, is not equal to γ_{sv}^{LW}.

It should be pointed out that most surface tensions for solids or polymers determined earlier by the VCG methodology without the inclusion of π_e are essentially equilibrium (experimental) surface tensions, γ_{sv}'s. Thus, if π_e's are substantial, initial (theoretical) surface tensions of solids and polymers should be higher than corresponding equilibrium values. We shall elucidate the difference between these two kinds of surface tensions in the experimental section.

2.5. Initial and Equilibrium Work of Adhesion

In the case of a liquid in contact with its vapor and a flat solid surface, an equilibrium contact angle, θ_e, is formed between the liquid and the solid, then the equilibrium work of adhesion can be represented by the Young-Dupre equation [21]

$$W_A = \gamma_{\ell v}(1 + \cos\theta_e) \tag{15}$$

Bangham and Razouk [20] also indicated that the equilibrium spreading pressure, π_e, of the adsorbed layer on the solid surface tended to lower the work of adhesion of the solid from that which might be determined in the absence of a vapor or in vacuum, thus W_{Ao}, the initial (theoretical) work of adhesion:

$$\pi_e = W_{Ao} - W_A \tag{16}$$

In the presence of the equilibrium spreading pressure, the initial work of adhesion between a clean solid and a liquid may be written as

$$W_{Ao} = W_A + \pi_e = \gamma_{\ell v}(1 + \cos\theta_e) + \pi_e \tag{17}$$

2.5.1. *Fowkes' Approach*

The work of adhesion can be determined in different ways. For example, Fowkes [19] proposed the following equation to determine the equilibrium (experimental) work of adhesion, W_A, for a system involving only dispersive interactions:

$$W_A = 2(\gamma_{\ell v}^d \gamma_s^d)^{1/2} \tag{18}$$

Thus, if π_e is substantial, the initial work of adhesion should be larger than the equilibrium one, and the difference between the two is the equilibrium spreading pressure:

$$W_{Ao} = 2(\gamma_\ell^d \gamma_s^d)^{1/2} + \pi_e \tag{19}$$

For the system involving both dispersive and acid–base interactions, Fowkes [19] applied Drago's four EC parameters [22] for determining the acid-base interaction enthalpy, ΔH^{ab}, and the acid-base component of the work of adhesion:

$$-H^{ab} = E_A E_B + C_A C_B \tag{20}$$

and,

$$W_A = 2(\gamma_\ell^d \gamma_d^d)^{1/2} - fn^{ab}(E_A E_B + C_A C_B) \tag{21}$$

where f is the conversion factor, generally smaller than one; n is the surface acid-base population; C is the susceptibility to the covalent interaction; E is that to the electrostatic interaction, and subscripts A and B are acid and base. Experimentally, the fraction of the surface participating in the interaction is difficult to determine.

If the adsorption is substantial, the initial work of adhesion should be expressed as:

$$W_{Ao} = 2(\gamma_\ell^d \gamma_s^d)^{1/2} - fn^{ab}(E_A E_B + C_A C_B) + \pi_e \tag{22}$$

For the interactions between liquids [19], the initial (theoretical) enthalpies (Tab. I) in terms of ΔH_{E+C} are in excellent agreement with the equilibrium (experimental) values of ΔH_{Exp}. Originally, Fowkes intended to show that the products of $\mu_1^2 \mu_2^2$ could not be correlated with the acid-base enthalpies. However, he might not have realized that these products, proportional to orientation enthalpies calculated with Keesom's formula, also show the clear coexistence of polarization interactions between acids and bases.

According to the following data, it is apparent that Fowkes' acid-base interaction, as estimated with Drago's parameters, is actually only hydrogen bonding. It does not include the polar component as in

TABLE I Enthalpies (kcal mol^{-1}) of acid-base interaction of acetone with acids of various dipole moments (Debye) (data of Fowkes [19])

Acid	$\mu_1^2 \mu_2^2$	ΔH_{E+C}	ΔH_{Exp}
Iodine	0	3.3	3.3
Aluminum trimethyl	2.1	20.0	20.3
Chloroform	8.6	3.6	3.6
Water	28.4	3.2	3.2
p-Chlorophenol	36.9	5.4	5.4

Eq. (5). The data also clearly show that the polarization (due to orientation alone) between acetone and iodine is, indeed, nil. Also, the polarization between acetone and aluminum is small in comparison with the acid–base interaction. However, for water and chlorophenol the polarization component is very strong. In comparing with the acid–base interaction, the strength in terms of enthalpies between aluminum trimethyl and acetone is the highest among the five pairs of liquids. These results also indicate that polarization can co-exist with the acid–base interaction. However, Drago's EC approach is used to estimate only the acid–base interaction in terms of hydrogen bonding, and polarization has to be calculated separately.

The agreement between the calculated and experimental interaction enthalpies is not always as good as that shown in Table I. Later, Drago *et al.* [23] also found out that some deviations were due to the enthalpy required to cleave the associated bonds between molecules in the initial liquid state. Thus, they introduced the fifth parameter, W, which is a constant contribution of the intramolecular interaction of a particular acid (or base). The ECW approach for the acid–base interaction enthalpy may be expressed as:

$$-H^{ab} = E_A E_B + C_A C_B - W \qquad (23)$$

If the nonspecific polarization, such as steric interaction, or π-back bonding donation, is substantial, further modification is needed. Though Drago's approach has been successful, it has reached a limit. Therefore, the Fowkes method, using Drago's parameters alone for the calculation of the work of adhesion, is still incomplete. So far, one still has to rely on the spreading pressure for estimating the polarization interaction, and Eq. (22) appears to be the best that one can get for the estimation of the initial work of adhesion. Therefore, we did not intend to expand our acid–base approach to include the entire Fowkes' method. For the unified approach, we prefer to use his dispersion component for our later calculations.

2.5.2. VCG's Method

In this paper, we plan, instead, to discuss mainly the unified acid–base approach with respect to the VCG methodology. VCG [2, 3] calculated the equilibrium work of adhesion for a liquid–solid system involving hydrogen-bonding with the following equation:

$$W_A = 2[(\gamma_{\ell v}^{LW}\,\gamma_s^{LW})^{1/2} + (\gamma_{\ell v}^{+}\,\gamma_{sv}^{-})^{1/2} + (\gamma_{\ell v}^{-}\,\gamma_{sv}^{+})^{1/2}] \tag{24}$$

When π_e is substantial, the initial work of adhesion should be higher:

$$W_{Ao} = 2[(\gamma_{\ell v}^{LW}\,\gamma_s^{LW})^{1/2} + (\gamma_{\ell v}^{+}\,\gamma_{sv}^{-})^{1/2} + (\gamma_{\ell v}^{-}\,\gamma_{sv}^{+})^{1/2}] + \pi_e \tag{25}$$

In the following sections, we shall demonstrate that without considering π_e, the original VCG approach is indeed incomplete and does encounter some difficulties. If π_e is considered, some of the VCG's equations can be modified. Now we are treating the polarization interaction, p, as a part of π_e, instead of as a part of the Lifshitz-van der Waals LW component, because the LW component is affected by polarization [3] as shown in the following relation:

$$\gamma_s^{LW} = [\gamma_{\ell v}(1 + \cos\theta_e) + \pi_e]^2/4\gamma_{\ell v} \tag{26}$$

2.6. Determination of Initial Surface Tension Components

In obtaining the initial surface tension components for a liquid, we should first determine the equilibrium contact angle of a reference liquid, *e.g.*, water, on a basic polymer, *e.g.*, PMMA, where γ_{sv}^{+} is zero. By using the dispersion component, d, we can derive a relation [3] related to water from Eq. (25) as follows:

$$\gamma_w(1 + \cos\theta_{w/s}) = 2[(\gamma_w^d\,\gamma_s^d)^{1/2} + (\gamma_w^{+}\,\gamma_{sv}^{-})^{1/2}] + \pi_w \tag{27}$$

and

$$\gamma_w^{+} = \{1/2[\gamma_w(1 + \cos\theta_{w/s})] - (\gamma_w^d\,\gamma_s^d)^{1/2} - \pi_w\}^2/\gamma_{sv}^{-} \tag{28}$$

Similarly for an equation related to a liquid

$$\gamma_\ell(1 + \cos\theta_{\ell/s}) = 2[(\gamma_\ell^d\,\gamma_s^d)^{1/2} + (\gamma_\ell^{+}\,\gamma_{sv}^{-})^{1/2}] + \pi_\ell \tag{29}$$

and

$$\gamma_\ell^{+} = \{1/2[\gamma_\ell(1 + \cos\theta_{w/s})] - (\gamma_\ell^d\,\gamma_s^d)^{1/2} - \pi_\ell\}^2/\gamma_{sv}^{-} \tag{30}$$

Upon dividing Eq. (28) by Eq. (30) we obtain the ratio of γ_w^+/γ_ℓ^+ as shown in Eq. (31)

$$\frac{\gamma_w^+}{\gamma_\ell^+} = \left[\frac{\gamma_w(1+\cos\theta_{w/s}) + \pi_w - 2(\gamma_w^d\gamma_s^d)^{1/2}}{\gamma_\ell(1+\cos\theta_{\ell/s}) + \pi_\ell - 2(\gamma_\ell^d\gamma_s^d)^{1/2}}\right]^2 \tag{31}$$

3. EXPERIMENTAL RESULTS

3.1. Equilibrium Surface Tension Components for Probe Liquids

VCG selected several probe liquids for the contact angle measurements. They determined the surface tension parameters, *e.g.*, γ^+ and γ^-, from the contact angles of polar liquids on a reference monopolar substrate, *e.g.*, PMMA, poly(methyl methacrylate). However, they did not contemplate the possible lowering of the initial surface tension of PMMA due to the vapor adsorption. They also assumed that the ratio of γ_w^+ and γ_w^- was unity for water as the reference. Later, we found [14, 15] that the proper ratio should be 1.8. Equilibrium (experimental) surface tension components ($\gamma_{\ell v}^+$ and $\gamma_{\ell v}^-$) for several probe liquids in the presence of vapor are shown in Table II. In the literature, these components have been incorrectly treated as initial (theoretical) surface tension components (γ_ℓ^+ and γ_ℓ^-).

With the new ratio, we calculated equilibrium surface tension components for many polymers and solids [14, 15]. Generally, after the recalculation most polymers still appeared to be rather basic. One of

TABLE II Equilibrium surface tension components for probe liquids in mJ m^{-2} at 20°C (Reference values for water: $\gamma_{\ell v}^+ = 34.2$ mJ m^{-2}; $\gamma_{\ell v}^- = 19$ mJ m^{-2})

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

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

the controversial examples is PVC, poly(vinyl chloride). Most researchers believe that this polymer should be acidic, but the VCG's results show the contrary. Our use of the new ratio for water as the reference raised the acidity scale slightly but not enough to render PVC acidic. Later, Volpe and Silboni [24] proposed an even higher ratio, but they still did not solve the problem. Thus, we suspected that there could be some other problem associated with the VCG approach. We shall demonstrate how our approach helps to solve the problem.

3.2. Initial Surface Tension Components for Probe Liquids

After we considered that the vapor adsorption on PMMA was substantial, we found many revealing results. There have been several reports claiming that the vapor of polar as well as apolar liquids [25, 26] can readily adsorb on PMMA. Furthermore, the adsorption was rather substantial, resulting in high π_e's. Bellon-Fontaine and Cerf [27] examined the adsorption of several liquids on four polymers, including PMMA. They indicated that their results had an experimental error of $\pm 12\,\mathrm{mJ\,m^{-2}}$. The validity of their results may be in question, because of their use of mercury as the reference. In comparison with the data generated by other workers, their results do appear somewhat high, so we used the lower limit of their π_e's for our calculations. For example, the lower limit of π_w for PMMA is $23\,\mathrm{mJ\,m^{-2}}$ which is comparable with the value of $26\,\mathrm{mJ\,m^{-2}}$ obtained by Busscher *et al.* [28] and $18.6\,\mathrm{mJ\,m^{-2}}$ by Erbil [29]. The lower limit π_e values are $31.7\,\mathrm{mJ\,m^{-2}}$ for formamide and $27.3\,\mathrm{mJ\,m^{-2}}$ for glycerol. For ethylene glycol, we estimated π_e by plotting π_e *versus* γ_ℓ of different liquids.

On the basis of Eq. (31) we are able to calculate the initial surface tension components $(\gamma_\ell^+, \gamma_\ell^-)$ for several probe liquids as shown in Table III. Since DMSO is a base, and γ_ℓ^+ is zero, we used an equation similar to Eq. (31) to calculate the ratio of γ_w^- (water)/γ_ℓ^- of DMSO on PTFE (where $\gamma_{sv}^+ = \gamma_{sv}^- = o$), not on PMMA, based on contact angles and π_e's reported in Ref. [27].

In Table III, initial surface tension components of liquids are listed as γ_ℓ^d for dispersion, γ_ℓ^h for hydrogen-bonding, instead of γ_ℓ^{ab} for the broader Lewis acid-base interaction, and π_e for the equilibrium

TABLE III Initial surface tension components for probe liquids in mJ m^{-2} at 20°C (Reference values for water: $\gamma_\ell^+ = 34.2\,\mathrm{mJ\,m^{-2}}$; $\gamma_\ell^- = 19\,\mathrm{mJ\,m^{-2}}$)

Liquid	γ_ℓ	γ_ℓ^d	γ_ℓ^h	γ_ℓ^+	γ_ℓ^-	θ_O *and* π_e (*on PMMA*)	
Water	72.8	21.8	51	34.2	19	67	23 [27]
Glycerol	64	34	30	17.4	12.9	62	27.3 [27]
Formamide	58	28	30	22.4	10.1	54	31.7 [27]
Diiodomethane	50.8	50.8	≈0	≈0	≈0	35.5	31.3 [26]
Ethylene glycol	48	29	19	15.1	6	52	36*
α-Bromonaphthalene	44.4	43.5	≈0	≈0	≈0	9.5	27.2 [26]
Dimethyl sulfoxide	44	29	15	2	28	16	38 [27]

*This value was extrapolated from the spreading pressure *versus* surface tension of liquids.

spreading pressure resulting from the polarization interaction. It is important to note that π_e, as defined, depends on polar interactions, p, between a solid and the vapor of a liquid, and π_e varies from liquid to liquid. Furthermore, we are using revised dispersion values later published by Fowkes [30]. For formamide, the dispersion component should be 28 mJ m^{-2}, instead of 39 mJ m^{-2} for the LW component used by VCG, and for DMSO it should be 29 mJ m^{-2}, instead of 36 mJ m^{-2}. Generally, with initial surface tension components, the liquids, *e.g.*, glycerol, formamide and ethylene glycol, become acidic, and the ratios of γ_ℓ^+ and γ_ℓ^- for these liquids become comparable with those of the α and β parameters of the linear free energy relationship [14, 15].

3.3. Determination of Equilibrium Surface Tensions for Polymers

In Table IV equilibrium surface tension components for four polymers, poly(tetrafluoroethylene), poly(propylene), poly(methyl methacrylate) and poly(vinyl chloride), were obtained with the values

TABLE IV Equilibrium surface tension components for polymers in mJ m^{-2} at 20°C (Reference values for water: $\gamma_{\ell v}^+ = 34.2\,\mathrm{mJ\,m^{-2}}$; $\gamma_{\ell v}^- = 19\,\mathrm{mJ\,m^{-2}}$)

Polymer	γ_s^{LW}	γ_{sv}^{ab}	γ_{sv}^+	γ_{sv}^-	γ_{sv}	π_w
Poly(tetrafluoroethylene)	19.6	0	0	0	19.6	0.2
Poly(propylene)	29.7	0	0	0	29.7	0.3
Poly(methyl methacrylate)	43.2	0	0	22.4	43.2	23
Poly(vinyl chloride)	43	0.8	0.04	3.5	43.8	6.5

for probe liquids listed in Table II. In addition, equilibrium spreading pressures are listed in the sixth column.

Based on the equilibrium surface tension components in Table IV, the first two polymers, PTFE and PP, are apolar, while PMMA and PVC appears to be basic. For PVC, the equilibrium surface tension, γ_{sv}, is 43.8 mJ m^{-2}, and related components γ_{sv}^{+} and γ_{sv}^{-} are 0.04 mJ m^{-2} and 3.5 mJ m^{-2}, respectively.

3.4. Determination of Initial Surface Tensions for Polymers

In Table V, initial surface tension components of these polymers were obtained with initial surface tension values of the probe liquids listed in Table III. It is noteworthy that the two initial surface tension components, γ_s^{+} and γ_s^{-}, for PVC are now 7.3 mJ m^{-2} and 2 mJ m^{-2}, respectively. Thus, PVC, when clean and unadsorbed, is surprisingly acidic. Furthermore, the determined initial surface tension, γ_s, is 50.3 mJ m^{-2} which is identical to the sum of π_w (6.5 mJ m^{-2}) and γ_{sv} (43.8 mJ m^{-2}) as listed in Table IV. Thus, for PVC, both values of γ_s are in excellent agreement. In Table V, the agreement of γ_s is also good for other polymers except PMMA.

At this juncture, we have at least overcome one of the major obstacles facing the VCG methodology. The acid–base parameters introduced by VCG have gained some new respect because we now can differentiate with the initial surface tension an "acid" (hydrogen-bond donor) from a "base" (hydrogen-bond acceptor), if the surface is clean and unadsorbed. For other polymers, we can calculate the initial surface tension using Eq. (10) after we determine π_e or from initial surface tension components for probe liquids listed in Table III. The exercise in this paper merely illustrates the theoretical importance of

TABLE V Initial surface tension components for polymers in mJ m^{-2} at 20°C (Reference values for water: $\gamma_\ell^{+} = 34.2$ mJ m^{-2}; $\gamma_\ell^{-} = 19$ mJ m^{-2})

Polymer	γ_s^d	γ_s^h	γ_s^+	γ_s^-	γ_s	$(\pi_w + \gamma_{sv})$
Poly(tetrafluoroethylene)	19.6	0	0	1.2	19.6	19.8
Poly(propylene)	29.7	0	0	0	29.7	30
Poly(methylmethacrylate)	43.2	12.9	1.3	32	56.1	66.2
Poly(vinyl chloride)	43	7.3	7.3	2	50.3	50.3

the spreading pressure on the Lewis acid–base theory. Since surface tensions of most polymers, in practice, are determined in the presence of the vapor of a liquid, it is really not necessary to revise all existing equilibrium surface tensions in the literature with spreading pressures into initial surface tensions. In practice, π_e is not easy to determine. In fact, all published data should be applicable to polymers at equilibrium at the liquid-polymer interface.

Though the VCG methodology is basically sound, there is, at least, one more revision needing to be made. If polar interactions are treated separately as in π_e, the Lifshitz-van der Waals component, γ^{LW}, proposed by VCG, is no longer relevant. Instead, by definition it is the dispersion component, γ^d (Fowkes), which should be used, and γ^d is not affected by polarization.

4. CONCLUSIONS

Our unified Lewis acid–base approach is based on a molecular bonding mechanism. The initial (theoretical) surface tension, γ_s, for a clean, unadsorbed solid should consist of dispersion, d, hydrogen-bonding, h, and polarization, p (a combination of induction i and orientation o interactions), components. Unlike the specific hydrogen-bonding component, the polar component, p, is nonspecific, and it is expressed as the equilibrium spreading pressure, π_e, between an immiscible pair, *e.g.*, a liquid and a solid (or polymer). For the unified approach, we consider both hydrogen bonding and polarization to take place simultaneously, if adsorption is substantial. Thus, the initial (theoretical) surface tension of a polymer in the absence of vapor adsorption can be expressed as: $\gamma_s = \gamma_s^d + \gamma_s^h$, while the equilibrium (experimental) surface tension in the presence ot vapor adsorption is $\gamma_{sv} = \gamma_s^d + \gamma_{sv}^h$. Furthermore, the initial surface tension is $\gamma_s = (\gamma_s^d + \gamma_{sv}^h) + \pi_e$. When the spreading pressure data are available, we can obtain both initial surface tensions and initial works of adhesion for polymers.

For "polar" materials, hydrogen-bonding is the major Lewis acid–base interaction on the surface. Fowkes used the Drago EC parameters to estimate the enthalpy of hydrogen bonding. VCG showed that hydrogen bonding should consist of two parameters; *i.e.*, hydrogen-bond donating (acidic) γ^+ and hydrogen-accepting (basic) γ^-. The hydrogen-bonding component of a solid obtained at equilibrium with the vapor of a liquid is $\gamma_{sv}^h = 2(\gamma_{sv}^+ \gamma_{sv}^-)^{1/2}$. In the literature, most surface tension components obtained at equilibrium are actually γ_{sv}. However, most equilibrium surface tension components cannot differentiate the polarity, or hydrogen-bonding tendency, of a polymer because the polymer surface is generally adsorbed by the vapor of a liquid. As a result of adsorption, more polymers appear to be "basic" as revealed by the equilibrium surface tension components. We have shown that the initial surface tension, though difficult to obtain, can serve much better to differentiate the polarity of a liquid or a polymer, *e.g.*, poly(vinyl chloride). This is the first time that we were able to show PVC to be an acid when the surface is clean and unadsorbed by a vapor.

In the Appendix, we shall reveal that the missing link between surface tension components and the LESR relationship is the equilibrium spreading pressure, π_e. Thus, the unified Lewis acid–base approach is relevant to both adhesion and solvation at the liquid-polymer interface.

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NOTATION

A	acid
B	base
C	susceptibity to covalent interaction
d	dispersion
E	susceptibity to electrostatic interaction
E	interaction energy
f	conversion factor
δH^2	the square of the Hildebrand solubility parameter of a solvent

ΔH^{ab}	enthalpy of the acid – base interaction
h	hydrogen bonding
I	ionization potential
i	induction
n^{ab}	acid – base population on the surface
o	orientation
p	polarization
r	interatomic distance
W	constant or Drago's fifth parameter
W_{Ao}	initial work of adhesion
W_A	equilibrium work of adhesion

Greek Letters

α	polarizability
α	empirical, quantitative measure of the hydrogen-bond-donating (HBD) ability of a bulk solvent toward a solute
β	empirical, quantitative measure of the hydrogen-bond-accepting (HBA) [or electron-pair-donating (EPD)] ability of a bulk solvent toward a solute for a hydrogen bond (or a Lewis coordination bond)
γ^{ab} (Fowkes)	acid – base component as defined by Fowkes
γ^{ab} (VCG)	acid – base component as defined by van Oss, Chaudhury and Good
γ^{h}	hydrogen bonding component of surface tension
γ^{d}	dispersion component of surface tension
γ^{LW}	Lifshitz-van der Waals component of surface tension
γ_s	initial surface tension of a clean, unadsorbed solid
γ_{sv}	equilibrium surface tension of a solid in the presence of a vapor
γ_ℓ	initial surface tension of a liquid
$\gamma_{\ell v}$	equilibrium surface tension of a liquid
γ^{+}	surface acidic or hydrogen-bond donating parameter
γ^{-}	surface basic or hydrogen-bond accepting parameter
θ_e	equilibrium contact angle
κ	Boltzmann constant
μ	dipole moment

π_e	equilibrium spreading pressure (or π_w in the presence of water vapor)
Π^*	a measure of the energetic effects (involving negative Gibbs free energy change) of solute–solvent, dipole–dipole, π, and dipole-induced dipole, i, interactions

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APPENDIX

Related Acid–Base Approach for Solvation

In studying the solvation problem, Taft and Kamlet [12, 13] developed a rather successful approach in describing hydrogen bonding systems. They did not depend on either the Brønsted-Lowrey approach, or the Lewis acid–base concept. Instead, Taft and Kamlet proposed a linear solvation energy relationship (LESR) to describe the parameters of a solvation process (XYZ) involving hydrogen bonding as:

$$\mathrm{XYZ} = (\mathrm{XYZ})\mathrm{o} + \mathrm{a}\alpha + \mathrm{b}\beta + \mathrm{s}\Pi^{*} + \mathrm{m}\delta\mathrm{H}^{2} \qquad (32)$$

where (XYZ)o, *a*, *b*, *s*, and *m* are solvent-independent coefficients characteristic of the process reflecting the sensitivity to the related solvent properties, *e.g.*, α, β and Π^{*} as UV/vis spectroscopically-derived parameters [12, 13]. Separately, α is an empirical, quantitative measure of the hydrogen-bond-donating (HBD) ability of a bulk solvent toward a solute [31]. β is an empirical, quantitative measure of the hydrogen-bond-accepting (HBA) [or electron-pair-donating (EPD)] ability of a bulk solvent toward a solute for a hydrogen bond (or a Lewis coordination bond). On the other hand, Π^{*} measures the energetic effects (involving negative Gibbs free energy change) of solute-solvent, dipole–dipole, o, 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. Thus, Π^{*} is a combination of dipolarity and polarizability of a solvent. Finally, $\delta\mathrm{H}^{2}$ is the square of the Hildebrand solubility parameter of a solvent, and it is equivalent to the cavity term which measures the work required to produce a cavity of unique volume in the solvent. This parameter is also equivalent to Fowkes dispersion component, γ^{d}.

In 1996, we [14, 15] first showed one aspect of the VCG approach to be analogous to the solvatochromic relationship; however, we had not

TABLE VI Solvatochromic parameters for some polymers

Polymer [32]	δH [33] $(cal/cc)^{1/2}$	α	β	Π^*
Fluoropolyol	0.84	0.42	0.8	–
Poly(isobutylene)	7.8–8.1	0.33	0.04	0.16
Poly(styrene)	8.5–9.3	0.08	0.06	0.65
Poly(ethylene-vinyl acetate) (60:40)	9.1	0.23	0.57	0.54
Poly(methyl methacrylate)	9.1–12.8	0.24	0.38	0.76
Poly(vinyl acetate)	9.4–11	0.02	0.44	0.76
Poly(2-hydroxyethyl methacrylate)	0.67	0.43	0.98	–
Poly(vinyl pyrrolidone)	−0.12	0.06	0.65	–
Poly(vinyl chloride)	9.4–11.4	0.06	0.07	0.65
Poly(carbonate)	9.3–9.9	−0.03	0.21	0.76
Poly(vinyl alcohol)	12.6	0.29	0.52	1.11

succeeded in linking all parameters of both methods together. In this paper, we have identified the missing link between the LESR parameter, Π^* (represented by the same symbol but in a different context), and the surface component, π_e. Furthermore, all four parameters in the original Taft-Kamlet relationship, δH, α, B, and Π^* are now somewhat equivalent to the surface tension components, γ^d, γ^+, γ^-, and π_e. Without π_e, the correlation has been incomplete. This equivalence is further manifested by the data on solvatochromic properties obtained by Paley [32] as shown in Table VI. In Table VI, poly(vinyl chloride) appears to be rather neutral and most polymers are rather basic, except poly(isobutylene). The pattern resembles those for the equilibrium surface tensions obtained in the presence of a vapor, but not those for the initial surface tensions of unadsorbed polymers. This is presumably due to the solvation between a solvent and a solute, but not an unadsorbed polymer.

Both surface and solvatochromic parameters can be used independently to describe adhesion as well as solvation at the liquid–solid interface. More work is needed for the actual comparative study between related parameters.