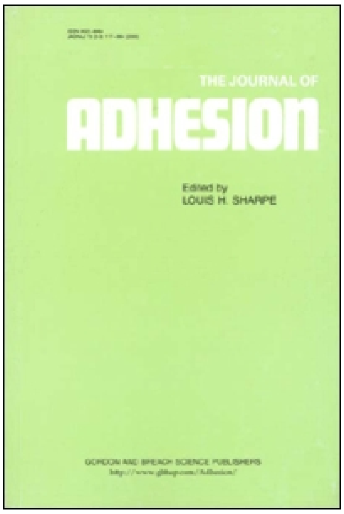

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Acid/Base Components in the Molecular Theory of Adhesion

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Acid/Base Components in the Molecular Theory of Adhesion*

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A method has been devised to determine the acid/base parameters of reference liquids as absolute numbers, and not as values relative to a conventional set of parameters for water. Contact angle measurements are employed, using three liquids on three solids. The theory calls for the solution of nine simultaneous, nonlinear equations in nine variables - and unreasonably formidable task.

A preliminary set of solutions has been computed, for one set of polar liquids on five solids. These results must be rejected on grounds of physical reasonableness. They also fail the test of predicting liquid-liquid interfacial tension, which for miscible liquids must be negative or zero.

Keywords: Adhesion; contact angle; interfacial tension; surface tension; solid surface free energy; acid/base interaction; hydrogen bonding

I. INTRODUCTION

Two phases adhere to each other when the following "necessary conditions" are met:

(1) Strong molecular forces across the interface.
(2) The existence of a mechanism for rapid dissipation of energy during separation, particularly when the separation occurs by crack propagation.

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(3) A matching of the mechanical (visco-elastic) properties of the phases.
(4) The absence of a "weak boundary layer" between the phases.
(5) Absence of geometrical conditions such as interfacial voids or edge cracks that would lead to stress intensification under load.

If conditions (2) to (5) are met, then (1) is a "sufficient condition".

The important kinds of interfacial force, in adhesion, are: electrostatic, covalent, acid-base (or hydrogen bonding) and van der Waals. Electrostatic (ionic) and covalent forces need no discussion here. The theory of hydrogen bonds at interfaces is still in its infancy. The van der Waals forces have been given extensive treatments, *e.g.*, by London [1] (the "dispersion force"), by Keesom [2] (the dipole-dipole force) and Debye [3] (the induction force). Of these, the first is by far the most important. The London theory of the dispersion force is now quite well accepted. It led to the so-called Good-Girifalco "geometric mean" theory of the free energy of adhesion, as the geometric mean of the free energies of cohesion of the separate phases [4, 5], for apolar substances.

$$\Delta G_{ij}^{a} = \sqrt{\Delta G_i^c \Delta G_j^c} \tag{1}$$

$$\gamma_i + \gamma_j - \gamma_{ij} = 2\sqrt{\gamma_i \gamma_j} \tag{2}$$

Fowkes [6, 7] pointed out the possibility of separating surface free energy into components,

$$\gamma_i = \gamma_i^d + \gamma_i^i + \gamma_i^p + \gamma_i^H \tag{3}$$

where d refers to dispersion force, i to induction force, p to the Keesom (dipole-dipole) force, and H to hydrogen bonding. Fowkes subsequently employed only the two most important terms, the d and H terms, in (3).

We have introduced the superscript LW, for d, honoring London and van der Waals [8–10]. Fowkes later used the notation, "AB" for, acid-base interaction, which is more general than "H".

The consequences of these definitions have recently been reviewed [11]. For interfacial tension,

$$\gamma_{ij}^{LW} = (\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}})^2 \tag{4}$$

For the contact angle, θ, of a liquid, l (whether polar or apolar), on an *apolar* solid,

$$\gamma_l(1 + \cos\theta_{sl}) = 2\sqrt{\gamma_l^{LW}\gamma_s} \tag{5}$$

$$= 2\sqrt{\gamma_l^{LW}\gamma_s^{LW}} \tag{6}$$

II. ACID/BASE THEORY

Eleven years ago [8–10], a combining rule for acid-base interactions was introduced, which had a basis in the molecular orbital theory of hydrogen bonding [12, 13].

$\gamma_i^{\oplus}$ = acidic parameter

$\gamma_i^{\ominus}$ = basic parameter

$$\gamma_{ij}^{AB} = 2(\sqrt{\gamma_i^{\oplus}} - \sqrt{\gamma_j^{\oplus}})(\sqrt{\gamma_i^{\ominus}} - \sqrt{\gamma_j^{\ominus}}) \tag{7}$$

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \tag{8}$$

For a single component, i, as a pure phase,

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^{\oplus}\gamma_i^{\ominus}} \tag{9a}$$

We want to determine $\gamma_{si}^{\oplus}$ and $\gamma_{si}^{\ominus}$, so that we can characterize the acid/base forces between a solid, s, and any acidic or basic (or bipolar) phase.

Incidentally, if $\sqrt{\gamma_i^{\oplus}} > \sqrt{\gamma_j^{\oplus}}$ and $\sqrt{\gamma_i^{\ominus}} < \sqrt{\gamma_j^{\ominus}}$, or *vice versa*, γ^{AB} will be negative, and its magnitude may be large. The magnitude of the free energy of adhesion will, then, be large and negative; and this will correspond to a condition conducive to strong adhesion.

Eqs. (4) to (6) can now be extended, to embrace the case where acid-base interactions are present. For the contact angle of liquid l on solid s,

$$\gamma_l(1+\cos\theta_{ls}) = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + 2\sqrt{\gamma_s^{\oplus}\gamma_l^{\ominus}} + 2\sqrt{\gamma_s^{\ominus}\gamma_l^{\oplus}} \qquad (10)$$

Then, the experiment that is to be carried out is the measurement of the contact angle, θ, of a set of reference liquids on the solid.

In view of Eqs. (5) and (6), we see that we can make an independent measurement of the contact angle of an apolar liquid (*e.g.*, CH_2I_2) on the solid, to determine γ_s^{LW}. Thus,

$$\gamma_s^{LW} = \gamma_{l(apolar)}(1+\cos\theta)^2/4 \qquad (11)$$

At the start of this effort, we did not know the values of $\gamma_l^{\oplus}$ or $\gamma_l^{\ominus}$ for any liquid. So Eq. (10) amounted to one equation in four variables: an underdetermined system. Equation (9a) provides a second equation, and Eq. (11) can be used in the form, Eq. (13):

$$\sqrt{\gamma_i^{\oplus}} = \gamma_i^{AB}/2\sqrt{\gamma_i^{\ominus}} \qquad (9b)$$

$$\gamma_i^{AB} = \gamma_i - \gamma_i^{LW} \qquad (12)$$

$$\gamma_l^{LW} = 4\gamma_s^{LW}/(1+\cos\theta_{ls})^2 \qquad (13)$$

Thus, a measurement of the contact angle of the liquid l_1 (say, water) on an apolar solid (say, Teflon TFE^{TM}) would yield a value of $\gamma_{l_1}^{LW}$ for use in Eq. (10). Then the quantity $\sqrt{\gamma_s^{LW}\gamma_l^{LW}}$ can be taken as "known", and we may write Eq. (10) as

$$\gamma_{l_1}(1+\cos\theta_{l/s}) - 2\sqrt{\gamma_s^{LW}\gamma_{l_1}^{LW}} = 2\sqrt{\gamma_{s_1}^{\oplus}}\sqrt{\gamma_{l_1}^{\ominus}} + 2\sqrt{\gamma_s^{\ominus}}\sqrt{\gamma_{l_1}^{\oplus}} \qquad (14)$$

At this point, we had two equations in four variables. If we measured the contact angle of a second reference liquid on the solid, we could write a second equation in the form of (14), and also a second equation like Eq. (9b). Then,

$$\gamma_{l_2}(1+\cos\theta_{l_2,s}) - 2\sqrt{\gamma_s^{LW}\gamma_{l_2}^{LW}} = 2\sqrt{\gamma_s^{\oplus}}\sqrt{\gamma_{l_2}^{\ominus}} + 2\sqrt{\gamma_s^{\ominus}}\sqrt{\gamma_{l_2}^{\oplus}} \tag{15}$$

$$\sqrt{\gamma_{l_2}^{\oplus}} = \gamma_{l_2}^{AB}/2\sqrt{\gamma_{l_2}^{\ominus}} \tag{16}$$

Now, we had six variables $(\gamma_{s_1}^{\oplus}, \gamma_{s_1}^{\ominus}, \gamma_{l_1}^{\oplus}, \gamma_{l_1}^{\ominus}, \gamma_{l_2}^{\oplus}, \gamma_{l_2}^{\ominus})$ and four equations – still two equations short of our needs.

III. A NEW APPROACH

We have discovered a path to a set of equations in which there are as many equations as variables. This is, to measure the contact angles of *three* polar liquids (1, 2, 3) on *three* solids ($s1, s2, s3$).

We combine Eqs. (9) and (11) for each liquid. We obtain for liquid 1 on solid 1,

$$\gamma_1(1+\cos\theta_{1,1}) - 2\sqrt{\gamma_{s1}^{LW}\gamma_1^{LW}} = 2\sqrt{\gamma_{s1}^{\ominus}}\sqrt{\gamma_1^{\oplus}} + \gamma_1^{AB}\sqrt{\gamma_{s1}^{\oplus}/\gamma_1^{\oplus}} \tag{17-1}$$

This becomes the first of 9 equations in the 9 variables, $\gamma_1^{\oplus}, \gamma_2^{\oplus}, \gamma_3^{\oplus}, \gamma_{s1}^{\oplus}, \gamma_{s2}^{\oplus}, \gamma_{s3}^{\oplus}, \gamma_{s1}^{\ominus}, \gamma_{s2}^{\ominus}, \gamma_{s3}^{\ominus}$.

$$\gamma_2(1+\cos\theta_{2,1}) - 2\sqrt{\gamma_{s1}^{LW}\gamma_2^{LW}} = 2\sqrt{\gamma_{s1}^{\ominus}}\sqrt{\gamma_2^{\oplus}} + \gamma_2^{AB}\sqrt{\gamma_{s1}^{\oplus}/\gamma_2^{\oplus}} \tag{17-2}$$

$$\gamma_3(1+\cos\theta_{3,1}) - 2\sqrt{\gamma_{s1}^{LW}\gamma_3^{LW}} = 2\sqrt{\gamma_{s1}^{\ominus}}\sqrt{\gamma_3^{\oplus}} + \gamma_3^{AB}\sqrt{\gamma_{s1}^{\oplus}/\gamma_3^{\oplus}} \tag{17-3}$$

$$\gamma_1(1+\cos\theta_{1,2}) - 2\sqrt{\gamma_{s2}^{LW}\gamma_1^{LW}} = 2\sqrt{\gamma_{s2}^{\ominus}}\sqrt{\gamma_1^{\oplus}} + \gamma_1^{AB}\sqrt{\gamma_{s2}^{\oplus}/\gamma_1^{\oplus}} \tag{17-4}$$

$$\gamma_2(1+\cos\theta_{2,1}) - 2\sqrt{\gamma_{s2}^{LW}\gamma_2^{LW}} = 2\sqrt{\gamma_{s2}^{\ominus}}\sqrt{\gamma_2^{\oplus}} + \gamma_2^{AB}\sqrt{\gamma_{s2}^{\oplus}/\gamma_2^{\oplus}} \tag{17-5}$$

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$$\gamma_3(1+\cos\theta_{3,3}) - 2\sqrt{\gamma_{s3}^{LW}\gamma_3^{LW}} = 2\sqrt{\gamma_{s3}^{\ominus}}\sqrt{\gamma_3^{\oplus}} + \gamma_3^{AB}\sqrt{\gamma_{s3}^{\oplus}/\gamma_3^{\oplus}} \tag{17-9}$$

We call this set, the "grand equations".

Since values of all the θ's and γ_l's are experimental, and since the values of all the γ^{LW} terms are obtained from contact angle and surface tension data by a reliable theory, the values of all the $\gamma^{\oplus}$ and $\gamma^{\ominus}$ parameters for the reference liquids, as determined by this method, will be absolute; and so will the parameters of the solids. Thus, the same solution for Eq. (17-1) to Eq. (17-9) will include a set of $\gamma_s^{\oplus}$ and $\gamma_s^{\ominus}$ parameters for the three solids. This will constitute a real advance over determining a set of *relative* parameters, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, which was all that could be obtained from measurement of contact angles of *two* liquids on *one* solid [8–11]. The evaluation of $\gamma^{\oplus}$ and $\gamma^{\ominus}$ for the two reference liquids, in our earlier approach, was based on the formalism,

$$\gamma^{\oplus}_{water} \equiv \gamma^{\ominus}_{water} \tag{18}$$

and the assumption that there are some usable monopolar solids, for which $\gamma_s^{\oplus} = 0$. See Ref. [10].

The "catch" to the grand equations is, of course, the question of how to solve them – and that cannot be done analytically. It is a formidable computer problem, though it looks do-able. A direct, brute force, trial and error technique, however, would take something over 10^{22} operations.

We have been able to simplify Eqs. 17-(1 to 9), to a set of three cubic equations which contained only the $\gamma^{\oplus}$ and $\gamma^{\ominus}$ parameters of the liquids. If these parameters can be found, then their use in pairs of equations containing $\gamma_s^{\oplus}$ and $\gamma_s^{\ominus}$ parameters of a single solid, *e.g.* Eqs. 17-1 and 17-2, will yield the values that will characterize each solid.

The set of three equations has been attacked by the Fortran "Do Looping" method. Table I shows the contact angles that we measured on five solids: PMMA, polystyrene, zein (a corn protein), polycarbonate (PC), and polypropylene (PPr). The liquids were water (W), formamide (FO), ethylene glycol (EG), 1,2 propanediol (PD), 1,3 butanediol (BD) and diiodomethane (DIM). All measurements were made at 21°C, using a modified Ramé-Hart contact angle instrument.

Table II shows the values of $\gamma_l^{\oplus}$ and $\gamma_l^{\ominus}$ of five reference liquids, obtained by the computer method mentioned above.

A major *caveat* must be emphasized, that these numbers are *not* conclusive results, as a test of the method. For example, we have not

TABLE I Advancing contact angles on five solids

	W	*EG*	*FO*	*1,2 PD*	*1,3 BD*	*DIM*
PMMA	75.4 ± 0.6°	51.4 ± 0.0°	55.5 ± 0.6°	22.3 ± 0.2°	22.7 ± 0.3°	43.6 ± 0.6°
PC	73.3 ± 0.2°	58.2 ± 0.8°	54.4 ± 0.15°	42.5 ± 0.1°	44.5 ± 0.2°	46.6 ± 0.2°
Zein	50.2 ± 0.5°	48.2 ± 0.5°	36.1 ± 0.4°	28.9 ± 0.5°	28.5 ± 0.1°	50.0 ± 0.4°
PS	80.0 ± 0.2°	53.8 ± 0.3°	55.8 ± 0.2°	23.8 ± 0.1°	24.5 ± 0.6°	35
PPr	95.1 ± 0.1°	65.3 ± 0.1°	70.6 ± 0.5°	43.3 ± 0.3°	43.8 ± 0.4°	54 ± 0.3°

TABLE II *Preliminary* results for the $\gamma^{\oplus}$ and $\gamma^{\ominus}$ parameters of five reference liquids

	$\gamma_l, mJ/m^2$	$\gamma_l^{LW}, mJ/m^2$	$\gamma_l^{\oplus}, mJ/m^2$	$\gamma_l^{\ominus}, mJ/m^2$
W	72.8	21.8	8.3	85.6
FO	58	39.9	7.0	11.7
EG	48	33.2	15.9	5.6
BD	37.8	32.0	16.5	0.5
PD	36.3	30.1	10.3	1.10

yet tested for the multiplicity of solutions (*e.g.*, as many as nine) which might well be expected for a set of nine simultaneous equations. If multiple solutions are found, then a criterion for choice will have to be developed. "Physical reasonableness" is one criterion.

A second *caveat* is the possibility of a false minimum, in the computer search for a solution. An analogy for this concern is the geographic exploration of a mountainous terrain, looking for the deepest valley. An explorer may move steadily downhill, to a valley floor, without knowing that if he went uphill and over a ridge, he would reach a deeper valley!

Table III casts some light on the *caveats* that we have just raised.

TABLE III Test of New Method: *Preliminary* estimates of parameters for five solids, based on measured contact angles, using parameters from Table II for the reference liquids

	$\gamma_i^{\oplus}, mJ/m^2$	$\gamma_i^{\ominus}, mJ/m^2$
PMMA	20.5	0.15
PS	10.34	0.12
Zein	0.2	0.5
PPr	0.8	0.02
PC	2.0	3.8

Some of the numbers in Table III are physically implausible. On the basis of chemical structure, PMMA and polystyrene would be expected to be Lewis bases, not Lewis acids. The numbers shown, 20.5 and 10.34, respectively, point to the rejection of the computation that gave us Tables II and III.

A further check, that leads to rejection of the results in Tables II and III, can be obtained by predicting liquid-liquid interfacial tension, *e.g.*, between water and formamide. Combining Eqs. (4) and (7),

$$\gamma_{ij}=(\sqrt{\gamma_i^{LW}}-\sqrt{\gamma_j^{LW}})^2+2(\sqrt{\gamma_i^{\oplus}}-\sqrt{\gamma_j^{\oplus}})(\sqrt{\gamma_i^{\ominus}}-\sqrt{\gamma_j^{\ominus}}) \qquad (19)$$

Substituting the data from Table II into Eq. (19), we estimate $\gamma_{water/formamide} = 6.8\,\mathrm{mJ/m^2}$. Since water and formamide are miscible in all proportions, the interfacial tension must be negative or zero. Therefore, the computed data in Table II cannot be accepted

This rejection means that we should continue attempting to find better computer solutions. There are numerous techniques that we plan to investigate.

Moreover, we have no certainty that the liquids and solids that were employed in the experiments so far were the optimum choices for testing the theory. So a continuation of our experimental program is in order.

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References

[1] London, F., *Trans. Faraday Soc.* **33**, 8 (1937).
[2] Keesom, W. K., *Phys. Z.* **22**, 126 (1921); **23**, 225 (1922).
[3] Debye, P., *Phys. Z.* **21**, 178 (1920); **22**, 302 (1921).
[4] Good, R. J., *et al*, WADC Report no. **55** **44**, (1953).
[5] Girifalco, L. A. and Good, R. J., *J. Phys. Chem.* **61**, 904–9 (1957).
[6] Fowkes, F. M., (a) *J. Phys. Chem.* **66**, 682 (1962); (b) *Advan. Chem. Ser.* (American Chemical Society, Washington, DC, 1964), **43**, p. 99.
[7] Fowkes, F. M., and Mostafa, M. A., *I. & E. C., Prod. Res. Dev.* **17**, 3 (1978).
[8] van Oss C. J., Good, R. J. and Chaudhury, M. K., *J. Colloid Interface Sci.* **111**, 378 (1986).

[9] van Oss C. J., Chaudhury, M. K. and Good, R. J., *Chem Rev.* **88**, 927–41 (1988).

[10] Good, R. J., Chaudhury, M. K. and van Oss C. J., in *Fundamentals of Adhesion*, Lee, L. H., Ed. (Plenum Press, NY, 1991), pp. 153–172.

[11] Good, R. J., *J. Adhesion Sci. & Technology* **6**, 1269–1302 (1992).

[12] Kollman, P., McKelvey, J., Johannson, A. and Rothenberg, S., *J. Am. Chem. Soc.* **97**, 955 (1975); Hobza, P. and Zahradnik, R., *Weak Intermolecular Interactions in Chemistry and Biology* (Elsevier, NY, 1980).

[13] Small, P. A., *J. Appl. Chem.* **3**, 71 (1953).