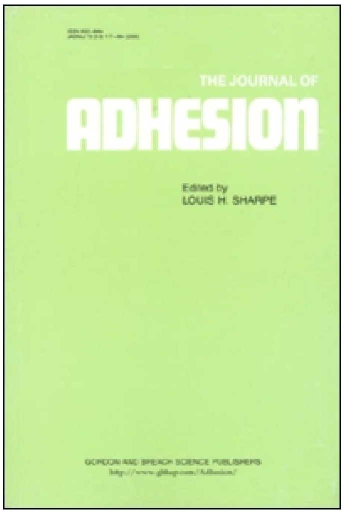

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Surface Hydrogen-Bond Components and Linear Solvation Energy Relationship Parameters*

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In 1987, van Oss, Chaudhury and Good introduced the Lewis acid (or hydrogen-bond acidic) component, γ^+, and Lewis base (or hydrogen-bond basic) component, γ^-, and assumed the ratio of γ^+ and γ^- for water at 20°C to be 1.0. With that ratio, the base components, γ^-, for other liquids and polymers appeared to be overestimated. Recently, we unexpectedly found a correlation between γ^+ and γ^- and the linear solvation energy relationship (LSER) parameters α (hydrogen-bond-donating ability, HBD) and β (hydrogen-bond-accepting ability, HBA), introduced by Taft and Kamlet in 1976. Interestingly, we found the ratio for the normalized α and β for water at ambient temperature to be 1.8 instead of 1.0. Based on this new ratio for the corresponding γ^+ and γ^-, the calculated total surface tensions for other liquids and polymers at 20°C are generally unchanged, as expected, despite the favorable changes in the γ^+ and γ^- ratio to make them less basic. In addition, the implications of other LSER parameters, *e.g.* Π^* and δ^2_H on surface properties will be briefly mentioned.

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

INTRODUCTION

One of Professor Robert J. Good's contributions to surface chemistry [1–3] is the splitting of the asymmetric acid-base parts of a dipolar

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(or bipolar) system into two separate surface tension or hydrogen-bond components [4]:

Lewis acid component of surface interaction (or the acidic parameter of hydrogen bonding), γ^+, and
Lewis base component of surface interaction (or the basic parameter of hydrogen bonding), γ^-.

Since hydrogen bonding is the major Lewis acid-base interaction, γ^+ is identical to the contribution of the hydrogen-bond donor (or Brϕnsted acid), while γ^- is that of the hydrogen-bond acceptor (or Brϕnsted base). This narrower definition than previously claimed based solely on hydrogen bonding has been given by Good [4].

Berg [5] has argued that most of the materials determined by van Oss, Chaudhury and Good (VCG) [1–2] appear to be rather basic in the Lewis sense, as originally claimed. Furthermore, poly(vinyl chloride) should be acidic, with low γ^+, instead of the contrary. Initially, we suspected that this could be partially due to using the assumed γ^+ and γ^- ratio of one for water at 20°C. Thus, we intend to improve the VCG method by finding a better γ^+ and γ^- ratio. Recently, we have reported our unexpected finding [6] about the new ratio based on the linear solvation energy relationship (LSER) solvatochromic parameters [7, 8]. In this paper we briefly describe the relationship between γ^+ and γ^- and LSER α and β parameters and then compare the surface tension component data for liquids and some polymers obtained with two respective ratios. At the end, we shall mention the limitation of the VCG method.

SURFACE TENSION COMPONENTS

Fowkes [9, 10] originally proposed the surface tension of a polar system to consist of the following components:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{i}} + \gamma^{\mathrm{p}} + \gamma^{\mathrm{h}}, \tag{1}$$

where superscripts **d**, **i**, **p**, and **h** represent dispersion, induction, polarization and hydrogen-bonding, respectively. Later, Fowkes [11] defined the acid-base component γ^{AB} to include the three terms in Eq. (1)

as follows:

$$\gamma^{AB}(\mathbf{Fowkes}) = \gamma^{i} + \gamma^{p} + \gamma^{h}. \tag{2}$$

However according to VCG [1], the induction, **i**, and polarization, **p**, components are of secondary importance in comparison with the dispersion, **d**, and hydrogen-bonding, **h**, components, and the first three components in Eq. (1) should instead be combined into the Lifshitz-van der Waals component, γ^{LW}:

$$\gamma^{LW} = \gamma^{d} + \gamma^{i} + \gamma^{p}. \tag{3}$$

Then, the acid-base component of the surface tension includes only the hydrogen-bonding component, and

$$\gamma^{AB}(\mathbf{VCG}) = \gamma^{h}. \tag{4}$$

According to VCG, the total surface tension for a polar system becomes:

$$\gamma = \gamma^{LW} + \gamma^{AB}. \tag{5}$$

By the VCG approach, the intrinsic asymmetry (or complementarity) of the two molecules should be taken into account for the acid-base interactions (or more appropriately hydrogen bonding), and the geometric mean rule can also be applied to the acid-base components of the change of the free energy of interaction, ΔG_{ij}^{AB}, and the maximum work of adhesion, W_{ij}^{AB}, between the i and the j phases. Thus,

$$\Delta G_{ij}^{AB} = -W_{ij}^{AB} = -2[(\gamma_i^{+}\gamma_j^{-})^{1/2} + (\gamma_i^{-}\gamma_j^{+})^{1/2}]. \tag{6}$$

Hence, the change of the free energy of interaction and the maximum work of adhesion for a polar system becomes

$$\Delta G_{ij} = -W_{ij} = -2[(\gamma_i^{LW}\gamma_j^{LW})^{1/2} + (\gamma_i^{+}\gamma_j^{-})^{1/2} + (\gamma_i^{-}\gamma_j^{+})^{1/2}]. \tag{7}$$

Since ΔG_{ij}^{AB} can also be derived from the Dupré equation

$$\Delta G_{ij}^{AB} = \gamma_{ij}^{AB} - \gamma_{i}^{AB} - \gamma_{j}^{AB},$$

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

$$\gamma_{ij}^{AB} = 2[(\gamma_i^{+}\gamma_i^{-})^{1/2} + (\gamma_j^{+}\gamma_j^{-})^{1/2} - (\gamma_i^{+}\gamma_j^{-})^{1/2} - (\gamma_i^{-}\gamma_j^{+})^{1/2}]. \qquad (8)$$

Finally, for a polar system, the Young-Good-Girifalco-Fowkes equation for the work of adhesion becomes

$$\gamma_{lv}(1 + \cos\theta_e) = 2[(\gamma_i^{LW}\gamma_j^{LW})^{1/2} + (\gamma_i^{+}\gamma_j^{-})^{1/2} + (\gamma_i^{-}\gamma_j^{+})^{1/2}]. \qquad (9)$$

The experimental procedure in determining different components has been described by Good *et al.* [3]. In fact, there are two methods for the determination. In view of Eq. (9), 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 are needed to solve Eq. (9). However, for both methods, each still lacks one more equation. Thus, the surface tension components for water have to be assumed for the purpose of calculation of the various components.

SOLVATOCHROMIC PARAMETERS

For obtaining a proper ratio for these hydrogen-bonding components, we unexpectedly found a relationship [6] between surface hydrogen-bond components and the LSER solvatochromic α and β parameters. In 1976, Taft and Kamlet [7] proposed a linear free energy relationship (LFER) or linear solvation energy relationship to describe the value of the solvent-dependent physicochemical property (XYZ) of the solute in a given solvent (*e.g.*, log *K*, log *k*, etc.) as:

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + a\,\alpha + b\,\beta + s\,\Pi^* + m\,\delta_H^2 + \cdots, \qquad (10)$$

where $(XYZ)_0$, a, b, s, and m are solvent-independent coefficients characteristic of the system under study and indicative of its suceptibility to the solvent properties, *e.g.*, α, β and Π^* as UV/vis spectroscopically-derived parameters [7, 8]. Separately, α is an empirical, quantitative measure of the hydrogen-bond-donating (HBD) ability of a bulk solvent toward a solute [12]. 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 exoergic effects (involving 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. Thus, Π^* is a combination of dipolarity and polarizability of a solvent. Finally, δ_H^2 is the squared Hildebrand solubility parameter [13] of a solvent equivalent to the cavity term [12], which measures the work required to produce a cavity of unique volume in the solvent.

For non-hydrogen-bond-donating (non-HBD) solvents [12], such as apolar, aliphatic and aromatic hydrocarbons, α values are zero (Tab. I). For polar aliphatic alcohols, $\alpha = 0.5–1.0$, and for fluoro-substituted alcohols and phenols, $\alpha > 1.0$, reaching a maximum of 1.96 for hexafluoro-2-propanol. For the convenience of comparison, we [6] arbitrarily normalize all α values between 0 and 1.0. Recently, this normalization method has also been used by Taft *et al.* to compare α and β [14]. Thus, beyond doubt, this normalization step is acceptable by those in the field. In Table I, the normalized values for these liquids are shown in parentheses.

In contrast, the β scale [12] is fixed by setting $\beta = 0.0$ for cyclohexane. For non-hydrogen-bond-accepting (non-HBA) solvents, such as apolar aliphatic hydrocarbons, β values are zero. However, for aromatic hydrocarbons, $\beta \approx 0.1$. For aliphatic ethers, $\beta \approx 0.7–0.9$. For hexamethylphosphoric triamide (HMPT), $\beta = 1.0$, and for aliphatic amines, generally $\beta \approx 0.5–0.7$, but reaches a maximum of 1.43 for 1, 2-diaminoethane. For comparison, all β values are also normalized between 0 and 1.0.

In addition to α and β, the third parameter, Π^* [12] is derived from solvent effects on $\Pi - \Pi^*$ absorptions of seven primary probe molecules (preferentially nitroaromatics). For measuring the Π^* value, the probe molecules should be insensitive to specific HBD or HBA interactions with solvents. For example, the UV/vis spectrum [8] of *N*, *N*-diethyl-4-nitroaniline (probe **1**), protonic indicator in non-HBA solvents, is shifted bathochromically (red) with increasing dipolarity of the solvent. From the Frank-Condon principle, the ground state and excited electronic states occupy the same volume, so that in Eq. (10), $m = 0$. Thus, the solvent effect on the wavenumber ν (in $10^3\ \mathrm{cm}^{-1}$) of the longest wavelength absorption ($\Pi \rightarrow \Pi^*$) peak of a dilute solution depends only on Π^*. For this case probe (1), the expression is given as

$$\nu(1)\ \mathrm{max} = 27.52 - 3.18\Pi^* \quad (10^3\ \mathrm{cm}^{-1}) \tag{11}$$

In general, the actual Π^* is the mean value of the Π^* values for several probes [15]. Values of Π^* of "selected solvents", nonchlorinated, nonprotonic, aliphatic solvents with a single dominant bond dipole, have been shown to be generally proportional to molecular dipole moments [8].

For this scale, $\Pi^* = 0.0$ for cyclohexane and $\Pi^* = 1.0$ for dimethyl sulfoxide, reaching a maximum of $\Pi^* = 1.2$ for 2-cyanopyridine. Strangely, there are negative values for a few aliphatic apolar hydrocarbons. However, so far no physical meaning for the negative values has been given. For comparison, all positive Π^* values are also normalized between 0 and 1.0.

RESULTS AND DISCUSSION

The above brief description of LSER parameters reveals a close relationship between surface hydrogen-bond components and the solvatochromic α and β parameters. Unlike acidity or basicity, the hydrogen-bonding ability of a free (or unassociated) molecule on the surface is identical to that in the bulk. Since the interaction, as recently defined [4], is limited only to hydrogen bonding instead of the broadly defined acid-base interactions, then γ^+ indeed resembles the HBD parameter α, and γ^- the HBA parameter β. Thus, we assume that the ratio of α and β (normalized) for water is equal to that of γ^+ and γ^- of water at 20°C. On this basis, we shall compare the data obtained by the original method with the ratio of 1.0 and those calculated by us with the new ratio of 1.8.

Marcus [15] compiled a partial list of solvatochromic parameters for 170 solvents at ambient temperature. From that list, we select several liquids which have been used as probes for the determination of contact angles on solid surfaces; for example, water, glycerol, formamide, ethylene glycol (1, 2-ethanediol), dimethyl sulfoxide, and diiodomethane. All of these liquids have distinctive and measurable solvatochromic parameters as shown in Table I. There are many more hydorgen-bond acceptors (or proton acceptors) than hydrogen-bond donors (or proton donors). We also would like to point out one more phenomenon; for water under ambient temperature, the α is not equal to the β, and the ratio of these two normalized parameters is 1.8. In brief, the solvatochromic evidence is rather convincing in providing a more realistic value of (α/β) because both of these two parameters are spectroscopically measurable.

On the basis of the assumed ratio of γ^+ and γ^- for water at 20°C to be 1.0, the revised surface tension components [16] of the probe liquids originally used by van Oss, Chaudhury and Good are shown in Table II. It is apparent that it is this ratio that caused the overestimation of the hydrogen-bond basic components because all materials were

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, Ref. 15.

determined with this ratio as the reference. In this paper, we assume that the ratio of the normalized α and β values of 1.8 is identical to that of γ^+ and γ^- of water at 20°C. Then, based on this new ratio, we calculated surface hydrogen-bond components for several probe liquids including water (Tab. III). According to our calculation, for water at 20°C, the hydrogen-bond acid component, γ^+, should be 34.2 mJm^{-2}, and the hydrogen-bond base component, γ^-, 19 mJm^{-2}. The only noticeable changes in Table III are the values of γ^+ and γ^- for all probe liquids. As expected, in general, by using the new ratio for water as the reference, the base components decrease substantially, while the acid components increase. On the other hand, despite the change in the ratio of γ^+ and γ^-, the products γ^{AB} due to the hydrogen-bond are unaffected. Thus, as a result, total surface tensions are

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

*See Good, R. J. and van Oss, C. J., Ref. 16.

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^-
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 $\gamma^+(H_2O)/\gamma^+(Gly)$, $\gamma^+(H_2O)/\gamma^+(For)$, $\gamma^+(H_2O)/\gamma^+(EG)$, and $\gamma^+(H_2O)/\gamma^+(DMSO)$ were kept at 6.5, 11, 13, and 51, respectively.

essentially unchanged. Consequently, we believe that the effect in using the spectroscopically measurable α and β ratio is beneficial to the VCG methodology. At least, one of the questions raised by the critiques [5] about the overestimation of Lewis basicity has been answered.

We selected the advancing contact angle data on several polymers determined with an apolar liquid and a pair of polar liquids consisting of water and glycerol. For the published data [3, 17–22] using water at 20°C with $\gamma^+ = \gamma^- = 25.5$ mJm^{-2} as the reference, we list surface tension components for those polymers in Table IV. Then, by using water at 20°C with γ^+ of 34.2 mJm^{-2} and γ^- of 19 mJm^{-2} as the reference, we list surface tension components for the same polymers in Table V.

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.*
Poly(tetrafluoroethylene)	19.6	19.6	0	0	0	20, 22
Poly(isobutylene)	25	25	0	0	0	20, 22
Poly(propylene)	29.7	29.7	0	0	1.4	21
Poly(ethylene)	33	33	0	0	0	3
Cellulose acetate	38	35	0	0	32.3	20
Poly(vinyl fluoride)	43.6	40.4	3.2	0.16	12.9	18
Poly(laurinlactam), PA 12	41.9	37.5	4.4	1	4.9	17
Poly(styrene)	42	42	0	0	1.1	2, 22
Poly(methyl methacrylate)	43.2	43.2	0	0	22.4	20
Nylon 6,6	37.7	36.4	1.3	0.02	21.6	20, 22
Poly(vinyl chloride)	43.8	43	0.8	0.04	3.5	21
Poly(oxyethlene), PEG-6000	43	43	0	0	64	2

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^-
Poly(tetrafluoroethylene)	19.6	19.6	0	0	2.4
Poly(isobutylene)	25	25	0	0	0
Poly(propylene)	29.7	29.7	0	0	0
Poly(ethylene)	33	33	0	0	0
Cellulose acetate	38	38	0	0	25
Poly(vinyl fluoride)	40.4	40.4	0	0	10.8
Poly(laurinlactam), PA 12	41	37.5	3.5	0.7	4.6
Polystyrene	42	42	0	0	0.1
Poly(methyl methacrylate)	43.2	43.2	0	0	8.8
Nylon 6,6	38.3	36.4	1.9	0.06	13.9
Poly(vinyl chloride)	44	43	1	0.1	2.4
Poly(oxyethylene), PEG-6000	46.7	43.5	3.2	0.06	43.5

By comparing the data in these two tables, it is apparent that the overall data are much improved by the lowering of the base components without affecting the total surface tensions. In Table VI, the surface tension data obtained by the contact angle measurements with both ratios are also compared with those directly determined [23] and those determined by the critical surface tension method [24]. In general, the contact angle method yields reasonably good, though not the most accurate, surface tensions of polymers as determined directly. It is well known that the critical surface tension method is the least accurate, as also shown in Table VI.

With the new ratio of γ^+ and γ^- of 1.8 for water at 20°C, the major improvement is in the lowering of the surface hydrogen-bond base components. However, as expected, with the new ratio, we are still unable to raise the surface hydrogen-bond acid components for some polymers, *e.g.* poly(vinyl chloride), to a level of being highly acidic, as reported by Fowkes [11]. This would indicate that γ^+ and γ^- are indeed mainly surface hydrogen-bond components, not suitable to differentiate broader Lewis acids from Lewis bases. For those truly Lewis acidic polymers, which are not due to hydrogen-bonding, the nonspecific interactions, perhaps as revealed in Π* or dipole moment, may play a more important role than that envisioned by VCG.

TABLE VI Comparison of Surface Tensions of Polymers in mJ m^{-2} at 20°C

Polymer	γ $(\gamma^+/\gamma^-)=1$	γ $(\gamma^+/\gamma^-)=1.8$	γ (*Direct*)*	γ (*Critical*)**
Poly(tetrafluoroethylene)	19.6	19.6	23.9	18
Poly(isobutylene)	25	25	33.6	27
Poly(propylene)	29.7	29.7	29	29
Poly(ethylene)	33	33	36.8	31
Cellulose acetate	38	38	45.9	–
Poly(vinyl fluoride)	43.6	40.4	38.4 (c)	28
Poly(laurinlactam) PA 12	41.9	41	35.8	–
Poly(styrene)	42	42	40.7	36
Poly(methyl methacrylate)	43.2	43.2	41.1	39
Nylon 6,6	37.7	38.3	38.4	46
Poly(vinyl chloride)	43.8	44	41.9	39
Poly(oxyethylene), PEG-6000	46.7–47.7	46.7–47.7	42.9	43

*Direct surface tension data were compiled by Wu, S., Ref. 23.

**Zisman's critical surface tension data were compiled by Lee, L. H., Ref. 24.

(c): contact angle method.

CONCLUSIONS

From the relationship between LSER sovatochromic parameters and surface hydrogen-bond components, we found a new ratio of γ^+ and γ^- of 1.8 for water at 20°C. The change of the ratio of water from 1.0 to 1.8 did lower the hydrogen-bond basicity of liquids and polymers, without affecting the overall surface tension values. However, more· significantly, our work also indicates that the VCG approach as defined appears to be applicable only to the hydrogen-bonding system, instead of the broad Lewis acid-base or electron donor-acceptor interactions. Since poly(vinyl chloride) is an acid in the broad Lewis acid-base sense, it can not be characterized by these hydrogen-bond components. For clarity, γ^+ should be named properly as the surface hydrogen-bond donor (or acid) component, and γ^- the surface hydrogen-bond acceptor (or base) component.

References

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

[2] van Oss, C. J., Chaudhury, M. K. and Good, R. J., *Adv. Colloid Interface Sci.* **28**, 35 (1987).

[3] Good, R. J., Chaudhury, M. K. and van Oss, C. J., *Fundamentals of Adhesion*, Lee, L. H., Ed. (Plenum Press, New York, 1991), p. 153.

[4] Good, R. J., *Proceedings of the 19th Annual Meeting of the Adhesion Society*, Ward, T. C., Ed., February, 1996, p. 1.

[5] Berg, J. C., in *Wettability*, Berg, J. C., Ed. (Marcel Dekker, New York, 1993).

[6] Lee, L. H., *Langmuir* **12**, 1681 (1996).

[7] Taft, R. W. and Kamlet, M. J., *J. Am. Chem. Soc.* **98**, 2866 (1976).

[8] Kamlet, M. J., Abboud, J.-L. M. and Taft, R. W., *J. Org. Chem.* **48**, 2877 (1983).

[9] Fowkes, F. M., in *Acid-Base Interactions*, Mittal, K. L., Ed. (VSP, Utrecht, The Netherlands, 1991), p. 93.

[10] Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40 (1964).

[11] Fowkes, F. M. and Mostafa, M. A., *Ind. Eng. Chem. Prod. Res. Dev.* **17**, 3 (1978).

[12] Reichardt, C., *Chem. Rev.* **94**, 2319 (1994).

[13] Hildebrand, J. H. and Scott, R. L., *The Soluthility of Non-electrolytes*, 3rd. ed. (Reinhold, New York, 1950).

[14] Taft, R. W., Berthelot, M., Laurence, C. and Leo, A. J., *CHEMTECH*, 20. July 1996.

[15] Marcus, Y., *Chem. Soc. Rev.* 409 (1993).

[16] Good, R. J. and van Oss, C. J., in *Modern Approaches to Wettability, Theory and Applications*, Shrader, M. E. and Loeb, G. I., Eds. (Plenum Press, New York, 1992), p. 1.

[17] Chibowski, E. and Gonzalez-Caballero, F., *J. Adhes. Sci. Technol.* **7**, 1195 (1993).

[18] Hollaender, A., *J. Colloid Interface Sci.* **169**, 493 (1995).

[19] van Oss, C. J., *Interfacial Forces in Aqueous Media* (Marcel Dekker, New York, 1994).

[20] van Oss, C. J., Good, R. J. and Busscher, H. J., *J. Dispersion Sci. Technol.* **11**, 75 (1990).

[21] van Oss, C. J., Chaudhury, M. K. and Good, R. J., *Sepr. Sci. Technol.* **24**, 15 (1989).

[22] van Oss, C. J. and Good, R. J., *J. Macromol. Sci.-Chem.* **A26**, 1183 (1989).

[23] Wu, S., in *Polymer Handbook*, Brandrup, J. and Immergut, E. H., Eds., 3rd. ed., Part VI (Wiley, New York, 1989), pp. 411–434.

[24] Lee, L. H., *J. Appl. Polym. Sci.* **12**, 719 (1968).