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Additive and Nonadditive Surface Tension Components and the Interpretation of Contact Angles

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It is demonstrated that, while the Lifshitz–van der Waals (γ^{LW}) and the polar, Lewis acid–base (γ^{AB}) surface tension components are additive, the Lewis acid–base electron-acceptor (γ^+) and electron-donor (γ^-) surface tension parameters (which on account of the intrinsic asymmetry of their interactions are connected in a more complex manner) are not additive. Contact angle data cannot, in general, be correlated with a *single* surface tension property. The relation between contact angles and the three controlling parameters γ_S^{LW}, γ_S^+, and γ_S^- of a polar solid, S, cannot be established by means of one single equation. These three unknowns can, however, be determined by means of contact angle measurements with three different liquids L (of which two must be polar and H-bonding), which are completely characterized as to their respective γ_L^{LW}, γ_L^+, and γ_L^- parameters by using a modified Young–Good–Girifalco–Fowkes equation 3 times. In view of these considerations, recent claims to have proven the applicability of a single "equation of state" are shown to be spurious.

Introduction

The potential importance of a successful theory of surface tension components, the concept of which was pioneered by Fowkes,[1] was recently reemphasized by Spelt et al.[2] These authors attempt to disprove the theory of surface tension components on experimental grounds and to vindicate their equation of state approach.[3] They reiterate, however, that the question of additivity or nonadditivity of surface tension components could have a crucial bearing on such a theory. Although their approach for vindicating their equation of state is seriously flawed, their view as to the importance of additivity is correct: on the basis of a theoretical structure that has evolved during the past few years, which fits in well with all the available experimental data, it does indeed follow that while certain surface tension components are additive, others are not.[4–6]

As can be shown rather readily, the combined contributions of apolar and polar components of the surface tension of solids, as well as of liquids, give rise to a set of multiterm equations, which relate the contact angles, the apolar surface tension components, and the different parameters making up the polar surface tension components (see below). However, the relative complexity of polar interfacial interactions makes it impossible to come to any simple conclusions relative to the various surface tension components. For example, demonstration that, in a few selected cases, apolar and "polar" liquids of the same surface tension have approximately the same contact angles on a given surface[2] does not constitute conclusive proof. If this demonstration were valid, it would work in the reverse sense, and liquids that have the same contact angle on a particular solid would be found to have the same surface tension. Table I shows that this is not the case. Water and glycerol form nearly the same contact angle on four of the solids. But the surface tensions of the two liquids differ by 12%, and the contact angles of the two liquids are significantly different on six other solids.

Further, while glycerol spreads on flat surfaces of a gel encasing water (which could be expected), it is a curious finding that water also spreads on flat surfaces of a gel encasing glycerol (see Table II). It is not possible to explain this result by means of the equation of state.

Table I. Contact Angles of Water and Glycerol on a Number of Solids

	polarity	θ_{H_2O}, deg	$\theta_{glycerol}$, deg
Teflon[a]	apolar	118	101
lysozyme (hydrated)[b]	bipolar	0	9
lysozyme (dry)[b]	monopolar	*58*[e]	*58*[e]
human serum albumin (dry)[b]	monopolar	*63.5*	*59.5*
Dextran T-150 (dry)[c]	monopolar	*44.6*	*41.5*
cellulose nitrate[c]	monopolar	*56*	*51*
cellulose acetate	monopolar	*53.7*	*52*
Zein (dry)[b,c]	monopolar	*64*	*65*
agarose (dry)[c]	monopolar	*57.3*	*57.3*
mica[d]	monopolar	0	20

[a] Reference 7. [b] Reference 15. [c] Reference 4. [d] Van Oss, C. J., unpublished results. [e] In studies with a wide range of biological surfaces, experience in this laboratory has shown that the contact angle of glycerol is practically the same as that of water, considerably more often than not; see the italic values.

Table II. Contact Angles on Gels, Encasing Liquids[a]

liquid in Gel	contact angle, deg	contact angle liquid
glycerol	0	H_2O
H_2O	0	glycerol

[a] Reference 5.

Table III. Contact Angles of Water on a Number of Solid Surfaces with a Surface Tension γ_S between 40.6 and 42.9 mJ/m² As Measured with Diiodomethane

solid surface	γ_S, mJ/m²	θ_{H_2O}, deg	$\gamma_{eq\,st}$, mJ/m²
cellulose acetate	42.9[a]	53.7[a]	50.4
poly(methyl methacrylate)	40.6[a]	70[a]	41.2
poly(ethylene terephthalate)	40.6[a]	81[a]	34.5
polystyrene	41.6[b]	91.4[c]	28.0

[a] Reference 4. [b] Unpublished results; see also: Good and Kotsidas (*J. Adhesion* **1979**, *10*, 17). [c] Reference 8.

Similarly, contact angles of a polar liquid such as water on solid surfaces of different "polarities" but of *close to*

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(1) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, Dec., 40–52.

(2) Spelt, J. K.; Absolom, D. R.; Neumann, A. W. *Langmuir* **1986**, *2*, 620.

(3) Neumann, A. W.; Good, R. J.; Hope, C. J.; Sejpal, M. *J. Colloid Inteface Sci.* **1974**, *49*, 291.

(4) Chaudhury, M. K.; van Oss, C. J.; Good, R. J., submitted for publication.

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Table IV. Contact Angles (Deg) of Dimethyl Sulfoxide (DMSO), α-Bromonaphthalene (αBrN), Diiodomethane (DIM), and Water on a Number of Surfaces

surface	DMSO	αBrN	DIM	H_2O
DNA (dry)[a]	0	28.5	42	57.4
lysozyme (hydrated)[b]	0	45.5	56	0
lysozyme (dry)[b]	*18.5*[e]	*22.5*[e]	36.5	58
human serum albumin (dry)[b]	*19.8*	*23.2*	37	63.5
Dextran T-150 (dry)[c]	*16*	*16*	29	30
poly(ethylene glycol) 6000 (dry)[c]	*13.8*	*10*	26	18.3
cellulose acetate[a]	*30*	*32*	55	54.5
RNA (dry)[a]	*42.7*	*41*	44	16.5
Zein (dry)[b,d]	*27*	*24*	36	64
poly(methyl methacrylate)[d]	*24*	*20.5*	32.8	70

[a] Reference 10. [b] Reference 15. [c] Reference 14. [d] Reference 4. [e] The contact angle values in italics, obtained with DMSO and αBrN, are fairly similar, for each of the individual polar surfaces shown. This is a prima facie indication for a γ^- monopolarity of known polar substances.

Table V. Interfacial Tensions γ_{12}, in mJ/m², between Water and a Number of Water-Immiscible Organic Liquids with Surface Tension (γ_1) between 26.9 and 27.5 mJ/m²

liquid	γ_1	γ_{12} (measured)	γ_{12} (eq state)[d]	deviation of γ_{12} (eq state) from γ_{12} (measured)
hexadecane	27.5[b]	51.1[a]	30.54	−40%
chloroform	27.15[c]	31.6[c]	30.89	−2%
ethyl *n*-octanoate	27.0[c]	25.5[c]	31.04	+2%
methyl *n*-hexyl ketone	26.9[c]	14.1[c]	31.14	+121%
1-octanol	27.5[c]	8.5[c]	30.54	+259%
octanoic acid	27.5[c]	8.5[c]	30.54	+259%

[a] Reference 5. [b] Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841. [c] Reference 9. [d] Obtained by the procedure given in ref 3.

the same total surface tension γ_S can differ widely (Table III). Also, two very different liquids with the same surface tension, dimethyl sulfoxide (DMSO) and α-bromonaphthalene (α-BrN), often though not invariably form the same contact angle on a number of surfaces of varying polarity (Table IV). Finally, the interfacial tensions between water and a number of organic liquids of virtually identical surface tension vary widely (Table V). These matters will be discussed in more detail, below.

Thus a few selected similarities in contact angles obtained with different liquids[2] by no means signify that different components of the surface tension do not contribute to different extents and in different ways to the contact angles formed by these liquids. We shall attempt to elucidate, below, the reasons for the similarities (see Spelt et al.[2] and Tables I and IV), for the differences (Tables III, V, and VII), and for other apparent paradoxes (Tables II and IV). To that purpose, we shall first briefly review the theory of surface tension components and of dipole vs polar interactions, and we shall then describe some of the earlier attempts to deal with the discrepancies caused by polar interactions. Finally, we shall discuss how the various anomalies, coincidences, similarities, and paradoxes, touched upon above, can be readily explained by the theory of surface tension components.

Theory

Recently it became possible to make a clear-cut distinction between apolar electrodynamic Lifshitz–van der Waals (LW) interactions, comprising the dispersion (London), orientation (Keesom), and the induction (Debye) interactions in the condensed state on the one hand,[7] and polar interactions on the other hand.[4-6,8] Excluding metal interactions[7] for the present purpose, the polar interactions under consideration are of the hydrogen-bonding type and can, in the largest sense, be designated as (Lewis) acid–base (AB) or electron-acceptor/electron-donor interactions. We shall, thus, deal in this paper with apolar (LW) and polar (AB) interactions among materials in the condensed state, and we shall briefly reiterate the equations pertinent to LW and AB interactions, respectively.

Apolar or LW Interactions. The LW interfacial tension is expressed according to the Good–Girifalco combining rule:[9]

$$\gamma_{ij}^{LW} = ((\gamma_i^{LW})^{1/2} - (\gamma_j^{LW})^{1/2})^2 \tag{1}$$

or

$$\gamma_{ij}^{LW} = \gamma_i^{LW} + \gamma_j^{LW} - 2(\gamma_j^{LW}\gamma_j^{LW})^{1/2} \tag{1a}$$

The latter version (1a) allows the expression of the Young equation (omitting the spreading pressure term) as

$$1 + \cos\theta = 2(\gamma_S^{LW}/\gamma_L^{LW})^{1/2} \tag{2}$$

where the subscripts S and L stand for solid and liquid, respectively. With purely LW liquids, one can thus directly obtain the γ_S^{LW} components of solid surfaces by contact angle measurement.

Polar or AB Interactions. It is of course obvious, but it may be useful to restate here, that while various substances can be exclusively apolar, polar substances always have apolar as well as polar properties. Thus for two polar substances *i* and *j*, the total free energy of interaction can be expressed as

$$\Delta G_{ij}^{TOT} = \Delta G_{ij}^{LW} + \Delta G_{ij}^{AB} \tag{3}$$

and similarly the total free energy of cohesion of any given material *i* (in the condensed state) as

$$\Delta G_{ii}^{TOT} = \Delta G_{ii}^{LW} + \Delta G_{ii}^{AB} \tag{3a}$$

Then, according to eq 3, the Young equation can be expressed as

$$(1 + \cos\theta)\gamma_L^{TOT} = -\Delta G_{SL}^{LW} - \Delta G_{SL}^{AB} \tag{4}$$

where

$$\Delta G_{SL}^{LW} = -2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} \tag{5}$$

according to eq 1a and the Duprê equation:

$$\Delta G_{ij} = \gamma_{ij} - \gamma_i - \gamma_j \tag{6}$$

This leaves us to define ΔG_{SL}^{AB}. Now, Lewis acid–base or electron-acceptor/electron-donor interactions are intrinsically asymmetrical[29] and thus nonadditive.[4,6] Also, one of the parameters will not be manifested at all unless the opposite parameter is present in another molecule or in another part of the same molecule. Selecting the symbols γ^+ for the electron-acceptor and γ^- for the electron-donor parameter of the surface tension, we may define the AB free energy of interaction between two substances in the condensed state[4,6,30] as

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(5) van Oss, C. J.; Ju, L.; Chaudhury, M. K.; Good, R. J. *J. Colloid Interface Sci.*, in press.

(6) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Adv. Colloid Interface Sci.* **1987**, *28*, 35.

(7) Chaudhury, M. K. "Short Range and Long Range Forces in Colloidal and Macroscopic Systems"; Ph.D. Thesis, SUNY at Buffalo, 1984.

(8) van Oss, C. J.; Good, R. J.; Chaudhury, M. K. *J. Colloid Interface Sci.* **1986**, *111*, 378.

(9) Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904.

$$\Delta G_{ij}^{\mathrm{AB}} = -2(\gamma_i^+\gamma_j^-)^{1/2} - 2(\gamma_\mathrm{i}^-\gamma_\mathrm{j}^+)^{1/2} \qquad (7)$$

The (polar) cohesive energy of a given material, *i*, then is

$$\Delta G_{ii}^{\mathrm{AB}} = -2(\gamma_i^+\gamma_i^-)^{1/2} - 2(\gamma_i^-\gamma_i^+)^{1/2} = -4(\gamma_i^+\gamma_i^-)^{1/2} \qquad (8)$$

We also know that

$$\Delta G_{ii}^{\mathrm{coh}} = -2\gamma_i \qquad (9)$$

where the superscript coh indicates the cohesive energy. From eq 8 and 9 it follows that

$$\gamma_i^{\mathrm{AB}} = 2(\gamma_i^+\gamma_i^-)^{1/2} \qquad (10)$$

and from eq 3a and 9

$$\gamma_i^{\mathrm{TOT}} = \gamma_i^{\mathrm{LW}} + \gamma_i^{\mathrm{AB}} \qquad (11)$$

We can now make an explicit definition of an LW liquid. It is a liquid, *i*, for which, in the free energy of cohesion (eq 3a), $\Delta G_{ii}^{\mathrm{AB}}$ is zero and for which, in the free energy of adhesion with any other material, *j*, $\Delta G_{ij}^{\mathrm{AB}}$ is zero. This means that the molecules have no (or negligible) capability of forming hydrogen bonds, or of acid–base interaction, with each other or with other molecules.

Additive and Nonadditive Surface Tension Components. From eq 11 it is clear that the apolar (LW) and the polar (AB) surface tension components are *additive*. However, the constituent electron-acceptor (γ^+) and electron-donor (γ^-) parameters of the polar (AB) component are *not* additive (eq 10). In most individual cases, $\gamma_i^+ \neq \gamma_i^-$. Indeed, as we have demonstrated earlier, there are many polar solids and liquids that are (usually) strong electron donors but have no (or very little) electron-acceptor capacity;[4,6] in other (rarer) instances, there are some polar solids and liquids that are electron acceptors but have no electron-donor capacity.[10] Such substances are best described as monopoles.[4,6,10] Monopolar compounds have a strong γ^+ *or* a strong γ^- parameter, but these parameters, in the absence of a surface tension parameter of the opposite sign, do not contribute to the energy of cohesion, i.e., their $\gamma_i^{\mathrm{AB}} = 0$ (see eq 10). But, paradoxically, while the total surface tension of *monopolar* compounds is the same as their γ^{LW}, they nevertheless can strongly interact with *bipolar*[4,6] liquids, such as water, through their one remaining polar parameter (e.g., their γ^-) and the opposing one of water (its γ^+). Thus, in eq 7, one of the right-hand terms remains, even if one of the compounds is monopolar.

Complete Young Equation. From the expression for the Young–Dupré equation given in eq 4, with insertion of the terms for ΔG^{LW} (eq 5) and for ΔG^{AB} (eq 7), a complete version of the Young equation can be written as

$$(1 + \cos\theta)\gamma_\mathrm{L}^{\mathrm{TOT}} = 2((\gamma_\mathrm{S}^{\mathrm{LW}}\gamma_\mathrm{L}^{\mathrm{LW}})^{1/2} + (\gamma_\mathrm{S}^+\gamma_\mathrm{L}^-)^{1/2} + (\gamma_\mathrm{S}^-\gamma_\mathrm{L}^+)^{1/2}) \qquad (12)$$

If we assume that (advancing) contact angles θ are determined with a liquid L, of which we not only know the (easily determined) total surface tension $\gamma_\mathrm{L}^{\mathrm{TOT}}$ but also its $\gamma_\mathrm{L}^{\mathrm{LW}}$ component and its $\gamma_\mathrm{L}{}^+$ and $\gamma_\mathrm{L}{}^-$ parameters, *there still are three independently variable unknowns*, i.e., $\gamma_\mathrm{S}^{\mathrm{LW}}$, γ_S^+, and γ_S^-, *which cannot be determined from only one equation.*

To solve for the three unknowns, three equations are required; i.e., one needs to determine the contact angles θ with three different, completely characterized, liquids.[4-6] It is therefore clear that attempts at a complete characterization of the surface tension properties of any given polar material by means of a contact angle determination with only one liquid, with the results expressed in only one equation,[2,3] cannot succeed. It also becomes clear why the Zisman methodology of extrapolating to cos θ = 1, in order to obtain a critical surface tension γ_c for various polar solids,[11] suffers from pronounced nonlinearity when strongly polar liquids are included among the liquids used for contact angle measurement. This nonlinearity has been noted previously,[12,13] but it is in fact even more pronounced than had been originally suspected.

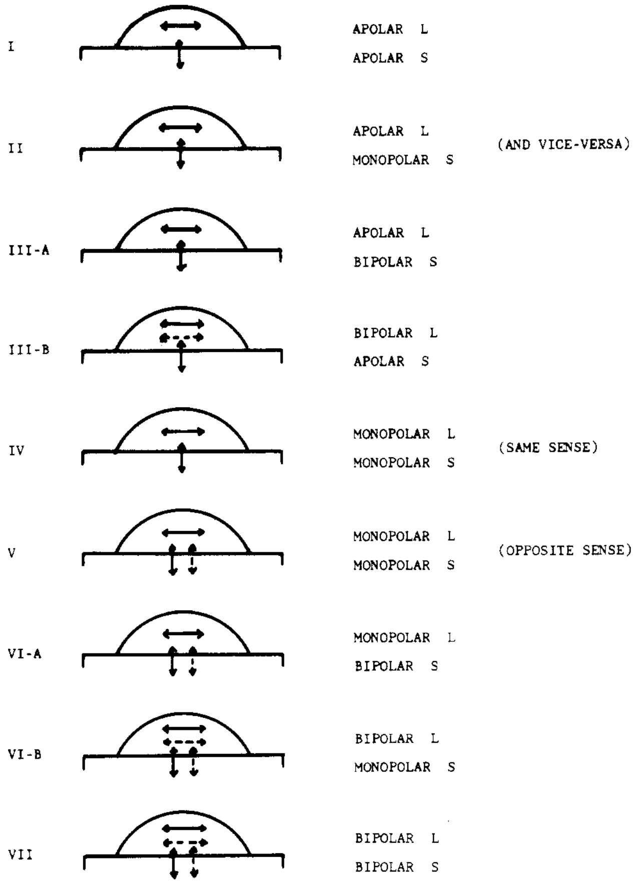

Figure 1. Schematic representation of the interactions that play a role in the shape of liquid drops on solid surfaces. Roman numerals: classification according to ref 4; see text. LW interactions are shown by arrows connected by solid lines; AB interactions are indicated by arrows connected by interrupted lines. Horizontal arrows indicate cohesion; vertical arrows indicate adhesion.

There are seven possible classes of binary systems, consisting of components 1 and 2:[4] I, 1 and 2 are apolar; II, 1 is apolar and 2 is monopolar; III, 1 is apolar and 2 is bipolar; IV, 1 and 2 are monopolar in the same sense; V, 1 and 2 are monopolar in the opposing sense; VI, 1 is monopolar and 2 is bipolar; and VII, 1 and 2 are bipolar.

In principle, any statement concerning 1 and 2 in the above list also holds symmetrically for 2 and 1.[4] However, when considering a liquid 1, forming a drop on a solid 2, a certain asymmetry may occur in a few cases, which gives rise to a total of nine different variants, illustrated in Figure 1 (the symmetrical cases being designated IIIA, IIIB and VIA,VIB). Here the solid arrows indicate LW interactions and the interrupted arrows AB interactions. Horizontal arrows designate cohesive and vertical arrows adhesive interactions. Cohesive interactions in the *solid*

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[10] van Oss, C. J.; Good, R. J.; Chaudhury, M. K. *J. Chromatog.* **1987**, *391*, 53.

[11] Zisman, W. A. *Adv. Chem. Ser.* **1964**, *43*, 1.

[12] Good, R. J.; Girifalco, L. A. *J. Phys. Chem.* **1960**, *64*, 561.

[13] Good, R. J.; Elbing, E. *Ind. Eng. Chem.* **1970**, *62*, 54.

are not indicated, as they do not, in general, have a direct bearing on the shape of the drop. Cohesive interactions in the liquid, on the other hand, play an important role in the ultimate shape of the drop (and thus in the value of θ), in the competition between the adhesion to the solid which tends to flatten the drop, and in the drop's cohesion, which tends to make it revert to a spherical shape.

In class I, polar interactions are totally absent, of course. In classes II, IIIa, and IV, polar properties do not contribute to the interaction across the interface, either because polar solids do not influence apolar liquids (II and IIIA) or because monopoles of the same sign do not influence each other (IV); see Figure 1. In other words, in classes I, II, IIIA, and IV, eq 12 reduces to eq 2. Examples are as follows: class I, hexadecane on Teflon; class II, no known example, but conceivably hexadecane on acetone encased in a gel; class IIIA, hexadecane on water encased in an agarose gel;[12] class IIIB, water on Teflon; and class IV, dimethyl sulfoxide[31] on surfaces of dried Dextran,[4,6,14] solid poly(ethylene glycol),[6,14] dried zein,[4,6] cellulose acetate,[10] cellulose nitrate,[10] and poly(methyl methacrylate);[4,5] see also Table IV.

The situation depicted in class IIIB (Figure 1) shows that it is possible to obtain γ_S^{LW} (i.e., γ_S^{TOT}) of an apolar solid surface with a bipolar liquid. The polarity of the liquid influences only its cohesion, and not its adhesion to the solid. In situations of this class, eq 12 reduces to

$$(1 + \cos \theta)\gamma_L^{TOT} = 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} \tag{12a}$$

An example is water on Teflon ($\theta \approx 118°$).

For classes V and VIA (Figure 1), eq 12 applies, with the slight modification that, here, $\gamma_L^{TOT} = \gamma_L^{LW}$. An example of class V is diiodomethane on dried DNA[10] (see Table IV). Examples of class VIA are dimethyl sulfoxide or diiodomethane on various hydrated proteins.[15]

For class VII (Figure 1), eq 12 is used. For class VIB, eq 12 is used, keeping in mind that one of the two polar terms is zero, depending on the sign of the monopolarity of the solid. Examples of class VIB are water or glycerol on dried DNA,[10] dried RNA,[10] dried Dextran,[4,14] dried poly(ethylene glycol),[4,14] various dried proteins,[15] cellulose acetate,[10] cellulose nitrate,[10] poly(methyl methacrylate),[4] dimethyl sulfoxide encased in a gel,[5] and glycerol on mica; see also Table IV. Examples of class VII are water on various hydrated proteins[5] and water on ethylene glycol or formaldehyde encased in gels.[17]

Interfacial Tensions. While the Good–Girifalco combining rule given in eq 1[9] allows one to obtain the interfacial tension between two exclusively apolar (LW) compounds quite accurately, there is no reason to assume that it also would apply to polar interactions.[4,6,16] If we rewrite the Dupré equation (eq 6) for polar interactions as

$$\gamma_{ij}^{AB} = \Delta G_{ij}^{AB} + \gamma_i^{AB} + \gamma_j^{AB} \tag{6a}$$

and if we insert the value found for ΔG_{ij}^{AB} in eq 7 into eq 6a, we find for the polar aspect of interfacial tension

$$\gamma_{ij}^{AB} = \gamma_i^{AB} + \gamma_j^{AB} - 2(\gamma_i^+\gamma_j^-)^{1/2} - 2(\gamma_i^-\gamma_j^+)^{1/2} \tag{13}$$

which, in view of eq 10, becomes[32]

$$\gamma_{ij}^{AB} = 2((\gamma_i^+\gamma_i^-)^{1/2} + (\gamma_j^+\gamma_j^-)^{1/2} - (\gamma_i^+\gamma_j^-)^{1/2} - (\gamma_i^-\gamma_j^+)^{1/2}) \tag{14}$$

Obviously, contrary to γ_{ij}^{LW}, γ_{ij}^{AB} can readily become *negative*. Indeed, after eq 1 and 14 are combined to yield

$$\gamma_{ij}^{TOT} = ((\gamma_i^{LW})^{1/2} - (\gamma_j^{LW})^{1/2})^2 + \\ 2((\gamma_i^+\gamma_i^-)^{1/2} + (\gamma_j^+\gamma_j^-)^{1/2} - (\gamma_i^+\gamma_j^-)^{1/2} - (\gamma_i^-\gamma_j^+)^{1/2}) \tag{15}$$

it is seen quite clearly that γ_{ij}^{TOT} can be negative[4,6,14] in the case of polar compounds; see also van de Ven et al.[18]

Interfacial or "Hydrophobic" Interactions. The total interfacial interaction ΔG_{132}^{TOT} between two entities 1 and 2, immersed in a polar liquid 3, in those cases when at least one of the two entities is of a relatively low cohesive energy, may be identified with what has been commonly alluded to as the "hydrophobic" interaction when the polar liquid in which such interactions take place is water; in which case, $\Delta G_{132}^{TOT} < 0$. According to eq 3

$$\Delta G_{132}^{TOT} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB} \tag{3b}$$

By use of the variants of the Dupré equation adapted to interactions of two condensed phases, 1 and 2, in a liquid, where the liquid phase is designated by the subscript 3

$$\Delta G_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23} \tag{6a}$$

the total interfacial (or "hydrophobic") interaction[4,6,10] is (by eq 3b, 6a, and 14):

$$\Delta G_{132}^{TOT} = \gamma_{12}^{LW} - \gamma_{13}^{LW} - \gamma_{23}^{LW} + \\ 2[(\gamma_3^+)^{1/2}((\gamma_3^+)^{1/2} + (\gamma_2^-)^{1/2} - (\gamma_3^-)^{1/2}) + (\gamma_3^-)^{1/2}((\gamma_1^+)^{1/2} + \\ (\gamma_2^+)^{1/2} + (\gamma_3^+)^{1/2}) - (\gamma_1^+\gamma_2^-)^{1/2} - (\gamma_1^-\gamma_2^+)^{1/2}] \tag{16}$$

When $\Delta G_{132}^{TOT} > 0$, the interaction becomes a repulsion, and is, inter alia, the driving force for phase separations of polymers in aqueous media,[14] for elution in various modes of liquid chromatography,[8] and for the generation of "hydration pressure". Simpler instances of hydrophobic interactions are designated by $G_{131}^{TOT} < 0$ pertaining to cases of bodies of identical entities, 1, in a medium 3.

Discussion

Once it had become clear that the only way of determining the three surface tension components of solids (γ_S^{LW}, γ_S^+, γ_S^-) from contact angle measurements (see eq 12) was by measuring contact angles with (at least) three different liquids for each solid[4,6] (in order to be able to solve three equations for three unknowns), we proceeded to do precisely that, with a number of solids[4,10,14,15] as well as with a number of liquids encased in gels so as to be able to treat them as solids.[5] A relatively unexpected outcome of these measurements was the finding that a large proportion of the measured materials turned out to have monopolar properties.[4,6,10,14] These materials include most proteins,[15] polysaccharides,[4,6,10] sucrose,[4] poly(ethylene glycol),[4,6,10] RNA,[10] cellulose esters,[4,10] and poly(methyl methacrylate),[4,6] all of which are γ^- monopoles. Also included is DNA,[10] which appears to have strong γ^+ properties. Moreover, aromatic compounds such as benzene and polystyrene have a monopolar γ^- character on account of the donor behavior of π electrons.

Findings of Spelt et al.[2] In the light of our findings, and also considering the chemical constitution of the liquids used by Spelt et al.[2] for measuring contact angles on certain low-energy surfaces, it becomes obvious that all liquids used by these authors obey $\gamma_L^{TOT} = \gamma_L^{LW}$. The li-

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[14] van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Sep. Sci. Technol.* **1987**, *22*, 1515.

[15] van Oss, C. J.; Good, R. J.; Chaudhury, M. K. *J. Protein Chem.* **1986**, *5*, 385.

[16] Fowkes, F. M. In *Physicochemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum: New York, 1983; Vol. 2, p 583.

[17] van Oss, C. J.; Roberts, M. J.; Good, R. J.; Chaudhury, M. K. *Colloids Surf.* **1987**, *23*, 369.

[18] Van de Ven, T. G. M.; Smith, P. G.; Cox, R. G.; Mason, S. G. *J. Colloid Interface Sci.* **1983**, *91*, 298.

quids used in ref 2 were pentadecane, α-methylnaphthalene, benzaldehyde, ethyl caprylate, heptaldehyde, methyl salicylate, and dibenzylamine.[33] The first of these is apolar, and the remaining six are largely or wholly γ^- monopoles. To obtain γ_S^{LW} from contact angles measured with these liquids, eq 2 may be used. In so doing, one obtains for FEP-A, $\gamma_S^{LW} = 16.9$ mJ/m^2 (minimum 16.4, maximum 17.8); for FEP-B, $\gamma_S^{LW} = 17.8$ mJ/m^2 (minimum 17.1, maximum 19.0); and for siliconized glass, $\gamma_S^{LW} = 22.1$ mJ/m^2 (two values only: 21.5 and 22.7). (For a precise description of the Teflon FEP-A and FEP-B samples, see ref 2.) In the cases of FEP-A and FEP-B, obviously $\gamma_S^{LW} = \gamma_S^{TOT}$ (see Figure 1, class I or II). In the case of siliconized glass, the Si–O–Si group makes the surface a mainly γ^- monopolar surface, so that here also $\gamma_S^{LW} = \gamma_S^{TOT}$ (see Figure 1, class IV). Therefore, γ^- liquids on a γ^- solid behave just like γ^{LW} liquids on a γ^{LW} solid.

Thus, while the results of Spelt et al.[2] can be completely explained by the theory of surface tension components that we have given above, the choice of their experiments was not appropriate for furnishing a decision as to the correctness of the general theory of surface tension components nor were these experiments sufficiently wide-ranging to reveal novel insights in the variegated role of surface tension components (see also van de Ven et al.[18]).

Findings from Tables I–V. Particularly germane to the influence of surface tension components are the data presented above, in Tables I–V, although many other data must also be taken into account to obtain the full picture. For instance, from contact angle measurements with both water and glycerol on γ^- monopolar surfaces, it could be determined that $\gamma^+_{water}/\gamma^+_{glycerol} \approx 4.5$. Thus, water interacts much more strongly than glycerol with γ^- monopolar surfaces, and consequently, relatively larger contact angles are observed with glycerol on γ^- monopolar surfaces than would be expected if γ^+ were larger. The ratio γ_1^+/γ_1^- for glycerol is smaller than that for water, by a factor of 0.14.[4] This difference between glycerol and water accounts for the fact that, in Table I, certain monopolar solids have an unexpected close value of θ for glycerol to that of water.

The paradoxical spreading of glycerol on water,[4,5] *and* of water on glycerol (mentioned above), is easily explained by the negative interfacial tension that exists between these two liquids as a result of their strong polar interaction[4,5] (see Table II). The great differences in water contact angles on a number of γ^- monopolar surfaces (Table III) are explicable by the fact that cellulose acetate is a strong γ^- monopole and polystyrene a very weak one, while poly(methyl methacrylate) and poly(ethylene terephthalate) are intermediate. Thus the polar adhesion between water and cellulose acetate is very strong and that between water and polystyrene rather weak.

One of the handier ways of detecting γ^- monopolarity is to measure contact angles with dimethyl sulfoxide (preponderantly a strong γ^- monopole) and α-bromonaphthalene (a very weak bipolar compound that as a first approximation, may just about be taken to be apolar). These liquids have almost identical surface tensions of $\approx$44 mJ/m^2. When a polar solid yields the same contact angle with both liquids (see the framed values in Table IV), it must be preponderantly a γ^- monopole, so that dimethyl sulfoxide shows no stronger polar interaction than α-bromonaphthalene in these cases. The different behavior of a γ^+ monopole (e.g., dried DNA) with these two liquids is quite striking (Table IV), as well as the different behavior of a strong bipole (hydrated lysozyme).

A clear example of the drastic influence of polar components on the total binary interaction is shown in Table V. According to the equation of state theory,[2] the interfacial tension for water vs pure organic liquids should be a unique function of the surface tension of the organic liquid. Table V provides a list of the interfacial tensions of water vs six organic liquids that all have surface tension of about 27 mJ/m^2 (varying only between 26.9 and 27.5 mJ/m^2). The interfacial tensions with water vary from 51.2 mJ/m^2 (hexadecane)[17] to as little as 8.5 mJ/m^2 (1-octanol and octanoic acid).[9] Equation 15 can, however, easily account for the differences in γ_{12} values shown in Table V. This is true even though the polar liquids listed are largely monopoles (γ^+ for chloroform and γ^- for the others), a condition which leaves only one positive and one negative term in the polar part of eq 15.

Table VI. Dipole Moments and Calculated and Experimental Enthalpies of Mixing of Pairs of Liquids

acid	base	$\mu_1^2\mu_2^2$ [a]	ΔH-(calcd),[a] kcal/mol	ΔH-(exptl),[a] kcal/mol
p-chlorophenol	trimethylamine	1.7	9.5	9.6
p-chlorophenol	ethyl acetate	14.1	5.0	5.1
p-chlorophenol	acetone	36.9	5.4	5.4
isothiocyanic acid	butyl ether	4.1	6.5	6.4
isothiocyanic acid	acetonitrile	46.6	4.6	5.0
aluminum trimethyl	acetone	2.1	20.0	20.3
chloroform	acetone	8.6	3.6	3.6

[a] Reference 16; in debyes.[4]

Dipole Moments. Spelt et al. observed that the polar liquids used in their contact angle measurements behaved as if they had no permanent dipole moments.[2] On the basis of this observation the authors concluded that Fowkes' γ^d[1,16] is an artifactual surface tension parameter with no real scientific basis. This is an untenable conclusion; Fowkes has argued that the surface tension component originating from dipole–dipole (Keesom) interaction does not contribute measurably to the total surface tension of a dipolar liquid and that the surface tension of nonassociated liquids is predominantly due to dispersion forces.[16]

Hence the Spelt conclusion is an unfortunate misrepresentation of Fowkes. A similar situation can also be noted in estimating the bulk enthalpy of mixing of polar liquids. Table VI demonstrates the noncorrelation between the enthalpy of mixing and the dipole moments of the various liquids quite clearly. The enthalpy of mixing can, however, be calculated from Drago's acid/base parameters[19] of the liquids, as can also be noted from Table VI.

A recent analysis of the surface interactions based on Lifshitz's theory has provided further theoretical justification for Fowkes' proposition.[5] For example, the true dipolar component of the surface tension of water, which is included in the zero-frequency component in Lifshitz's equation, is only about 1–4 mJ/m^2. The conventionally accepted value of 51 mJ/m^2, which was calculated on the basis of pairwise additivity theory[13] for interactions in the gas phase, is very much larger than that value. It can be shown that the zero-frequency interactions are so coupled with the higher frequency interactions that it becomes totally unnecessary to decouple the polar and dispersion interactions for liquids with either zero or finite dipole moments. For nonpolar liquids, the zero-frequency electronic induction term substitutes for the orientation term of polar liquids. For Lifshitz–van der Waals interactions,

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(19) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* 1971, *93*, 6014.

Table VII. Advancing Contact Angles of Various Liquids on Teflon and the γ^{LW} Found for Teflon FEP from These Data by Using Eq 12a

liquid	liquid surface tension, mJ/m²	temp, °C	contact[a] angle θ, deg	γ^{LW}, mJ/m²
1-methylnaphthalene	39	24	72.6	16.45
methyl salicylate	39	24	72.8	16.36
dibenzylamine	41.8	3	75.4	16.38
benzaldehyde	42.9	3	73.4	17.72
dibenzylamine	41.9	3	75.4	16.38
methyl salicylate	41.5	3	72.9	17.37
pentadecane	25.6	39	52.4	16.59
heptaldehyde	25.5	39	53.2	16.3
pentadecane	27.7	14	53.6	17.58
ethyl caprylate	27.7	14	53.0	17.76

[a] Reference 2.

the Good–Girifalco interaction parameter, ϕ,[9,13] is found to be so close to unity[7,8] for most common substances that it has become necessary to modify Fowkes' γ^d slightly, with the aid of a different notation, to γ^{LW} (LW stands for Lifshitz–van der Waals; see above). Then, LW interactions, by definition, comprise the dispersion, dipolar, *and* induction terms[4,6,7] (see above). It should be noted that the numerical values of γ^{LW} are the same as Fowkes' γ^d.[1,16] Numerical arguments show that one can generally neglect the Keesom and Debye interaction terms in condensed phases[16] and be content with only the dispersion interaction term. As long as a liquid is nonassociated, the presence of permanent dipoles will have a negligible effect on its energy of cohesion or on its spreading behavior on a nonpolar substance.

The fact that the contact angles of the liquids used by Spelt et al.[2] all yield close to the same value of γ^{LW} for Teflon FEP (see Table VII) indicates that these liquids are nonassociated and interact with the substrate only through *LW* interactions (see also Fowkes).[20] If, however, the authors had chosen H-bonded liquids, very different results would have been obtained on even slightly polar surfaces (see, e.g., ref. 7), because the H-bonding component of the surface tension of such test liquids has very little in common with the non-H-bonding properties of nonpolar surfaces.

ϕ Factor. The publications on the interaction parameter, or ϕ factor,[9,12] drew the attention of various workers (see, e.g., Fowkes[1,16]) to the various anomalies caused by polar contributions to the energy of cohesion of polar liquids, especially water (which tends to give rise to the condition $\phi < 1$), as well as anomalies caused by polar interactions in adhesion (which tends to cause an increase in ϕ). The ϕ factor also played an essential role in the elaboration of the equation of state[3] (see above). While it is not now in practical use, its concept was of crucial importance in the realization of the importance of the polar aspects of the surface tension, as well as in the further quantitative development of these polar aspects. We may, incidentally, reiterate that ϕ may be taken as equal to unity for interfaces between two apolar phases, between an apolar phase and a monopolar phase, or between two phases that are monopolar in the same sense (see also van de Ven et al.).[18] It is not, to any important extent, a function of relative molecular volume.[21]

Zisman Approach. For apolar materials the Zisman approach[11] is correct (or would be correct if $\cos\theta$ were plotted against $\gamma/(\gamma_L)^{1/2}$ instead of γ/γ_L).[20] The use of the slope of the plotted line to obtain a measure of the polar contribution to γ_S[11] is qualitatively instructive but does not suffice to express the polar contributions quantitatively.

With apolar solids, provided the solid is extremely smooth, it is in principle superfluous to use a plurality of apolar liquids and to make a graph and extrapolate to $\cos\theta = 1$, as any one of the apolar liquids should yield the same γ_S, according to eq 2. All apolar liquids yield the same γ_S, according to eq 2 rearranged in the form

$$\gamma_S = [\gamma_L(1 + \cos\theta)^2]/4$$

since $\gamma_S = \gamma_S^{LW}$.

It is possible to identify the presence of roughness that is "appreciable"[7] by graphing $\cos\theta$ vs $(\gamma_L^{LW})^{1/2}/\gamma_L$. (If the liquids in the series that is employed are LW liquids, then $\gamma_i^{LW} = \gamma_i^{TOT}$, and a plot may be made of $\cos\theta$ vs $\gamma/(\gamma_L)^{1/2}$. If the graph is linear and if when extrapolated to $((\gamma_L^{LW})^{1/2}/\gamma_L) = 0$ the line passes through -1.00, then the solid may be regarded as smooth, for the purposes of contact angle studies. If the intercept is more negative than -1, then the roughness area ratio $\rho \equiv A(\text{true})/A(\text{apparent,macroscopic})$ is given by the negative value of the intercept.

Equation of State. Like the concept of the ϕ factor, the elaboration of one simple, universal equation that would incorporate the anomalies of polar origin into the Young equation was an interesting idea.[3] However, in the light of the multiplicity of unknown components of the equation, as outlined above, any proposal to solve for three components with only one equation becomes untenable.

To begin with, the equation of state has as a built-in postulate[3] that the interfacial tension γ_{LV} cannot be negative, as is readily apparent from the γ_{LV} tables[21] generated from the computer program given in the Appendix of the original paper.[3] As has already been pointed out by van de Ven et al.,[18] that postulate is erroneous.[4,5] Most values pertaining to polar compounds, found by the methods of ref 3 and 22, for high γ_L and γ_S data points, are likely to be wrong.

More fundamentally, for a known contact angle θ and a known liquid surface tension γ_L^{TOT}, the interesting unknown is not γ_S^{TOT} but the set, γ_S^{LW}, γ_S^{+}, and γ_S^{-}. All three of these vary independently of each other, according to the chemical composition of the solid in question (see eq 12). These three unknowns obviously require three equations for their solution[4,6,10,14,15] (assuming we know γ_L^{LW}, γ_L^{+}, and γ_L^{-} for the three different liquids used in the three contact angle determinations). It is impossible to determine even γ_S^{TOT} with only one equation. Thus, eq 11 and 12 must be used jointly, for example, in the form

$$\gamma_S^{TOT} = \gamma_S^{LW} + 2(\gamma_S^{+}\gamma_S^{-})^{1/2} \qquad (17)$$

which illustrates that γ_S^{TOT} is composed of its three independently variable components in a complex manner. Some of the errors in γ_S caused by use of the equation of state can be seen in Table III, where $\gamma_{\text{eq state}}$ is 17.5% too high for cellulose acetate and 32.7% too low for polystyrene. Similar errors are also reported by Busscher et al.[23] in their Table IV, where the discrepancies between $\gamma_{\text{eq state}}$ obtained with water and $\gamma_{\text{eq state}}$ obtained with α-bromonaphthalene, on the same materials, range between +47.4% and −42.9%. Finally, referring to Table V, the interfacial tension between water and all six of the

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(20) Fowkes, F. M. *J. Adhesion Sci. Technol.* **1987**, *1*, 7.

(21) Good, R. J. *J. Colloid Interface Sci.* **1977**, *59*, 398.

(22) Neumann, A. W.; Absolom, D. R.; Francis, D. W.; van Oss, C. J. *Sep. Purif. Methods* **1980**, *9*, 69.

(23) Busscher, H. J.; Kip, G. A. M.; van Silfhout, A.; Arends, J. *J. Colloid Interface Sci.* **1986**, *114*, 307.

organic liquids listed would be from 30.54 to 31.14 mJ/m^2 according to the equation of state. The observed values range from ’40% too low (for hexadecane/water) to 259% too high (for 1-octanol/water and octanoic acid/water).

But even supposing that γ_S^{TOT} somehow could in general be approximated via only one equation in one independent variable, i.e., by measuring contact angles with only one liquid (and that approximation is by coincidence, occasionally, surprisingly close when using the equation of state), the question may be raised, what can one do with γ_S^{TOT} once its value is known? The answer is not much. It does, of course, allow one to calculate the energy of cohesion of the solid (eq 9 and 11). But contrary to γ_L^{TOT}, which is an essential factor in the Young equation (see also Figure 1), γ_S^{TOT} plays no role in that or any equation other than eq 11 and is in itself of no direct use in the determination of interaction energies between a solid and a liquid (eq 3, 6, 7) or between a solid and other solids (eq 3, 6, 7, 16).

Advancing Solidification Fronts. In a more recent paper Spelt et al. renew their critique on what they call "the Fowkes approach" by comparing rejection and engulfment results obtained with various particles in advancing solidification front experiments in various liquids/solids with contact angle results, obtained on the various solids with drops of glycerol.[24] In so doing they use the simplified Young equation, which, as we have pointed out, must be reserved for apolar liquids or apolar solids.[12a] However, with an extremely polar and H-bonded liquid such as glycerol, and even slightly polar solids, the use of the complete Young equation[12] is imperative, because contrary to their postulate, with the exception of Teflon, none of their solid compounds may be assumed to be solely "dispersive". Spelt et al. assume, for glycerol, a γ_L^{LW}/γ_L ratio of 0.58 (this ratio, however, in reality is probably closer to 0.53).[7] But their main error arises out of neglecting the polar interactions between the very polar glycerol and the (slightly but not negligibly) monopolar solids studied, such as nylon, polystyrene, and siliconized glass, as well as the strongly monopolar organic alcohols (see case VIB, Figure 1). It should therefore come as no surprise that from data thus processed predictions as to rejection or engulfment in advancing solidification front experiments are not uniformly confirmed. No definitive comment can be offered on the agreement between the observed rejection or engulfment behavior reported by Spelt et al.[24] and the free energies predicted by using the authors' equation of state, as it was not made clear whether these free energy calculations were based on the contact angle data obtained with glycerol or on other data. But assuming the first supposition to be the correct one, a rather good agreement obtained by the use of the equation of state may be likened to the surprisingly good predictions obtained earlier with the equation of state concerning phase separation or miscibility in different organic solutions of two polymers.[25] However, upon closer scrutiny these predictions[24] turned out to be actually based on the cancellation of various errors.[26] Given the fact that $\gamma_W^+/\gamma_{GLY}^+$ for water (W) and glycerol (GLY) is of the order of 4.5,[4,6] it may well be that if contact angles on the various solids and polymers are determined with water, instead of with glycerol, somewhat greater discrepancies will be found between free energies calculated with the equation of state and the observed behavior in advancing solidification fronts than were noted with glycerol.

It is obvious that other single equations of state that have been proposed[27] necessarily are equally spurious.

General Comment

It is a dangerous departure from standard scientific methodology to try to draw too broad empirical conclusions from a small, selected set of data. To do so is to risk the error of overgeneralization or generalization to fit the personal bias of the investigator.

There are two remedies by which this risk can be reduced to an acceptable level. One of them, Popper's method of "falsification",[28] has come into extremely wide acceptance in recent years. It states that the author of a hypothesis (or theory) should look not for further confirmatory cases but for cases that would provide the proposition, as a generalization, law, or theory, to be false. The failure of a diligent search for falsification is taken as giving support for the proposition, though not absolute confirmation. If an investigator does not carry out this tactic, he leaves it to others to do so.

The second remedy is to use theory to identify relevant principles and to draw deductions from them. This tactic enables the investigator to establish whether his hypothesis can be embedded in the matrix that can be described as "all the rest of scientific knowledge"; if it cannot, then one of two things must happen. First, the items in the rest of scientific knowledge that conflict with the hypothesis must

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(24) Spelt, J. K.; Smith, R. P.; Neumann, A. W. *Colloids Surf.* **1987**, *28*, 85.

(25) van Oss, C. J.; Omenyi, S. N.; Neumann, A. W. *Colloid Polym. Sci.* **1979**, *257*, 737.

(26) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Sep. Sci. Technol.*, in press.

(27) Gerson, D. F. *Colloid Polym. Sci.* **1982**, *260*, 539.

(28) Popper, V. *The Logic of Scientific Discovery*; Hutchinson: London; Basic Books: New York, 1959; Julius Springer-Verlag: Vienna, 1934.

(29) Jensen, W. B. In *The Lewis Acid–Base Concepts*; Wiley-Interscience: New York, 1980. Jensen uses the term "reciprocal".

(30) P. Kollman (*J. Am. Chem. Soc.* **1977**, *99*, 4875) has expressed the asymmetrical interaction in a similar manner. We must stress the fact that eq 7 cannot be regarded as a "geometric mean" relation. It must not be confused with an expression of the form $\Delta G_{ij}^{AB} = -2(\gamma_i^P\gamma_j^P)^{1/2}$, where "p" refers to the "polar component" of surface tension. Equation 7 supersedes all equations of this form. The right-hand side of eq 7 expresses the *sum* of two complementary interactions, i.e., the interaction between available electron donors of substance *i* with available acceptors of substance *j plus* the interaction between available electron acceptors of substance *i* and available donors of *j*, *each of which* is in accordance with a geometric mean rule. This new formalism is needed because the formalism of the form above (ΔG_{ij}^{AB}), which has been used previously by many authors (e.g., Schakenraad, J. M.; Busscher, H. J.; Wildevuur, C. R. H.; Arends, J. *J. Biomed. Mater. Res.* **1986**, *20*, 773. Nyilas, E.; Morton, W. A.; Cumming, R. D.; Leberman, D. M.; Chiu, T. H.; Baier, R. E. *J. Biomed. Mater. Res.* **1977**, *8*, 51 is inadequate and, in most cases, erroneous (ref 16; see also the *caveat* in ref 8). The complementarity of the interactions is also made evident by the fact that only those γ_i^+ and/or γ_i^- values are manifested (e.g., in contact angle measurements) that are available for interaction across a phase boundary. Such interactions may be either with a different material, *j* (adhesion), or with the same material, *i* (cohesion).

(31) This is to some extent an oversimplification: DMSO is largely monopolar, with a strong γ^- parameter, but also appears to have a small γ^+ parameter (Fowkes, F. M. *J. Adhesion Sci. Technol.* **1987**, *1*, 7).

(32) An equation of this type has been proposed earlier by P. A. Small (*J. Appl. Chem.* **1953**, *3*, 71); see also W. B. Jensen *Surface and Colloid Science in Computer Technology*; Mittal, K. L., Ed.; Plenum: New York, 1987; p 27).

(33) Until extremely recently, it was believed that ammonia and the primary and secondary amines were amphoteric in the sense of being both Lewis bases and proton-donor Lewis acids. In a just-published review (a) of spectroscopic and other studies that have been made since 1983, Nelson, Fraser, and Klemperer have given convincing evidence that the protons of NH_3 do not take part in "hydrogen-bond donation" interactions. Hence NH_3 is a γ^- monopole. It is therefore extremely probable that the same is true of dibenzylamine. A number of years ago, Good (b) reported that the molar surface entropy of hydrogen bonding substances such as water is about 45% of that of non-hydrogen-bonding liquids. NH_3 and various amines constituted an exception, having molar surface entropy values close to the mean for the non-hydrogen-bonding substances. This earlier finding also indicates that dibenzylamine, like NH_3 is a γ^- monopole. (a) Nelson, D. D.; Fraser, G. T.; Klemperer, W. *Science (Washington, DC)* *238*, 1670. (b) Good, R. J. *J. Phys. Chem.* **1957**, *61*, 810.

be independently overthrown. An example for the present instance is the generalized acid–base theory, which Neumann and his associates[2] would have to overthrow if the equation of state were to be given ultimate acceptance. Second, if the advocate of a new hypothesis cannot overthrow the concepts and results in the rest of scientific knowledge that conflict with the hypothesis, then he must concede that the hypothesis is not valid.

Our purpose in this paper has been to develop and expound the modern theory of surface tension components. Until recently, we had thought that an equation of state could (at least as an approximation that was useful in a limited range of cases) coexist with the theory of surface tension components. Reference 2 closes the door on this coexistence. Spelt et al. have brought forward their equation of state, and some data taken with a very limited number of liquids on apolar or monopolar solids, as being "in direct conflict with the theory of surface tension components".

We have, above, laid out a number of ways in which this equation of state is in conflict with accepted theory, in regard to intermolecular forces *in general*, and with a large number of experiments in surface chemistry. On the basis of these arguments, we conclude that this "equation of state", and Spelt's experiments, do not raise any serious challenge to the theory of surface tension components.

Soot Oxidation in Fibrous Filters. 1. Deposit Structure and Reaction Mechanisms

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Soot generated in an acetylene flame was collected in quartz and glass fiber filters and oxidized by placing the loaded filters in a tube furnace at 1 atm and temperatures of 400 and 525 °C. The rate of soot oxidation was about 2 orders of magnitude higher on glass filters than on quartz filters. Elementary spheroids present in the soot flame were about 20 nm in diameter. When the soot loading was low, the spheroids deposited as single particles on the fiber surface, and the soot/fiber contact was good. At higher loadings the spheroids agglomerated in the gas and grew further on the fibers to form clusters as large as a few microns in size; most of the particles were not in contact with the fiber surface. The oxidation rate of soot on glass fiber filters was proportional to the total soot loading even when most of the elementary soot particles were not in contact with the fiber surface. EDX analysis of partially oxidized soot particles showed that sodium from glass fibers was transported to the soot and catalyzed the surface reaction. Because the sodium species uniformly covered the soot surface after a short induction period, the rate per unit soot surface area is independent of the filter loading when the loading is 3.1 $\mu g/cm^2$ or less.

Introduction

Fibrous filters are widely used for the high-efficiency, low-pressure drop filtration of small particles from gases. The fundamental filtration mechanisms[1] are well understood, and good estimates can be made of the efficiency of filtration of spherical particles when the filters are clean, before significant buildup of deposits has occurred.

Although the filtration removal mechanisms are well understood, chemical reactions of particles in filters have not been carefully studied. Despite this, combustion in filters has been used to measure the mass of different fractions of the carbon-containing components of ambient aerosols.[2–5] Fibrous filters may offer an alternative to current diesel trap technologies for the removal of soot from exhaust gases followed by the oxidation of the deposited particles in situ.[6–9] The cellular ceramic traps now in use generally have a collection efficiency of 34.5–98.8% depending on the operating conditions.[10] The fibrous filter is lightweight and highly efficient (>99%), and the fibers can be made of materials resistant to high temperatures and corrosion. Moreover, we have found that catalytic agents can be incorporated into the fibers.

The goal of this research was to elucidate the kinetics of reactions of small particles deposited in fibrous filters, which we call "immobilized aerosol reactors". Soot was chosen for study because of its practical importance in atmospheric pollution.

Soot is made up of aggregated carbon particles with varying ratios of organic compounds to carbon. Soot formation in flames has been extensively studied.[11–14] The

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(1) Friedlander, S. K. *Smoke, Dust and Haze*; Wiley-Interscience: New York, 1977.

(2) Novakov, T. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimish, R. L., Eds.; Plenum: New York, 1982; p 19.

(3) Macias, E. S.; Chu, L.-C. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimish, R. L., Eds.; Plenum: New York, 1982; p 131.

(4) Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimish, R. L., Eds.; Plenum: New York, 1982; p 131.

(5) Cadle, S. H.; Groblicki, P. J. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimish, R. L., Eds.; Plenum: New York, 1982; p 131.

(6) Howitt, J. S.; Montierth, M. R. *SAE Paper 810114* 1981.

(7) Öser, P.; Thomas, U. *SAE Paper 830087* 1983.

(8) Enga, B. E.; Buchman, M. F.; Lichtenstein, I. E. *SAE Paper 820184* 1982.

(9) Murphy, M. J.; Hillenbrand, L. J.; Trayser, D. A. *Interagency Energy/Environment R and D Program Report*; EPA-600/7-79-232b, 1979.

(10) Miller, P. R.; Scholl, J.; Bagley, S.; Leddy, D.; Johnson, J. H. *SAE Paper 830457* 1983.

(11) Haynes, B. S.; Wagner, H. Gg. *Prog. Energy Combust. Sci.* 1981, 7, 229.

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