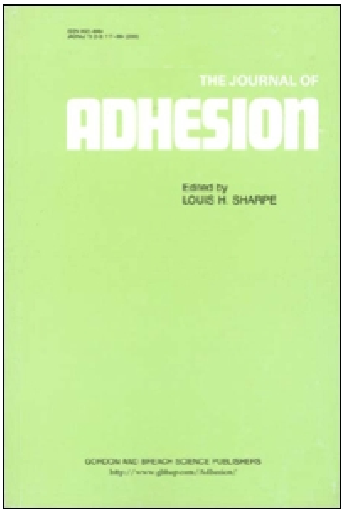

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On the Predominant Electron-Donicity of Polar Solid Surfaces

C. J. Van Oss[a]; R. F. Giese[b]; W. Wu[c]
[a] Departments of Microbiology, Chemical Engineering and Geology, State University of New York at Buffalo, Buffalo, NY, USA [b] Department of Geology, State University of New York at Buffalo, Buffalo, NY, USA [c] Department of Chemistry, State University of New York at Buffalo, Buffalo, NY, USA

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On the Predominant Electron-Donicity of Polar Solid Surfaces*

C. J. VAN OSS[a,]**, R. F. GIESE[b] and W. WU[c]

[a]Departments of Microbiology, Chemical Engineering and Geology,
State University of New York at Buffalo, Buffalo, NY 14214-3000, USA;
[b]Department of Geology, State University of New York at Buffalo,
Buffalo, NY 14214-3000, USA;
[c]Department of Chemistry, State University of New York at Buffalo,
Buffalo, NY 14214-3000, USA

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The reasons for the predominant electron-donicity of almost all solid polar surfaces and its implications are discussed in this paper. By contact angle or interfacial tension measurements, the electron-accepting as well as the electron-donating properties of polar liquids can be ascertained, through the interplay between their energies of *adhesion* and *cohesion*. For the solid-liquid interface, direct interfacial tension measurements are not possible, but indirectly, solid/liquid interfacial tensions of polar systems can be obtained by contact angle measurement. However, as the energy of cohesion of a solid does not influence the contact angle formed by a liquid drop placed upon its surface, one can only measure the solid surface's *residual* polar property, manifested by the energy of *adhesion* between solid and liquid. This residual polar property is of necessity the dominant component; in most cases this turns out to be its electron donicity. When, by means of contact angle measurements with polar liquids, *both* electron-accepting and electron-donating potentials are found on a polar solid, it is most likely still partly covered with a polar liquid: usually water. The *amount* of residual water of hydration of a polar solid follows from its polar (Lewis acid-base) surface tension component (γ^{AB}). The *degree of orientation* of the residual water of hydration on a polar solid can be expressed by the ratio of the electron-donating to electron-accepting potentials ($\gamma^{\ominus}/\gamma^{\oplus}$), measured on the hydrated surface.

Keywords: Bipolar liquids; electron-acceptors; electron-donors; energy of cohesion of liquids; energy of cohesion of solids; Lewis acid-base interactions; Lifshitz-van der Waals interactions; monopolar liquids; monopolar solid surfaces; surface tension components; water of hydration

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**Corresponding author.

1 PROPERTIES OF POLAR LIQUIDS

Fowkes *et al.* defined "polar" liquids as: "those which are self-associated through... (Lewis acid-base interactions, including hydrogen bonds), which have an acid-base contribution to their cohesive energy and surface tension, γ_L^{AB}, and therefore have a surface tension γ_L greater than the van der Waals contribution to their surface tension γ_L^{LW}" [1]. He went on to state that "By this definition polar liquids must have both acidic and basic sites, and... such polar liquids are easily identifiable by their insolubility in the higher alkanes, especially squalane. Typical polar liquids include alcohols, nitriles, amides, and even the lower ketones. Liquids which are acidic or basic, but do not have both acidic and basic sites, are quite miscible in the higher alkanes; van Oss and co-authors [2] prefer to refer to these as "monopolar" liquids [1]."

Among these monopolar liquids are: benzene (basic), toluene (basic), chloroform (acidic) [2, 3], as well as methyl ethyl ketone, tetrahydrofuran [3, 4], and octanol [3] (all basic). To distinguish "polar" from monopolar liquids, it seems appropriate to designate "polar" liquids [1] which have both acidic and basic sites (see above), as "bipolar" liquids [5].

1.1 The Polar Properties of Liquids

The polar properties of liquids (L) are linked to their polar surface tension component *i.e.*, the Lewis acid-base component (γ_L^{AB}), in such a manner that the total surface tension of a liquid (γ_L) is expressed as [1-5]:

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} \tag{1}$$

where

$$\gamma_L^{AB} = 2(\gamma_L^{\oplus} \gamma_L^{\ominus})^{1/2} \tag{2}$$

and where $\gamma_L^{\oplus}$ is the Lewis acid (electron-acceptor) and $\gamma_L^{\ominus}$ the Lewis base (electron-donor) parameter of the polar surface tension component ($\gamma_{\mathrm{L}}^{\mathrm{AB}}$); $\gamma_{\mathrm{L}}^{\mathrm{LW}}$ is the Lifshitz-van der Waals, or apolar component, which is *always present*. The values of $\gamma_{\mathrm{L}}^{\mathrm{LW}}, \gamma_{\mathrm{L}}^{\oplus}$ and $\gamma_{\mathrm{L}}^{\ominus}$ of a liquid can be obtained in two ways:

A) By contact angle (θ) measurements with the liquid (L) on several different solid surfaces (S), using the following version of Young's equation[2–5]:

$$(1+\cos\theta)\gamma_L = 2((\gamma_{\mathrm{L}}^{\mathrm{LW}}\gamma_{\mathrm{S}}^{\mathrm{LW}})^{1/2} + (\gamma_{\mathrm{L}}^{\oplus}\gamma_{\mathrm{S}}^{\ominus})^{1/2} + (\gamma_{\mathrm{L}}^{\ominus}\gamma_{\mathrm{S}}^{\oplus})^{1/2}) \tag{3}$$

B) By interfacial tension (γ_{L2}) measurements of liquid (L), with a (known) liquid
(2), with which it is immiscible, using[2–5]:

$$\gamma_{\mathrm{L}2} = \overbrace{[(\gamma_{\mathrm{L}}^{\mathrm{LW}})^{1/2} - (\gamma_{2}^{\mathrm{LW}})^{1/2}]}^{a}{}^{2}$$

$$+ \overbrace{2[(\gamma_{\mathrm{L}}^{\oplus}\gamma_{\mathrm{L}}^{\ominus})^{1/2}}^{b} + \overbrace{(\gamma_{2}^{\oplus}\gamma_{2}^{\ominus})^{1/2}}^{c}$$

$$- \overbrace{(\gamma_{L}^{\oplus}\gamma_{2}^{\ominus})^{1/2}}^{d} - \overbrace{(\gamma_{L}^{\ominus}\gamma_{2}^{\oplus})^{1/2}]}^{e} \tag{4}$$

As there are three unknowns ($\gamma^{\mathrm{LW}}, \gamma^{\oplus}$ and $\gamma^{\ominus}$), in both the contact angle (Eq. (3)) and the interfacial tension with immiscible liquids approaches (Eq. (4)), measurements have to be done on three different solids (Eq. (3)), or with three different immiscible liquids (Eq. (4)), to find out the surface properties of a bipolar liquid.

1.2 Monopolar Liquids

With a *monopolar* liquid usually only one interfacial measurement (using Eq. (4)) suffices, as in all cases γ_{L} is also known[6], or can easily be determined. For monopolar liquids, $\gamma^{\mathrm{AB}} = 0$, by definition (*cf.* Eq. (2)), so that here, $\gamma_{\mathrm{L}} = \gamma_{\mathrm{L}}^{\mathrm{LW}}$. A number of monopolar liquids have been enumerated in the introductory part of Section 1, above.

2 POLAR LIQUIDS USED IN CONTACT ANGLE MEASUREMENTS

2.1 The Need to Use High Energy Liquids

The most important prerequisite of any liquid destined to be used in contact angle measurements on solids, is that the liquid's surface tension has to be higher than the surface tension of the solid that must be measured, or else the liquid will spread on the solid's surface. As most organic and inorganic solids have a surface tension [3] of at least about 35 mJ/m^2, and usually more of the order of 40 mJ/m^2, contact angle liquids must have a $\gamma_L > 40$ mJ/m^2 to be useful.

2.2 Apolar Contact Angle Liquids

For apolar liquids, the requirement of $\gamma_L > 40$ mJ/m^2 rules out all alkanes that are liquid at 20°C. In practice, one is left with α-bromonaphthalene ($\gamma_L = 44.4$ mJ/m^2) and diiodomethane (methylene iodide) ($\gamma_L = 50.8$ mJ/m^2). Neither liquid is 100% apolar, judging by a somewhat lower interfacial tension with water [7] than the ideal 55 mJ/m^2 (for α-bromonaphthalene) or 57 mJ/m^2 (for diiodomethane). Nonetheless, for most practical purposes one may assume that, for both liquids, $\gamma_L^{\oplus}$ and $\gamma_L^{\ominus}$ are negligibly small. Kerkeb *et al.*, on the other hand, prefer to assign a $\gamma^{\oplus}$ value of 0.7 mJ/m^2 to diiodomethane [8], which is easily derived from the published interfacial tension of diiodomethane with water [7] of $\gamma_{LW} = 48.5$ mJ/m^2, assuming $\gamma_L^{\ominus} = 0$, and using Eq. (4). However, in most cases this finite $\gamma_L^{\oplus}$ – value may safely be neglected.

2.3 Polar Contact Angle Liquids in General

Among polar liquids, one does not find *any* monopolar liquid (with either a sizable $\gamma_L^{\oplus}$ or $\gamma_L^{\ominus}$ value) with $\gamma_L > 35$ mJ/m^2. For measuring $\gamma_S^{\oplus}$ and $\gamma_S^{\ominus}$ (using Eq. (3)) one, therefore, needs at least two bipolar liquids of $\gamma_L > 40$ mJ/m^2. There are only a few such liquids. The most important of these is water.

2.4 Water as a Polar Contact Angle Liquid

Water (w) is *the* most used liquid for contact angle measurements. Apart from its general availability, the most important reason for this is its unusually high surface tension: $\gamma_w = 72.8$ mJ/m^2 at 20°C. The reason for the high value of γ_w is the high hydrogen-bonding energy of cohesion of water, which is responsible for 70% of its cohesion: $\gamma_w^{\mathrm{AB}} = 51.0$ mJ/m^2, whilst [9] $\gamma_w^{\mathrm{LW}} = 21.8$ mJ/m^2 (yielding in total: $\gamma_w = 72.8$ mJ/m^2; *cf.* Eq. (1)). Although $\gamma_w^{\oplus} \cdot \gamma_w^{\ominus}$ is known: $\gamma_w^{\mathrm{AB}} = 2(\gamma_w^{\oplus} \cdot \gamma_w^{\ominus})^{1/2} = 51$ mJ/m^2 (*cf.* Eq. (2)) $\gamma_w^{\oplus}/\gamma_w^{\ominus}$ unfortunately remains unknown. What is known is that *both* $\gamma_w^{\oplus}$ and $\gamma_w^{\ominus}$ are sizable entities, *cf.* Gutmann [10], and Ref. 3, pp. 27–28.

2.5 The Polar Properties of Water at 20°C Adopted as Standard

An arbitrary but plausible ratio of $\gamma_w^{\oplus}/\gamma_w^{\ominus} = 1.00$ (at 20°C) was adopted to serve as the reference point on the basis of which any polar system (i) can be defined in terms of its $\gamma_i^{\oplus}$ and $\gamma_i^{\ominus}$ values [2, 3]. The uncertainty (inherent in the assumed standard ratio of $\gamma_w^{\oplus}/\gamma_w^{\ominus} = 1$ at 20°C) disappears by expressing [2, 3] $\gamma_i^{\oplus}$ in terms of $\delta_{iw}^{\oplus}$, such that $\delta_{iw}^{\oplus} = (\gamma_i^{\ominus}/\gamma_w^{\ominus})^{1/2}$. In so doing, Young's equation (Eq. (3)) for θ_w becomes [2, 3]:

$$(1 + \cos\theta)\gamma_w = 2(\gamma_i^{\mathrm{LW}}\gamma_w^{\mathrm{LW}}) + 51\delta_{iw}^{\oplus} + 51\delta_{iw}^{\ominus} \tag{3a}$$

However, this device for avoiding any assumption relative to the $\gamma_w^{\oplus}$ and $\gamma_w^{\ominus}$ values introduces new symbols ($\delta^{\oplus}$ and $\delta^{\ominus}$) pertaining to polar surface tension parameters, which is both confusing and unnecessary. It should be realized that in calculating $\gamma_{ij}^{\mathrm{AB}}$ values (*cf.* Eqs. (1), (2) and (4)), the assumptions about $\gamma_w^{\oplus}$ and $\gamma_w^{\ominus}$ *cancel out* [2, 3], so that the resulting $\gamma_{ij}^{\mathrm{AB}}$-values, expressed in S.I. units, (*e.g.*, mJ/m^2) are not dependent on these assumptions [2, 3, 5]. Similarly, the other entities derived from $\gamma_{ij}^{\mathrm{AB}}$, such as $\Delta G_{ij}^{\mathrm{AB}}$, $\Delta G_{iji}^{\mathrm{AB}}$ and $\Delta G_{ijk}^{\mathrm{AB}}$ are also independent of the value of $\gamma_w^{\oplus}/\gamma_w^{\ominus}$, because all three terms can be derived from $\gamma_{ij}^{\mathrm{AB}}$ (and/or from γ_i^{AB}, which is directly measurable, *cf.* Eqs. (1), (2), (4)):

$$\Delta G_{ij}^{\mathrm{AB}} = \gamma_{ij}^{\mathrm{AB}} - \gamma_i^{\mathrm{AB}} - \gamma_j^{\mathrm{AB}} \tag{5}$$

$$\Delta G_{iji}^{\mathrm{AB}} = -2\gamma_{ij}^{\mathrm{AB}} \tag{6}$$

$$\Delta G_{ikj}^{\mathrm{AB}} = \gamma_{ij}^{\mathrm{AB}} - \gamma_{ik}^{\mathrm{AB}} - \gamma_{jk}^{\mathrm{AB}} \tag{7}$$

where $\Delta G_{ij}^{\mathrm{AB}}$ is the polar free energy of interaction between condensed state materials *i* and *j in vacuo*, $\Delta G_{iji}^{\mathrm{AB}}$ is the polar free energy of interaction between two molecules or particles of condensed state material *i*, immersed in liquid *j*, and ΔG_{ikj}^{AB} the polar free energy of interaction between two molecules or particles of condensed state materials *i* and *j*, immersed in liquid *k*.

Thus the "real" value of the ratio $\gamma_w^{\oplus}/\gamma_w^{\ominus}$, while unknown at this time, (and probably unknowable for the foreseeable future), *is not needed for expressing the polar free energies* of interaction alluded to above (Eqs. (5)–(7)); the *assumed value* of $\gamma_w^{\oplus}/\gamma_w^{\ominus}=1$, (together with $\gamma_w^{\oplus}+\gamma_w^{\ominus}=51$ mJ/m^2) [9], at 20°C, suffices to yield *absolute values* for $\Delta G_{ij}^{AB}, \Delta G_{iji}^{AB}, \Delta G_{ikj}^{AB}$ as well as for $\Delta G_{ii}^{AB}(=-2\gamma_i^{AB})$, in S.I. units.

2.6 Other Polar Contact Angle Liquids

Two other high energy bipolar liquids, useful for measuring contact angles, in addition to water, are: *glycerol* [3, 11] ($\gamma_G=64$ mJ/m^2, $\gamma_G^{LW}=34$ mJ/m^2, $\gamma_G^{AB}=30$ mJ/m^2, $\gamma_G^{\oplus}=3.92$ mJ/m^2 and $\gamma_G^{\ominus}=57.4$ mJ/m^2, all at 20°C) and *formamide* [3, 11] ($\gamma_F=58$ mJ/m^2, $\gamma_F^{LW}=39$ mJ/m^2, $\gamma_F^{AB}=19$ mJ/m^2, $\gamma_F^{\oplus}=2.28$ mJ/m^2, $\gamma_F^{\ominus}=39.6$ mJ/m^2, all at 20°C). A third non-aqueous high-energy bipolar liquid is *ethylene glycol* (useful for contact angle measurements when glycerol cannot be used because of its high viscosity, *e.g.*, in thin layer wicking [12]). Its surface properties are estimated as [3]: $\gamma_{EG}=48$ mJ/m^2, $\gamma_{EG}^{LW}=29$ mJ/m^2, $\gamma_{EG}^{AB}=19$ mJ/m^2, $\gamma_{EG}^{\oplus}=1.92$ mJ/m^2 and $\gamma_{EG}^{\ominus}=47$ mJ/m^2 (all at 20°C).

The properties of these high energy bipolar liquids have been obtained from contact angle measurements on known monopolar ($\gamma^{\ominus}$) surfaces, such as solid polyethylene oxide and polymethyl methacrylate [3, 11], etc.

3 PREDOMINANT ELECTRON-DONICITY OF BIOPOLYMERS, OTHER POLAR POLYMERS AND SOLID POLAR PARTICLES AND SURFACES

3.1 Reasons for the Prevalent Electron-Donicity of Polar Materials

The predominant electron-donicity that can be observed through contact angle measurements on proteins, polysaccharides and other polar polymers [2], as well as on various clay particles [3–5] and other mineral surfaces [6, 7], is largely a consequence of the prevalence of oxygen in the Earth's lower atmosphere (≈ 20 vol. %) and in the Earth's surface (≈ 46.6 weight %) [13]. Thus, all the biopolymers and common minerals and mineral particles (especially silicates) are oxides and/or hydroxides, which makes them preponderantly electron-donors.

For instance, glycerol, with $\gamma_G^\oplus = 3.92$ and $\gamma_G^\ominus = 57.4$ mJ/m^2 as best values [3, 11] (*cf.* Section 2.6) clearly is predominantly a Lewis base. From the pronounced miscibility, or solubility of glycerol in water:

$$\ln s = -2\gamma_{1w}/kT \tag{8}$$

(where s is the solubility in mol fraction, k is Boltzmann's constant and T the temperature in degrees K; at 293° K, 1 $kT = 4.04 \times 10^{21}$J) [3, 14], it is easily shown that for glycerol $\gamma_1^\ominus$ must be larger than 35 mJ/m^2 and $\gamma_1^\oplus$ must be smaller than 6.4 mJ/m^2. A large $\gamma_1^\ominus/\gamma_1^\oplus$ value for glycerol also follows from the fact that not only does glycerol spread on water (contained in a gel), but water (even though it has a higher surface tension than glycerol) also spreads on glycerol (contained in a gel) [15]; see also Ref. 3, pp. 102, 103. Thus the values for $\gamma_1^\oplus$ and $\gamma_1^\ominus$ for glycerol, mentioned above [11], are entirely plausible. One important reason why a strong asymmetry between $\gamma_1^\oplus$ and $\gamma_1^\ominus$ is a prerequisite for pronounced aqueous solubility, is the fact that the hydrophobic attraction, which counteracts solubility, has to be overcome in all cases. This is exemplified in term b of Eq. (4), which represents the omnipresent polar free energy of cohesion of water [3, 16, 17].

A high $\gamma_1^\ominus/\gamma_1^\oplus$ ratio is also a prerequisite for the aqueous solubility of the linear polymer of glucose, *i.e.*, dextran. Also, using Eq. (8), it is easily shown that the ratio of $\gamma_1^\ominus/\gamma_1^\oplus$ has to be significantly greater than 2.5 (where $\gamma_1^\ominus$ must be greater than about 29 mJ/m^2). In reality, a value of $\gamma_1^\ominus \approx 55$ mJ/m^2 was found for dextran, with $\gamma_1^\oplus \approx 0$ [2, 3]. Further reasons for this are discussed in Section 3.2, below.

3.2 Occurrence of Monopolar Electron-Donicity Among Polar Solids

Whilst the reason for the prevalent electron-donicity of condensed-phase polar materials thus appears clear, the frequent occurrence of *monopolar* electron-donicity in such materials also needs to be discussed.

The ($\gamma^{\ominus}$) monopolarity of polyethylene oxide (PEO) is readily understandable from its chemical composition. However, the apparent ($\gamma^{\ominus}$) monopolarity of many polysaccharides, such as dextran (DEX), which is a mainly linear polymer of glucose, is somewhat less obvious, as DEX has polar O as well as OH groups. As shown in the preceding Section (3.1), it is necessary for DEX that $\gamma_1^{\oplus} \ll 11.6$ mJ/m^2 and $\gamma_1^{\ominus} \gg 29$ mJ/m^2, which means that, in any case, $\gamma^{\ominus}$ dominates. There are two ways by which values of $\gamma^{\oplus} = 0$ and $\gamma^{\ominus} = 55$ mJ/m^2 for DEX [2, 3] can occur, as measured by contact angle determinations on dried layers of DEX, on a flat plate: 1) the dominant $\gamma_1^{\ominus}$ sites of DEX neutralize, and thus mask, the few $\gamma_1^{\oplus}$ sites by *intermolecular* interaction, upon or after deposition of an aqueous DEX solution on a flat surface, or: 2) the dominant $\gamma_1^{\ominus}$ sites of DEX neutralize, and thus mask, the few $\gamma_1^{\oplus}$ sites by *intramolecular* interaction, even prior to deposition on a flat surface. Now, apart from the more favorable higher concentration, and thus closer proximity between DEX molecules in the first case, it would appear that if the many $\gamma_1^{\ominus}$ sites of DEX can neutralize a few $\gamma_1^{\oplus}$ sites on adjoining molecules, the $\gamma_1^{\ominus}$ sites on one DEX polymer molecule should be equally capable of neutralizing the few $\gamma_1^{\oplus}$ sites that are present on the same molecular strand by folding appropriately. The distance between $\gamma^{\ominus}$ and $\gamma^{\oplus}$ sites on a single molecular strand of DEX is unlikely to be greater than if they were situated on adjoining strands. It is, therefore, reasonable to assume that the $\gamma^{\ominus}$ monopolarity of DEX, as well as of many other water-soluble biopolymers, is a property of the individual polymer molecules through *intramolecular* compensation. However, the $\gamma^{\ominus}$ monopolarity observed for mono and oligo-saccharides, dried from aqueous solutions deposited on glass slides (Ref. 3, pp. 180, 181), is clearly a consequence of *intermolecular* $\gamma^{\ominus} - \gamma^{\oplus}$ interactions.

3.3 Occurrence of Bipolarity Among Polar Solids

By direct contact angle measurement, as well as by thin layer wicking on solid surfaces, one often encounters $\gamma^{\ominus}$ monopolarity, *e.g.*, among some smectites (*e.g.*, hectorite [18]), and other clay particles [19] [*e.g.*, tremolite [20], illite [21], sepiolite [22], palygorskite [23], as well as various solid polymer surfaces [3, 11] (*e.g.*, poly(methyl methacrylate) [3, 11], poly(vinyl alcohol) [3], poly(ethylene oxide) [3], variousproteint [3], etc.].

However, many other mineral particles and surfaces [19], such as solid polymers (*e.g.*, nylon [3]) and, especially, ***hydrated proteins*** [3], tend to show a small but not negligible $\gamma^{\oplus}$, in addition to a (usually more sizable) $\gamma^{\ominus}$. In all cases where finite $\gamma^{\oplus}$ and $\gamma^{\ominus}$ values are found, it is essential also to consider the γ^{AB} values (Eq. (2)) they give rise to; see Table I.

It should be noted that the free energy of cohesion of a given homogeneous surface (1) traditionally tends to be expressed as:

$$\Delta G_{11}^{coh} \equiv -2\gamma_1 \tag{9}$$

where γ_1 would comprise γ_1^{LW} and γ_1^{AB} (*cf.* Eq. (1)), the polar part of the free energy of cohesion of material (1) then would be:

$$\Delta G_{11}^{AB} \equiv -2\gamma_1^{AB} \tag{9A}$$

while the apolar part is:

$$\Delta G_{11}^{LW} \equiv -2\gamma_1^{LW} \tag{9B}$$

One might then be tempted to continue this sequence, by expressing the internal *covalent* energy of cohesion of a solid material as:

$$\Delta G_{11}^{covalent} = -2\gamma_1^{covalent}. \tag{9C}$$

However, in solids the (internal) covalent energy of cohesion does not manifest itself through a measurable influence on their (surface) adhesion to liquids, *i.e.*, the covalent energy of cohesion of solids has no effect whatsoever on the shape of drops of liquids deposited on their surface. Thus, in this context, Eq. (9C) has no meaning when considered with respect to the surface properties of a solid material. Eq. (9A) has only meaning for solid surfaces (1) insofar as one may assume a complete neutralization of, *e.g.*, $\gamma_1^{\oplus}$ in the presence of a much larger $\gamma_1^{\ominus}$, so that for a dry, flat, homogeneous surface, $\gamma_1^{AB} = 0$. Its excess $\gamma_1^{\ominus}$, on the other hand, remains measurable through contact angle measurement with high-energy polar liquids with a sizable $\gamma_L^{\oplus}$. Finally, Eq. (9B) does remain valid, as attractive Lifshitz-van der Waals forces remain measurable as medium to long-range interactions between the

TABLE I $\gamma_1^{LW}, \gamma_1^{\oplus}, \gamma_1^{\ominus}, \gamma_1^{AB}$ and ΔG_{1w} Values (in mJ/m^2) of Various Solid Surfaces

Surface(1)[a]	γ_1^{LW}	$\gamma_1^{\oplus}$	$\gamma_1^{\ominus}$	γ_1^{AB}	ΔG_{1w}^b	ΔG_{1w}^c	$\Delta\Delta G_{1w}^d$	$\gamma_1^{\ominus}/\gamma_1^{\oplus e}$
Polyethylene oxide[3]	43.0	0	64.0	0	−142.0	−142.0	0	—
Teflon FEP[3]	17.9	0	0	0	−39.5	−39.5	0	—
Human Serum albumin (HSA)[3] (dry, pH 7.0)	41.0	0.126	17.2	2.9	−105.2	−101.7	−3.5	136.5
HSA, 1 layer of hydration, pH 7.0[3]	26.6	0.6	75.9	13.5	−144.0	−136.2	−7.8	126.5
HSA, 2 layers of hydration, pH 7.0[3]	26.8	6.0	51.5	35.2	−145.6	−120.8	−24.8	8.6
Talc[19, 20]	31.5	2.4	2.7	5.1	−84.7	−69.0	−15.7	1.1
Talc[f]	34.2	0.1	6.9	1.7	−84.4	−82.5	−1.9	69
Hectorite (dry)[18, 19]	39.9	0	23.7	0	−108.2	−108.2	0	—
Montmorillonite SWa−1 [19, 21]	43.6	1.8	36.8	16.3	−136.5	−122.9	−13.6	20.4
Muscovite (mica) [19, 22]	40.6	1.8	51.5	19.3	−148.1	−132.0	−16.1	28.6

[a] See References.

[b] From the Dupré equation: $\Delta G_{1w} = \gamma_{1w} - \gamma_1 - \gamma_w$ (*cf.* Eqs. (1), (4), (5), and (11); $\gamma_w = 21.8\,(LW) + 51(AB) = 72.8$ mJ/m^2.

[c] $\Delta G'_{1w}$ calculated by neglecting $\gamma_1^{\oplus}$.

[d] $\Delta\Delta G_{1w} = \Delta G_{1w} - \Delta G'_{1w}$ (the value of $\Delta\Delta G_{1w}$ indicates the energy of residual hydration remaining on the solid surface; $\Delta\Delta G_{1w}$ is quite similar in absolute value to γ_1^{AB}).

[e] Dimensionless ratio.

[f] Heated overnight to 400°C, then cooled in vacuum desiccator until ready for thin layer wicking.

atoms and molecules of material (1) and those of a probe, *e.g.*, an apolar contact angle liquid.

Thus, if, on a solid surface, a non-negligible value for $\gamma_1^{\oplus}$ is found by contact angle measurement with polar liquids, one may assume the presence of a residual polar liquid on that surface (see Tab. I). In most cases, that liquid will be simply water of hydration. In the presence of a measurable $\gamma^{\ominus}$ value, the occurrence of a non- negligible $\gamma^{\oplus}$ necessarily gives rise to a finite γ^{AB} (Eq. (2)). The value of that γ^{AB}, then, is a measure of the degree of residual hydration. The extent of this residual hydration can also, somewhat more accurately, be expressed as $\Delta\Delta G_{1w}$:

$$\Delta\Delta G_{1w} = \Delta G_{1w} - \Delta G'_{1w} \tag{10}$$

where $\Delta G_{1\omega}$ is the free energy of hydration of surface (1), using Dupré's equation:

$$\Delta G_{1w} = \gamma_{1w} - \gamma_1 - \gamma_w \tag{11}$$

(*cf.* Eq. (5)), and $\Delta G'_{1w}$ is an expression of the free energy of hydration of surface (1) that would manifest itself when $\gamma_1^{\oplus}$ is taken to be zero. The difference between ΔG_{1w} and $\Delta G'_{1w}$, then, approximates the residual free energy of hydration, due to imperfect drying of surface (1). In Table I the values of $\Delta\Delta G_{1w}$ are shown for a number of solid materials, most of them with a residual layer of water of hydration. It can be seen that the $|\Delta\Delta G_{1w}|$ values are fairly similar to the γ_1^{AB} values; the latter, thus, may be regarded as a rough semi-quantitative measure of the degree of residual hydration of a supposedly dry surface (1); see also Section 3.5.1, below, and Table II.

TABLE II $\gamma_1^{LW}, \gamma_1^{\oplus}, \gamma_1^{\ominus}$ and γ_1^{AB} values (in mJ/m^2) of encapsulated and non-capsulated Staphylococci

Staphylococcus[a]	γ_1^{LW}	$\gamma_1^{\oplus}$	$\gamma_1^{\ominus}$	γ_1^{AB}
S. epidermidis [29, 30] (encapsulated)	25.6	6.1	47.2	33.9
S. epidermidis [29, 30] (non-capsulated)	35.1	0	50.0	0

[a] See References.

The degree of orientation of the residual water of hydration remaining on a solid surface (1) can be found in the ratio $\gamma_1^\ominus/\gamma_1^\oplus$ (*cf.* right-hand column of Tab. I). The percentage of oriented (as compared with random) water of hydration has earlier been expressed by: $100 \times (51 - \gamma_1^{AB}/51)$, yielding, for instance, for concentrated human serum albumin (HSA) with one layer of water of hydration, 75% orientation, whilst in the second layer only 31% of the water of hydration appears oriented by this approach [3, 23]; see Table I. However, the $\gamma_1^\ominus/\gamma_1^\oplus$ ratio provides a more realistic expression of the orientation of the residual water molecules of hydration, showing a quasi-total orientation on "dry" HSA and on HSA with only one layer of hydration, and a still sizable but already exponentially attenuated orientation of the water molecules in the second layer of hydration surrounding HSA. The $\gamma_1^\ominus/\gamma_1^\oplus$ ratio for talc (first entry) indicates a virtual absence of orientation of the water molecules still adhering to talc particles. However, the tiny amount of residual water of hydration present on the surface of talc (see second entry of talc, Tab. I), even after heating to 400°C for 16 hours, appears strongly oriented, which would be indicative of a modest but still dominant electron-donicity of talc.

3.4 Occasional Occurrence of Negative Values of $(\gamma^\oplus)^{1/2}$

Whilst most three-liquid contact angle measurements on $(\gamma_1^\ominus)$ monopolar or virtually monopolar surfaces yield a $\gamma_1^\oplus$ value that is zero, or close to zero [so that concomitantly the value of $(\gamma_1^\oplus)^{1/2}$ is also zero or close to zero], in some cases the calculations result in a small negative value for $(\gamma_1^\oplus)^{1/2}$. A number of publications contain speculations [24, 25] on the origin of this phenomenon, while others have utilized the occasional occurrence of a negative value of $(\gamma_1^\oplus)^{1/2}$ as an argument against the applicability of Lewis acid-base interactions to surface and interfacial chemistry in polar systems [26, 27]. These arguments can easily be disproved [28]. Very simply, small but often unavoidable errors in contact angle measurements with polar liquids on a polar surface can give rise to a small negative value of $(\gamma_1^\oplus)^{1/2}$ (Eq. (3)) which in reality is zero, or close to zero in the case of $(\gamma_1^\ominus)$ monopolar surfaces.

Taking, for instance, a flat layer of co-poly(ethylene oxide-propylene oxide) (molecular weight 2,000), on which the following contact angles were found: $\theta_{1-\text{bromonaphthalene}} = 19°$, $\theta_{\text{water}} = 19°$, $\theta_{\text{glycerol}} = 48°$ (Ref. 3, Tab. XIII-5). This yields $\gamma_i^{LW} = 42$ mJ/m^2, $(\gamma_i^{\oplus})^{1/2} = -0.05$ and $(\gamma_i^{\ominus})^{1/2} = 8.081$. However, if θ_{glycerol} had been 0.7° smaller, or if θ_{water} had been 1.3° smaller, $(\gamma_i^{\oplus})^{1/2}$ would have had a positive value, *i.e.*, respectively, $+0.0018$ and $+0.0017$. Errors in contact angle measurement of the order of one or two degrees are quite normal when using polar liquids on polar surfaces. Thus, the occasional occurrence of small negative values for $(\gamma_i^{\oplus})^{1/2}$, on $(\gamma^{\ominus})$ monopolar or virtually monopolar surfaces, should not be a cause for alarm, or for speculation about deeper underlying causes, nor is it a plausible ground for questioning the applicability of Lewis acid-base interactions to surface and interface chemistry in polar systems.

3.5 Changes Occurring in $\gamma_i^{\ominus}$ of Solid Surfaces

3.5.1 Changes in $\gamma_i^{\ominus}$ as a Function of Time

Flat surfaces of, *e.g.*, polymers, can be obtained by depositing a solution of the polymer in a given solvent on a flat (*e.g.*, glass) plate, and allowing the solvent to evaporate. With poly(methyl methacrylate) (PMMA), dissolved in toluene, a flat, smooth surface is obtained after evaporation of the solvent. Soon after an apparently dry PMMA plate is obtained, a $\gamma_i^{\ominus}$ value of about 12 mJ/m^2 can be measured. However, in the following weeks $\gamma_i^{\ominus}$ gradually increases, ultimately reaching a value of about 22 mJ/m^2. The mechanism of this increase in $\gamma_i^{\ominus}$ may be complex. Slow evaporation of the solvent, toluene, may have something to do with it: toluene has a $\gamma_{\text{toluene}}^{\ominus} \approx 2.4$ mJ/m^2 (Ref. 3, Tab. XIII-2). Thus, in an early stage one may be measuring a compromise between the $\gamma_i^{\ominus}$ of PMMA and the much lower $\gamma_{\text{toluene}}^{\ominus}$. Upon further evaporation of the solvent the influence of toluene on the measured $\gamma_i^{\ominus}$ would tend to diminish, until dry PMMA obtains, with a fairly high $\gamma_i^{\ominus}$ value. However, a possible gradual reorientation of oxygen-containing groups of PMMA toward the air interface may also play a role.

Bacteria as well as mammalian cells can be deposited in a flat layer from a cell suspension onto a porous membrane, *e.g.*, by suction. However, such cells initially are soaking wet and will yield a contact angle with water of 0°, which is not very informative. To obtain the "real" contact angle such cell layers must first undergo a mild degree of air drying. With water as contact angle liquid, one then follows the drying process, to establish a "plateau value" of a constant θ_{water}, which value tends to persist for a period, of typically, about one hour. If, for instance, one establishes that for a given type of cell layer, the plateau value sets in after about 50 minutes, and lasts for 60 minutes, one can then measure contact angles on a cell layer dried in that manner, between 51 and 110 minutes after onset of drying [29]. Table II indicates that encapsulated bacteria still show a significant amount of water of hydration ($\gamma_1^{\text{AB}} = 33.9$ mJ/m^2) which is substantially oriented ($\gamma_1^{\ominus}/\gamma_1^{\oplus} \approx 7.74$) (see also Tab. I). Furthermore, the γ^{LW} of non-capsulated Staphylococci is significantly higher than the γ^{LW} of the encapsulated variety, which also agrees with the presence of water of hydration on the latter (25.6 mJ/m^2 being much closer to the γ_1^{LW} of pure water, of 21.8 mJ/m^2, than the non-capsulated γ_1^{LW} of 35.1). Contrary to bacterial cells, mammalian cells always show considerable residual water of hydration, when using plateau contact angle values [30, 31]. There does not, at the moment, exist a contact angle approach for studying mammalian cells, by which the real totally dehydrated cell surface can be studied without incurring denaturation.

Another example of time-related changes in the degree of surface hydration is that of freshly split mica (muscovite). Immediately after splitting, a contact angle with diiodomethane (θ_{DIM}) of 20°, or less, is found. Within seconds θ_{DIM} *increases* to about 40°, indicative of rapidly increasing hydration: For $\theta_{\text{DIM}} = 20°$, $\gamma_{\text{mica}}^{\text{LW}} = 47.8$ mJ/m^2, which soon falls to 39.6 mJ/m^2 ($\theta_{\text{DIM}} = 40°$)[3]. Thus, contrary to the decrease in surface hydration observed as a function of time elapsed, when air-drying layers of cells (see above), freshly split mica undergoes a rapid increase in surface hydration. In both states θ_{water} on mica is, and remains, zero or close to zero.

3.5.2 Changes in $\gamma_1^{\ominus}$ Through Chemical Interactions

There is, of course, a vast number of possible chemical interactions that can influence the properties of the surfaces of various solids. However, one specific example is worth mentioning as it also has some bearing on the gradual oxidizing influence of the sun, and other weather conditions, *i.e.*, corona-treated poly(propylene). The surface properties of pure poly(propylene) are: $\gamma_1^{\text{LW}} = 25.7$ mJ/m^2, $\gamma_1^{\oplus} = 0, \gamma_1^{\ominus} = 3$.

However, after corona-charge treatment, a significant degree of oxidation appears to occur, leading to: $\gamma_1^{LW} = 33.0, \gamma_1^{\oplus} = 0$ and $\gamma_1^{\ominus} \doteq 11.1$ mJ/m^2 [3, 11]. Thus, a process which may be called accelerated weathering, can make a totally apolar polymer significantly more polar. (The increase in γ_1^{LW} is indicative of the presence of oxygen).

3.5.3 Changes in $\gamma^{\ominus}$ Induced by Changes in the Surface (ζ)-Potential

In organic as well as in inorganic compounds, hydrophilicity correlates strongly with high $\gamma^{\ominus}$-values [32]. Such high $\gamma^{\ominus}$-values readily occur in the absence of any significant surface (ζ)-potential, *e.g.*, among neutral polysaccharides. However, when a sizable ζ-potential exists [*e.g.*, of the order of -40 mV or more (negative)], it tends to be accompanied by a high $\gamma^{\ominus}$. If one causes the ζ-potential to decrease (*e.g.*, by pH-changes [3, 33], or by the admixture of plurivalent counterions [3, 22, 34–36]), the $\gamma^{\ominus}$ will decrease with it. Thus, upon depressing the ζ-potential of a hydrophilic compound or particle (1), its initially high $\gamma^{\ominus}$ (which connotates its hydrophilicity), will decrease and thus severely diminish its hydrophilicity or, more often, become so low as to change from hydrophilic to hydrophobic [3, 22, 35, 36].

This effect is strongly noticeable in: a) flocculation of mineral particles by the admixture of plurivalent counterions [34], b) the hydrophobization of phospholipid bilayers (*e.g.*, of phosphatidylic acid and phosphatidyl serine), by the admixture of Ca^{2+} [36], and c) the hydrophobization of proteins and other polyelectrolytes at pH-values close to their isoelectric point [33].

4 CONCLUSIONS

Through contact angle measurements with appropriate apolar and polar liquids on surfaces of polar organic or inorganic *solids*, one observes that virtually all these solid surfaces are predominantly electron-donating, with an electron-acceptor parameter that only varies between zero and very small values. Polar *liquids*, on the other hand, tend to have sizable values for both their electron-donor and their electron-acceptor parameters.

The reason for this observed difference between polar liquid and polar solid surfaces lies in the difference between liquids and solids with respect to the correlation, or absence of correlation, between their surface tension and their energy of cohesion. The surface tension of a pure homogeneous *liquid* is proportional to its free energy of cohesion. On the other hand, the concept of surface tension of a *solid* has nothing to do with its energy of cohesion, and if the surface tension of a solid has any meaning at all (which has been doubted [1]), such a meaning can only be found through the energy of adhesion between the solid and a liquid [1]; see also Ref. 3, page 113.

The surface of a dry polar solid is obligatorily monopolar, because the covalent as well as the electron-donor/electron-acceptor bonds between the atoms and/or molecules of the solid are completely coordinated inside the solid. Therefore, none of the covalent bonds is available for surface interactions, whereas only *either* excess electron-donating *or* excess electron-accepting sites are available for surface interactions. On solid polar surfaces, these almost always turn out to be excess electron-donating sites, thus making them monopolar electron-donors.

Although one usually finds a value of zero, or close to zero, for the electron-acceptor parameter ($\gamma_s^{\oplus}$) of a dry polar solid surface (using Eq. (3)), one occasionally arrives at a small negative value for $(\gamma_S^{\oplus})^{1/2}$. It has been shown that such a small deviation of $(\gamma_S^{\oplus})^{1/2}$ to the wrong side of zero can readily arise through a slight error (of the order of 0.5° to 1.5°) in contact angle measurement.

Finally, a correlation was found between the observation of a non-negligible value for $\gamma_S^{\oplus}$, together with a larger value for $\gamma_S^{\oplus}$, and the presence of residual water of hydration on the surface of imperfectly dried solids. A finite value for $\gamma_S^{\oplus}$, gives rise to a sizable value for γ_S^{AB} (Eq. (2)). The amount of residual water of hydration then is a function of the value of γ_S^{AB}, and its degree of orientation is denoted by the $\gamma_s^{\oplus}/\gamma_s^{\ominus}$ ratio.

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