

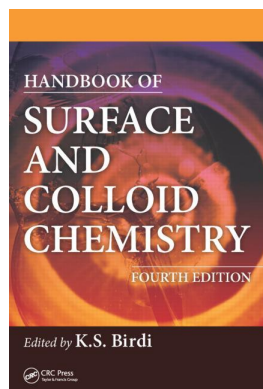
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11 Adhesion and Wetting

A Quantum Mechanics–Based Approach

Costas G. Panayiotou

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11.1 INTRODUCTION

Adhesion and wetting of solid surfaces are major fields in interface science with a remarkable range of technological applications. In spite their importance, their precise determination still remains a challenge due, primarily, to the challenges associated with the practical implementation of an operational definition of the surface tension, γ_s , of solids. The latter is often determined from extrapolations from the melt state and, most commonly, indirectly from the contact angle of liquid drops deposited on the surface and the application of a model/equation for the interfacial tension, γ_{SL} , with the liquid. In general, the work of adhesion of two unit surfaces or the negative of the surface free energy change upon the formation of a unit interface ij from the component unit surfaces i and j is obtained from the Dupre equation [1,2]:

$$W_{ij}^{adh} = \gamma_i + \gamma_j - \gamma_{ij} = -\Delta G_{ij}^s \quad (11.1)$$

The work of adhesion of a solid with a liquid, forming a contact angle θ with the solid surface, is given by the classical Young equation [3]:

$$W_{SL}^{adh} = \gamma_L(1 + \cos\theta) \quad (11.2)$$

As seen, a combination of Equations 11.1 and 11.2 does not give the interfacial tension unless we know the surface tension of the solid surface, and vice versa. The use of additional liquids will provide for more equations, but one unknown will always be left undetermined. Thus, it is essential to have an additional model/equation for the interfacial tension or the work of adhesion.

One of the most, if not the most, widely used equations for the interfacial tension is the van Oss–Chaudhury–Good (vOCG) equation [4–6]:

$$\gamma_{SL} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_S^A} - \sqrt{\gamma_L^A} \right) \left(\sqrt{\gamma_S^B} - \sqrt{\gamma_L^B} \right) \quad (11.3)$$

or

$$W_{SL}^{adh} = 2 \left[\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^A \gamma_L^B} + \sqrt{\gamma_S^B \gamma_L^A} \right] \quad (11.4)$$

Superscript *LW* in these equations stands for Lifshitz–van der Waals and indicates that in the vOCG model this term encompasses the contributions from the weak London dispersion interactions, as well as the Debye dipole–induced dipole and the Keesom dipole–dipole orientation interactions. Superscripts *A* and *B* stand for acid and base, respectively, and indicate that Lewis acid–base interactions are also considered in the vOCG model but via the asymmetric product of the second term on the rhs of Equation 11.3 and not by a quadratic always positive term like the first term. This model gives the working Equations 11.3 and 11.4 but does not give equations for the separate *LW* and *A* or *B* surface tension components of the compounds in contact. The latter are, in practice, determined by a simultaneous multiparameter fit to experimental contact angle data for various liquid–solid pairs or to experimental interfacial tension data for liquid–liquid interfaces. Through this multifitting process it is attempted to obtain unique values for the surface tension components valid for all kinds of interfaces, including pure liquid–vapor or pure solid–vacuum (or air) interfaces. This results, very often, to very high values of base surface tension components, which are difficult to reconcile with our current understanding of intermolecular interactions. Numerous corrective attempts have been made in the literature [7–9] for reducing the values of these base components but the problem still remains. An often common element to these corrective attempts is the drastic increase of the acid surface tension component of water and the concomitant reduction of the base component, which were equal in the original vOCG model [4–6]. In addition to the preceding problems, there is experimental evidence (and, thus, criticism of the vOCG model for not accounting) for *polarization* of the solid surface by the contacting liquid, that is, for the change of the surface tension components of solids in response to the interaction with (some) contacting liquids [10,11].

This chapter presents a quantum mechanics–based alternative to the vOCG approach whose predictive capacity offers a new way of addressing the previously mentioned controversial interfacial issues. The new approach is built upon the recently introduced molecular descriptors called partial solvation parameters (PSP) [12–16]. The rationale and the working equations of partial solvation parameters are described in this series of recent papers [12–16] where the reader is referred to for the details. A short review is presented in Chapter 3.

Briefly, the PSP approach heavily resides on the quantum mechanics–based COSMO-RS theory of solutions [17–22]. The COSMO model belongs to the class of continuum solvation models (CSM) of quantum mechanics. For the solvation picture, it considers the molecule embedded in a conductor of infinite permittivity that screens perfectly the molecular charges on the surface of its molecular cavity. This molecular cavity is characterized by a volume, V_{cosm} , and a molecular surface area, A_{cosm} . The crucial information is contained in the so-called COSMO file of each compound obtained from quantum chemical calculations at various levels of theory. COSMO files give the detailed surface charge distribution or the σ -profile of each molecule. The σ -profile may be analyzed into its moments of various orders, known as COSMOMents, out of which a large number of properties may be calculated, among them the molecular descriptors of Abraham's QSPR/LSER model [23,24].

There are two PSP schemes, the s and the σ -scheme. The two schemes have identical hydrogen bonding parameters but they differ in the way they partition the non-hydrogen-bonding interactions of the molecule. In the s -scheme this partitioning leads to the dispersion, s_d , and polar, s_p PSP, which are equivalent to the more familiar Hansen's dispersion solubility parameter, δ_d , and polar solubility parameter, δ_p , respectively [25]. In the σ -scheme the partitioning leads to the van der Waals, σ_w , and polarity/polarizability, σ_{pz} PSP. The van der Waals PSP is, simply, the weak van der Waals energy density:

$$\sigma_w = \sqrt{\frac{E_{vdW}}{V_{mol}}} \quad (11.5)$$

where

E_{vdW} is the weak van der Waals molar energy

V_{mol} is the molar volume of the compound

Regardless of the partitioning, energy balance implies the following equation:

$$\delta_d^2 + \delta_p^2 = s_d^2 + s_p^2 = \sigma_w^2 + \sigma_{pz}^2 \quad (11.6)$$

Although Equation 11.6 entails a slight recalculation of partial solubility parameters, it is useful in orienting the reader on the physical content of each quantity and in obtaining σ_{pz} from a simple subtraction. The thus calculated σ_{pz} PSP is close to the dielectric PSP obtained from the equation:

$$\sigma_{diel} = \sqrt{\frac{E_{diel}}{V_{mol}}} \quad (11.7)$$

where E_{diel} is the dielectric molar energy of the compound. Both, E_{vdW} and E_{diel} , are directly available from COSMO-RS theory [19], which is the basic source of information for getting PSPs. The name, *van der Waals*, has been retained for the corresponding, σ_w , PSP although it clearly accounts for the atom-specific weak dispersive or London interactions. Similarly, the name, *dispersion* PSP, has been retained for s_d in order to specify the equivalence with the more familiar partial solubility parameter, δ_d . This is not a very accurate terminology, however, since s_d (and δ_d) accounts for the London as well as the Debye induction forces. On the other hand, s_p (and δ_p) account for permanent dipole–dipole (Keesom orientation) interactions and is equal to zero for compounds with zero dipole moment. Thus, σ_{pz} accounts for, both, Keesom and Debye interactions.

In the PSP approach the compounds are divided into two major classes, the homosolvated and the heterosolvated. Heterosolvated are the compounds that can hydrogen bond only with another (heteron, in Greek) different compound, that is, they cannot self-associate. All other compounds are homosolvated. The hydrogen bonding PSPs, σ_{Ga} for the proton donor (electron acceptor or acidic) and σ_{Gb} for the proton acceptor (electron donor or basic) capacity of the compound, are obtained from the corresponding Abraham's LSER descriptors, A and B , which are in turn obtained from the COSMOments of the molecule [19]. For water, $A = 0.676$ and $B = 0.663$ or $A = 1.0198B$. The PSP approach considers perfect neutrality for water and this requires a slight shift of the B scale by ca. 2%. By setting $m\text{-SUM} = A + 1.0198B$, the following defining equations for our hydrogen bonding PSPs are obtained:

$$\sigma_{Ghb}^2 = \sigma_{Ga}^2 + \sigma_{Gb}^2 \quad (11.8)$$

$$\frac{\sigma_{Ga}^2}{\sigma_{Ghb}^2} = 1 - \frac{\sigma_{Gb}^2}{\sigma_{Ghb}^2} = \frac{A}{m-SUM} \quad (11.9)$$

$$\sigma_{Ghb} = 5.5 \sqrt{\frac{m-SUM}{V_{\text{cosm}}}} \quad (11.10)$$

It is clear from the above description that PSPs may be obtained in a straightforward manner as long as the COSMO file of the molecule is available. COSMO files are already available for thousands of compounds in free or commercial databases. They may also be obtained directly from quantum chemical calculation suites such as the TURBOMOLE [26] or the DMol³ incorporated in the MaterialStudio suite of Accelrys® and other suites. The PSPs for a number of common solvents are reported in Table 11.1. The PSPs for high polymers cannot be obtained at present from quantum chemical calculations due to their enormous number of conformers and to cpu time limitations. They may be obtained, however, from inverse-gas chromatography (IGC) and other experimental methods [15,16]. It should be made clear that PSPs heavily depend on COSMO-RS model. Any changes in COSMO-RS parameterization or any miscalculations of LSER descriptors in the multi-linear regressions with COSMOments will have an impact on PSPs. However, in Reference 14, the PSP approach has been developed into a full activity-coefficient model for concentrated as well as infinitely dilute systems. In this development, the free energy change upon formation of a hydrogen bond between acidic molecule *i* and basic molecule *j* is given by the universal equation

$$G_{ab,ij}^H = -1.70\sigma_{Ga,i}\sigma_{Gb,j}\sqrt{V_{mol,i}V_{mol,j}} + 2.50 \quad (\text{kJ/mol}) \quad (11.11)$$

in direct analogy with the QSPR/LSER model [23]. Thus, PSPs may be checked now against experimental data on activity coefficients and derived thermodynamic quantities.

With this introduction and the tables with PSPs we may now proceed to the presentation of the new approach to interfacial energies, wetting, and adhesion. This is done in the next section while examples of calculations are shown in Section 11.3. A preliminary version of the new approach is presented in the Appendix of Reference 15.

11.2 MOLECULAR SURFACE TENSION COMPONENTS

The central task and focus in this section is on a one-to-one mapping of PSPs onto the corresponding surface tension components of the molecule. In other words, the molecular descriptors that were designed for properties of bulk phases will now lead to their counterparts for properties of surfaces and interfaces. This is by no means a simple or straightforward task and it will necessarily involve a number of approximations.

For our purpose, we should recall a key distinction between the weak van der Waals or London dispersive intermolecular interactions, reflected by σ_w , and all other intermolecular interactions: Only the first are atom-specific interactions with practically no orientational or directional character. This is crucial when discussing surface properties and interfacial phenomena. A polar molecule, such as ethanol, will exhibit some kind of preferential orientation on the surface and will find itself in a density gradient in order to minimize its surface free energy: Most likely, ethanol molecule will orient its hydroxyl toward the bulk, where there is higher probability to find another hydroxyl and form a hydrogen bond with it. Quantum chemical calculations for molecules able to form inter- and intra-molecular hydrogen bonds, such as ethylene-glycol and glycerol, indicate that their conformers with cooperative intramolecular hydrogen bonds are most likely the most stable ones in the gas phase. In contrast, their more open conformations shown in Figure 11.1 are most likely the most

TABLE 11.1
Partial Solvation Parameters (PSP) of Pure Compounds

Part A: The PSPs for Non-hydrogen-Bonded Compounds					
Compound	σ_w (MPa ^{1/2})	σ_{pz} (MPa ^{1/2})	Compound	σ_w (MPa ^{1/2})	σ_{pz} (MPa ^{1/2})
<i>n</i> -Pentane	13.65	5.00	Cyclohexane	13.85	8.35
<i>n</i> -Hexane	13.75	6.50	Cycloheptane	13.85	8.55
<i>n</i> -Heptane	13.75	7.00	1-Pentene	13.80	4.35
<i>n</i> -Octane	13.75	7.00	1-Hexene	13.85	5.75
<i>n</i> -Nonane	13.75	7.50	Benzene	14.84	11.43
<i>n</i> -Decane	13.75	7.50	Toluene	14.59	11.09
<i>n</i> -Undecane	13.75	7.50	Ethylbenzene	14.41	10.77
<i>n</i> -Dodecane	13.75	8.00	<i>n</i> -Propylbenzene	14.30	10.36
<i>n</i> -Hexadecane	13.75	8.00	<i>n</i> -Butylbenzene	14.24	10.17
<i>n</i> -Octadecane	13.75	8.00	<i>n</i> -Pentylbenzene	14.17	10.22
<i>n</i> -Eicosane	13.75	8.50	<i>n</i> -Hexylbenzene	14.13	10.20
<i>n</i> -Tetracosane	13.75	8.50	<i>m</i> -Xylene	14.40	10.89
<i>n</i> -Octacosane	13.75	8.50	<i>o</i> -Xylene	14.40	11.45
<i>n</i> -Dotriacontane	13.75	8.50	<i>p</i> -Xylene	14.38	10.67
Isobutane	13.17	2.90	Styrene	14.70	12.06
Isopentane	13.37	3.65	Naphthalene	14.43	13.04
2-Methylpentane	13.48	5.10	Carbon tetrachloride	16.97	6.06
3-Methylpentane	13.48	5.80	Methyl chloride	16.92	10.14
2,3-Dimethylpentane	13.37	6.40	Monochlorobenzene	15.51	11.57
2,3,4-Trimethylpentane	13.22	6.95	Benzyl chloride	15.45	12.89
Cyclopentane	14.10	8.05	Carbon disulfide	18.42	8.77
Part B: The PSPs for Hydrogen-Bonded Compounds					
Compound	σ_w	σ_{pz}	σ_{Gb}	σ_{Ga}	
<i>Homosolvated</i>					
Methanol	15.18	10.62	18.34	15.01	
Ethanol	14.65	10.92	15.12	11.28	
1-Propanol	14.45	10.96	13.17	9.87	
1-Butanol	14.30	11.33	11.91	8.74	
1-Pentanol	14.23	10.46	11.19	8.59	
1-Hexanol	14.16	9.79	10.51	7.96	
1-Heptanol	14.10	10.42	9.95	7.41	
1-Octanol	14.07	10.23	9.49	6.96	
1-Nonanol	14.03	10.96	9.10	6.58	
1-Decanol	13.98	10.82	8.83	6.27	
Isopropanol	14.23	10.03	13.39	9.57	
2-Butanol	14.23	9.24	11.39	8.43	
2-Methyl-1-propanol	14.11	7.76	11.21	9.24	
2-Methyl-2-propanol	13.87	8.81	11.82	7.75	
2-Pentanol	14.07	10.29	10.61	7.73	
3-Pentanol	14.07	10.30	10.27	6.83	
Cyclohexanol	14.10	14.04	10.91	7.42	
Phenol	14.95	13.93	8.35	11.89	
Benzyl alcohol	14.84	15.44	10.63	8.07	
<i>m</i> -Cresol	14.73	13.63	8.07	10.73	
<i>o</i> -Cresol	14.76	12.21	7.71	10.62	

(Continued)

TABLE 11.1 (Continued)
Partial Solvation Parameters (PSP) of Pure Compounds

Part B: The PSPs for Hydrogen-Bonded Compounds

Compound	σ_w	σ_{pz}	σ_{Gb}	σ_{Ga}
<i>p</i> -Cresol	14.67	14.18	8.09	10.70
4-Hydroxystyrene	14.03	11.57	7.69	10.67
Ethylene glycol	15.16	20.36	17.51	13.94
1,2-Propylene glycol	14.67	17.76	15.19	11.30
1,3-Propylene glycol	14.65	18.61	16.02	11.62
Glycerol	14.56	24.13	16.59	11.38
Diethylene glycol	14.54	17.36	15.56	7.73
Triethylene glycol	14.46	13.57	15.28	6.70
Tetraethylene glycol	14.37	11.67	15.24	6.05
Formic acid	15.06	8.78	13.90	20.34
Acetic acid	14.27	9.01	13.84	15.55
Propionic acid	14.03	8.38	12.19	13.48
<i>n</i> -Butyric acid	13.90	9.41	11.07	12.09
<i>n</i> -Pentanoic acid	13.86	7.95	10.30	11.05
<i>n</i> -Hexanoic acid	13.81	9.85	9.69	10.25
Methylamine	15.01	4.33	20.55	8.85
Ethylamine	14.24	8.32	17.20	5.70
<i>n</i> -Propylamine	14.07	9.17	15.15	4.35
<i>n</i> -Butylamine	14.05	9.54	13.75	4.00
<i>n</i> -Pentylamine	13.95	8.57	12.15	3.95
<i>n</i> -Hexylamine	13.90	8.36	11.95	3.00
Dimethylamine	14.41	7.48	16.50	5.50
Diethylamine	14.02	6.45	12.55	3.05
DI- <i>n</i> -Propylamine	13.93	6.99	10.05	2.75
DI- <i>n</i> -Butylamine	13.86	8.27	9.15	2.60
Formamide	15.31	21.85	20.29	18.3
Water	16.26	15.40	28.28	28.28
Hydrogen peroxide	15.80	24.62	17.25	28.70
<i>Heterosolvated</i>				
Acetone	14.10	10.05 ¹	10.25	0.00
Methyl ethyl ketone	13.98	8.65	8.65	0.00
2-Pentanone	13.91	8.90	7.95	0.00
Acetaldehyde	14.33	10.25	12.00	0.00
1-Propanal	14.11	10.10	12.50	0.00
1-Butanal	14.00	9.60	11.00	0.00
1-Pentanal	13.93	9.65	8.90	0.00
Ethyl acetate	13.85	8.20	8.15	0.00
<i>n</i> -Propyl acetate	13.80	8.05	8.00	0.00
<i>n</i> -Butyl acetate	13.78	8.45	8.05	0.00
Methyl propionate	13.93	9.25	8.10	0.00
Ethyl propionate	13.79	7.73	7.95	0.00
Propyl propionate	1.01	8.07	7.25 ²	0.00
Methyl isobutyrate	1.01	8.17	8.40 ²	0.00
Butyl isobutyrate	1.02	6.46	8.00 ²	0.00
Dimethyl ether	13.81	2.10	9.80	0.00

(Continued)

TABLE 11.1 (Continued)
Partial Solvation Parameters (PSP) of Pure Compounds

Part B: The PSPs for Hydrogen-Bonded Compounds

Compound	σ_w	σ_{pz}	σ_{Gb}	σ_{Ga}
Diethyl ether	1.11	3.80	8.70	0.00
DI- <i>n</i> -propyl ether	13.76	4.50	6.70	0.00
DI- <i>n</i> -butyl ether	1.04	5.25	7.35	0.00
DI- <i>n</i> -octyl ether	1.00	7.40	4.60	0.00
Tetrahydrofuran	14.29	8.50	10.25	0.00
Chloroform	17.25	3.20	0.00	7.90
Vinyl chloride	1.00	3.20	0.00	3.55
Trimethylamine	13.80	2.75	11.20	0.00
Triethylamine	13.46	4.15	9.25	0.00
Dimethyl sulfoxide	15.46	9.17	19.52	0.5

stable and preferred ones in the liquid state, not only for entropic reasons but, mainly, because they allow for a more efficient and extensive intermolecular hydrogen bonding network. Across the interface, the molecules will assume various conformations and orientations between those shown in Figure 11.1 that will ultimately lead to surface free energy minimization.

Molecules like ethanol or acetone and the higher member of their homologous series may preferably orient themselves and keep away from the liquid–vapor interface their polar sites. In this way, these molecules (and the majority of polar molecules) will exhibit a polar character on the

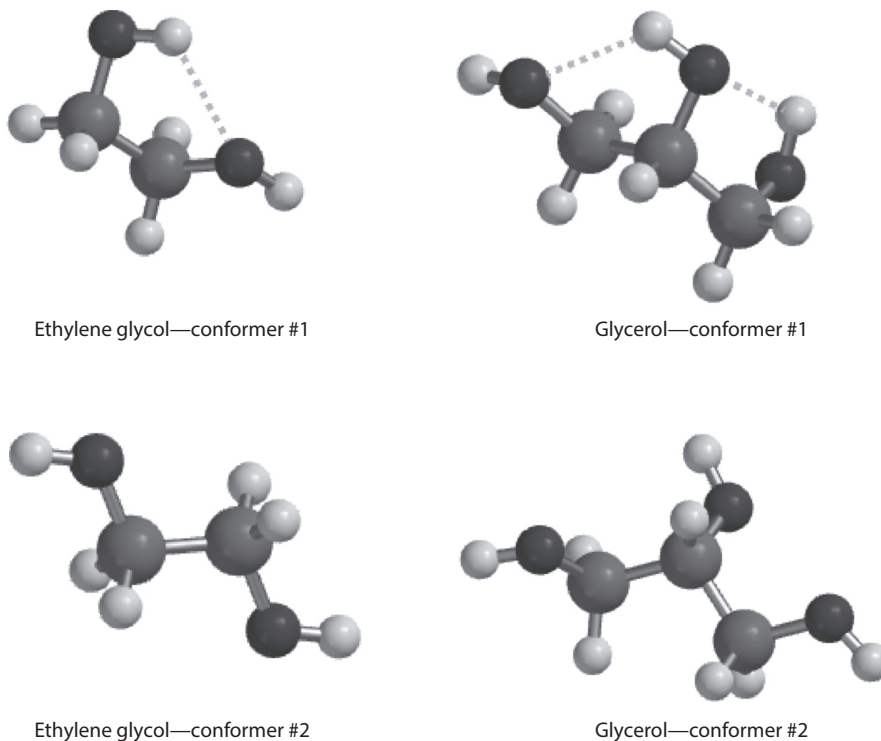


FIGURE 11.1 Conformers of ethylene glycol and glycerol with and without intramolecular hydrogen bonds (shown by dashed lines).

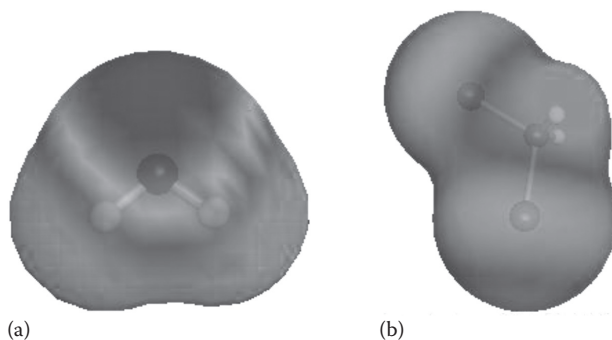


FIGURE 11.2 The COSMO surfaces of (a) water and (b) diiodomethane (DIM). The charge densities vary from highly negative (electron donor or proton acceptor) sites typically marked in deep red over oxygen atom to highly positive (electron acceptor or proton donor) sites marked in deep blue over hydrogen atoms. Intermediate densities are marked with intermediate colors of the visible color spectrum.

interface lower than its corresponding character in the bulk liquid. Such a possibility, however, is not very much available for molecules like water whose COSMO surface is shown in Figure 11.2 with its surface charge density marked in colors. No matter how oriented at the interface, the water molecule will always expose its polar/hydrogen-bonding sites away from the bulk liquid phase. As a consequence, the water molecule is expected to exhibit nearly its full hydrogen bonding capacity at the interface. On the other hand, apolar or less polar molecules, like diiodomethane shown also in Figure 11.2, are relatively more indifferent for specific orientations at interfaces other than those dictated by stereochemical constraints or space filling requirements. Since these two molecules are extensively used in the interface/wetting/adhesion literature, it is worth commenting briefly on their σ -profiles shown in Figure 11.3.

According to COSMO-RS convention, only charge densities in excess of $0.01 \text{ e}/\text{\AA}^2$ in absolute values are capable of participating in hydrogen bonds. As observed in Figure 11.3, the σ -profile of water molecule is nearly symmetric and extended beyond the hydrogen bonding cutoffs on both sides of the profile. This is in contrast to arguments often appearing in the literature for a much more acidic than basic character of water. The nearly symmetric σ -profile of water leads to nearly equal A and B LSER molecular descriptors, as we have seen in the previous section and corroborates our

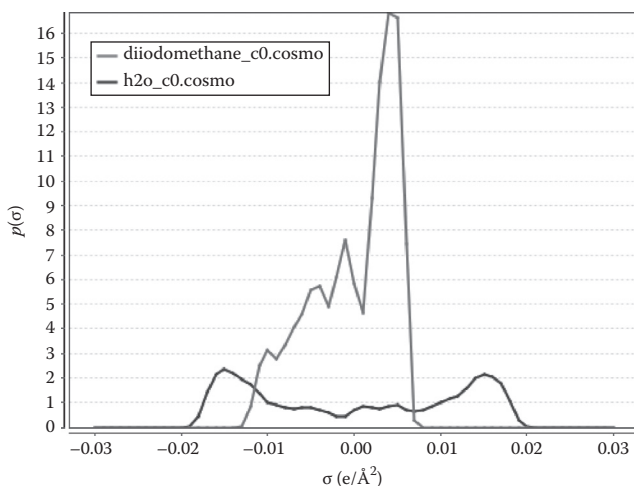


FIGURE 11.3 The sigma profiles of water and diiodomethane. The charge densities refer to the screening charges, that is, to the counter-charges of the real molecular charges.

selection of acidity/basicity scale based on the water neutrality. On the other hand, the σ -profile of the much used diiodomethane is somewhat asymmetric with a minor protrusion into the acidic domain, although its main polarity sites are populating the opposite domain of the profile. In other words, diiodomethane is not an apolar molecule and in no way we may consider it interacting with dispersion forces only.

From the preceding exposition, it becomes clear that preferential orientations and molecular conformations are of central importance at interfaces and ultimately dictate interfacial free energies. This free energy character of interfacial tension makes difficult the mapping of PSPs onto the corresponding surface tension components, γ_w , γ_{pz} , γ_a , and γ_b . We may proceed, however, by confining ourselves, first, to the weakest van der Waals interactions, namely, the London dispersive interactions and the mapping of σ_w into the dispersion or van der Waals surface tension component, γ_w .

From its very definition, σ_w is an energy density (energy per unit volume), while the corresponding surface tension component, γ_w , will be energy per unit area. In a real pure liquid, we could allocate to each molecule an average solvation area and an average solvation volume. The COSMO area, A_{cosm} , and COSMO volume, V_{cosm} , could be considered good measures for this solvation area and the solvation volume, respectively. We could, then, relate the preceding components through the basic defining equations:

$$V_{\text{cosm}}\sigma_w^2 = A_{\text{cosm}}\gamma_w = E_w \quad (11.12)$$

or

$$\gamma_w = \frac{V_{\text{cosm}}}{A_{\text{cosm}}}\sigma_w^2 \quad (11.13)$$

Equation 11.13 is an approximate equation, but it may satisfactorily serve our purpose. Of course, the other components of surface tension cannot be obtained by such a simple equation and, in order to proceed, we should turn to their free energy character. The appropriate equations in this case should resemble Equation 11.11 giving the hydrogen bonding free energy of interacting acidic and basic molecules. Quite generally, this free energy character may simply be expressed as follows:

$$\gamma = \gamma_w + \gamma_{pz} + \gamma_{hb} = \Gamma^h - T\Gamma^s \quad (11.14)$$

The components with superscript h will be referred to as enthalpic or energetic components and those with superscript s as entropic ones. γ_{pz} and γ_{hb} are the surface tension components arising from polarity/refractivity and hydrogen bonding interactions, respectively. Regarding hydrogen bonding quantities of interacting molecules i and j , their relation to PSPs could then be obtained from defining equations of the form (cf. Equations 11.11 and 11.13):

$$\Gamma_{ij}^h = h\sigma_{a,i}\sigma_{b,j}\sqrt{\frac{V_i}{A_i}\frac{V_j}{A_j}} = 2\sqrt{\Gamma_{a,i}^h\Gamma_{b,j}^h} \quad (11.15)$$

and

$$\gamma_{hb,ij} = f\sigma_{Ga,i}\sigma_{Gb,j}\sqrt{\frac{V_i}{A_i}\frac{V_j}{A_j}} + g = 2\sqrt{\gamma_{a,i}\gamma_{b,j}} \quad (11.16)$$

The ratios under the square roots are the solvation volume-to-surface area ratios for each type of interaction. It is not obvious how these ratios could be obtained but we will not need them here. Subscripts hb , a , and b in these equations are referring to the overall hydrogen bonding, to acidic, and to basic components, respectively. For simplicity, in this work, we will consider only one type of acidic and/or basic group per molecule. For pure hydrogen-bonded compounds, then, the defining Equation 11.16 becomes

$$\gamma_{hb} = 2\sqrt{\gamma_a\gamma_b} \quad (11.17)$$

For a molecule with similar acidic and basic character, there is no reason to expect that it will lose this similarity at the interface. For the purposes of this work then and on account of Equation 11.16, we will adopt the following equations:

$$\frac{\gamma_a}{\gamma_b} = \frac{\sigma_{Ga}\sigma_{Ghb}}{\sigma_{Ga}\sigma_{Ghb}} = \frac{\sigma_{Ga}}{\sigma_{Ga}} \quad (11.18)$$

If γ_{hb} were known, Equations 11.17 and 11.18 would form a system of two equations with two unknowns that could be solved for γ_a and γ_b . Even then, however, we would need additional information in order to calculate γ_{pz} . From the preceding discussion, we may expect that, as the molecule at the pure liquid–vapor interface is adopting orientations that will minimize its surface energy, its polar or hydrogen bonding groups are more likely to be oriented toward the bulk liquid phase rather than the interface. As a consequence, this tendency will affect, both, hydrogen bonding and polarity/polarizability components of its surface tension, at least to the extent that high surface charge densities may be counted either as hydrogen bonding sites when interacting with complementary hydrogen bonding sites or as polarity/polarizability sites when interacting with non-hydrogen bonding counterparts [17–21]. In view of this COSMO picture of real solvents and in order to proceed, we will also adopt the following equations:

$$\frac{\gamma_{pz}}{2\gamma_a} = \frac{\sigma_{pz}^2}{u\sigma_{Ga}\sigma_{Ghb}}, \quad \frac{\gamma_{pz}}{2\gamma_b} = \frac{\sigma_{pz}^2}{u\sigma_{Gb}\sigma_{Ghb}} \quad (11.19)$$

or

$$\frac{\gamma_{pz}}{2\sqrt{\gamma_a\gamma_b}} = \frac{\sigma_{pz}^2}{u\sigma_{Ghb}\sqrt{\sigma_{Ga}\sigma_{Gb}}} \quad (11.20)$$

The factor u should be, in general, a characteristic property of the molecule and should reflect the peculiarities of the molecular structure and the surface charge distribution that are not accounted for by the PSP terms in the rhs of the equations. This assumption facilitates calculations very much. If the total surface tension, γ , is known, then, Equation 11.14 along with Equations 11.17 through 11.19 form a system of four equations with four unknowns, namely, γ_{pz} , γ_{hb} , γ_a , and γ_b . The solution of this system is facilitated by noting from Equations 11.17 and 11.20 that

$$\gamma_{hb} = 2\sqrt{\gamma_a\gamma_b} = \gamma_{pz}u \frac{\sigma_{Ghb}\sqrt{\sigma_{Ga}\sigma_{Gb}}}{\sigma_{pz}^2} \quad (11.21)$$

Combining with Equation 11.14, we obtain

$$\gamma_{pz} + \gamma_{hb} = \gamma_{pz} \left(1 + u \frac{\sigma_{Ghb} \sqrt{\sigma_{Ga} \sigma_{Gb}}}{\sigma_{pz}^2} \right) = \gamma - \gamma_w \quad \text{or}$$

$$\gamma_{pz} = \frac{\gamma - \gamma_w}{\left(1 + u \left(\sigma_{Ghb} \sqrt{\sigma_{Ga} \sigma_{Gb}} / \sigma_{pz}^2 \right) \right)} \quad (11.22)$$

Then, from Equations 11.19 and 11.22 we may obtain γ_a , γ_b , and γ_{hb} . It is worth mentioning that the preceding equations hold for, both, homosolvated and heterosolvated compounds. For the latter, Equation 11.21 gives $\gamma_{hb} = 0$ while Equation 11.22 gives $\gamma_{pz} = \gamma - \gamma_w$. The important point is that the method (Equation 11.19) provides also with γ_a or γ_b components of heterosolvated compounds, for which $\gamma_{hb} = 0$.

The experimental surface tensions of many common liquids are available in the open literature or in critical compilations such as the DIPPR database [27]. From these total surface tensions, one may then obtain the partial surface tensions by using the preceding set of simple equations. Equation 11.13 should be used first in order to obtain γ_w . The value of factor u , however, has not been specified yet.

It is important to point out that for a compound with equal acidic and basic PSPs ($\sigma_{Ga} = \sigma_{Gb}$), the preceding method implies that its corresponding acidic and basic surface tension components will also be equal. This is the case for water in the PSP approach. The COSMO volume and area for water are equal to 0.0256 and 0.4306 nm², respectively [19]. Substituting in Equation 11.13, we obtain $\gamma_w = 15.71$ mN/m. The DIPPR value for the total surface tension of water at 20°C is 72.8 mN/m. By replacing in Equations 11.19 through 11.22, we obtain the other three surface tension components as functions of factor u . The results are reported in Table 11.2 while in Figure 11.4 is shown the variation of the hydrogen bonding component, γ_a or γ_b , with factor u . In the same figure is also shown that the van Oss [4–6,28] value of 25.5 mN/m for these components corresponds to a value near 2 for the factor u . In order, then, to further simplify our method and have a nearly common reference point with the vOCG approach [4–6,28], we set $u = 2$ and consider it a universal constant applicable to all compounds.

In Table 11.3 are reported the COSMO volumes and areas and the surface tension components for a number of common solvents as calculated by the preceding method. In the last column are reported the total surface tensions as obtained from DIPPR [27]. It should be stressed that the values of the surface tension components in Table 11.3 are predicted ones and not fitted to experimental data other than the overall surface tension of the compound.

TABLE 11.2
The Polar and Hydrogen-Bonding Surface Tension Components of Water for Various Values of the Factor u (Equations 11.19 through 11.22)

u	γ_{pz}	γ_a, γ_b	$\gamma_{hb}/\gamma_{total}$
0.75	12.47	22.31	0.61
1	9.90	23.60	0.65
2	5.42	25.84	0.71
3	3.73	26.68	0.73
4	2.84	27.12	0.75

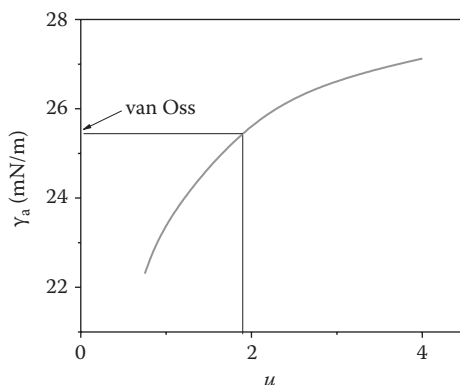


FIGURE 11.4 The HB component of surface tension, γ_a or γ_b , of water as a function of the factor u in the defining Equations 11.19 through 11.22. As shown, the adopted value of 25.5 mN/m by the vOCG approach [4–6,28] corresponds to a value of u near 2.

The major part of the sum of γ_W and γ_{pz} , presumably, corresponds to the widely used Lifshitz–van der Waals surface tension [4–6,28], or

$$\gamma_W + \gamma_{pz} \cong \gamma^{LW} \quad (11.23)$$

The calculations with Equation 11.23 and Table 11.3 are in reasonably good agreement with the reported values for the Lifshitz–van der Waals surface tension component in the literature [4–6,28]. As an example, the γ^{LW} calculated from Equation 11.23 for methanol, ethanol, glycerol, and water are 17.23, 18.03, 31.97, and 21.13 mN/m, respectively, while the corresponding reported values [28] are 18.5, 20.1, 34.0, and 21.8 mN/m, respectively. Having the partial surface tensions of pure solvents, we may now proceed to the next step and propose a method for the surface-tension characterization of polymers and solid surfaces.

The preceding procedure may be applied to polymers and smooth solid surfaces although there are some noticeable difficulties. The problems in this case start with the estimation of γ_W . As already mentioned, it is not possible at present to run quantum chemical calculations for high polymers. The required ratio of COSMO volume-to-surface area of a polymer could be obtained, as an example, from its monomer or its oligomer analogs through the following equation:

$$\left(\frac{V_S}{A_S}\right)_{\text{polymer}} = \left(\frac{V_{\text{cosm}}}{A_{\text{cosm}}}\right)_{\text{monomer}} \left(\frac{r}{q}\right)_{\text{polymer}} \left(\frac{q}{r}\right)_{\text{monomer}} \quad (11.24)$$

q , r being the UNIQUAC/UNIFAC-type parameters [29,30]. The higher the oligomer analog the better is expected to be the approximation with Equation 11.24. When the molecular structures of the solid surface are more complex (branched, cross-linked, dendritic, etc.), Equation 11.24 will be a rather poor approximation. The simplest solution in these cases is the use of one or two experimental data of contact angles with non-hydrogen bonding solvents in order to obtain γ_W and substitute in Equations 11.19 through 11.22 in order to obtain all other surface tension components. However, this requires first an equation for the contact angle or for the work of adhesion or for the interfacial tension. This is done in the next section.

11.2.1 DERIVATION OF THE PSP EQUATION FOR THE WORK OF ADHESION

The contributions of the various PSP terms in mixing quantities in the case of bulk phases have been discussed in References 14–16. In Reference 14 it was shown that the van der Waals and the

TABLE 11.3
The Partial Surface Tensions of Common Pure Compounds

Compound	V_{cosm} (nm ³) [19]	A_{cosm} (nm ²) [19]	γ_w (mN/m)	γ_{pz} (mN/m)	γ_b (mN/m)	γ_a (mN/m)	γ (mN/m) [27]
<i>n</i> -Hexane	0.1457	1.569	17.56	0.35	0	0	17.91
<i>n</i> -Heptane	0.1676	1.7689	17.91	1.90	0	0	19.83
<i>n</i> -Octane	0.1895	1.9684	18.21	2.90	0	0	21.13
<i>n</i> -Nonane	0.2113	2.1679	18.46	3.95	0	0	22.40
<i>n</i> -Decane	0.2333	2.3678	18.68	4.70	0	0	23.39
<i>n</i> -Dodecane	0.2768	2.7664	18.97	5.95	0	0	24.93
<i>n</i> -Hexadecane	0.3664	3.5686	19.49	7.65	0	0	27.15
<i>n</i> -Octadecane	0.4089	3.9657	19.49	8.55	0	0	28.01
<i>n</i> -Eicosane	0.4527	4.3648	19.46	9.10	0	0	28.56
<i>n</i> -Docosane	0.4965	4.7636	19.45	9.50	0	0	28.97
<i>n</i> -Tetracosane	0.5403	5.1626	19.42	9.80	0	0	29.29
<i>n</i> -Octacosane	0.6274	5.9555	19.36	10.35	0	0	29.71
Cyclohexane	0.1263	1.3149	18.20	6.45	0	0	24.64
Cycloheptane	0.1498	1.4863	19.25	7.75	0	0	26.99
Benzene	0.1100	1.2137	19.95	8.25	0	0	28.21
Toluene	0.1318	1.4055	19.95	8.00	0	0	27.92
Ethylbenzene	0.1539	1.5860	20.14	8.40	0	0	28.59
<i>n</i> -Propylbenzene	0.1762	1.7865	20.18	8.40	0	0	28.50
<i>n</i> -Butylbenzene	0.1980	1.9860	20.20	8.45	0	0	28.64
Acetaldehyde	0.0643	0.8288	15.93	4.83	6.62	0	20.76
1-Propanal	0.0853	1.0150	16.73	5.23	8.01	0	21.96
1-Butanal	0.1074	1.2153	17.32	7.63	10.02	0	24.95
1-Pentanal	0.1294	1.4194	17.69	7.64	6.50	0	25.33
Acetone	0.0863	1.0268	16.72	6.32	6.57	0	23.04
Methyl ethyl ketone	0.1070	1.2065	17.34	6.62	6.62	0	23.96
Methanol	0.0484	0.6756	16.51	0.72	2.76	2.26	22.22
Ethanol	0.0700	0.8811	17.04	0.99	2.36	1.76	22.10
1-Propanol	0.0918	1.0805	17.04	0.99	2.36	1.76	23.39
1-Butanol	0.1139	1.2814	17.75	1.37	2.47	1.85	24.37
1-Pentanol	0.1355	1.4820	18.18	1.85	2.53	1.86	25.30
1-Hexanol	0.1578	1.6831	18.51	1.92	2.78	2.13	25.90
1-Heptanol	0.1794	1.8818	18.79	2.02	2.92	2.21	26.71
1-Octanol	0.2014	2.0812	18.96	2.62	2.97	2.22	27.10
1-Decanol	0.2449	2.4766	19.15	2.81	3.00	2.20	28.38
2-Pentanol	0.1354	1.4548	18.42	1.55	2.04	1.49	23.45
Cyclohexanol	0.1391	1.4226	19.43	6.35	4.63	3.15	33.42
Ethylene glycol	0.0805	0.9784	18.92	10.82	10.23	8.14	47.99
Glycerol	0.1118	1.2151	19.51	22.46	12.88	8.83	63.30
Tetraethylene glycol	0.2468	2.5551	19.94	8.05	14.77	5.87	46.61
Ethyl acetate	0.1173	1.3316	16.9	6.34	7.33	0.00	23.24
<i>n</i> -Propyl acetate	0.1393	1.5329	17.31	6.55	6.52	0.00	23.86
<i>n</i> -Butyl acetate	0.1611	1.7323	17.65	7.1	5.55	0.00	24.75
Carbon tetrachloride	0.1284	1.3421	26.00	1.00	0	0	27.00
Diiodomethane	0.1164	1.2537	32.71	17.21	0	0	49.92
<i>n</i> -Propylamine	0.0968	1.1245	16.16	1.29	3.67	1.05	21.38
<i>n</i> -Butylamine	0.1186	1.3228	17.2	1.93	4.17	1.21	23.62
Formamide	0.0575	0.7675	17.56	12.74	14.79	13.34	58.40
Dimethyl sulfoxide	0.0988	1.1167	21.14	8.90	40.34	1.03	42.95
Water	0.0256	0.4306	15.71	5.42	25.84	25.84	72.80

polarity/polarizability interactions are contributing with quadratic terms of PSP differences while the hydrogen bonding interactions with logarithmic terms of equilibrium constants, K_{ij} , for the hydrogen bonding between a proton donor (acidic) molecule i and a proton acceptor (basic) molecule j . Assuming analogous contributions at interfaces, Equation 69 of Reference 14 for the residual free energy at infinite dilution per unit volume or the compatibility of components i and j , rewritten here for convenience,

$$\frac{\Delta G_{ij}^{r,\infty}}{V_{mol,i}} = \left\{ (\sigma_{wi} - \sigma_{wj})^2 + (\sigma_{pzi} - \sigma_{pzj})^2 - \frac{RT}{V_{mol,i}} \ln \left(1 + \frac{a}{r_j} K_{ij} \right) \right\} \quad (69, \text{Reference 14})$$

could be translated into the following equation for the interfacial tension (or compatibility of surfaces i and j):

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{w,i}} - \sqrt{\gamma_{w,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 - \frac{RT}{V_{mol,i}} \ln \left(1 + \frac{a}{r_j} K_{ij} \right) \right\} \quad (11.25)$$

Assuming one interacting site per segment (or, $a/r_j = 1$) and equilibrium constants significantly larger than 1, Equation 11.25 reduces to the following simple equation for cross-associating compounds:

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{w,i}} - \sqrt{\gamma_{w,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 - \frac{RT}{V_{mol,i}} \ln(K_{ij}) \right\} \quad (11.25a)$$

The corresponding equation for molecules able to self-associate and cross-associate becomes:

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{w,i}} - \sqrt{\gamma_{w,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 - \frac{RT}{V_{mol,i}} \ln \left(\frac{K_{ij}}{K_{ii}} \right) - \frac{RT}{V_{mol,j}} \ln \left(\frac{K_{ji}}{K_{jj}} \right) \right\} \quad (11.26)$$

The equilibrium constants K_{ij} are related to hydrogen bonding free energies through the classical equation:

$$-RT \ln K_{ij} = G_{ij}^H \quad (11.27)$$

Substituting from Equation 11.27, Equations 11.25a and 11.26 further simplify to the following forms:

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{w,i}} - \sqrt{\gamma_{w,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 + \frac{G_{ij}^H}{V_{mol,i}} \right\} \quad (11.25b)$$

and

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{w,i}} - \sqrt{\gamma_{w,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 + \frac{G_{ij}^H - G_{ii}^H}{V_{mol,i}} + \frac{G_{ji}^H - G_{jj}^H}{V_{mol,j}} \right\} \quad (11.26a)$$

The last terms, however, in these equations are energy densities and are more appropriate to PSPs rather than to surface tension components that are energies per unit area. Thus, they also need to

be translated into γ terms. This translation is facilitated by the inspection of Equations 11.11 and 11.16 or 11.17, which are the defining equations for the bulk and interface free energy changes upon hydrogen bond formation. Substituting the analogous terms, Equations 11.25b and 11.26a become

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{W,i}} - \sqrt{\gamma_{W,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 + 2\sqrt{\gamma_{a,i}\gamma_{b,j}} \right\} \quad (11.25c)$$

and

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{W,i}} - \sqrt{\gamma_{W,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 + 2 \left(\sqrt{\gamma_{a,i}\gamma_{b,j}} - \sqrt{\gamma_{a,i}\gamma_{b,i}} \right) + 2 \left(\sqrt{\gamma_{a,j}\gamma_{b,i}} - \sqrt{\gamma_{a,j}\gamma_{b,j}} \right) \right\} \quad (11.26b)$$

or

$$\gamma_{ij} = \left\{ \left(\sqrt{\gamma_{W,i}} - \sqrt{\gamma_{W,j}} \right)^2 + \left(\sqrt{\gamma_{pz,i}} - \sqrt{\gamma_{pz,j}} \right)^2 + 2 \left(\sqrt{\gamma_{a,i}} - \sqrt{\gamma_{a,j}} \right) \left(\sqrt{\gamma_{b,i}} - \sqrt{\gamma_{b,j}} \right) \right\} \quad (11.26c)$$

Equation 11.25c is a special case of Equation 11.26c and holds for molecules that cross-associate but do not self-associate (heterosolvated; we avoid the terms monopolar and bipolar used with vOCG model because polar interactions are distinct from hydrogen bonding interactions here). Our discussion will focus then on the general Equation 11.26c. As observed, the last term in this equation is identical to the hydrogen bonding term of the vOCG equation [4–6,28]. The preceding derivation was useful in delineating the assumptions behind this term. Expanding terms in Equation 11.26c and replacing for pure components, we obtain

$$\gamma_{ij} = \gamma_i + \gamma_j - 2 \left\{ \sqrt{\gamma_{W,i}\gamma_{W,j}} + \sqrt{\gamma_{pz,i}\gamma_{pz,j}} + \sqrt{\gamma_{a,i}\gamma_{b,j}} + \sqrt{\gamma_{a,j}\gamma_{b,i}} \right\} \quad (11.27)$$

which, combined with Dupre equation (11.1), gives for the work of adhesion:

$$W_{ij}^{adh} = 2 \left\{ \sqrt{\gamma_{W,i}\gamma_{W,j}} + \sqrt{\gamma_{pz,i}\gamma_{pz,j}} + \sqrt{\gamma_{a,i}\gamma_{b,j}} + \sqrt{\gamma_{a,j}\gamma_{b,i}} \right\} \quad (11.28)$$

From Young's Equation 11.2, then, we obtain for the contact angle of a drop of liquid, L , on a solid surface, S , the following working equation:

$$\gamma_L(1 + \cos\theta) = 2 \left\{ \sqrt{\gamma_{W,L}\gamma_{W,S}} + \sqrt{\gamma_{pz,L}\gamma_{pz,S}} + \sqrt{\gamma_{a,L}\gamma_{b,S}} + \sqrt{\gamma_{a,S}\gamma_{b,L}} \right\} \quad (11.29)$$

This is the desired equation, which may be now applied for the characterization of polymer and solid surfaces.

11.3 APPLICATIONS

In this section, we apply Equation 11.29 for the characterization of polymer surfaces on the basis of their PSPs. PSPs for some common polymers [15,16] are reported in Table 11.4. In order to use Equation 11.29 for the prediction of surface tension components of polymers, as we did for liquids in the previous section, we must have first γ_W , which in turn requires A_{cosmo} and V_{cosmo} values. Since

TABLE 11.4
Partial Solvation Parameters of Common Polymers

Polymer	σ_w	σ_{pz}	σ_{Gb}	σ_{Ga}
Polyethylene, HDPE	13.75	9.00	0.0	0.0
Polyethylene, LDPE	13.75	7.75	0.0	0.0
Polypropylene, PP	14.05	5.05	0.0	0.0
Poly(ethyl ethylene), PEE	14.60	5.00	0.0	0.0
Polystyrene, atactic, PS	15.20	7.00	0.0	0.1
Poly(methyl acrylate), PMA	18.00	15.80	9.85 ± 0.40	0.0
Poly(ethyl acrylate), PEA	18.30	11.50	9.0 ± 0.15	0.0
Poly(methyl methacrylate), PMMA	18.50	7.80	7.55 ± 0.70	0.0
Poly(butyl methacrylate), PBMA	17.80	7.50	7.6 ± 0.25	0.0
Poly(hydroxy-ethylacrylate), PHEA	20.80	19.55	4.0 ± 0.20	7.5
Poly(vinyl chloride), PVC	18.50	13.95	0.0	4.2 ± 1.2
Polyepichlorohydrin, PECH	17.30	15.45	7.5	3.0 ± 1.1
Poly(ϵ -caprolactone), PCL	18.55	9.80	8.25 ± 0.25	0.0
Hyperbranched, Boltorn H ₂ O	19.95	5.65	10.45 ± 0.15	0.0
Poly(dimethyl siloxane), PDMS	14.50	3.70	5.15 ± 0.15	0.0
Poly(vinyl methyl ether), PVME	16.55	11.25	6.9 ± 0.20	0.0
Polytetrahydrofuran, PTHF	14.85	11.20	9.2	0.0
Poly(ethylene oxide), PEO	16.40	15.70	10.6	0.0

these values cannot be obtained directly for high polymers, we should resort to approximate values from analog oligomers. In Table 11.5 are reported such values for a number of analogs. As observed, there is a non-negligible scatter of values around the average ratio of 0.096. Even for polyethylene, the uncertainty from using data from its analogs may be as high as 5%. From Table 11.3, we observe that γ_w tends to a limiting value of 19.4 mN/m as the size of *n*-alkane increases. On the other hand, using the two ratios of Table 11.5 and the value of 13.75 MPa^{1/2} for the σ_w PSP of polyethylene

TABLE 11.5
The $V_{\text{cosmo}}/A_{\text{cosmo}}$ Ratio for Analog Oligomers

Polymer	Analog	A_{cosmo} (nm ²)	V_{cosmo} (nm ³)	$V_{\text{cosmo}}/A_{\text{cosmo}}$	γ_w , Pred (mN/m)
PE	Tetradecane	3.1652	0.3211	0.101	19.5 ± 0.5
PE	Hexatriacontane	7.5481	0.8034	0.106	
PP	2,4-Dimethylpentane	1.847	0.190	0.101	20.0 ± 1.0
PP	2,4,6-Trimethylheptane	2.2058	0.2355	0.107	
PVC	Vinyl chloride	0.934	0.076	0.082	28.0 ± 4.0
PVC	2,4-Dichloropentane	1.6962	0.1707	0.101	
PEO	Triethyleneglycol <i>n</i> -propylether	2.6554	0.2561	0.096	26.5 ± 0.5
PEO	Tetraethyleneglycol monomethylether	2.7662	0.2687	0.097	
PEO	Tetraethyleneglycol monobutylether	3.4051	0.3352	0.098	
PS	Styrene	1.5445	0.1476	0.096	22.5 ± 1.0
PS	Ethylbenzene	1.5902	0.1544	0.097	
PVAc	Vinylacetate	1.296	0.1127	0.087	23.0 ± 4.0
PVAc	Ethylacetate	1.3345	0.1175	0.088	
PMMA	Methylmethacrylate	1.4487	0.1342	0.093	33.0 ± 1.0
Average				0.096	

[15,16], we obtain for γ_w the values of 19.1 and 20.0 mN/m. These results lead to an estimated or predicted value of 19.5 ± 0.5 mN/m for the γ_w of polyethylene. Following this procedure, predicted values for γ_w have been obtained for other polymers and are reported in the last column of Table 11.5. The observed large uncertainties for poly(vinyl acetate) (PVAc) and poly(vinyl chloride) (PVC) are due to the large discrepancies between the σ_w of high polymers and of their analog oligomers. Such discrepancies are sometimes unavoidable in view of the fact that the available inverse-gas chromatography (IGC) data are for relatively high temperatures. In these cases of large uncertainties, one may resort to the use of Equation 11.29 with experimental contact angle data for a couple of solvents. Having γ_w , in the one or in the other way, one may follow the procedure of the previous section and predict all other surface tension components of the polymers. Surface tensions of pure polymer surfaces are, however, needed in this procedure.

In their seminal paper, Owens and Wendt [31] have reported surface tension and contact angle data for a number of polymers, which have been widely used as reference data in the literature. These data are reproduced in Table 11.6 for the polymers with available PSPs. In each row of the table there are two sets of data. The upper set uses the experimental contact angle data and calculates the surface tension components of the polymers on the basis of these experimental data. The lower set (in *italics*) gives the predicted surface tension components by the present approach and uses these components in order to predict the contact angles as well. As observed, the calculated surface tension components are in rather satisfactory agreement with the predicted ones. On the other hand, the predicted contact angles with diiodomethane (DIM) are in very good agreement with the experimental ones. As regards contact angles with water, this approach overpredicts them for polystyrene and to a lesser extent for poly(vinyl chloride). The failure for polystyrene may be due to the fact that COSMO-RS and, thus, PSP does not consider the interactions with the pi-electrons of the aromatic ring as hydrogen bonding. This holds true, unless this particular polystyrene surface had acquired extraneous polar groups, which is often the case with such data in the literature. The failure for PVC originates from a rather too high value for σ_w from IGC data, which leads to a high value for γ_w , which, in turn, leads to a low value for γ_{pz} and, thus, a low value for γ_a . The overall picture, however, is rather satisfactory. The important message of the calculations reported in Table 11.6 is that Equation 11.29 along with the surface tension components of solvents from Table 11.3 may be used for a rather reliable estimation of the surface tension components of polymers. In fact, they may be used for the characterization of any smooth solid surface regardless of whether PSP data are available or not.

Before proceeding further or before embarking into calculations of surface tension components for surfaces with unknown PSPs, we should clarify the methodology and set guidelines for the procedure. The first thing we should keep in mind is the potential existence of numerous surfaces

TABLE 11.6
The Surface Tension Components of Polymers

Polymer	γ_{total} (mN/m)	θ , Water	θ , DIM	γ_w	γ_{pz}	γ_a	γ_b
Polyethylene	33.2	104	53	19.7	13.5	0	0
		<i>106</i>	<i>51</i>	<i>19.5</i>	<i>13.7</i>	0	0
Poly(vinyl chloride)	41.5	87	36	24.4	17.1	3.2	0
		<i>92</i>	<i>35</i>	<i>28.0</i>	<i>13.5</i>	<i>1.2</i>	0
Poly(methyl methacrylate)	40.2	80	41	32.7	7.5	0	7.0
		<i>81</i>	<i>40</i>	<i>33.0</i>	<i>7.2</i>	0	<i>6.8</i>
Polystyrene	42.0	91	35	23.5	18.2	0	1.5
		<i>100</i>	<i>35</i>	<i>22.5</i>	<i>19.5</i>	0	0

Source: Data by Owens, D.K. and Wendt, R.C., *J. Appl. Polym. Sci.*, 13, 1741, 1969.

for the same polymer, depending on intrinsic and extrinsic factors ranging from molecular size distribution, microstructure or end groups, up to specific surface treatment and conditioning. The second thing to keep in mind is that a theoretical approach like PSP can predict unique properties of surfaces if there are such unique properties. If the surface is not clean and not at equilibrium or the probe affects the surface properties, it is difficult to extract unique surface properties. An inspection in the compilation of experimental contact angles on polymers by Lyklema [32] reveals this non-unique property problem. As an example, even for polyethylene, the reported advancing contact angle with water ranges from 28 to 116. Obviously, these polyethylene surfaces are not identical (if the measurements have been conducted properly).

The probe effect on the surface properties is a crucial issue in the study of these interfacial phenomena. It is then worth examining if the current approach can predict contact angles with other solvents on the polymers of Table 11.6. In Table 11.7 are reported such predicted contact angles with four additional solvents.

The results in Table 11.7 deserve several comments. First of all, there are two sets of predictions. Those marked in *italics* are absolute predictions directly from the corresponding PSPs. The other set was obtained from the calculated (modified) surface tension components reported in Table 11.6 in order to reproduce the experimental contact angle data with water and/or DIM. As observed, the predictions with both sets fall, essentially, within the range of measured values. With the expected exception of PVC, the predictions by the two sets are very similar. A similar to PVC discrepancy was expected for polystyrene, on the basis of the data in Table 11.6. As observed in Table 11.7, the absolute predictions for polystyrene are much better than the predictions with the modified surface tension components. This probably indicates that the surface of the polystyrene sample in Table 11.6 may have not been very clean. It is essential to point out that with both sets of predictions, the defining Equations 11.18 through 11.20, which interrelate the polarity/polarizability, acidity, and basicity components, were respected. This is important when a hydrogen bonding solvent is used as a probe of the corresponding character of the solid surface as it cannot attribute arbitrary values in one surface tension component disregarding the others. This in turn guarantees that the hydrogen bonding character of all surfaces, liquid or solid, will be compatible with their bulk-phase hydrogen bonding character and, thus, the information may be interchanged.

TABLE 11.7
Experimental and Predicted Contact Angles on the Polymers of Table 11.6

Polymer	θ , Ethylene Glycol		θ , Formamide		θ , Glycerol		θ , DMSO	
	Predicted	Experim.	Predicted	Experim.	Predicted	Experim.	Predicted	Experim.
Polyethylene	72	69 ^a	85	a77–81	80	a79–94	63	
	72		85		80	r53–56	63	
Polystyrene	52	60 ^a	67	a69–88	64	a71–80	44	
	62		77	r35–70	71		49	
PVC	45	45.7 ^b	63	a55–66	59	a67–69	<0	Swollen ^b
	52		69	56.9 ^a	65	61.8 ^a	14	
PMMA	43	36.8 ^b	61	a51–64, 41 ^a	63	a60–69	43	12 ^b
	44		61		63	58.1 ^b	45	

Experimental data from the compilation of Lyklema [32] unless otherwise specified. Advancing and receding contact angle data are marked with a and r in front, respectively. Calculations in italics are absolute predictions.

^a Dann [33].

^b Della Volpe et al. [34] equilibrium data.

11.4 DISCUSSION AND CONCLUSIONS

The new approach to wetting/adhesion and contact angles described and tested in the previous two sections is based on a drastically different picture of interfacial interactions from that of the vOCG approach [4–6,28]. In the new approach, the surface character of a liquid or a solid at equilibrium is dictated by the solvation character of the compound as expressed by its partial solvation parameters and the requirement for interfacial free energy minimization. This forces the molecules to assume conformations and preferential orientations at interface that will probably keep the molecular sites with high interaction energies toward the bulk phase and away from the interface. As a consequence, the polar or hydrogen bonding character of surfaces of pure compounds is, in general, significantly lower than the corresponding bulk-phase character. We may get a feeling of this difference by calculating the ratio of hydrogen bonding character over the non-hydrogen bonding character in bulk liquid and at the liquid–vapor interface for alkanols. The results are summarized in Table 11.8. As seen, methanol has over five times higher hydrogen bonding character in bulk over the vapor–liquid interface. Even octanol has near two-times higher hydrogen-bonding character in its bulk liquid phase over the liquid–vapor interface. The last column in Table 11.8 indicates the extent of the earlier-mentioned preferential orientations at the interface. Obviously, when these surfaces will come in contact with a polar or hydrogen bonding liquid, these orientations will change and the molecule will exercise its full hydrogen bonding capacity. Depending on the liquid in contact, this may lead to full miscibility.

The case of solid polymer surfaces may be somewhat different depending on whether the polymer is below or above its glass transition temperature and/or melting point. Chain molecules in the glassy or crystalline state are frozen or possessing reduced flexibility for translation and rotation. In order to assume their equilibrium surface conformations, they should be given sufficient time at annealing conditions so that they keep their polar sites with high interaction energies preferentially oriented toward the bulk. When a liquid drop comes in contact with the surface, it will first sense this equilibrium surface character of the polymer, which may be significantly less polar compared to the bulk character. However, if the liquid will remain on the surface for sufficient time, depending on its own polarity, it may act as a local surface plasticizer facilitating main chain or pendant group rotations that may bring on the surface its polar sites. In other words, the liquid may “polarize” the polymer surface [10,11] and reveal (part of) its polar character. Depending on the extent or speed of plasticization, this may take some time. This lag in time may explain the observed contact angle hysteresis and why the advancing angles are always higher than the receding ones. As observed in Table 11.7, the predictions with the modified set of surface tension components are always lower than the absolute predictions of the present approach. The latter reflect the initial equilibrium state

TABLE 11.8
Comparison of Hydrogen Bonding Character in Bulk and in Liquid–Vapor Interface

Alkanol	$B = \frac{\sigma_{hb}^2}{\sigma_w^2 + \sigma_{pz}^2}$	$S = \frac{\gamma_{hb}}{\gamma_w + \gamma_{pz}}$	B/S
Methanol	1.636	0.290	5.645
Ethanol	1.066	0.226	4.716
Ethanol	1.066	0.226	4.716
1-Propanol	0.823	0.223	3.685
1-Butanol	0.656	0.217	3.025
1-Pentanol	0.638	0.238	2.680
1-Hexanol	0.587	0.244	2.399
1-Heptanol	0.501	0.238	2.104
1-Octanol	0.458	0.234	1.956
1-Decanol	0.375	0.227	1.652

of the pure polymer surface while the former its “polarized” state. Contact angles of absolute predictions are, thus, expected to be closer to advancing contact angles while the ones predicted with the modified surface tension components could be considered to be closer to the receding ones if one could exclude solvent molecules adsorbed on the surface in the receding front.

There are two important points to be made in relation with the vOCG model [4–6,28]. As we have seen, in the present approach there is a direct correspondence of the acidity/basicity surface character of a compound to its corresponding bulk character. In contrast, in the vOCG approach, this correspondence is lost and the basicity character appears disproportionately prevailing. In parallel, the water neutrality hypothesis (equal acidity and basicity) of the original vOCG model is sound and fully supported by quantum chemical calculations and QSPR/LSER data. Any attempts in the literature to drastically alter this neutrality may have improved the fitting performance but they may have obscured the physical basis and the insight in the studied interfacial phenomena.

It should be stressed again that the polymer PSPs used in this work are those obtained from IGC (cf. Table 11.4) at relatively high temperatures. No attempt was made to correct for any temperature dependence. In a refinement of the model, one could certainly account for it. Such an account of temperature dependence could bring σ_w from IGC for high polymers closer to the corresponding one from oligomers.

In conclusion, the present approach to surface tension components has some apparent similarities with the vOCG model [4–6,28] but, in essence, it is a drastically different approach. The key feature is that it provides with a sound basis for the interactions dictating interfacial phenomena, which is fully compatible with the picture we have about intermolecular interactions from quantum chemical calculations. The new approach has not been tested extensively yet, but the tests of this work are indicating a rather satisfactory agreement with experiment. Work is underway in our laboratory toward a more extensive testing of the new approach against experimental data.

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