INTERACTIONS OF COMPONENTS AND ELEMENTS OF THE SURFACE FREE ENERGY AT INTERFACES

Jan KLOUBEK

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 182 23 Prague 8

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A new hypothesis is suggested for the evaluation of the components (γ^{d} and γ^{ab}) and the elements (γ^{a} and γ^{b}) of the surface free energy. The respective equations are introduced for the interactions at interfaces between a non-polar acid and non-polar base, a polar phase and non-polar acid or base, and two polar phases. The dispersion component, γ^{d}, equals the total surface free energy of non-polar phases. However, they can interact at the interface as an acid or a base through their single permanent elements γ^{a} or γ^{b}, respectively. Otherwise, induced elements γ^{ia} and γ^{ib} can also be effective. The surface free energy of polar phases is additively composed of the dispersion, γ^{d}, and acid-base components, $\gamma^{ab} = 2(\gamma^{a}\gamma^{b})^{1/2}$. The proposed equations are verified using the known values of the surface and interfacial free energies for the liquid–liquid systems and they are applied to the solid–liquid interfaces. The values of the elements are determined for water, $\gamma^{a}_{W} = 67{\cdot}7$ and $\gamma^{b}_{W} = 10{\cdot}6$ mJ/m^2, and for other liquids, such as glycerol, formamide, mercury, benezene, diethyl ether and trichloromethane.

The determination of the surface free energy of solids, γ_S, is one of the problems which have not yet been solved satisfactorily. There are various methods of calculation, based on the evaluation of the contact angles of liquids on solid surfaces, but the accuracy and the correctness of these methods remain a matter for controversial discussion, as there is no independent method for reliable verification of the calculated γ_S values. The work of adhesion, W_A, between two liquids can be used as a criterion of the correctness of calculation methods because the surface free energy of liquids and the respective interfacial free energy, in contrast to solids, can be measured directly. Fowkes[1] employed this procedure when he proposed his theory. Various related methods were checked in the same way[2].

Fowkes[1] suggested the distribution of the surface free energy into the ever-present London (dispersion) component, γ^{d}, and the other components, such as the Keesom (polar), γ^{p}, Debye (induction), γ^{i}, and hydrogen bond, γ^{h}, components, These non-dispersion components have often been combined and denoted as γ^{n}. Accordingly, the equation

$$\gamma = \gamma^{d} + \gamma^{n} \qquad (1)$$

has been used. Later, Fowkes[3] introduced the acid-base component, γ^{ab}. He also proposed the additivity of the partial works of adhesion, which he expressed by the relationship

$$W_A = W_A^d + W_A^p + W_A^i + W_A^h + W_A^{ab} + \ldots \qquad (2)$$

The dispersion component of the work of adhesion is given by the geometrical mean of the dispersion components of the surface free energies of the adjoining phases 1 and 2

$$W_A^d = 2\,(\gamma_1^d \gamma_2^d)^{1/2}\,. \qquad (3)$$

In contrast to Eq. (*3*), Fowkes[3] denied the validity of the geometrical mean for other components, i.e., $W_A^h \neq 2(\gamma_1^h \gamma_2^h)^{1/2}$ or $W_A^{ab} \neq 2(\gamma_1^{ab} \gamma_2^{ab})^{1/2}$. Nevertheless, the equations introduced by Owens and Wendt[4],

$$W_A = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^h \gamma_2^h)^{1/2}\,, \qquad (4)$$

or by Kaelbe and Uy[5],

$$W_A = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2}\,, \qquad (5)$$

or by Kitazaki and Hate[6],

$$W_A = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} + 2(\gamma_1^h \gamma_2^h)^{1/2}\,, \qquad (6)$$

were accepted by many authors and they are still frequently used.

On the other hand, Neumann at al.[7,8] argued against the validity of Eqs (*3*)–(*6*). They believe that the dispersion and polar forces do not act separately at the interface. They tried to prove that the work of adhesion is a function of the total values of the surface free energy and not of any of the separate components.

Van Oss et al.[9] combined all the long range forces, i.e., London, Keesom and Debye forces into one component, which they call Lifshits–van der Waals or apolar and denote γ^{LW}. Their second component represents the short range forces which cause the acid–base interaction and it is denoted γ^{AB}. Accordingly, instead of Eq. (*1*), the authors[9] write

$$\gamma = \gamma^{LW} + \gamma^{AB}\,. \qquad (7)$$

In later communications[10,11], these authors divided the component γ^{AB} into an element acting as the Bronsted or Lewis acid (i.e. proton donor or electron acceptor), γ^+, and an element acting as the Bronsted or Lewis base (i.e. proton acceptor or electron donor), γ^-. They suggested the relationships

$$\gamma^{AB} = 2(\gamma^+ \gamma^-)^{1/2} \qquad (8)$$

and

$$W_A = 2(\gamma_1^{LW}\gamma_2^{LW})^{1/2} + 2(\gamma_1^+\gamma_2^-)^{1/2} + 2(\gamma_1^-\gamma_2^+)^{1/2} \,. \qquad (9)$$

The authors call substances with surface free energy corresponding to Eq. (*7*) bipolar. In addition to apolar substances, which contain no elements and have $\gamma = \gamma^{LW}$, they also define monopolar substances, which contain either single γ^+ or single γ^- elements and also have $\gamma = \gamma^{LW}$. When, e.g., one phase with $\gamma_1 = \gamma_1^{LW}$ contains γ_1^+ and the second phase with $\gamma_2 = \gamma_2^{LW}$ contains γ_2^- or $\gamma_2 = \gamma_2^{LW} + \gamma_2^{AB}$, Eq. (*9*) reduces to

$$W_A = 2(\gamma_1^{LW}\gamma_2^{LW})^{1/2} + 2(\gamma_1^+\gamma_2^-)^{1/2} \,. \qquad (10)$$

Unfortunately, Eqs (*9*) and (*10*) can only be solved when the values of elements γ^+ and γ^- of one phase are assumed. No actual values have yet been determined and the results can only be expressed as a ratio between elements of the same sign. It seems that Eq. (*9*) cannot be generally valid because it did not yield a reasonable result in an investigated case[12] while the concept of induction[2,12] yielded a better solution. However, some similarity can be found between the ideas of the induction components in non-polar compounds and of single elements in monopolar compounds.

In this paper, the idea of the acid–base interaction will be further developed and demonstrated on pairs of liquids. In contrast to Neumann et al.[13] it is believed that the same approach can be applied to solid–liquid interfaces because there is no substantial difference from the interaction at liquid–liquid interfaces.

THEORETICAL

First it is necessary to elucidate the separation of the surface free energy into components. The London forces cause attraction among all the molecules, while the Keesom or hydrogen bond forces contribute to the cohesion of molecules having permanent dipoles or an intrinsic acid–base interaction, respectively. There is no need to separate the attraction forces when evaluating the cohesion because they all act jointly. On the other hand, the forces should be separated for the evaluation of adhesion because the polar Keesom and hydrogen bond forces of one phase cannot cause an attraction across the interface when no response appears in the adjoining phase. The polar forces of one phase can either interact with the polar forces of the second phase or induce a response in a non-polar phase and thus increase the adhesion. Therefore, accepting the Fowkes principle of attraction between components of the same kind across the interface is incompatible with the van Oss et al.[10,11] idea of the γ^{LW} component. On the other hand, all Keesom, Debye and hydrogen bond interactions are intermolecular attractions between positive and negative charges.

(with or without formation of a chemical bond) and, therefore, they can be combined into one polar component such as, e.g., γ^{n} in Eq. (*1*). It is not important to consider the difference between the rates at which the forces decay with distance because the equilibrium distance at the interface does not change.

To emphasize the interaction between charges of the opposite sign, the polar component is further denoted γ^{ab}. The positive, proton donor, electron acceptor or acid element is denoted as γ^{a}, and the negative, proton acceptor, electron donor or base element as γ^{b}. Thus, equation

$$\gamma = \gamma^{d} + \gamma^{ab} \tag{11}$$

instead of Eq. (*1*) will now be used. Component γ^{ab} can be considered to equal half of the work of adhesion (or, better, half of the work of cohesion) between elements γ^{a} and γ^{b} at an imaginary interface inside the phase. Therefore, similar to the work of adhesion between the two dispersion components in Eq. (*3*), γ_1^{ab} (for the phase 1) will be given by the relationship

$$\gamma_1^{ab} = 2(\gamma_1^{a}\gamma_1^{b})^{1/2} \tag{12}$$

(which is similar to Eq. (*8*) introduced by van Oss et al.[10] without proper justification).

The work of adhesion according to Dupré is

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}\,. \tag{13}$$

This is a thermodynamic relationship which gives the difference between the equilibrium energies before and after bringing phases 1 and 2 in contact. Because the sum $\gamma_1 + \gamma_2$ is the arithmetic mean of the works of cohesion, $\overline{W}_C$, Eq. (*13*) can be rewritten as

$$\gamma_{12} = \overline{W}_C - W_A\,, \tag{14}$$

which shows that the interfacial free energy is equal to the difference between the mean work of cohesion and the work of adhesion. Similarly as in Eq. (*11*), we can write

$$\gamma_{12} = \gamma_{12}^{d} + \gamma_{12}^{ab}\,, \tag{15}$$

$$\overline{W}_C = \overline{W}_C^{d} + \overline{W}_C^{ab}\,, \tag{16}$$

$$W_A = W_A^{d} + W_A^{ab}\,. \tag{17}$$

The dispersion component of the interfacial free enery, γ_{12}^{d}, can be resolved according to equation

$$\gamma_{12}^{d} = [(\gamma_1^{d})^{1/2} - (\gamma_2^{d})^{1/2}]^2 \tag{18}$$

as was mentioned earlier[4-6]. According to Eq. (*18*), the dispersion component of the interfacial free energy originates from the difference between the dispersion parts of the cohesion forces in the adjoining phases. However, the idea (which agrees with Eq. (*14*)) that the cohesion force of phase 1 is decreased at the interface by the attraction from the side of the phase 2, i.e., $(\gamma_1^d)^{1/2}\,[(\gamma_1^d)^{1/2} - (\gamma_2^d)^{1/2}]$, seems to be more explicit. A similar action takes part on the other side of the interface and this leads to the equation

$$\gamma_{12}^d = (\gamma_1^d)^{1/2}\,[(\gamma_1^d)^{1/2} - (\gamma_2^d)^{1/2}] + (\gamma_2^d)^{1/2}\,[(\gamma_2^d)^{1/2} - (\gamma_1^d)^{1/2}]\,. \qquad (19)$$

Both Eqs (*18*) and (*19*) yield the same result, i.e.,

$$\gamma_{12}^d = \gamma_1^d + \gamma_2^d - 2(\gamma_1^d\gamma_2^d)^{1/2}\,, \qquad (20)$$

which is identical with Eq. (*3*) and justifies the expression of the partial work of adhesion as the geometrical mean of the respective components (or elements) of the surface free energies.

For an imaginary interface in the bulk of the phase, $\gamma_1^d = \gamma_2^d$ and $\gamma_{12}^d = \gamma_{11}^d = 0$ should be substituted into Eq. (*20*) which yields $\overline{W}_C^d = W_A^d$. Similarly, cohesion of the polar elements has been expressed by the relationship for adhesion in Eq. (*12*).

Now let us consider the interaction of polar forces at interfaces. In the ideal arrangement of molecules shown in Fig. 1*a*, the cohesive attraction of dipoles or of hydrogen bonds between the molecules of one phase is decreased at the interface by the adhesive attraction from the adjoining phase between charges of the opposite sign. The difference between the cohesion and adhesion gives to rise the interfacial free energy (cf. Eqs (*14*) and (*19*)). Thus, it may seem that, for the polar interaction, the equation

$$\begin{aligned}\gamma_{12}^{ab} = {} & (\gamma_1^a)^{1/2}\,[(\gamma_1^b)^{1/2} - (\gamma_2^b)^{1/2}] + (\gamma_1^b)^{1/2}\,[(\gamma_1^a)^{1/2} - (\gamma_2^a)^{1/2}] + \\ & + (\gamma_2^a)^{1/2}\,[(\gamma_2^b)^{1/2} - (\gamma_1^b)^{1/2}] + (\gamma_2^b)^{1/2}\,[(\gamma_2^a)^{1/2} - (\gamma_1^a)^{1/2}] \qquad (21)\end{aligned}$$

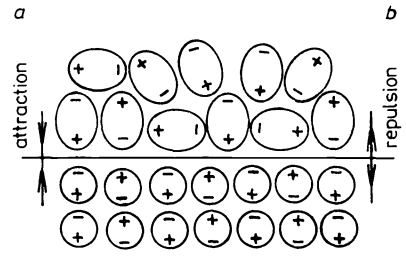

FIG. 1

Scheme of the interface between two polar liquids with the molecular orientation causing *a* attraction, *b* repulsion could be valid. Neglecting the different meaning of γ^{d} and γ^{ab} from γ^{LW} and γ^{AB}, respectively, Eq. (*21*) leads formally to the relationship introduced by van Oss et al.[10,11] (see Eq. (*9*)). However, the molecules are in continuous motion during which they change their mutual position. Therefore, in addition to attraction between charges of the opposite sign, repulsion between charges of the same sign should also take place (see Fig. 1*b*) which decreases adhesion. Analysis of the long range forces showed[14] that the dispersion and induction contributions are always attractive. However, the coulombic contribution may be attractive or repulsive depending on the mutual orientation of molecules. Hence, Eq. (*21*) is not complete. It should be supplemented for this repulsion and then, the following relationship is obtained:

$$\begin{aligned}\gamma_{12}^{ab} = {} & (\gamma_1^{a})^{1/2}\,[(\gamma_1^{b})^{1/2} - (\gamma_2^{b})^{1/2} + (\gamma_2^{a})^{1/2}] + (\gamma_1^{b})^{1/2}\,[(\gamma_1^{a})^{1/2} - \\ & + (\gamma_2^{a})^{1/2} + (\gamma_2^{b})^{1/2}] + (\gamma_2^{a})^{1/2}\,[(\gamma_2^{b})^{1/2} - (\gamma_1^{b})^{1/2} + \\ & + (\gamma_1^{a})^{1/2}] + (\gamma_2^{b})^{1/2}\,[(\gamma_2^{a})^{1/2} - (\gamma_1^{a})^{1/2} + (\gamma_1^{b})^{1/2}]\,. \end{aligned} \tag{22}$$

Equations (*22*) and (*12*) give

$$\gamma_{12}^{ab} = \gamma_1^{ab} + \gamma_2^{ab} - 2(\gamma_1^{a}\gamma_2^{b})^{1/2} - 2(\gamma_1^{b}\gamma_2^{a})^{1/2} + 2(\gamma_1^{a}\gamma_2^{a})^{1/2} + 2(\gamma_1^{b}\gamma_2^{b})^{1/2}\,. \tag{23}$$

All the cohesion, attraction and repulsion forces at interfaces are assumed to be proportional to the geometrical mean of the involved elements.

The bulk phase is always electroneutral. Each charge should be equilibrated with the charge of the opposite sign regardless of the difference between the γ^{a} and γ^{b} values. Similarly, the charge at one side of the interface of two different phases is equilibrated with the charge of the opposite sign at the other side of the interface. The net charge at one side is proportional to $(\gamma_1^{a}\gamma_2^{b})^{1/2} - (\gamma_1^{b}\gamma_2^{a})^{1/2}$ and at the other side to $(\gamma_2^{a}\gamma_1^{b})^{1/2} - (\gamma_2^{b}\gamma_1^{a})^{1/2}$. Then, the phase at the interface is no longer electroneutral and a polar attraction between the two adjoining phases takes place, proportional to the sum of all charges, i.e., $2(\gamma_1^{a}\gamma_2^{b})^{1/2} + 2(\gamma_1^{b}\gamma_2^{a})^{1/2}$. The values of γ^{a} and γ^{b} are proportional to the number of sites with the negative and positive charges, respectively. Therefore, the terms $2(\gamma_1^{a}\gamma_2^{b})^{1/2}$ and $2(\gamma_1^{b}\gamma_2^{a})^{1/2}$ are also proportional to the probability of a close approach of charges of the opposite sign at the interface. Similarly, the probability of approach of charges of the same sign is $2(\gamma_1^{a}\gamma_2^{a})^{1/2}$ and $2(\gamma_1^{b}\gamma_2^{b})^{1/2}$, which determines the polar repulsion. However, the repulsion terms cannot be involved when the acid and base elements result from induction. They will be denoted γ^{ia} and γ^{ib}, respectively.

When $\gamma_2^{ab} = 0$ and γ_1^{ab} interacts with element γ_2^{b} (a non-polar compound with the character of a base, or briefly non-polar base), Eq. (*23*) reduces to

$$\gamma_{12}^{ab} = \gamma_1^{ab} - 2(\gamma_1^{a}\gamma_2^{b})^{1/2} + 2(\gamma_1^{b}\gamma_2^{b})^{1/2}\,. \tag{24}$$

Similarly, when $\gamma_2^{ab} = 0$ and γ_1^{ab} interacts with element γ_2^{a} (a non-polar compound with the character of an acid, or briefly non-polar acid), the equation

$$\gamma_{12}^{ab} = \gamma_1^{ab} - 2(\gamma_1^{b}\gamma_2^{a})^{1/2} + 2(\gamma_1^{a}\gamma_2^{a})^{1/2} \tag{25}$$

is obtained. Finally, when $\gamma_1^{ab} = 0$, $\gamma_2^{ab} = 0$, and the compounds are a non-polar acid and a non-polar base, respectively, the equation

$$\gamma_{12}^{ab} = -2(\gamma_1^{a}\gamma_2^{b})^{1/2} \tag{26}$$

results.

Combining Eqs (*20*) and (*23*) leads to $W_A = W_{12} = W_{12}^{d} + W_{12}^{ab}$ where

$$W_{12} = 2(\gamma_1^{d}\gamma_2^{d})^{1/2} + 2(\gamma_1^{a}\gamma_2^{b})^{1/2} + 2(\gamma_1^{b}\gamma_2^{a})^{1/2} - 2(\gamma_1^{a}\gamma_2^{a})^{1/2} - 2(\gamma_1^{b}\gamma_2^{b})^{1/2} . \tag{27}$$

Similarly, Eq. (*20*) can be combined with Eqs (*24*), (*25*) or (*26*) (depending on the respective conditions) to yield

$$W_{12} = 2(\gamma_1^{d}\gamma_2^{d})^{1/2} + 2(\gamma_1^{a}\gamma_2^{b})^{1/2} - 2(\gamma_1^{b}\gamma_2^{b})^{1/2} , \tag{28}$$

$$W_{12} = 2(\gamma_1^{d}\gamma_2^{d})^{1/2} + 2(\gamma_1^{b}\gamma_2^{a})^{1/2} - 2(\gamma_1^{a}\gamma_2^{a})^{1/2} , \tag{29}$$

$$W_{12} = 2(\gamma_1^{d}\gamma_2^{d})^{1/2} + 2(\gamma_1^{a}\gamma_2^{b})^{1/2} . \tag{30}$$

It seems possible that, in some non-polar compounds with $\gamma = \gamma^{d}$ and $\gamma^{ab} = 0$, both elements γ^{a} and γ^{b} can be induced at the interface depending on the properties of the adjoining phase.

Non-polar acids or bases have no charge in the bulk and, therefore, there is neither polar attraction nor repusion, i.e., single γ^{a} or γ^{b} forces do not affect either the surface free energy or the cohesion. Polar attraction takes place in the bulk between elements γ^{a} and γ^{b} only. At the imaginary interface in the bulk of a polar liquid, $\gamma_1^{ab} = \gamma_2^{ab}$, $\gamma_1^{a} = \gamma_2^{a}$, $\gamma_1^{b} = \gamma_2^{b}$ and $\gamma_{12}^{ab} = 0$. For a non-polar base or acid with $\gamma_1^{ab} = \gamma_1^{a} = 0$ or $\gamma_1^{ab} = \gamma_1^{b} = 0$, Eqs (*24*) and (*25*) yield $\gamma_1^{b} = 0$ or $\gamma_1^{a} = 0$, respectively. These results only mean that the contribution of the single elements to cohesion is zero irrespective of their actual value for adhesion. For the imaginary interface in the bulk of a polar liquid, Eq. (*23*) yields $\gamma_1^{ab} = 2(\gamma_1^{a}\gamma_1^{b})^{1/2} - \gamma_1^{a} - \gamma_1^{b}$. Because the contribution of the single terms γ_1^{a} and γ_1^{b} to the cohesion is zero, as stated in the previous cases, Eq. (*23*) then reduces to Eq. (*12*) which shows the conformity of these two equations.

Solution of Eqs (*27*)–(*30*) with unknown γ^a and γ^b values is not possible. A further relationship is needed. To this purpose, the relationship of the base or acid elements to the empirical donor or acceptor numbers, respectively, will be considered.

RESULTS AND DISCUSSION

Calculation of the Acid and Base Elements of Water

Gutmann[15] evaluated the donor numbers, D_L, and acceptor numbers, A_L, as empirical parameters of liquids to describe their nucleophilic and electrophilic behavior, respectively. His values for water, $D_W = 33$ and $A_W = 54{\cdot}8$, will be further used together with the recently determined[16] values $\gamma_W^d = 19{\cdot}09$ and $\gamma_W^{ab} = 53{\cdot}66$ (at 20°C). All data for the surface free energy, interfacial free energy and work of adhesion are given in mJ/m^2. The data for some other liquids are given in Table I. The dipole moments, μ, are also included. The μ value for water is $6{\cdot}17 \,.\, 10^{-30}$ C m. No relationship of μ to D_L and A_L can be found. Therefore, no relationship can be expected between μ and the values of the surface free energy elements.

Direct proportionality,

$$(\gamma_W^a)^{1/2} = x_1(A_W)^{1/2}\,, \qquad (31a)$$

$$(\gamma_W^b)^{1/2} = y_1(D_W)^{1/2}\,, \qquad (31b)$$

is assumed for water. However, this relationship cannot be valid for other liquids as follows from a comparison of the D_L and A_L values in Table I. Both benzene

TABLE I

Basic data used in the calculations: donor and acceptor numbers (D_L and A_L, ref.[15]); surface and interfacial free energy and work of adhesion for the liquid–water interface (γ_L, γ_{WL}, and W_{WL} (in mJ/m^2), ref.[17]); dipole moment (μ (in C m), ref.[18])

Liquid	D_L	A_L	γ_L	γ_{WL}	W_{WL}	$\mu \,.\, 10^{30}$
Benzene	0·1	8·2	28·88	33·90	67·73	0·00
Nitrobenzene	4·4	14·8	43·9	25·7	90·95	14·24
Diethyl ether	19·2	3·9	17·0	10·7	79·05	3·84
Butyronitrile	16·6	—	28·1	10·4	90·45	13·58
Dichloromethane	—	20·4	26·5	28·3	70·95	5·14
Trichloromethane	—	23·1	27·15	31·6	68·3	3·40

and diethyl ether should be predominantly nucleophilic. However, while $D_L > A_L$ for diethyl ether, the ratio is the reverse for benzene. Therefore, the relationships

$$(\gamma_L^a)^{1/2} = x_1(A_L)^{1/2} + x_2\,, \qquad (32a)$$

$$(\gamma_L^b)^{1/2} = y_1(D_L)^{1/2} + y_2\,, \qquad (32b)$$

are used for organic liquids, which give reasonable results as will be shown below.

For the interaction between water and non-polar bases (L_1 and L_2), two Eqs (*28*) can be rearranged after substituting Eqs (*12*), (*31*) and (*32*) to give

$$\gamma_W^b = [W_{WL1} - W_{WL2} + 2(\gamma_W^d)^{1/2}(\gamma_{L1}^{1/2} - \gamma_{L2}^{1/2}) + \\ + \gamma_W^{ab}(D_{L1}^{1/2} - D_{L2}^{1/2})/D_W^{1/2}]/[2(D_{L1}^{1/2} - D_{L2}^{1/2})/D_W^{1/2}]\,. \qquad (33)$$

Similarly, for the interaction between water and non-polar acids, equation

$$\gamma_W^a = [W_{WL1} - W_{WL2} + 2(\gamma_W^d)^{1/2}(\gamma_{L1}^{1/2} - \gamma_{L2}^{1/2}) + \\ + \gamma_W^{ab}(A_{L1}^{1/2} - A_{L2}^{1/2})/A_W^{1/2}]/[2(A_{L1}^{1/2} - A_{L2}^{1/2})/A_W^{1/2}] \qquad (34)$$

is obtained. The values of γ_W^b from Eq. (*33*) are given in Table II. The average value is $\gamma_W^b = 10{\cdot}43 \pm 2{\cdot}70$. For the interfaces of dichloromethane and trichloromethane with water, Eq. (*34*) yields $\gamma_W^a = 67{\cdot}71$. From this γ_W^a value and from $\gamma_W^{ab} = 53{\cdot}66$, Eq. (*12*) yields $\gamma_W^b = 10{\cdot}63$. The acceptable standard deviation of γ_W^b values from Eq. (*33*) and the accordance with the value from Eq. (*34*) justify the applicability of Eqs (*31*) and (*32*). The results also show that, in this case, the influence of dipole moments on the interaction mechanism can be neglected and the organic liquids used for the calculations can be considered as non-polar bases or acids.

It should be noted that van Oss et al.[10] only assumed that $\gamma_W^+ = \gamma_W^- = 25{\cdot}5$, but nonetheless they admit[19] $\gamma_W^+ > \gamma_W^-$ (equivalent to $\gamma_W^a > \gamma_W^b$). Their values for other liquids, γ_L^+ and γ_L^-, are only expressed as a ratio to γ_W^+ and γ_W^-, respectively.

Calculation of Elements of Organic Liquids from their Interaction with Water

Using the above obtained $\gamma_W^a = 67{\cdot}71$ and $\gamma_W^b = 10{\cdot}63$ values, the values of γ_L^b for non-polar compounds (with $\gamma_L^d = \gamma_L$) can be calculated from Eq. (*28*), which we rearrange to give

$$(\gamma_L^b)^{1/2} = [W_{WL} - 2(\gamma_W^d\gamma_L)^{1/2}]/2[(\gamma_W^a)^{1/2} - (\gamma_W^b)^{1/2}]\,. \qquad (35)$$

If there is no repulsion, i.e., the polar interaction is caused by the induced element

γ_L^{ib}, then

$$(\gamma_L^{ib})^{1/2} = [W_{WL} - 2(\gamma_W^d\gamma_L)^{1/2}]/2(\gamma_W^a)^{1/2} \,. \tag{36}$$

The difference between γ^b and γ^{ib} is in that γ^b is a permanent or durable property while γ^{ib} can only exist in one phase when an acid group from the adjoining phase, γ_2^a, is in immediate vicinity.

The values for aromatic compounds calculated from Eqs (*35*) and (*36*) are given in Table III. The interactions of these liquids with water and mercury were evaluated earlier[2] using other relationships. It was found from the interactions with mercury that the aromatic hydrocarbons have $\gamma_L = \gamma_L^d$ but they can interact with water through an induced polar component. The average of the values in Table III for aromatic hydrocarbons (excluding benzene) is $\gamma_L^b = 3{\cdot}15 \pm 0{\cdot}54$ from Eq. (*35*) or $\gamma_L^{ib} = 1{\cdot}15 \pm 0{\cdot}20$ from Eq. (*36*). It will further be shown that, for benzene, γ_L^b should be employed while, for the other aromatic compounds, γ_L^{ib} is more likely. For a comparison, values of γ_L^b obtained from Eq. (*35*) for some other organic liquids are also included in Table III.

It follows from Eq. (*29*) that the same right-hand side as in Eq. (*35*) is valid for calculations of $-(\gamma_L^a)^{1/2}$ for non-polar acids. Thus, $-(\gamma_L^a)^{1/2} = 2{\cdot}61$ is obtained for dichloromethane ($\gamma_L = 26{\cdot}5$, $W_{WL} = 70{\cdot}95$) and $-(\gamma_L^a)^{1/2} = 2{\cdot}29$ for trichloromethane ($\gamma_L = 27{\cdot}15$, $W_{WL} = 68{\cdot}3$). However, the negative values of $(\gamma_L^a)^{1/2}$ lead to the strange conclusion that the effects of the terms $2(\gamma_W^b\gamma_L^a)^{1/2}$ and $2(\gamma_W^a\gamma_L^a)^{1/2}$ are, in contrast to the above hypothesis, repulsive and attractive, respectively. This result cannot be explained at present. On the other hand, after leaving-out the repulsion term, Eq. (*29*) can be rewritten to

$$(\gamma_L^{ia})^{1/2} = [W_{WL} - 2(\gamma_W^d\gamma_L)^{1/2}]/2(\gamma_W^b)^{1/2} \,, \tag{37}$$

which yields reasonable values $(\gamma_L^{ia})^{1/2} = 3{\cdot}98$ for dichloromethane and 3·49 for trichloromethane. However, using Eq. (*37*) is not compatible with Eq. (*34*) which was aplied to calculate γ_W^a.

The values of γ_{L1}^b can be checked for liquids with known D_L (see Table I) using γ_{L2}^b from Table III and the relationship derived from Eqs (*31b*) and (*32b*),

$$(D_{L1}^{1/2} - D_{L2}^{1/2})/D_W^{1/2} = [(\gamma_{L1}^b)^{1/2} - (\gamma_{L2}^b)^{1/2}]/(\gamma_W^b)^{1/2} \,. \tag{38}$$

The results are summarized in Table II. The best agreement of the γ_L^b values from Eq. (*38*) with those from Eq. (*35*) is obtained when compounds with similar μ values are used together, i.e., when Eq. (*38*) is solved for the pairs benzene–diethyl ether and nitrobenzene–butyronitrile. A comparison of the γ_L^b values from Tables II and III, e.g., for diethyl ether and nitrobenzene, shows that dipole moments cannot play an important role at interfaces where the hydrogen bond interaction takes place. Therefore, the compounds with a relatively high μ can also be regarded as non-polar bases or acids.

TABLE II

Base elements (in mJ/m^2) of water, γ_W^b, and liquids L_1, γ_{L1}^b, calculated for pairs water–L_1 from Eq. (*33*) and L_1–L_2 from Eq. (*38*)

L_1	L_2	γ_W^b Eq. (*33*)	γ_{L1}^b Eq. (*38*)
Benzene	nitrobenzene	7·03	5·36
Nitrobenzene	benzene		9·62
Benzene	diethyl ether	11·11	4·09[a]
Diethyl ether	benzene		19·34[a]
Benzene	butyronitrile	8·98	5·33
Butyronitrile	benzene		17·84
Nitrobenzene	diethyl ether	14·29	9·20
Diethyl ether	nitrobenzene		21·38
Nitrobenzene	butyronitrile	10·74	11·02[a]
Butyronitrile	nitrobenzene		19·79[a]
Diethyl ether	butyronitrile	—	21·31
Butyronitrile	diethyl ether		17·27

[a] Values which agree best with the results from Eq. (*35*) given in Table III.

TABLE III

Base elements (in mJ/m^2), γ_L^b and γ_L^{ib}, calculated for aromatic hydrocarbons and for some organic liquids from the data in ref.[17]

Aromatic hydrocarbon	γ_L^b Eq. (*35*)	γ_L^{ib} Eq. (*36*)	Organic liquid	γ_L^b Eq. (*35*)
Benzene	4·37	1·59	Chlorobenzene	3·39
Toluene	3·47	1·26	Bromobenzene	3·41
o-Xylene	3·58	1·31	Nitrobenzene	11·07
m-Xylene	2·85	1·04	Diethyl ether	18·75
p-Xylene	2·85	1·04	Butyronitrile	19·73
Ethylbenzene	2·70	0·98	Ethyl acetate	22·50
Mesitylene	2·58	0·94	2-Pentanon	23·11
p-Cymene	4·02	1·47	Aniline	28·05

Interactions of Liquids with Mercury

The values, $\gamma_M = 480$, $\gamma_M^d = 190{\cdot}6$, $\gamma_{WM} = 415$, $W_{WM} = 137{\cdot}75$ for mercury from ref.[2], $\gamma_W = 72{\cdot}75$, $\gamma_W^d = 19{\cdot}09$, $\gamma_W^{ab} = 53{\cdot}66$ for water from ref.[16] and $\gamma_W^a = 67{\cdot}71$, $\gamma_W^b = 10{\cdot}63$ from the present communication, are used in Eq. (*27*), which then becomes

$$W_{WM} = 2(\gamma_W^d\gamma_M^d)^{1/2} + 2(\gamma_W^a\gamma_M^b)^{1/2} - 2(\gamma_W^b\gamma_M^b)^{1/2}\,. \qquad (39)$$

Mercury is assumed to be a non-polar base with $\gamma_M = \gamma_M^d + \gamma_M^m$ (γ_M^m being the metallic component, $\gamma_M^{ab} = \gamma_M^a = 0$). Equation (*39*) yields $\gamma_M^b = 2{\cdot}97$.

In the previous paragraph, aromatic hydrocarbons were considered to be non-polar bases. It has been found earlier[2] that aromatic hydrocarbons, except for benzene, behave toward mercury as non-polar compounds. Thus, the equation

$$W_{ML} = 2(\gamma_M^d\gamma_L)^{1/2} \qquad (40)$$

is valid (see Table IV). However, the interaction of benzene with mercury includes the repulsion between γ_L^b and γ_M^b, according to the equation

$$W_{ML} = 2(\gamma_M^d\gamma_L)^{1/2} - 2(\gamma_M^b\gamma_L^b)^{1/2} \qquad (41)$$

which yields $W_{ML} = 141{\cdot}2$ (using γ_L^b for benzene from Table III), in agreement with $W_{ML} = 140{\cdot}9$ from Eq. (*13*) ($\gamma_{ML} = 368$).

Nitrobenzene appears to be a non-polar base for interaction with water. It also interacts as a non-polar base with mercury. Equation (*41*) (with γ_L^b from Table III) yields $W_{ML} = 171{\cdot}5$ in good agreement with $W_{ML} = 173{\cdot}9$ from Eq. (*13*). It can be

TABLE IV

Comparison of work of adhesion (in mJ/m^2) for the mercury–aromatic hydrocarbon interfaces calculated from Eqs (*40*) and (*41*) with the actual value according to Eq. (*13*)

Hydrocarbon	W_{ML}		
	Eq. (*13*)	Eq. (*40*)	Ea. (*41*)
Benzene	140·9	148·4	141·2
Toluene	147·5	147·4	141·0
o-Xylene	151·1	151·5	145·0
m-Xylene	151·9	148·4	142·6
p-Xylene	147·4	147·1	141·3

concluded that the dipole moment of nitrobenzene does not play an important role at the interface with mercury. The electron-donor properties of the oxygens seem to be the only significant factor for the polar interaction. Similarly, chlorobenzene gives $W_{\mathrm{ML}} = 153{\cdot}7$ from Eq. (*41*), in agreement with $W_{\mathrm{ML}} = 153{\cdot}2$ from Eq. (*13*). On the other hand, interactions of aniline and bromobenzene with mercury correspond to Eq. (*40*) yielding $W_{\mathrm{ML}} = 180{\cdot}9$ and $166{\cdot}8$ in agreement with the values $W_{\mathrm{ML}} = 181{\cdot}9$ and $166{\cdot}5$ from Eq. (*13*), respectively.

The acid–base interaction of a non-polar acid with mercury can be demonstrated on the example of trichloromethane. In this case, Eq. (*30*) becomes

$$W_{\mathrm{ML}} = 2(\gamma_{\mathrm{M}}^{\mathrm{d}}\gamma_{\mathrm{L}})^{1/2} + 2(\gamma_{\mathrm{M}}^{\mathrm{b}}\gamma_{\mathrm{L}}^{\mathrm{ia}})^{1/2} \qquad (42)$$

which yields $W_{\mathrm{ML}} = 150{\cdot}3$ in agreement with $W_{\mathrm{ML}} = 150{\cdot}2$ from Eq. (*13*).

A number of examples indicates that the hypothesis of interactions at interfaces presented in this paper is more reliable than the methods of van Oss et al.[10] and of the other previous authors[4–6]. Of course, examples can be found which cannot be routinely solved using the above equations and a special explanation becomes necessary which is not yet available. It is, e.g., not clear why the mechanism of interactions of benzene with water and mercury differs from that of other aromatic hydrocarbons. Deviations can be caused by an inaccuracy in the measured values. The interfacial tension of dichloromethane with mercury[17], e.g., seems to be low ($\gamma_{\mathrm{ML}} = 343$) compared to the values for trichloromethane ($\gamma_{\mathrm{ML}} = 357$) and tetrachloromethane ($\gamma_{\mathrm{ML}} = 359$). Consistent values of W_{ML} from Eqs (*13*) and (*42*) would be obtained if γ_{ML} for dichloromethane equals $357{\cdot}5$.

Calculation of the Surface Free Energy Elements of Alcohols

The intersection points of the curves representing the dependence of the calculated $\gamma_{\mathrm{L}}^{\mathrm{b}}$ on the chosen $\gamma_{\mathrm{L}}^{\mathrm{ab}}$ values for the liquid–mercury and liquid–water interfaces have been used to obtain the actual $\gamma_{\mathrm{L}}^{\mathrm{b}}$ and $\gamma_{\mathrm{L}}^{\mathrm{ab}}$ values of alcohols. For this purpose, $\gamma_{\mathrm{L}} = \gamma_{\mathrm{L}}^{\mathrm{d}} + \gamma_{\mathrm{L}}^{\mathrm{ab}}$ is assumed and Eq. (*27*) is rearranged to give

$$\gamma_{\mathrm{L}}^{\mathrm{b}}\, 2(\gamma_{\mathrm{M}}^{\mathrm{b}})^{1/2} + (\gamma_{\mathrm{L}}^{\mathrm{b}})^{1/2}\,[W_{\mathrm{ML}} - 2(\gamma_{\mathrm{M}}^{\mathrm{d}})^{1/2}/(\gamma_{\mathrm{L}} - \gamma_{\mathrm{L}}^{\mathrm{ab}})^{1/2}] + \gamma_{\mathrm{L}}^{\mathrm{ab}}(\gamma_{\mathrm{M}}^{\mathrm{b}})^{1/2} = 0 \qquad (43)$$

and

$$\begin{aligned}\gamma_{\mathrm{L}}^{\mathrm{b}}\, 2[(\gamma_{\mathrm{W}}^{\mathrm{a}})^{1/2} - (\gamma_{\mathrm{W}}^{\mathrm{b}})^{1/2}] - (\gamma_{\mathrm{L}}^{\mathrm{b}})^{1/2}\,[W_{\mathrm{WL}} - 2(\gamma_{\mathrm{W}}^{\mathrm{d}})^{1/2}\,(\gamma_{\mathrm{L}} - \gamma_{\mathrm{L}}^{\mathrm{ab}})^{1/2}] - \\ + \gamma_{\mathrm{L}}^{\mathrm{ab}}[(\gamma_{\mathrm{W}}^{\mathrm{a}})^{1/2} - (\gamma_{\mathrm{W}}^{\mathrm{b}})^{1/2}] = 0\,. \qquad (44)\end{aligned}$$

The intersections of the curves were obtained using the absolute values of $(\gamma_{\mathrm{L}}^{\mathrm{b}})^{1/2}$: (A) from the first root of Eq. (*43*) and the second root of Eq. (*44*) and (B), vice versa, from the second root of Eq. (*43*) and the first root of Eq. (*44*). The second roots of both equations yield negative values of $(\gamma_{\mathrm{L}}^{\mathrm{b}})^{1/2}$. The same $\gamma_{\mathrm{L}}^{\mathrm{ab}}$ value results from both solutions, solution A gives the low $\gamma_{\mathrm{L}}^{\mathrm{a}}$ and the high $\gamma_{\mathrm{L}}^{\mathrm{b}}$ values, solution B gives the opposite values, i.e., $\gamma_{\mathrm{L}}^{\mathrm{b}}(\mathrm{B}) = \gamma_{\mathrm{L}}^{\mathrm{a}}(\mathrm{A})$ and $\gamma_{\mathrm{L}}^{\mathrm{b}}(\mathrm{A}) = \gamma_{\mathrm{L}}^{\mathrm{a}}(\mathrm{B})$. The results from solution B, which fit Eq. (*27*) for the water–alcohol interface, yielding the same W_{WL} as Eq. (*13*), are given in Table V. On the other hand, solution A fits Eq. (*27*) for the mercury–-alcohol interface. This is a strange result, suggesting that $\gamma_{\mathrm{L}}^{\mathrm{a}}$ may be interchanged in some cases for $\gamma_{\mathrm{L}}^{\mathrm{b}}$, which was also found elsewhere and cannot be explained satisfactorily here. The values are certainly not precise: the $\gamma_{\mathrm{L}}^{\mathrm{ab}}$ values for butanol and hexanol are too high. However, deviations might arise from inaccurate values of the work of adhesion, especially for the interface with mercury. The low values of $\gamma_{\mathrm{L}}^{\mathrm{a}}$ for the water–alcohol interfaces suggest that alcohols might interact as non-polar bases. Then, Eqs (*35*) and (*41*) can be used to calculate $\gamma_{\mathrm{L}}^{\mathrm{b}}$ from the work of adhesion of alcohols with water and mercury, respectively. Reasonable values are obtained only for the interaction with water and they are also given in Table V. To obtain the same values of $\gamma_{\mathrm{L}}^{\mathrm{b}}$ from the interaction with mercury as from the interaction with water, the measured interfacial tensions between alcohol and mercury should be corrected as shown in Table V (cf. also the remark on γ_{ML} for dichloromethane in the preceding paragraph). Thus, an inaccuracy in the measured values may lead to great confusion in the evaluations.

TABLE V

Surface free energies γ_{L}, their components $\gamma_{\mathrm{L}}^{\mathrm{d}}$, $\gamma_{\mathrm{L}}^{\mathrm{ab}}$ and elements $\gamma_{\mathrm{L}}^{\mathrm{a}}$, $\gamma_{\mathrm{L}}^{\mathrm{b}}$, interfacial free energies γ_{ML}, and works of adhesion W_{ML}, W_{WL} of mercury (M)–alcohol (L) and water (W)–alcohol (L) interfaces; all quantities given in mJ/m^2

Alcohol	1-Butanol	1-Hexanol	1-Octanol
γ_{L} [a]	24·6	25·8	27·5
$\gamma_{\mathrm{L}}^{\mathrm{d}}$ [b]	15·4	17·2	25·3
$\gamma_{\mathrm{L}}^{\mathrm{ab}}$ [b]	9·20	8·59	2·18
$\gamma_{\mathrm{L}}^{\mathrm{a}}$ [b]	0·45	0·47	0·05
$\gamma_{\mathrm{L}}^{\mathrm{b}}$ [b]	46·76	39·32	25·26
$\gamma_{\mathrm{L}}^{\mathrm{b}}$ [c]	27·66	22·77	21·41
γ_{ML} [a]	375·	372·	352·
γ_{ML} [d]	385·8	382·0	378·65
W_{WL} [a]	95·6	91·8	91·8
W_{ML} [a]	129·6	133·8	155·5

[a] Data from ref.[17]; [b] values obtained from intersection points of curves constructed from Eqs (*43*) and (*44*); [c] calculated from Eq. (*35*); [d] corrected value yielding $\gamma_{\mathrm{L}}^{\mathrm{b}}$ from Eq. (*41*) equal to $\gamma_{\mathrm{L}}^{\mathrm{b}}$ from Eq. (*35*).

Application of the Hypothesis to Solid–Liquid Interface

Using data on contact angles, Θ, for liquids on solids from the literature[20], the surface free energy of non-polar solids with $\gamma_S = \gamma_S^d$ can be calculated from the equation

$$\gamma_L(1 + \cos\Theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} \tag{45}$$

when no interaction of the surface free energy elements takes place. The average values of γ_S^d obtained with methylene iodide, α-bromonaphthalene, tricresyl phosphate and hexadecane are given in Table VI (larger deviations were excluded from the average). The values of γ_S^d calculated using the same equation for the interaction

TABLE VI

Dispersion components and base elements of the surface free energy of solids and works of adhesion (in mJ/m^2) calculated using contact angles of liquids

Solid	γ_S^d Eq. (*45*) non-polar liquids	γ_S^d Eq. (*45*) water	$(\gamma_S^b)^{1/2}$ Eq. (*35*) water	$(\gamma_S^{ib})^{1/2}$ Eq. (*36*) water	W_{SL} Eq. (*47*) glycerol		W_{SL} Eq. (*47*) formamide	
					left	right	left	right
Polyethylene	34·57 ± 2·18	43·49	0·63	0·38	75·50	73·90	71·29	71·00
Polytetrafluoroethylene	19·17 ± 0·61	33·09	1·21	0·73	52·39	51·86	56·17	52·97
Paraffin wax	23·96 ± 1·64	33·09	0·75	0·46	56·77	60·56	57·18	59·14
Hexatriacontane	19·38 ± 2·04	28·53	0·83	0·50	55·67	53·80	56·17	53·21
Polystyrene	42·56 ± 0·75	66·91	1·46	0·88	74·41	78·74	74·24	78·88
Polytrifluoroethylene	23·07 ± 1·30	64·56	2·84	1·72	72·22	70·80	72·28	69·76
Poly(vinylidene fluoride)	30·56 ± 5·33	89·95	3·48	2·10	79·81	82·34	88·18	81·23
Poly(vinyl fluoride)	36·26 ± 1·43	95·47	3·30	1·99	89·19	87·69	92·41	86·31
Poly(vinylidene chloride)	42·99 ± 2·36	95·47	2·83	1·71	94·14	92·37	86·42	90·61
Poly(vinyl chloride)	41·68 ± 2·05	76·76	2·03	1·22	88·17	87·88	81·87	85·87
Poly(chlorotrifluoroethylene)	29·19 ± 2·55	69·31	2·57	1·55	72·22	77·09	66·30	65·52
Poly(methyl methacrylate)	40·23 ± 2·31	95·47	3·01	1·82	86·12	90·47	83·71	88·85
Poly(hexamethylene adipamide)	41·00 ± 2·68	124·83	4·19	2·53	95·10	96·07	95·61	94·79
Poly(ethylene terephthalate)	41·85 ± 1·76	92·69	2·78	1·68	90·19	91·09	86·42	89·34

with water (also given in Table VI) deviate conspicuously from the previous ones, indicating that a polar interaction takes place between water and even those solids that are generally accepted as non-polar, i.e., polyethylene, polytetrafluoroethylene, paraffin wax and hexatriacontane. Assuming that the solids listed in Table VI are non-polar bases, their γ_S^b elements were calculated using the γ_W^a and γ_W^b values in the relationship corresponding to Eq. (*35*). The induction effect was also considered and the γ_S^{ib} elements were calculated using Eq. (*36*) (with γ_S instead of γ_L).

Polymers from Table VI can be divided into two groups: the first consisting of typical non-polar solids with lower γ_S^b (or γ_S^{ib}) and the second with higher γ_S^b (or γ_S^{ib}) values. In the first group, $\gamma_S^d = \gamma_S$ may be assumed while, in the second one, either $\gamma_S^d < \gamma_S$ or γ_S^a (γ_S^{ia}) instead of γ_S^b (γ_S^{ib}) can complicate the evaluation (cf. the calculation for dichloromethane and trichloromethane).

With the first group of solids, pairs of equations (for the same liquid and two different solids)

$$\gamma_L(1 + \cos \Theta) = 2(\gamma_S\gamma_L^d)^{1/2} + 2(\gamma_S^{ib}\gamma_L^a) \qquad (46)$$

were solved using $\gamma_S = \gamma_S^d$ (obtained with non-polar liquids) and γ_S^{ib} from Table VI along with the γ_L and Θ values of glycerol to determine its γ_L^d and γ_L^a values. The average values obtained, $\gamma_L^d = 44{\cdot}06 \pm 22{\cdot}48$ and $(\gamma_L^a)^{1/2} = -3{\cdot}23 \pm 2{\cdot}84$, have rather high standard deviation. The negative value of $(\gamma_L^a)^{1/2}$, in fact, indicates a repulsion between the opposite charges for the interaction according to Eq. (*46*). Therefore, the mechanism assuming the induced element γ_S^{ib} in the respective group of polymers cannot be valid either for glycerol or for water and other polar liquids. Similarly, the hypothesis of van Oss et al.[10] on the interaction of monopolar bases with polar liquids would yield $\gamma_S^- = \gamma_S^{ib}$ and, therefore, it cannot be valid.

The relationship corresponding to Eq. (*28*),

$$\gamma_L(1 + \cos \Theta) = 2(\gamma_S\gamma_L^d)^{1/2} + 2(\gamma_S^b\gamma_L^a)^{1/2} - 2(\gamma_S^b\gamma_L^b)^{1/2}\,, \qquad (47)$$

was rearranged to give

$$\gamma_L^b\, 2(\gamma_S^b)^{1/2} + (\gamma_L^b)^{1/2}\left[\gamma_L(1 + \cos \Theta) - 2(\gamma_S)^{1/2}(\gamma_L - \gamma_L^{ab})^{1/2}\right] - \gamma_L^{ab}(\gamma_S^b)^{1/2} = 0 \quad (48)$$

to determine the dependence of the calculated $(\gamma_L^b)^{1/2}$ values on the chosen γ_L^{ab} values using $\gamma_S = \gamma_S^d$ from the contact angles of non-polar liquids in Eq. (*45*) and γ_S^b from the interaction with water according to Eq. (*35*) (see Table VI). The intersection points of curves for the first five solids (from polyethylene to polystyrene) and glycerol gave the average values $\gamma_L^{ab} = 20{\cdot}97 \pm 7{\cdot}50$ and $(\gamma_L^b)^{1/2} = 4{\cdot}48 \pm 1{\cdot}32$, from which $\gamma_L^d = 42{\cdot}43$ and $(\gamma_L^a)^{1/2} = 2{\cdot}34$ (Eq. (*12*)). The dependence of $(\gamma_L^b)^{1/2}$ on γ_L^{ab} for the second group of solids (from polytrifluoroethylene to poly(ethylene terephthalate)) is different from the dependence for the first group and the average values of the intersection points for glycerol, γ_L^{ab} = 25·41 ± 8·98 and $(\gamma_L^b)^{1/2}$ = 4·73 ± 1·40 from which γ_L^d = 37·99 and $(\gamma_L^a)^{1/2}$ = 2·69, deviate slightly from the former result. The average values obtained from the curves according to Eq. (*48*) were used in Eq. (*47*) to calculate $(\gamma_S^b)^{1/2}$. For the second group of polymers, the calculated $(\gamma_S^b)^{1/2}$ values are negative, indicating that the respective positive values correspond to $(\gamma_S^a)^{1/2}$. The average difference between the absolute $(\gamma_S^b)^{1/2}$ values calculated for the interface with water and with glycerol is 0·08 ± 0·65. A better comparison gives the work of adhesion (see Table VI) calculated for the left and right-hand sides of Eq. (*47*) in which the $(\gamma_S^b)^{1/2}$ values obtained from Eq. (*35*) for interaction with water were used (for the second group of solids as $-(\gamma_S^a)^{1/2}$). The average deviation of these two sides is −0·94 ± 2·80.

Using the same procedure as for glycerol, formamide and the first group of solids from Table VI yield γ_L^{ab} = 21·84 ± 5·91 and $(\gamma_L^b)^{1/2}$ = 3·27 ± 1·64, from which γ_L^d = 36·36 and $(\gamma_L^a)^{1/2}$ = 3·34. For the second group of solids, γ_L^{ab} = 22·73 ± 10·03 and $(\gamma_L^b)^{1/2}$ = 2·44 ± 0·33, from which γ_L^d = 35·47 and $(\gamma_L^a)^{1/2}$ = 4·65. The values obtained from both the left and right-hand side of Eq. (*47*) are also given in Table VI. The values of $\gamma_S = \gamma_S^d$ obtained from Eq. (*45*) for the interaction with the non-polar liquids and $(\gamma_S^b)^{1/2}$ from Eq. (*35*) for interaction with water were used in the calculations. The data for the first group of solids were also used for poly(chlorotrifluoroethylene). The average deviation of the left from the right-hand side of Eq. (*47*) is 0·06 ± 3·98.

When $\gamma_S^d < \gamma_S$, the interaction with polar liquids is given by Eq. (*27*), from which $(\gamma_S^b)^{1/2} - (\gamma_S^a)^{1/2}$ can be calculated:

$$(\gamma_S^b)^{1/2} - (\gamma_S^a)^{1/2} = [\gamma_L(1 + \cos \Theta) - 2(\gamma_S^d \gamma_L^d)^{1/2}]/2[(\gamma_L^a)^{1/2} - (\gamma_L^b)^{1/2}] \,. \qquad (49)$$

However, Eq. (*49*) yields $(\gamma_S^b)^{1/2} - (\gamma_S^a)^{1/2}$ with the same value as $(\gamma_S^b)^{1/2}$ from Eq. (*35*).

It may be interesting to compare the components and elements determined in this paper with those of van Oss et al.[19]. For glycerol, they found γ_L^{AB} = 30, $(\gamma_L^+/\gamma_W^+)^{1/2}$ = 0·392 and $(\gamma_L^-/\gamma_W^-)^{1/2}$ = 1·500, which yields $(\gamma_L^+)^{1/2}$ = 1·98 and $(\gamma_L^-)^{1/2}$ = 7·57 for their assumed $\gamma_W^+ = \gamma_W^-$ = 25·5, or $(\gamma_L^+)^{1/2}$ = 3·23 and $(\gamma_L^-)^{1/2}$ = 4·89 for our γ_W^a and γ_W^b used as γ_W^+ and γ_W^-, respectively. Our values, $(\gamma_L^a/\gamma_W^a)^{1/2}$ = 0·284 or 0·327 and $(\gamma_L^b/\gamma_W^b)^{1/2}$ = 1·374 or 1·451 (from the first or second group of solids), do not deviate much from $(\gamma_L^+/\gamma_W^+)^{1/2}$ and $(\gamma_L^-/\gamma_W^-)^{1/2}$, respectively, found by van Oss et al.. Furthermore, for formamide, they determined γ_L^{AB} = 18·6, $(\gamma_L^+/\gamma_W^+)^{1/2}$ = 0·299 and $(\gamma_L^-/\gamma_W^-)^{1/2}$ = 1·246, which yields $(\gamma_L^+)^{1/2}$ = 1·51 and $(\gamma_L^-)^{1/2}$ = 6·29 for $\gamma_W^+ = \gamma_W^-$ = 25·5, or $(\gamma_L^+)^{1/2}$ = 2·64 and $(\gamma_L^-)^{1/2}$ = 4·06 for our γ_W^a and γ_W^b, respectively. Our values are $(\gamma_L^a/\gamma_W^a)^{1/2}$ = 0·406 or 0·565 and $(\gamma_L^b/\gamma_W^b)^{1/2}$ = 1·003 or 0·748.

CONCLUSIONS

In the present paper, the surface and interfacial free energies as well as the works of adhesion and cohesion are separated into the dispersion and acid-base components. The Fowkes equation for the dispersion forces interactions is extended for the acid--base interactions in which not only the attraction forces but also the repulsion forces are included. The origin of the interfacial free energy is explained and the relationship between the acid-base component, γ^{ab}, and the respective surface free energy elements, γ^a and γ^b, is substantiated. Equations are proposed for interactions between: (i) two polar phases, (ii) a polar phase and a non-polar acid or base, and (iii) a non--polar acid and a non-polar base.

On the basis of the interaction of water with various liquids, the acid and base elements of water, γ_W^a and γ_W^b, are determined using the known donor and acceptor numbers. Benzene is characterized as a non-polar base and its γ_L^b element is determined from the interactions with water and mercury. Other aromatic liquids interact with water and mercury through their induced base element, γ_L^{ib}, which, in contrast to γ_L^b, does not lead to repulsion. Also other organic liquids investigated, irrespective of their dipole moments, behave rather as non-polar compounds with a single polar element than as polar compounds.

The suggested equations are applied to polymer solids and the polar elements of these solids are determined from their interaction with water. Using their γ_S^b or γ_S^a values for the evaluation of the interaction with glycerol and formamide, the polar components and the elements of the surface free energy of these two liquids are determined.

Some data obtained at 20°C in mJ/m^2 are summarized here. Water: $\gamma_W = 72{\cdot}75$, $\gamma_W^d = 19{\cdot}09$, $\gamma_W^{ab} = 53{\cdot}66$, $\gamma_W^a = 67{\cdot}71$, $\gamma_W^b = 10{\cdot}63$. Glycerol: $\gamma_L = 63{\cdot}4$, $\gamma_L^d = 42{\cdot}4$ to $38{\cdot}0$, $\gamma_L^{ab} = 21{\cdot}0-25{\cdot}4$, $\gamma_L^a = 5{\cdot}5-7{\cdot}2$, $\gamma_L^b = 20{\cdot}1-22{\cdot}4$. Formamide: $\gamma_L = 58{\cdot}2$, $\gamma_L^d = 36{\cdot}4-35{\cdot}5$, $\gamma_L^{ab} = 21{\cdot}8-22{\cdot}7$, $\gamma_L^a = 11{\cdot}2-21{\cdot}6$, $\gamma_L^b = 10{\cdot}7-6{\cdot}0$. Mercury: $\gamma_M = 480$, $\gamma_M^d = 190{\cdot}6$, $\gamma_M^b = 2{\cdot}97$. Diethyl ether: $\gamma_L = \gamma_L^d = 17{\cdot}0$, $\gamma_L^b = 18{\cdot}75$. Benzene: $\gamma_L = \gamma_L^d = 28{\cdot}88$, $\gamma_L^b = 4{\cdot}37$. The average γ_L^{ib} of other aromatic liquids is $1{\cdot}15$.

The surface free energy, its components and elements are important characteristics which can help to understand the interactions at interfaces. To this purpose, the correct relationships should be known. It is shown that the evaluation cannot be carried out according to a uniform scheme without a thorough consideration of the mechanism of the interaction, as can sometimes be found in the literature. Equations previously suggested and frequently used by other authors do not seem to have a general validity. They often yield inaccurate results and may lead to erroneous conclusions. A correct approach to solving this problem should be clarified and, therefore, an attempt is made in this paper to find relationships representing the true interactions at interfaces. However, further investigation will be needed to confirm the presented hypothesis and to clear some vague questions.

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