INTERACTION AT INTERFACES AND INDUCTION OF SURFACE FREE ENERGY COMPONENTS*

Jan KLOUBEK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Máchova 7, 121 38 Prague 2*

A set of published data on surface free energy (γ_1, γ_2) and interfacial energy (γ_{12}) for interfaces mercury–organic liquid, mecury–water, and water–organic liquid (125 pairs altogether) has been critically evaluated. It has been found that the Antonow rule does not hold, that the Neumann equation is suitable for determining the work of adhesion, if γ_1 and γ_2 are not too different, and that the Fowkes equation can be used to assess the type of interaction at the interface. A hypothesis has been suggested which states that, besides the interaction between dispersion components of the surface free energies of the adjoining phases and the interaction between the non-dispersion components of the same type in bulk, a non-dispersion component of one phase may interact by inducing a component of the same type in the other phase near the interface. Relations concerning the mechanism of interaction at the interface have been derived. Also, the relation between the Girifalco–Good, Neumann and complemented Fowkes equation has been evaluated. For the particular liquids the dispersion portion of their surface free energies and the interaction mechanism at their interface with water and mercury have been estimated. For water, *e.g.* the polar component of the surface free energy ($14 \cdot 7$ mJ m^{-2}) and the hydrogen-bond component ($36 \cdot 3$ mJ m^{-2}) have been determined. The introduction of the induced component of the surface free energy is shown, as an example, for water–aromatic hydrocarbons and water––alcohols systems.

Surface free energy, γ_i, interfacial free energy, γ_{ij}, and the thermodynamic work of adhesion W_A, are characteristic quantities of interfaces. The relation between them is given by the Dupré equation

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \,.\tag{1}$$

According to this equation the work of adhesion is given by the arithmetic mean of the work of cohesion of the adjoining phases diminished by the interfacial free energy, γ_{12}.

Application of the Antonow rule[1] for $\gamma_2 > \gamma_1$

$$\gamma_{12} = \gamma_2 - \gamma_1 \,,\tag{2}$$

leads to

$$W_A = 2\gamma_1 \,.\tag{3}$$

Though it was shown that the Antonow rule was basically incorrect[2], the literature[3] acknowledges that it fits experimental results, if γ_1 and γ_2 refer to the surface free energy of mutually saturated phases.

Girifalco and Good[4] expressed the work of adhesion by

$$W_A = 2\Phi \sqrt{(\gamma_1\gamma_2)} \qquad (4)$$

and joined it with equation (1); later on, Φ was called the interaction parameter. The geometric mean was used, in analogy with the Berthelot equation related to the attraction constants for unlike molecules.

Neumann and coworkers[5-8] formulated an empirical relation between Φ and γ_{12},

$$\Phi = 1 - 0.0075\gamma_{12} \qquad (5)$$

and used it to eliminate Φ from equation (4). In this way, W_A can be calculated from Eq. (6)

$$W_A = (2 - 0.015\gamma_{12}) \sqrt{(\gamma_1\gamma_2)} . \qquad (6)$$

Fowkes[9-11] separated the surface free energy into components of which the London dispersion force component was always present. In general, the separation can be written as

$$\gamma = \gamma^a + \gamma^b + \gamma^c + \dots ; \qquad (7)$$

indices a, b, c denote various components of the surface free energy. The plausibility of such a separation γ was later on confirmed by Tamai[12].

A particular case, where intermolecular attraction interaction occurs only *via* dispersion forces, was expressed by Fowkes as

$$W_A = 2 \sqrt{(\gamma_1^d\gamma_2^d)} . \qquad (8)$$

This relation is satisfactory, if the surface free energy of at least one of the adjoining phases contains only the dispersion component. Nevertheless, equation (8) has been subjected to criticism[13,14].

It was also found that even so good results can be obtained if the arithmetic mean[15] or other average values were used (*e.g.*, the quadratic mean[16]) instead of the geometric mean in Eq. (8).

In those cases, where the interfacial interaction involves other than dispersion forces, the value of W_A in equation (1) is higher than that one given by equation (8); this was noted by Fowkes, too. Therefore, some other authors[17-21] added to equation (8) the geometric means of non-dispersion components of the surface free energies. This procedure was widely used, though regarded by Fowkes[22] himself as an incorrect one. According to Wu[23,24], better results can be obtained, if the harmonic mean is used instead of the geometric mean.

Using the geometric means of components of the same type in both phases, one can write in general[25]

$$W_A = 2 \sqrt{(\gamma_1^a\gamma_2^a)} + 2 \sqrt{(\gamma_1^b\gamma_2^b)} + 2 \sqrt{(\gamma_1^c\gamma_2^c)} + \dots \qquad (9)$$

which can be arranged, if connected with equation (1), as

$$\gamma_{12} = (\sqrt{\gamma_1^a} - \sqrt{\gamma_2^a})^2 + (\sqrt{\gamma_1^b} - \sqrt{\gamma_2^b})^2 + (\sqrt{\gamma_1^c} - \sqrt{\gamma_2^c})^2 + \dots \qquad (10)$$

If equations (4) and (7) are correct, equations (9) and (10) must hold, too. It follows from

(4) and (9) (ref.[26]) that

$$\Phi = \sqrt{(a_1 a_2)} + \sqrt{(b_1 b_2)} + \sqrt{(c_1 c_2)} + \dots , \qquad (11)$$

where $a = \gamma^a/\gamma$, $b = \gamma^b/\gamma$, $c = \gamma^c/\gamma$, etc.

In connection with equation (10) it is worth mentioning that Bikerman[27], when criticising equation (2), regarded as reasonable the relation

$$\gamma_{12} = (\sqrt{\gamma_1} - \sqrt{\gamma_2})^2 \qquad (12)$$

though he did not find for it an agreement with experimental data. However, equation (12) is in agreement with (4) and (10) only in a special case, namely, if $\Phi = 1$, which in turn holds (cf. Eq. (11)) only if $\gamma_1/\gamma_2 = \gamma_1^a/\gamma_2^a = \gamma_1^b/\gamma_2^b = \gamma_1^c/\gamma_2^c$, etc..

Recently, a hypothesis has appeared[28] which states that at the interface, besides the interaction between the surface free energy components of the same type existing in separated phases, also an interaction between a non-dispersion component of one phase and the component of the same type induced in the region of the interface of the other phase may take place.

Equation (9) in connection with the Young–Dupré equation has been often used to determine the surface free energy of solid substances from measurements of the contact angle of liquids.

In this paper, the applicability of equation (9) is checked on the measurements of a series of pairs of liquids, used earlier by Girifalco and Good[4] in the evaluation of Φ. Equation (10) is used in this communication as a start in estimating various possible interaction mechanisms including the earlier mentioned induced components of the surface free energy. At the same time, solutions are examined of equations (3) and (6) used earlier in evaluations of the surface free energy of solids[5-8,29-32]. All values of the work of adhesion, surface and interfacial free energy are given in mJ m^{-2}.

THEORY AND RESULTS

Interface Mercury (M)–Organic Liquid (L)

The evaluation of W_A from the surface free energy data of pure liquids can be complicated by their mutual solubility. These complications do not take place, if one of the liquids is mercury. The surface free energy of mercury is composed, according to Fowkes, from the dispersion and metallic components, i.e.,

$$\gamma_M = \gamma_M^d + \gamma_M^m . \qquad (7a)$$

If the interaction at the mercury–organic liquid interface is determined solely by the dispersion components of the surface free energies, equation (8) holds. If then $\gamma_L = \gamma_L^d$ one may write, in agreement with Fowkes

$$\sqrt{\gamma_M^d} = W_A/2 \sqrt{\gamma_L} . \qquad (8a)$$

The values of γ_M^d as calculated from (8a) are given in the fourth column of Table I.

TABLE I

Data for liquid(L) — mercury(M) interface calculated with the use of equations indicated in parentheses above the columns

L	γ_L	$W_A(1)$	$\gamma_M^d(8a)$	$\gamma_L^d(8b)$	$\gamma_L^d(13b)$	$\gamma_L^d(14a)$
n-Hexane	18·4	120·4	197·0[c]	19·0[a]	19·3[a]	18·4[a]
n-Heptane	20·4	122·4	183·6[c]	19·7[a]	19·3[b]	—
n-Octane	21·8	126·8	184·4[c]	21·1[a]	20·7[a]	—
Isooctane	18·8	122·8	200·5	19·8	20·2	18·8[a]
n-Nonane	22·8	130·8	187·6[c]	22·4[a]	22·3[a]	—
Benzene	28·2	140·2	174·3[b]	25·8[b]	24·4[b]	—
Toluene	28·5	147·5	190·8[c]	28·5[a]	28·6[a]	28·5[a]
o-Xylene	30·1	151·1	189·6[c]	29·9[a]	29·8[a]	—
m-Xylene	28·9	151·9	199·6[c]	30·3[a]	31·2	28·9[a]
p-Xylene	28·4	147·4	191·3[c]	28·5[a]	28·6[a]	28·4[a]
n-Propylbenzene	29·0	146·0	183·8[c]	28·0[a]	27·3[b]	—
n-Butylbenzene	29·2	146·2	183·0[c]	28·0[a]	27·3[b]	—
Dichloromethane	23·0	160·0	278·3	33·6	42·0	22·2[a]
Trichloromethane	27·1	150·1	207·8	29·6	31·2	27·1[a]
Tetrachloromethane	27·0	148·0	203·1	28·7	29·8	26·9[a]
1,1-Dichloroethane	24·6	167·6	285·5	38·6	47·7	23·6[a]
1,2-Dichloroethane	32·2	154·2	184·6[c]	31·2[a]	30·5[b]	—
1,2-Dibromoethane	38·7	172·7	192·7[c]	39·1[a]	39·5[a]	38·7[a]
1,1,2,2-Tetrabromoethane	49·7	236·7	282·8	73·5	141·8	47·9[a]
Iodomethane	30·1	206·1	352·8	55·7	99·7	26·6[b]
Iodoethane	28·2	186·2	307·4	45·5	65·5	26·5[b]
Chlorobenzene	33·2	153·2	176·7[b]	30·8[b]	29·2[b]	—
Bromobenzene	36·3	166·3	190·5[c]	36·3[a]	36·3[a]	36·3[a]
Nitroethane	32·2	206·2	330·1	55·8	94·7	29·5[b]
Nitrobenzene	43·9	173·9	172·2[b]	39·7[b]	36·3[b]	—
n-Butyl acetate	25·2	130·2	168·2[b]	22·2[b]	20·7[b]	—
Diethyl ether	17·0	118·0	204·8	18·3	18·8	17·0[a]
Ethanthiol	23·2	189·2	385·7	47·0	78·3	19·2[b]
Bis(3-methylbutyl)amine	24·2	132·2	180·5[b]	22·9[b]	22·3[b]	—
Aniline	42·9	181·9	192·8[c]	43·4[a]	43·9[a]	42·9[a]
Methanol	22·6	119·6	158·2[b]	18·8[b]	17·1[b]	—
Ethanol	22·8	113·8	142·2[b]	17·0[b]	14·6[b]	—
Propanol	23·8	125·8	166·2[b]	20·8[b]	19·3[b]	—
Butanol	24·6	129·6	170·7[b]	22·0[b]	20·7[b]	—
2-Methylpropanol	23·0	161·0	281·7	34·0	42·9	22·2[b]
3-Methylbutanol	25·7	131·7	168·7[b]	22·8[b]	21·2[b]	—
Hexanol	25·8	133·8	173·5[b]	23·5[b]	22·3[b]	—
2-Octanol	26·5	158·5	237·0	33·0	37·8	26·2[a]
Octanol	27·5	155·5	219·8	31·7	34·7	27·4[a]
Cyclopentanol	32·0	147·0	168·8[b]	28·3[b]	26·1[b]	—
Acetic acid	27·8	178·8	287·5	41·9	56·4	26·7[a]

TABLE I
(*Continued*)

L	γ_L	$W_A(1)$	$\gamma_M^d(8a)$	$\gamma_L^d(8b)$	$\gamma_L^d(13b)$	$\gamma_L^a(14a)$
Pentanoic acid	27·3	177·3	287·9	41·2	55·3	26·2[a]
Undecenoic acid	30·6	157·6	202·9	32·6	34·0	30·6[a]
Oleic acid	32·5	190·5	279·2	47·6	65·5	31·4[a]

[a] Value within ±5% of the measured value γ_L (second column); [b] value lower by more than 5% of the average of γ_M^d (190·6), or γ_L^d indicating that γ_L contains a non-dispersion component; [c] value within ±5% of the average γ_M^d calculated for mercury–aliphatic saturated hydrocarbons.

The respective published values[4] of γ_L and W_A (for γ_M = 480) are summarized in the second and third column of the table. Using equation (*8a*), Fowkes determined from the data for aliphatic and aromatic hydrocarbons an average value of γ_M^d = 200 ± 7 using γ_M = 484. In our case the overall average value for all aliphatic hydrocarbons in Table I is γ_M^d = 190·6 ± 7·7, for aromatic hydrocarbons (disregarding benzene) it is γ_M = 189·7 ± 6·0. As the surface free energy of aliphatic saturated hydrocarbons contains only the dispersion component, it also holds for aromatic hydrocarbons that $\gamma_L = \gamma_L^d$. A lower value for benzene is an indication of the fact that a non-dispersion component is active in γ_L which does not play a role in the interaction across the interface with mercury. An analogous case represent other liquids, for which γ_M^d < 190·6 was calculated with the use of equation (*8a*).

For those values in the fourth column of Table I which differ by less than ±5% from the value 190·6, the calculations using (*8a*) and the respective interaction mechanism may be regarded as satisfactory; these values are denoted by the index *c* (in Table I). For values lower than 190·6 by more than 5%, it is probable that the use of equation (*8a*) is doubtful and that the low value is due to the presence of a non--dispersion component in γ_L which neither interacts with γ_M^m nor causes an induction (index *b* in Table I). We may assume that, instead of equation (*8a*), the following relation would be more suitable

$$\sqrt{\gamma_M^d} = W_A/2\sqrt{\gamma_L^d}. \tag{8b}$$

On the other hand, values larger than 190·6 by more than 5% are not satisfactory either, and using equation (*8a*) leads to erroneous results. We assume that the increase is due to neglecting the induction effect. If, *e.g.*, γ_L^n induces at the mercury interface γ_M^n of the same magnitude, we obtain from equation (*10*)

$$\gamma_{ML} = \left(\sqrt{\gamma_M^d} - \sqrt{\gamma_L^d}\right)^2 + \left(\sqrt{\gamma_M^n} - \sqrt{\gamma_L^n}\right)^2 + \gamma_M^m \tag{13}$$

and if $\gamma_M^n = \gamma_L^n$, it holds

$$\sqrt{\gamma_M^d} = (W_A - \gamma_L^n)/2 \sqrt{\gamma_L^d} \, . \tag{13a}$$

Neglecting γ_L^n in equation $(13a)$ leads to $(8b)$ and thus to an incorrect increase of the calculated value of γ_M^d.

If we use now the assumption that the component γ_L^n is present (which does not interact across the interface), then by substituting into equation $(8b)$ $\gamma_M^d = 190{\cdot}6$, we ought to obtain $\gamma_L^d < \gamma_L$ with the limiting case $\gamma_L^d = \gamma_L$ for $\gamma_L^n = 0$. The results calculated in this way are given in the fifth column of Table I. The values which differ by less than $\pm 5\%$ from the respective measured value of γ_L are denoted by the index a, and ought to be related to the liquids whose surface free energy contains only the dispersion component. Values differing from γ_L by more than 5% downwards are denoted by the index b and indicate that the surface free energy of the liquid contains a non-disperion component. However, in many cases the calculations give un-realistic values $\gamma_L^d > \gamma_L$. Similarly as stated above for γ_M^d, in that case the use of equation $(8b)$ is incorrect, and the results suggest that at the interface an induction takes place.

In case γ_L^n induces γ_M^n of the same magnitude, equation (13) may be reformulated for γ_L^d calculations to

$$\sqrt{\gamma_L^d} = \sqrt{\gamma_M^d} - \sqrt{(\gamma_M^d + \gamma_{LM} - \gamma_M)} \, . \tag{13b}$$

The values of γ_L^d calculated with the use of equation $(13b)$ are shown in the sixth column of Table I. Again, the index a is used to denote the results which agree with γ_L within $\pm 5\%$. In this case, γ_L^n is zero or negligibly small, and thus the induction is negligible, too. The values of γ_L^d differing from γ_L by more than 5% downwards are denoted by the index b. However, in all cases, where equation $(13b)$ gives satis-factory results (indexed by a and b), equation $(8b)$ leads to good results, too. There-fore, it cannot be decided, if the induction originating γ_M^n plays any significant role or if it takes place at all. Unsatisfactory results $\gamma_L^d > \gamma_L$ were obtained when using equation $(13b)$ in the same cases as when using $(8b)$.

Besides the above mentioned induction mechanism another mechanism may be considered: let us assume that the non-dispersion component of the surface free energy of the liquid changes by the induction into a component which can interact with γ_M^m. In this case we obtain from equation (10)

$$\gamma_{LM} = (\sqrt{\gamma_M^d} - \sqrt{\gamma_L^d})^2 + (\sqrt{\gamma_M^m} - \sqrt{\gamma_L^n})^2 \tag{14}$$

which can be written as

$$\sqrt{\gamma_L^d} = [W_A - 2 \sqrt{\gamma_M^m} \sqrt{(\gamma_L - \gamma_L^d)}]/2 \sqrt{\gamma_M^d} \, . \tag{14a}$$

From here we can evaluate γ_L^d by a stepwise approximation. Equation $(14a)$ assumes the form of equation $(8a)$ for $\gamma_L = \gamma_L^d$. Though equation $(14a)$ does not give a suitable solution in some cases, it offers reasonable results just for those liquids for which both $(8b)$ and $(13b)$ fail. In particular, this concerns halogenated hydrocarbons, alcohols, and acids in which the latter type of induction may take place.

It follows clearly from a comparison of the second and third column of Table I $(\gamma_L$ and $W_A(1))$ that equation (3) in no case gives satisfactory results and that Antonow rule does not hold. Similarly, equation (6) does not suit either, as large values of γ_{LM} lead to negative values of W_A.

Interface Water (W)–Mercury (M)

In the following calculations these values have been used: $\gamma_W = 72·8$; $\gamma_M = 480$; $\gamma_{WM} = 415$ (ref.[33]); $\gamma_M^d = 190·6$. In case the interaction could be described by dispersion forces only, equation (8) would be valid, and from there $\gamma_W^d = 24·9$. This value is higher than the one which results from the interaction water–aliphatic hydrocarbons (see further on, $\gamma_W^d = 21·8$); this indicates that an induction takes place. On the other hand, Fowkes — who regarded as a correct one the value $\gamma_{WM} = 425$ — found equation (8) quite satisfactory for this particular case.

The surface free energy of water contains, besides the dispersion component, the polar component, γ_W^p, and the hydrogen-bond component, γ_W^h. We may assume that the non-dispersion component of the surface free energy of water, γ_W^n (which may be γ_W^p or γ_W^h, or both these components together), induces a component of the same magnitude, γ_M^n. It follows from equation (10) for this case

$$\gamma_W^n = W_A - 2 \sqrt{\gamma_W^d} \sqrt{\gamma_M^d} . \tag{15}$$

There is still another possible type of induction, namely a transformation of γ_W^n into a component capable of an interaction with γ_M^m; this can be evaluated by deriving from equation (10) the following relation

$$\sqrt{\gamma_W^n} = (W_A - 2 \sqrt{\gamma_W^d} \sqrt{\gamma_M^d})/2 \sqrt{\gamma_M^m} . \tag{16}$$

If one uses in both cases $\gamma_W^d = 21·8$, one obtains from equation (15) a reasonable value $\gamma_W^n = 8·9$, while equation (16) offers $\gamma_W^n = 0·1$ — a value too low. Because $\gamma_W^d + \gamma_W^n < \gamma_W$, γ_W^n represents only one of both non-dispersion components of the surface free energy of water. The results of Panzer[34], derived from solubility parameters, give $\gamma_W^h > \gamma_W^p$. Therefore, it is probable that the calculated value is $\gamma_W^n = \gamma_W^p$, and that the induced interaction water–mercury takes place *via* $\gamma_W^p = 8·9$, according to equation (15). Then the corresponding value $\gamma_W^h = \gamma_W - \gamma_W^d - \gamma_W^p = 42·1$; this is to be compared with the value of Panzer, $\gamma_W^h = 38·5$. If, of course, the induction

effect γ_W^p led to $\gamma_M^p < \gamma_W^p$, the correct value γ_W^p would be higher than 8·9 and γ_W^h lower than 42·1 (compare further on, interaction water–aromatic hydrocarbons).

Interface Water(W)*–Organic Liquid*(L)

The values γ_L and W_A, earlier used by Girifalco and Good[4], are summarized in the second and third column of Table II. The fourth column gives the values of γ_W^d calculated under the condition $\gamma_L = \gamma_L^d$ from

$$\sqrt{\gamma_W^d} = W_A / 2 \sqrt{\gamma_L} \,. \tag{8c}$$

The procedure is analogous to the earlier mentioned calculation of γ_M^d with the use of equation (8a). The average value of γ_W^d for all saturated hydrocarbons (in Table II from n-pentane to "liquid petroleum") is 22·3 ± 2·4, and it is characterized by a fairly large scatter of values. The average of all values determined for straight-chain aliphatic hydrocarbons from C_6 upwards (indexed by a in Table II) agrees with the value of Fowkes, $\gamma_W^d = 21·8 \pm 0·7$. This value will be used from now on in this paper. For all other pairs the calculated values of γ_W^d are substantially higher. It follows from this fact that the use of equation (8c) is in these cases unsuitable, because it neglects the effect of non-dispersion forces.

As stated above, the values γ_M^d calculated with the use of equation (8a) for the mercury–aromatic hydrocarbons interface agree with the values for the mercury–aliphatic hydrocarbons interface. Accordingly, it ought to hold for aromatic hydrocarbons that $\gamma_L = \gamma_L^d$. However, for the interface with water there is a difference between aromatic and aliphatic hyrocarbons in the results, calculated with the use of equation (8c). We may assume, therefore, that in the region of the interface the polar component of the surface free energy of water causes a γ_L^p contribution, though in the organic liquid bulk it remains $\gamma_L = \gamma_L^d$. If $\gamma_W^p = \gamma_L^p$, we obtain from equation (10)

$$\gamma_{WL} = (\sqrt{\gamma_W^d} - \sqrt{\gamma_L^d})^2 + \gamma_W^h \,, \tag{17a}$$

which can be written as

$$\gamma_W^p = W_A - 2 \sqrt{\gamma_W^d} \sqrt{\gamma_L} \,. \tag{17b}$$

The values γ_W^p obtained with the use of equation (17b) (for $\gamma_W^d = 21·8$) are given in the fifth column of Table II. The average value of γ_W^p for all aliphatic hydrocarbons (the values are denoted by b in Table II) is $\gamma_W^p = 0·0 \pm 2·8$. By inserting $\gamma_W^p = 0$ into equation (17b) one obtains equation (8c); this means that the interaction of water with aliphatic hydrocarbons is due to dispersion forces only, without any contribution of induced components of the surface free energy.

For aromatic hydrocarbons the average value of γ_W^p calculated from equation (17b) (index c in Table II) is $\gamma_W^p = 14·7 \pm 1·6$. This value is in a reasonably good

agreement with the value obtained above from the interaction water–mercury. If $\gamma_W^p = 14\cdot7$, then it follows from the summation of the particular components that $\gamma_W^h = 36\cdot3$.

Equation ($17b$) gives satisfactory results on γ_W^p even for the interface between water and several halogenated hydrocarbons. Though we assume for most of them the presence of the component γ_L^p, equation ($17b$) may be at least approximately suitable, if γ_L^p is small and the induction by water increases its value at the interface from an originally low value to a value equal ot γ_W^p. With symmetric halogenated hydrocarbons the induction effect will be probably weaker. Therefore, equation ($17b$) does not give satisfactory results: e.g., for tetrachloromethane or tetrachloroethylene the calculated values of γ_W^p are much smaller than the expected value of $14\cdot7$. On the other hand, higher values of γ_W^p in Table II (mainly for oxygen-containing compounds) may be caused by the fact that hydrogen-bond induction takes place and the calculated values represent γ_W^h rather than γ_W^p, as can be derived from equation (10).

Let us assume that induction does not occur, but only an interaction between existing γ_W^p and γ_L^p takes place. Then for $\gamma_L = \gamma_L^d + \gamma_L^p$ equation (10) can be written as

$$\sqrt{\gamma_L^d} = \left[W_A - 2\sqrt{\gamma_W^p}\sqrt{(\gamma_L - \gamma_L^d)}\right]/2\sqrt{\gamma_W^d}. \qquad (18a)$$

From here, using $\gamma_W^d = 21\cdot8$ and $\gamma_W^p = 14\cdot7$, the values given in the sixth column of Table II were calculated by stepwise approximation. The conditions under which equation ($18a$) gives realistic values are: $\gamma_L \geqq \gamma_L^d$, and $W_A > 2\sqrt{\gamma_W^p}\sqrt{(\gamma_L - \gamma_L^d)}$. If in the calculations these conditions cannot be met, the respective values in Table II are omitted.

For aliphatic hydrocarbons, where $\gamma_L = \gamma_L^d$, equation ($18a$) assumes the form of equation ($8c$) and the calculated values of γ_L^d in the sixth column agree with the values of the second column. Both for aromatic and halogenated hydrocarbons the calculated values of γ_L^d are too low, with regard to the results with mercury. Therefore, the mechanism of interaction according to equation ($18a$) does not seem probable. For most of other liquids equation ($18a$) does not have a solution; this finding is also not in favour of the mechanism which the equation assumes.

Calculations according to equation ($18a$) may be modified in such a way that instead of γ_W^p one uses in it γ_W^h; this represents an interaction via the hydrogen-bond components of the surface free energy. The equation acquires the form

$$\sqrt{\gamma_L^d} = \left[W_A - 2\sqrt{\gamma_W^h}\sqrt{(\gamma_L - \gamma_L^d)}\right]/2\sqrt{\gamma_W^d} \qquad (18b)$$

and the results are shown in the seventh column of Table II. Similarly to the previous case, the calculated and measured values agree for aliphatic hydrocarbons. However, in contrast with the calculations using ($18a$), equation ($18b$) gives reasonable

TABLE II

Data for liquid(L)–water(W) interface calculated with the use of equations indicated in parentheses above the columns

L	γ_L	$W_A(1)$	$\gamma_W^d(8c)$	$\gamma_W^p(17b)$	$\gamma_L^d(18a)$	$\gamma_L^d(18b)$	$W_A(3)$	$W_A(6)$
n-Pentane	15·8	39·6	24·8	2·5[b]	15·7	15·8	31·6	42·9
Isopentane	13·4	37·5	26·2	3·3[b]	13·2	13·3	26·8	39·7
n-Hexane	18·4	40·1	21·8[a]	0·0[b]	18·4	18·4	36·8	45·1
n-Heptane	20·4	43·0	22·6[a]	0·8[b]	20·4	20·4	40·8[a]	48·1
n-Octane	21·8	43·8	22·0[a]	0·2[b]	21·8	21·8	43·6[a]	49·3
n-Decane	23·9	45·5	21·6[a]	−0·2[b]	—	—	47·8[a]	51·4
2,7-Dimethyloctane	22·2	48·2	26·1	4·2[b]	21·9	22·1	44·5	52·2
n-Tetradecane	25·6	46·2	20·8[a]	−4·6[b]	—	—	51·2	52·5
Cyclohexane	25·5	48·1	22·6	0·9[b]	25·5	25·5	51·0	53·7
Decalin	29·9	51·3	22·0	0·2[b]	29·9	29·9	59·8	57·3
"Stanolax"	30·7	47·9	18·7	−3·8[b]	—	—	61·4	55·2
"Liquid Petroleum"	31·1	48·6	18·9	−3·5[b]	—	—	62·2	55·7
Benzene	28·9	66·6	38·4	16·4[c]	—	26·5	57·7	67·6[d]
Toluene	28·5	65·2	37·2	15·3[c]	—	26·5	57·0	66·4[d]
o-Xylene	30·1	66·8	37·0	15·6[c]	—	28·0	60·2	68·3[d]
m-Xylene	28·9	63·8	35·2	13·6[c]	22·3	27·4	57·8	65·7[d]
p-Xylene	28·4	63·4	35·3	13·6[c]	21·5	26·8	56·8	65·1[d]
Ethylbenzene	29·2	63·6	34·6	13·1[c]	23·5	27·8	58·4	66·0[d]
Mesitylene	28·8	62·9	34·3	12·8[c]	10·2	27·5	57·6	65·0[d]
p-Cymene	28·1	66·3	39·0	16·8[c]	—	25·6	56·2	67·0[d]
Dichloromethane	26·5	71·0	47·5	22·9	—	21·0	53·0	69·2[d]
Trichloromethane	27·2	68·3	43·0	19·6	—	23·5	54·3	67·8[d]
Tetrachloromethane	27·0	54·7	27·8	6·2	26·1	26·7	53·9[d]	58·7
Tetrachloroethylene	31·7	57·0	25·6	4·4	31·3	31·6	63·4	61·9
1-Chloro-2-methylpropane	21·9	70·3	56·3	26·6	—	11·9	43·8	65·2

2-Chloro-2-methylpropane	19·6	68·6	60·0	27·3	—	—	39·2	62·1
1-Chloro-3-methylbutane	23·5	80·9	69·5	35·6	—	—	47·0	73·2
Tribromomethane	41·5	73·4	32·4	13·2	36·7	40·1	83·0	76·2[d]
Tetrabromomethane	49·7	83·7	35·2	17·9	38·3	47·0	99·4	85·3[d]
Bromoethane	24·2	65·8	44·7	19·9	—	20·3	48·4	64·3[d]
1,2-Dibromoethane	38·7	75·0	36·3	16·9	20·6	36·3	77·4[d]	77·1[d]
1,1,2,2-Tetrabromoethane	49·7	83·7	35·2	17·9	20·5	47·0	99·4	85·3[d]
1,2,3-Tribromopropane	45·4	79·7	34·9	16·8	17·8	43·1	90·8	81·8[d]
Diiodomethane	50·8	75·1	27·7	8·5	6·7	50·3	101·6	77·4[d]
Chlorobenzene	33·6	69·0	35·4	14·9	14·3	31·8	67·2[d]	71·2[d]
Bromobenzene	36·5	71·2	34·7	14·8	13·8	34·7	73·0[d]	73·6[d]
Iodobenzene	39·7	70·7	31·4	11·9	9·2	38·6	79·4	73·8[d]
o-Bromotoluene	35·8	67·4	31·7	11·5	8·6	34·7	71·6	70·6[d]
o-Chloronaphthalene	41·8	73·9	32·6	13·5	11·5	40·3	83·6	76·7[d]
o-Bromonaphthalene	44·6	75·3	31·7	12·9	10·8	43·3	89·2	78·0[d]
Ethanthiol	23·2	69·9	52·6	24·9	—	15·8	46·4	66·1
Bis(2-chloroethyl) ether	42·8	87·2	44·4	26·1	—	36·2	85·6[d]	87·9[d]
Phenyl isothiocyanate	41·5	75·3	34·1	15·1	14·3	39·6	83·0	77·8[d]
Carbon disulfide	32·3	56·7	24·8	3·6	32·0	32·2	64·6	61·8
Butanenitrile	28·1	90·5	72·8	41·0	—	—	56·2	83·4
3-Methylbutanenitrile	26·0	84·7	68·9	37·1	—	—	52·0	77·8
Nitromethane	36·8	100·1	68·0	43·5	—	—	73·6	96·1[d]
Nitrobenzene	43·9	91·0	47·1	29·1	—	35·2	87·8[d]	91·3[d]
o-Nitrotoluene	41·5	87·1	45·6	26·9	—	34·2	83·0[d]	87·5[d]
m-Nitrotoluene	41·4	86·5	45·1	26·4	—	34·5	82·8[d]	87·0[d]
Diethyl ether	17·0	79·1	91·9	40·6	—	—	34·0	64·7
Bis(2-methylethyl) ether	17·3	72·2	75·2	33·4	—	—	34·6	61·4
Dipropylamine	25·5	96·6	91·4	49·4	—	—	51·0	85·1
Dibutylamine	22·1	84·5	81·0	40·7	—	—	44·1	73·9
Aniline	42·9	109·9	70·3	48·7	—	—	85·8	106·9[d]

TABLE II
(Continued)

L	γ_L	$W_A(1)$	$\gamma_W^d(8c)$	$\gamma_W^P(17b)$	$\gamma_L^d(18a)$	$\gamma_L^d(18b)$	$W_A(3)$	$W_A(6)$
Heptanal	26·9	86·0	68·7	37·6	—	—	53·8	79·4
Benzaldehyde	40·0	97·3	59·1	38·2	—	—	80·1	95·4[d]
2-Pentanon	24·7	91·2	84·1	44·8	—	—	49·4	80·8
3-Hexanon	25·5	84·7	70·3	37·5	—	—	51·0	77·4
2-Hexanon	25·0	88·2	77·7	41·5	—	—	50·0	79·2
2-Heptanon	26·2	86·6	71·5	38·8	—	—	52·4	79·2
2-Octanon	26·9	85·6	68·0	37·2	—	—	53·8	79·1
1-Chloro-2-propanon	35·3	101·0	72·2	45·5	—	—	70·6	96·0[d]
1,1-Dichloro-2-propanon	31·9	90·3	63·8	37·6	—	—	63·8	86·0[d]
Butanol	24·6	95·6	92·8	49·3	—	—	49·2	83·5
2-Methylpropanol	23·0	93·8	95·5	49·0	—	—	46·0	80·6
Pentanol	25·7	94·1	86·0	46·8	—	—	51·4	83·7
3-Methylbutanol	23·2	91·2	89·5	46·2	—	—	46·4	79·2
Hexanol	25·8	91·8	81·6	44·4	—	—	51·6	82·3
Heptanol	24·5	89·6	81·8	43·4	—	—	49·0	79·6
Octanol	27·5	91·8	76·5	42·8	—	—	55·0	83·8
2-Octanol	26·5	89·7	75·8	41·6	—	—	53·0	81·5
Cyclohexanol	32·7	101·6	78·8	48·2	—	—	65·4	94·7
3-Methylbutanoic acid	25·5	95·6	89·5	48·4	—	—	51·0	84·4
Heptanoic acid	28·3	94·1	78·1	44·4	—	—	56·6	86·0
Octanoic acid	27·5	91·8	76·5	42·8	—	—	55·0	83·8
Undecenoic acid	30·6	93·3	71·0	41·6	—	—	61·2	87·2
Oleic acid	32·5	89·6	61·7	36·4	—	—	65·0	85·8[d]
Perfluorodibutyl ether	12·2	33·1	22·5	0·5	12·2	12·2	24·4	36·4
Perfluorotributylamine	16·8	64·0	61·0	25·7	—	—	33·6	56·5

[a] Values used to calculate the average $\gamma_W^d = 21·8$; [b] values for which the average $\gamma_W^P = 0$ indicated that only the interaction *via* dispersion forces takes place; [c] values used to calculate the average $\gamma_W^P = 14·7$; [d] values within $\pm 5\%$ of $W_A(1)$.

values of γ_L^d for aromatic and halogenated hydrocarbons. This means that the surface free energy of these compounds may contain a small non-dispersion component which is able to interact with the hydrogen-bond component of the surface free energy of water. Thus, there are two possible ways of explaining the interaction of water with aromatic and halogenated hydrocarbons: on the one hand, by induction of the polar component (cf. equation (17b)), on the other hand, by the existence of a small non-dispersion component which is able to interact with the hydrogen-bond component according to equation (18b).

For most of the other liquids the results indicate that both a partial induction of the non-dispersion component and an interaction between the existing components of the surface free energy takes place. In order to illustrate this case, we report in the following a simplified calculation for alcohols. Let us assume that $\gamma_L =$ $= \gamma_L^d + \gamma_L^p$, that both the interaction between dispersion components and between polar components of water and alcohols takes place, and that water induces $\gamma_L^h = \gamma_W^h$. For this case we can derive from equation (10)

$$\gamma_W^h = W_A - 2\sqrt{\gamma_W^d}\sqrt{\gamma_L^d} - 2\sqrt{\gamma_W^p}\sqrt{\gamma_L^p}. \qquad (19)$$

By substituting $\gamma_W^d = 21\cdot8$, $\gamma_W^p = 14\cdot7$, $W_A(1)$ from Table II, and γ_L^d and γ_L^p (according to (13b) or (14a) from Table I) into equation (19), we obtain the following values of γ_W^h: 38·0 (n-butanol), 42·9 (2-methylpropanol), 31·9 (3-methylbutanol), 33·4 (n--hexanol), and 40·5 (n-octanol). The average value of $\gamma_W^h = 37\cdot3 \pm 4\cdot6$ agrees well with the above mentioned value derived from the induction effect of the polar component of water on aromatic hydrocarbons; this seems to confirm this particular mechanism of the interaction at the interface. Panzer[34] calculated from solubility parameters very low values of γ_L^h for alcohols: e.g., for n-butanol 1·2 and for 2-methyl-propanol 1·3. These are negligibly small values in comparison with those assuming the existence of induction, and thus equation (19) may be used in calculating the approximate value of γ_W^h.

Finally, Table II shows values of W_A calculated with the use of equations (3) and (6); the results are compared with those obtained with equation (1). In case the values in eighth and nineth column of Table II agree with $W_A(1)$ within $\pm5\%$, we regard the results as acceptable (denoted by index d in Table II). It turns out, however, that the agreement of the $W_A(3)$ values is rather fortuitous and in many cases the deviation is quite large. The values $W_A(6)$, in comparison with $W_A(1)$, are systematically higher for aliphatic hydrocarbons and lower for oxygen-containing compounds. However, the differences are not as large as those for $W_A(3)$, and in many cases (e.g., aromatic hydrocarbons and halogenated compounds) the agreement with $W_A(1)$ is good. Equation (6) is thus not suitable in general for interfaces of two liquids, but in many cases W_A can be obtained from it with a reasonable accuracy.

Comparison of the Equations Used and Summary of Results

A certain contradiction may be seen in the Girifalco–Good equation (joined equations (*1*) and (*4*)), namely in that the work of adhesion is expressed in it twice in a different way: first, as a corrected $(-\gamma_{12})$ arithmetic mean of the cohesion energies $(\gamma_1 + \gamma_2)$, second, as a corrected (Φ-times) geometric mean $(2\sqrt{(\gamma_1\gamma_2)})$. In another words, the interfacial free energy is determined in the equation as a difference between the work of cohesion, expressed by the arithmentic mean, and the work of adhesion, expressed as a geometric mean. However, for a particularly chosen value of Φ equation (*4*) must be of a general validity.

A factor f can be chosen in such a way that the ratio of the arithmetic and the geometric mean multiplied by it equals unity, $f(\gamma_1 + \gamma_2)/2\sqrt{(\gamma_1\gamma_2)} = 1$; introduced into the Girifalco–Good equation, it leads to an expression identical with the Neumann equation (*5*), if $f/2\sqrt{(\gamma_1\gamma_2)} = 0.0075$. However, the Neumann interaction parameter (Φ_N) is identical with the Girifalco–Good interaction parameter (Φ_G) only if $f = 1$, *i.e.* for $\gamma_1 = \gamma_2$, because

$$\Phi_N = \Phi_G f = f(\gamma_1 + \gamma_2)/2\sqrt{(\gamma_1\gamma_2)} - f\gamma_{12}/2\sqrt{(\gamma_1\gamma_2)} \,. \tag{20}$$

According to equation (*5*), Φ_N can be $\Phi_N \leqq 1$; however, Girifalco and Good[4] report $\Phi_G > 1$ for the interface between water and alcohols or some other oxygen-containing compounds. This is, of course, not allowed by equation (*11*), according to which $\Phi \leqq 1$. Therefore, neither (*11*) nor (*9*) have a general validity. However, if we start from equation (*10*), and assume that at the interface a surface free energy component is induced, then the calculated W_A can give in equation (*4*) $\Phi_G > 1$. Thus, equation (*10*) agrees with equation (*4*), if we consider in it all the interaction mechanisms at the interface, including the induced components of the surface free energy.

The results of calculations of the work of adhesion based on the Antonow rule (equation (*3*)), $W_A(3)$, only rarely conform with the definition of the thermodynamic value of the work of adhesion, $W_A(1)$ (*i.e.* W_A according to equation (*1*)). This is the case, even if the mutual solubility of both phases is negligible. The agreement of $W_A(1)$ and $W_A(3)$ has to be regarded as fortuitous, and the use of equation (*3*) cannot be correct in general. The standard deviation of the difference $W_A(1) - W_A(3)$ of all values in Table II is $+15 \pm 19.9$. The values of $W_A(1)$ are thus on the average higher than those of $W_A(3)$; this may be a consequence of the fact that the lowered values of the surface free energy of water, saturated by the particular organic liquid, were not used in calculating $W_A(1)$. On the other hand, against this argumentation speaks that in 16 cases in Table II the value of $W_A(3)$ is higher than that one of $W_A(1)$ by more than 5%. After all, for the mercury–liquid interfaces γ_M cannot be lowered by the solubility, and still the difference $W_A(1) - W_A(3)$ has a high positive value.

Equation (*20*) shows that equation (*4*) corresponds practically to equation (*5*), if,

first, there is not a large difference between γ_1 and γ_2 and, second, if $\gamma_1 + \gamma_2 \approx 133$. In these cases equation (6) is valid. The values in Table II give the standard deviation of the difference $W_A(1) - W_A(6)$ for the interfaces of water with aromatic hydrocarbons and halogenated compounds as $-1\cdot0 \pm 3\cdot0$, and for the interfaces between water and all liquids as $+2\cdot0 \pm 5\cdot9$. This shows that equation (6) represents a good approximation for calculations of the respective values. However, equation (6) cannot be used for interfaces mercury–liquids.

Fowkes equation (8) holds for those interfaces, where there is an interaction between dispersion components of the surface free energies of both phases only. The complemented Fowkes equation (9) is valid, if there is an interaction between respective non-dispersion components of both phases, but if no induction takes place.

It has been shown in this contribution that in many cases very probably a non-dispersion component of the surface free energy of one phase induces a component of the same type at the interface of the other phase, and thus it influences the value of W_A. In such a case, it is possible to start in the evaluation of the work of adhesion from equation (10) and use it in a suitable form, according to the corresponding interaction at the interface, as demonstrated here on several specific cases. Besides that, equation (10) expresses a disequilibrium of the forces acting at both sides of the interface — a phenomenon which originates the interfacial tension. Also, it specifies the nature of the interfacial tension, as suggested by Birkeman[27], and elucidates the proper use of the geometric mean in equations (8) and (9).

A comparison of the value of the dispersion component, calculated according to equation (8), $\gamma^d(c)$, with the known real value, $\gamma^d(r)$, can indicate the type of interaction at the interface. If $\gamma^d(c)$ agrees with $\gamma^d(r)$, then the interaction is due to dispersion forces only. If $\gamma^d(c) < \gamma^d(r)$, when using equation (8), then in the other phase a non-dispersion component plays a role which does not participate in the interaction. If $\gamma^d(c) > \gamma^d(r)$, then at the interface an induction of a component of the surface free energy takes probably place.

The calculated results show that for aromatic hydrocarbons $\gamma_L = \gamma_L^d$, but the polar component of the surface free energy of water induces at the interface γ_L^p. However, aromatic hydrocarbons also may contain a small non-dispersion component which is capable of an interaction with the hydrogen-bond component of water. Halogenated and oxygen-containing compounds either induce, through their polar component of the surface free energy, a component of the same type in mercury, or — due to mercury — their polar component changes to a component capable of an interaction with γ_M^m. At the interface with water both an interaction between non-dispersion components and an induction of non-dispersion components in organic liquids takes place.

The values of γ_W^p and γ_W^h were calculated from the water–mercury interaction, under the assumption that γ_W^p induces γ_M^p of the same magnitude. A similar assump-

tion made it possible to calculate γ_w^p and γ_w^h from the water–aromatic hydrocarbons interaction. Finally, the value of γ_w^h was determined from the interaction water––alcohols assuming that γ_L^h arizes through induction. All calculated values of γ_w^h exhibit both a good mutual agreement (the average value is $38\cdot6 \pm 3\cdot1$) and an agreement with the value $\gamma_w^h = 38\cdot5$ determined earlier[34] from the solubility parameter.

REFERENCES

1. Antonow G.: J. Chim. Phys. *5*, 372 (1907).
2. Defay R., Prigogine I., Bellemans A., Everett D. H.: *Surface Tension and Adsorption*, p. 182. Longmans, London 1966.
3. Shchukin E. D., Pertsov A. V., Amelina E. A.: *Kolloidnaya Chimiya*, p. 86. Izdatelstvo Moskovskogo Universiteta, Moskva 1982.
4. Girifalco L. A., Good R. J.: J. Phys. Chem. *61*, 904 (1957).
5. Driedger O., Neumann A. W., Sell P. J.: Kolloid Z. — Z. Polym. *204*, 101 (1965).
6. Sell P. J., Neumann A. W.: Angew. Chemie *78*, 321 (1966).
7. Neumann A. W., Sell P. J.: Kunststoffe *57*, 829 (1967).
8. Neumann A. W.: Adv. Colloid Interface Sci. *5*, 105 (1974.)
9. Fowkes F. M.: J. Phys. Chem. *66*, 328 (1962).
10. Fowkes F. M.: J. Phys. Chem. *67*, 2538 (1963).
11. Fowkes F. M.: Ind. Eng. Chem. *56*, 40 (1964).
12. Tamai Y.: J. Phys. Chem. *79*, 965 (1975).
13. Bikerman J. J.: J. Adhesion *3*, 19 (1971).
14. Zisman W. A.: J. Paint Technology *44*, 42 (1972).
15. Zettlemoyer A. C.: J. Colloid Interface Sci. *28*, 343 (1968).
16. Cortes J.: J. Colloid Interface Sci. *45*, 209 (1973).
17. Owens D. K., Wendt R. C.: J. Appl. Polym. Sci. *13*, 1741 (1969).
18. Dahlquist C. A., *Aspects of Adhesion* (D. J. Alner, Ed.), Vol. V, p. 183. University of London Press, London 1969.
19. Kaelble D. H., Uy N. C.: J. Adhesion *2*, 50 (1970).
20. Kaelble D. H.: J. Adhesion *2*, 66 (1970).
21. Wu S.: J. Phys. Chem. *74*, 632 (1970).
22. Fowkes F. M., J. Adhesion *4*, 155 (1972).
23. Wu S.: J. Polym. Sci. C *34*, 19 (1971).
24. Wu S.: J. Adhesion *5*, 39 (1973).
25. Kitazaki Y., Hata T.: J. Adhesion *4*, 123 (1972).
26. Kloubek J.: J. Adhesion *6*, 293 (1974).
27. Bikerman J. J.: *Physical Surfaces*, p. 122, Academic Press, New York 1970.
28. Kloubek J.: *Poster at the VIIIth Conference on Surface Forces*, Academy of Sci. U.S.S.R., Moscow, December 1985.
29. Elton G. A.: J. Chem. Phys. *19*, 1066 (1951).
30. Wolfram E.: Kolloid Z. — Z. Polym. *182*, 75 (1962).
31. Lipatov Yu. S., Feinerman A. E.: J. Adhesion *6*, 165 (1974).
32. Lipatov Yu. S., Feinerman A. E.: Adv. Colloid Interface Sci. *11*, 195 (1979).
33. Butler E. B.: J. Phys. Chem. *67*, 1419 (1963).
34. Panzer J.: J. Colloid Interface Sci. *44*, 142 (1973).

Translated by Z. Herman.