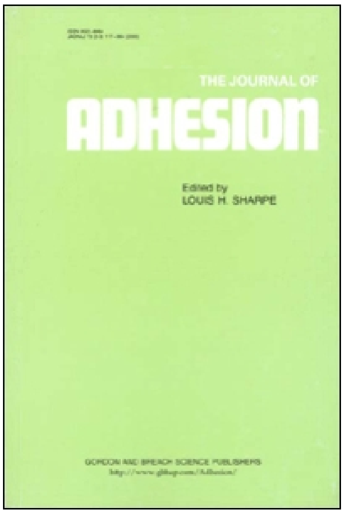

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Interaction of Polar Forces and Their Contribution to the Work of Adhesion

J. Kloubek[a]
[a] J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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Interaction of Polar Forces and Their Contribution to the Work of Adhesion

J. KLOUBEK

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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It is shown that the best fit of experimental data to the correlation equation as used by Fowkes[1] cannot be considered as a criterion of correctness with which the mathematical formula expresses the way of polar interaction at interfaces. Examples of other evidence are given that the polar part of work of adhesion may be well represented by the geometrical mean of polar components of surface energies.

INTRODUCTION

Fowkes[1] selected some of Dann's[2] experimental data concerning the contact angles of four polar liquids on seven polymer solids to show that the non-dispersion part of work of adhesion, $W_A - W_A^d$, is directly proportional to the non-dispersion part of surface tension of liquids, $\gamma_L - \gamma_L^d$. This direct proportionality was already indicated before by Dann[3] who, however, mentioned that either a linear or a second-order quadratic model could fit the data.

Several authors[4-12] expressed the part of polar interaction at the interface of adjacent phases by the geometrical mean of polar components of surface free energies, $2(\gamma_S^p\gamma_L^p)^{1/2}$, i.e., analogously to the formerly proved[13, 14] relation concerning the interaction of dispersion forces, $2(\gamma_S^d\gamma_L^d)^{1/2}$. If we simply denote the non-dispersion part of surface energy as γ^p we can write in conformity with the above authors[4-12] (for zero spreading pressure conditions)

$$W_A = 2(\gamma_S^d\gamma_L^d)^{\frac{1}{2}} + 2(\gamma_S^p\gamma_L^p)^{\frac{1}{2}}. \tag{1}$$

This correlation is considered by Fowkes as incorrect. He produced evidence by showing in a graph of his paper[1] that the experimental points deviate distinctly from (1) while they fit the correlation

$$W_A = 2(\gamma_S^d\gamma_L^d)^{\frac{1}{2}} + K\gamma_L^p \tag{2}$$

which he holds to be true.

The above two correlations have been supplemented in this paper by the third one,

$$W_A = 2(\gamma_S^p\gamma_L^p)^{\frac{1}{2}} + K\gamma_L^d, \tag{3}$$

which has no theoretical basis and is undoubtedly incorrect from the point of view of providing information about the way of interaction. The purpose of it is to find out if the better fit of data used by Fowkes[1] can determine the correctness of mathematical formulation of the mode of interaction at interfaces.

EVALUATION OF CORRELATIONS (1)–(3) AND OF THE DATA USED

Properties of liquids used by Fowkes are given in Table I because of some misprints in the respective paper.[1] Values γ_L^d and γ_L^p were calculated by Eqs. (4) and (5),

$$\gamma_L^d = \gamma_L^2(1 + \cos\theta)^2/4\gamma_S, \tag{4}$$

$$\gamma = \gamma^d + \gamma^p, \tag{5}$$

using the respective data[1, 2] of surface tension of liquids and their contact angles θ on paraffin of $\gamma_S = 25.5$ dyn/cm.

Equations (1)–(3) were evaluated by the least squares method using γ_L^d and γ_L^p given in Table I and advancing contact angles given by Dann[2]. Results are summarized in Table II.

TABLE I

Surface tension, its components and contact angle of liquids on paraffin

Liquid	θ^a	γ_L	γ_L^d [b]	γ_L^p [c]
water	110	72.2	22.1	50.1
glycerol	96	64.0	32.2	31.8
formamide	91	58.3	32.2	26.1
ethylene glycol	83	48.3	28.8	19.5

[a] Advancing contact angles according to Dann.[2]
[b] Calculated by Eq. (4).
[c] Evaluated by Eq. (5).

TABLE II

Components of surface free energy of polymers as calculated by Eqs. (1)–(3) and the respective standard deviations of work of adhesion

Polymer [a]	Correlation equation	γ_S^d	γ_S^p	K	S [b]
PMA	(1)	20.54	12.16	—	2.65
	(2)	37.35	—	0.69	2.59
	(3)	—	19.21	1.34	2.97
PET	(1)	24.66	12.13	—	1.56
	(2)	42.77	—	0.69	1.20
	(3)	—	19.77	1.47	1.30
PCT	(1)	20.07	15.06	—	3.98
	(2)	38.82	—	0.77	3.76
	(3)	—	22.38	1.33	3.54
Nylon 11	(1)	21.70	11.17	—	0.76
	(2)	38.07	—	0.66	0.32
	(3)	—	18.12	1.37	1.40
Nylon 6.6	(1)	24.36	15.60	—	1.44
	(2)	45.34	—	0.77	1.81
	(3)	—	24.64	1.44	3.30
PS	(1)	23.17	6.14	—	1.90
	(2)	35.16	—	0.49	1.66
	(3)	—	11.60	1.43	1.46
PVC	(1)	40.77	2.18	—	3.69
	(2)	49.69	—	0.29	3.64
	(3)	—	7.45	1.88	4.00

[a] Abbreviations as follows: PMA = poly(methylmethacrylate), PET = poly(ethylene terephthalate), PCT = poly(1,4-cyclohexanedimethylene terephthalate), PS = poly(styrene), PVC = poly(vinylchloride).

[b] $S = (\Sigma\Delta^2/(n-2))^{1/2}$, $\Delta = W_A - W_A(\text{regr.})$, $n = 4$.

Eq. (1) seems to give too low γ_S. Wu[9] estimated γ_S of PMA at 20°C by extrapolating surface tension of the melt and found it to be equal to that resulting from parachor (41.1 dyn/cm) and γ_S of PS by these two methods as 40.7 and 37.5 dyn/cm respectively. The disadvantage of Eqs. (2) and (3) is that they do not make it possible to estimate γ_S. In no case does standard deviation of work of adhesion differ in such a way as to determine which one of the respective correlations is correct or which should be preferred, and which can be rejected because of nonconformity with experimental values. Even in some cases Eq. (3) gives the best fit. However, this correlation does not agree with Eq. (4) which was verified by a good approximation of calculated results to the experimental values measured with pairs of liquids interacting only by dispersion forces.[13, 14] Standard deviations are summarized in Table III. For all polymers together correlation (2) gives the smallest deviation, for nylons correlation (1) is the best. However, in contrast to the Fowkes' paper[1] the differences are not significant. It must be further considered that the results depend on γ_L^d and γ_L^p used. Fowkes[13, 14] gives, e.g. for water $\gamma_W^d = 21.8$ dyn/cm. Dann[2] gives averaged dispersion components for water 22.0, glycerol 34.0, formamide 32.3, and ethylene glycol 29.3 dyn/cm. The differences between the above values and those corresponding with the contact angle on paraffin (cf. Table I) are considerable. They influence the sequence in accuracy of correlations so that even in most cases correlation (3) could be the best. This fact clearly shows that the best fit of the data cannot be used in the present case to judge the correctness of interaction evaluation. Other criteria must be looked for. However, the data of Dann[2] should be inspected first.

TABLE III

Standard deviations of W_A of polymer classes

Polymer class	Equation [a] (1)	 (2)	 (3)
Polyesters	2.90	2.73	2.77
Nylons	1.15	1.30	2.54
Oxygen-free polymers	2.94	2.83	3.01
All polymers investigated	2.54	2.44	2.78

[a] Standard deviations concerning the respective correlation equations, $S = (\Sigma^m \Sigma^n \Delta^2/(n-2)m)^{1/2}$, n is the number of liquids used on each polymer, m is the number of polymers evaluated.

As shown by Murphy and coworkers[15] solid surfaces cannot be evaluated correctly when using solutions because surface energy changes as a result of the preferential adsorption of one or another component of solution. Therefore, in our calculations summarized in Table II we have not used Dann's components of surface tension obtained by averaging the data including solutions[2] but the values corresponding to the contact angles only of the pure liquids on paraffin.

Dann likewise gives in his paper[2] contact angles of methylene iodide and α-bromonaphthalene on polymers. These data are not included directly in Fowkes' paper.[1] However, because Fowkes[1] writes that his "Figure 1 shows Dann's results" it may be supposed that he used γ_S^d estimated by Dann[2] to calculate $W_A^d = 2(\gamma_S^d\gamma_L^d)^{1/2}$. Dann[2] denoted as γ_c^d the critical surface tension of polymers which relates to the liquids interacting only by dispersion forces. This he considered to equal γ_S^d. According to his own data he could use only water, glycerol, formamide, methylene iodide, and α-bromonaphthalene to determine γ_c^d. To make possible an extrapolation to similar γ_c^d values wetting by ethylene glycol should have been omitted from the Dann's data. However, indeterminate γ_c^d result as it follows from divergent values in Dann's following paper.[3] For a comparison both his $\gamma_S^d = \gamma_c^d$ are given in Table IV.

It can hardly be considered that the first three liquids interact with polymers only by dispersion forces. Suitability of methylene iodide and α-bromonaphthalene to characterize the surfaces is questionable because the author himself mentioned that the surface of PS was attacked by them. When we draw a straight line through the respective points of these two liquids in the plot of cos θ against γ_L we get γ_c given in the fourth column of Table IV. All values are very close together and they do not seem to characterize polymers. They all approach conspicuously to the surface tension of α-bromonaphthalene.

Linearly extrapolated dependencies of cos θ on γ_L of four polar liquids (water, glycerol, formamide, and ethylene glycol) yield γ_c values given in the fifth column of Table IV. These data were evaluated by the least squares method and the standard deviation of γ_L at cos $\theta = 1$ is enclosed. These γ_c are much lower than those determined by "non-polar" liquids.

TABLE IV

Critical surface tension of polymers

			Extrapolated values		
Polymers	Literature data $\gamma_S^d = \gamma_c^d$		non-polar liquids	polar liquids	Calculated values
a	*b*	*c*	*d*	*e*	*f*
PMA	43	41	44.0	26.0 ± 6.0	28.4
PET	43	43	44.1	32.3 ± 3.7	35.6
PCT	44.6	43	—	29.7 ± 9.1	31.5
Nylon 11	43	41	44.2	25.5 ± 3.1	29.8
Nylon 6.6	46	47	43.7	38.6 ± 1.1	39.1
PS	42.5	40	43.8	20.3 ± 7.3	26.7
PVC	43	40	43.5	37.2 ± 5.5	40.0

[a] Abbreviations as in Table II.

[b] According to Dann.[2]

[c] According to Dann.[3]

[d] By linear extrapolating wetting data of methylene iodide and α-bromonaphthalene.

[e] By linear extrapolating wetting data of water, glycerol, formamide and ethylene glycol by least squares method. The standard deviation attached is $S_c = S[(1/n) + (1 - x)^2/\Sigma(x - \bar{x})^2]^{1/2}$ in which $S = [\Sigma\Delta^2/(n-2)]^{1/2}$, $n = 4$, $\Delta = \gamma_L - \gamma_L(\text{regr.})$, $x = \cos\theta$, $\bar{x} = \Sigma\cos\theta/n$.

[f] Calculated by Eq. (11) using d_c and p_c extrapolated together with γ_S and γ_S^d calculated by Eq. (1).

JUSTIFICATION OF USING THE GEOMETRICAL MEAN IN EVALUATION OF POLAR FORCE INTERACTION

As already mentioned by Dann[3], K in Eq. (2) undoubtedly should be a function of γ_S^p. It does not seem likely that the polar components of both phases could interact in a different way. Thus, we may consider $K = K'\gamma_S^p$. In that case the meaning of K' is obscure because of its low value without any explicit significance. Eq. (2) as well as Eq. (3) seem to have hardly any other meaning than just a casual correlation of the data.

If the reasoning which justifies the geometrical mean of dispersion forces interaction[13, 14] is accepted the same principle may also be considered for the polar interaction. Interfacial energy can be dissolved in surface energy components when rearranging (1) in (7) as it has been already done by Owens and Wendt[4] and by Kaelble and Uy.[5]

$$\gamma_{SL} = [(\gamma_S^d)^{1/2} - (\gamma_L^d)^{1/2}]^2 + [(\gamma_S^p)^{1/2} - (\gamma_L^p)^{1/2}]^2 \qquad (7)$$

Eq. (7) expresses the principle of compensation of forces action across the interface. The less the difference between the respective components, the less the interfacial tension. In the case of ideal interaction γ_{SL} should be zero. The necessary condition for it, according to (7), is $\gamma_S^d = \gamma_L^d$ and $\gamma_S^p = \gamma_L^p$. Then the work of adhesion becomes equal to that of cohesion. On the contrary, Eq. (7) explains why the interfacial tension has usually a non-zero value at $\gamma_L = \gamma_S$.

Similar to Eq. (5) relation (7) can be written in terms of interfacial energy components (8).

$$\gamma_{SL} = \gamma_{SL}^d + \gamma_{SL}^p \qquad (8)$$

Fowkes' theory has been already interpreted in this way.[16] According to Fowkes[13] his excess energy ($E_{SL} = K\gamma_L^p$) would be represented by $-\gamma_{SL}^p$ because he considered

$$\gamma_{SL}^d = \gamma_S + \gamma_L - 2(\gamma_S^d\gamma_L^d)^{1/2}$$

and

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d\gamma_L^d)^{1/2} - E_{SL}$$

(cf. Eq. (2)) in the case of a polar interaction. He used the above equations with a simplification that he considered $\gamma_L = \gamma_L^d$ for many organic liquids. Unlike Fowkes, it follows from Eqs. (7) and (8) that

$$W_A^d = \gamma_S^d + \gamma_L^d - \gamma_{SL}^d = 2(\gamma_S^d\gamma_L^d)^{1/2} \qquad (9a)$$

and

$$W_A^p = \gamma_S^p + \gamma_L^p - \gamma_{SL}^p = 2(\gamma_S^p\gamma_L^p)^{1/2}. \qquad (9b)$$

By summation of Eqs. (9) we obtain the known relation

$$W_A = W_A^d + W_A^p = \gamma_S + \gamma_L - \gamma_{SL} = 2\phi(\gamma_S\gamma_L)^{1/2} \qquad (10)$$

in which $\phi = (d_S d_L)^{1/2} + (p_S p_L)^{1/2}$, $d = \gamma^d/\gamma$ and $p = \gamma^p/\gamma$. In this way Eq. (1) agrees with the work of adhesion according to Girifalco and Good.[17, 18]

To show explicitly the relation between γ_c and γ_S or γ_S^d Eq. (1) can be rearranged (for $\cos\theta = 1$) in

$$(\gamma_c/\gamma_S)^{1/2} = (d_c d_S)^{1/2} + (p_c p_S)^{1/2}. \qquad (11)$$

Values d_c and p_c were extrapolated for hypothetical liquids of $\gamma_L = \gamma_c$ by the best fit linear relation between d_L and γ_L of the respective polar liquids (water, glycerol, formamide, and ethylene glycol), $d_L = 1.208 - 0.01169\gamma_L$. Thus γ_c were calculated using d_c and p_c in Eq. (11) together with γ_S and γ_S^d (i.e. d_S and p_S) obtained by Eq. (1) (Table II). The results are given in Table IV (column *f*) and show a good agreement with γ_c extrapolated by the Zisman plot (column *e*).

However, the above γ_S may be considered only as an average of a variable because of a surface modification by adsorbed layers of autophobic liquids. Deviating values of γ_S were calculated by the empirical method of Neumann and Sell[19, 20] which was recently reexamined on a theoretical basis.[21] The results are given in Table V. They show with few exceptions that γ_S becomes smaller with liquids of lower γ_L. This indicates that the surfaces are modified by an adsorption of some liquids. This fact was already mentioned by Dann.[3] In such a case the fit of correlations (1)–(3) cannot be taken for a criterion of their correctness at all because of neglecting the unequal spreading pressures π.

TABLE V

Surface free energy of polymers calculated by the method of Neumann and Sell[19-21]

	γ_S [b]			
Polymer [a]	water	glycerol	formamide	ethylene glycol
PMA	38.6	36.2	37.6	32.9
PET	40.4	40.2	39.8	36.1
PCT	40.9	38.5	40.8	33.8
Nylon 11	38.0	37.3	36.0	33.3
Nylon 6.6	43.9	41.9	42.4	40.8
PS	32.4	33.9	31.1	29.1
PVC	33.0	35.1	38.7	33.8

[a] Denoted as in Table II.

[b] Calculated by using contact angles given by Dann[2] for the respective liquids.

Let us assume that water, as the most polar and with the highest γ_L of the liquids used, does not spread and that γ_S calculated by the methods of Neumann and Sell[19-21] using contact angle data of water on polymers represents the correct values. We can calculate surface energy components using the known γ_S, γ_L^d, γ_L^p and $\cos\theta$ by solving Eqs. (1) and (5). Thus, we obtain

$$(\gamma_S^d)^{\frac{1}{2}} = (\gamma_L^d)^{\frac{1}{2}}A \pm (\gamma_L^p)^{\frac{1}{2}}[(\gamma_S/\gamma_L) - A^2]^{\frac{1}{2}} \tag{12a}$$

and

$$(\gamma_S^p)^{\frac{1}{2}} = (\gamma_L^p)^{\frac{1}{2}}A \mp (\gamma_L^d)^{\frac{1}{2}}[(\gamma_S/\gamma_L) - A^2]^{\frac{1}{2}} \tag{12b}$$

in which $A = (1 + \cos\theta)/2$. The calculated γ_S^d and γ_S^p make it possible to evaluate π by Eq. (13).

$$\pi = 2(\gamma_S^d \gamma_L^d)^{\frac{1}{2}} + 2(\gamma_S^p \gamma_L^p)^{\frac{1}{2}} - \gamma_L(1 + \cos\theta). \tag{13}$$

Results of calculations according to (12) and π of ethylene glycol, as an example, are given in Table VI. Both π calculated by (13), on one hand, and the difference of surface energies, calculated according to Neumann and Sell for wetting by water and by ethylene glycol, on the other, are in a reasonable agreement.

TABLE VI

Components of surface free energy as calculated by Eqs. (12) and spreading pressure of ethylene glycol on polymers

Polymer [a]	γ_S^d [b]	γ_S^p [b]	π [c]	π [d]
PMA	30.6	8.0	6.3	5.7
PET	31.0	9.4	4.3	4.3
PCT	31.1	9.8	8.3	7.1
Nylon II	30.4	7.6	4.8	4.6
Nylon 6.6	31.4	12.5	3.0	3.1
PS	27.8	4.6	3.0	3.3
PVC	28.2	4.8	−3.0	−0.8

[a] Denoted as in Table II.

[b] Calculated by using contact angles given by Dann[2] and γ_S from Table V for water.

[c] Calculated by Eq. (13).

[d] Difference of values for water (surface without any spread liquid) and for ethylene glycol (surface with an adsorbed autophobic layer of liquid) from Table V.

Eq. (1) recently helped also to explain the different behavior of ice and water surfaces.[22] All the above facts and results of cited authors[4–12] testify that the geometrical mean of polar components of surface free energy may be used to represent the mode of polar interaction at interfaces in a good approximation.

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