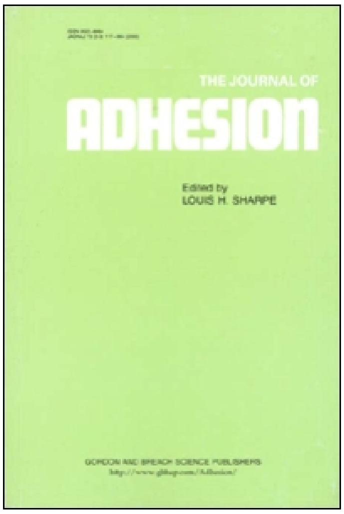

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Further Comments on Contact Angle Measurements on Polymer Solids

Jan Kloubek[a]; H. P. Schreiber[b]
[a] Tessek Ltd., Praha, Czech Republic [b] Department of Chemical Engineering, Ecole Polytechnique, Montreal, Quebec, Canada

To cite this Article Kloubek, Jan and Schreiber, H. P.(1993) 'Further Comments on Contact Angle Measurements on Polymer Solids', The Journal of Adhesion, 42: 1, 87 — 90

To link to this Article: DOI: 10.1080/00218469308026572

URL: http://dx.doi.org/10.1080/00218469308026572

J. Adhesion, 1993, Vol. 42, pp. 87–90
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America.

NOTE
Further Comments on Contact Angle Measurements on Polymer Solids

JAN KLOUBEK

TESSEK Ltd., Radlicka 117/520, 158 01 Praha 5, Czech Republic

H. P. SCHREIBER*

Department of Chemical Engineering, Ecole Polytechnique, P.O. Box 6079, Stn. A., Montreal H3C 3A7, Quebec, Canada

(Received November 27, 1992; in final form March 3, 1993)

KEY WORDS acid/base interaction; contact angle; adhesion; work of adhesion; Gutmann's theory.

In recent years much emphasis has been placed on the importance of specific interactions in determining a wide range of polymer properties. Following the work of Fowkes and coworkers,[1,2] all non-dispersion force interactions falling into the "specific" category may be considered to arise from acid/base interactions. This places heavy emphasis on methods for determining suitable acid/base parameters for polymers, with inverse gas chromatography (IGC) as a convenient choice. The IGC approach employed by one of us[3] uses Gutmann's theory[4] of (Lewis) acids and bases, and determines polymer interaction properties by placing these in contact with vapors of selected fluids for which acid/base indexes, AN and DN, are available. Retention volume data for interacting vapor/polymer combinations are compared with the retention volumes of dispersion-force probes (*e.g.*, n-alkanes), leading to the identification of AN and DN parameters for the polymer.[3]

The capability of polymer surfaces to interact with contacting fluids through electron acceptor/donor mechanisms raised the question whether or not such fundamental procedures in surface science as contact angle determinations may be affected by acid/base interactions between substrate and contacting fluid. A positive answer to this query was given in a recent article,[3] which noted that the contact angle of polar fluids on an acidic polymer (PVC) and a basic polymer (PS) varied with the magnitude of acid/base interactions for contacting solid/liquid pairs. It was possible to obtain initial and equilibrium values of the contact angle, Θ_0 and Θ_e. Differences between these values, labelled $\Delta\Theta$, are recalled in Table I along with

---

*Corresponding author.

TABLE I
Acceptor (AN) and donor (DN) numbers, contact angle decrease, $\Delta\Theta$ (deg), and work of adhesion, W_A (mJ/M^2), of liquids on PVC and PS

			PVC			PS		
	AN	**DN**	**$\Delta\Theta$**	**W_A**	**W_A^d**	**$\Delta\Theta$**	**W_A**	**W_A^d**
PVC	8.1	2.6	—	—	—	—	—	—
PS	1.7	4.3	—	—	—	—	—	—
W	54.8	18.0	3	84	59.6 55.5[a]	8	104	57.8 53.9[a]
FM	39.8	24.0	1	72	72.2 75.6[a]	9	88	70.1 73.5[a]
B	8.2	0.1	5	39	69.4	7	45	66.4
P	14.2	33.1	9	56	77.4	2	50	75.2
THF	8.0	22.5	9	57	74.7	3	73	72.5

[a] Values calculated using $\gamma_L^d = 19.1$ mJ/m^2 at 20°C for water[5] and 35.5 mJ/m^2 for formamide; all other γ_L and γ_S^d correspond to those in Table I of Ref. 3.

pertinent AN and DN parameters for the polymers and for the following contacting fluids: water (W), formamide (FM), benzene (B), pyridine (P) and tetrahydrofurane (THF). Also entered in Table I are values of the work of adhesion, W_A, and of its dispersion component, W_A^d, as calculated respectively from

$$W_A = \gamma_L (1 + \cos \Theta_e) \tag{1}$$

and

$$W_A^d = 2 (\gamma_S^d \gamma_L^d)^{1/2} \tag{2}$$

It can be seen that in several cases $W_A^d > W_A$. This suggests that the liquids change the solid surface by spreading or swelling and that, therefore, the polar (acid/base) portion of the work of adhesion, W_A^{ab}, may not be determined reliably from the expression generally used,

$$W_A = W_A^d + W_A^{ab} \tag{3}$$

The major impact of solid/liquid interactions may then be noted in W_A and W_A^{ab}, but not necessarily in W_A^d.

W_A^{ab} is not available from data published in Ref. 3. An alternative approach can be taken by writing the polar interaction for acidic solids as

$$P_{ab} = AN_S (DN_L - AN_L) \tag{4}$$

and for basic solids as

$$P_{ab} = DN_S (AN_L - DN_L) \tag{5}$$

An acceptable relationship between P_{ab} and the contact angle difference, $\Delta\Theta$, was reported in Ref. 3., albeit that acceptability was, for the moment, based on limited experimental information. The relationship under consideration may be expressed as in eqn. 6, below, and empirical linear regression parameters may be calculated for the equation

$$\Delta\Theta = A + BP_{ab} \tag{6}$$

The regression parameters are entered in Table II. A comparison is made between parameters obtained from analyses including all five liquids, and those obtained after exclusion of the most deviating value (identified in the Table). The reason for deviation in the specified cases has not been ascertained. As mentioned in recent communications, however,[6–8] irregularities in literature values of AN and DN for vapors used in the IGC experiments may be responsible. A somewhat more inclusive, but still empirical, evaluation of a specific interaction parameter may be obtained by writing

$$\begin{aligned} P'_{ab} &= (AN_S - DN_S)\,(DN_L - AN_L) \\ &= AN_S DN_L + DN_S AN_L - AN_S AN_L - DN_S DN_L \end{aligned} \tag{7}$$

The P'_{ab} may be substituted in eqn. 6, with the result, as shown in Table II, that the constant $A' = A$ of eqn. 6, and the regression coefficient, r^2, is the same in both cases. Only the slope of the straight line B' differs from B in eqn. 6. The empiricism of these statements notwithstanding, eqns. 4, 5 and 7 suggest that the net interaction potential at interfaces between two polar condensed phases should include an evaluation of forces resulting from opposite donor/acceptor tendencies and also of modifying forces arising from the pairing of like (*i.e.* donor/donor and acceptor/acceptor) species.

Eqn. 7 appears to be a better candidate than are eqns. 2 and 3 for expressing the magnitude of interfacial interactions due to acid/base forces. It is an analogue to an equation relating W^{ab} to the acid/base components of the surface free energy[9,10]

$$\begin{aligned} W_A^{ab} &= 2[(\gamma_S^a)^{1/2} - (\gamma_S^b)^{1/2}]\,[(\gamma_L^b)^{1/2} - (\gamma_L^a)^{1/2}] \\ &= 2[(\gamma_S^a \cdot \gamma_L^b)^{1/2} + (\gamma_S^b \cdot \gamma_L^a)^{1/2} - (\gamma_S^a \cdot \gamma_L^a)^{1/2} - (\gamma_S^b \cdot \gamma_L^b)^{1/2}] \end{aligned} \tag{8}$$

The linear relationship between $\Delta\Theta$ and P'_{ab}, as generated by applying eqn. 7, supports the validity of eqn. 8, and thus also the concept of representing interactions at interfaces of condensed phases by including contributions from forces generated by unlike (acid/base) as well as by like (acid/acid or base/base) pairings. The possibility is not excluded that the latter may, in some cases, exceed the effects of acid/base coupling at interfaces. Such an event has been reported earlier[11] for interfaces between perfluorohydrocarbons and water.

As noted already, in the case of data from Ref. 3, it is not possible to evaluate

TABLE II

Constants of the linear regression, Eq. (6), for the dependence of $\Delta\Theta$ on P_{ab} (A, B) and on P'_{ab} (A′, B′); the correlation coefficient, r^2, is identical in both cases

	A = A′	**B**	**B′**	**r²**
PVC	6.136	0.017	0.024	0.740
PVC[a]	6.830	0.014	0.021	0.955
PS	5.137	0.028	0.047	0.794
PS[b]	5.712	0.045	0.075	0.996

[a]Computation excludes the value for FM (see Table I).
[b]Computation excludes the value for W (see Table I).

TABLE III
Constants of the linear regression, Eq. (9), for the dependence of W_A on P_{ab} (A, B) and on P'_{ab} (A′, B′) (absolute values); the correlation coefficient, r^2, is identical in both cases

	A = A′	B	B′	r^2
PVC	36.03	0.167	0.247	0.733
PVC[a]	30.05	0.183	0.269	0.958
PS	39.27	0.404	0.669	0.565
PS[a]	30.50	0.445	0.737	0.767

[a] Computation excludes value for FM.

W_A^{ab} explicitly. Assuming, however, that acid/base interaction has the dominant effect on the equilibrium value of the contact angle, Θ_e, then a linear relationship may be expected between W_A and P_{ab} or P'_{ab}, leading to the statement

$$W_A = A + B \ | P_{ab} | \qquad (9)$$

This is similar to eqn. 6 but uses the absolute value of P_{ab}. Results computed from this convention are shown in Table III. The procedure implies that an acidic substance interacts with a stronger acid as though it were a base, and similarly that a base interacts with a stronger base as though it were an acid. Similar observations were advanced in an earlier publication by one of us.[9] Additional experimental data will be sought to clarify further the issues raised in this note.

References

1. F. M. Fowkes, in *Physicochemical Aspects of Polymer Surfaces*, Vol. 2, K. L. Mittal, Ed. (Plenum Press, New York, 1983), p. 583.
2. F. M. Fowkes, *J. Adh. Sci. Tech.* **1**, 7 (1987).
3. H. P. Schreiber, *J. Adhesion* **37**, 51 (1992).
4. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1983).
5. J. Kloubek, *Coll. Czech. Chem. Commun.* **54**, 3171 (1989).
6. P. C. Maria and J. F. Gal, *J. Phys. Chem.* **89**, 1296 (1985).
7. F. L. Riddle and F. M. Fowkes, *J. Amer. Chem. Soc.* **112**, 3259 (1990).
8. W. B. Jensen, *J. Adh. Sci. Tech.* **5**, 1 (1991).
9. J. Kloubek, *Coll. Czech. Chem. Commun.* **56**, 277 (1991).
10. J. Kloubek, *Adv. Colloid Interface Sci.* **38**, 99 (1992).
11. J. Kloubek, *Colloids and Surfaces* **55**, 191 (1991).