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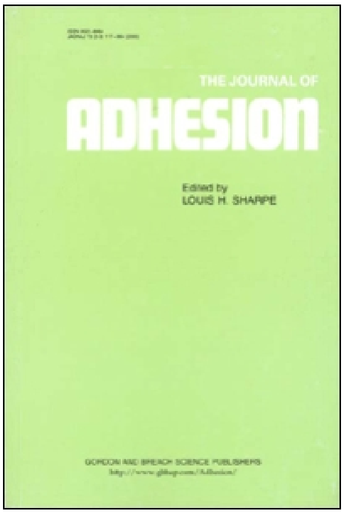

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Donor-Acceptor Interactions at Interfaces

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Donor-Acceptor Interactions at Interfaces†

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The free energy change per unit area on separating an interface (the work of adhesion, W_A) is composed of a variety of interactions:

$$W_A = W_A{}^d + W_A{}^h + W_A{}^{ab} + W_A{}^p + W_A{}^i + \cdots$$

where superscripts are d for London dispersion forces, h for hydrogen-bonding, ab for acid-base interaction, p for dipole-dipole interaction, and i for induced dipole-dipole interaction. The work of cohesion can be similarly separated into components of surface tension($\gamma^d, \gamma^h, \gamma^{ab}, \gamma^p, \gamma^i$). The success of predicting $W_A{}^d$ by $2\sqrt{\gamma_1{}^d\gamma_2{}^d}$, as derived from London force theory, has led others to propose that $W_A{}^h = 2\sqrt{\gamma_1{}^h\gamma_2{}^h}$, etc. However, there is no theoretical basis for the latter and we see that present experimental data indicate rather clearly that at a solid-liquid interface $W_A{}^h$ is directly proportional to $\gamma_L{}^h$:

$$W_A{}^h = K\gamma_L{}^h$$

Contact angles of liquid drops on polymer surfaces are relatively easy to measure and the literature abounds with hundreds or thousands of such measurements[1-5]. These data tempt many of us to propose analytical expressions for correlation. Some of these expressions are provided only to help correlate and predict contact angles; these may be judged by accuracy of prediction. Other correlations are purported to shed light on the interaction of various kinds of intermolecular forces at the liquid/solid interface, a very immature field of physical chemistry, even less understood than intermolecular forces in liquids. In addition the literature is filled with contact angle correlations which fall in between these categories, suggesting some physical significance, but really more concerned with a simple mathematical form.

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The same situation exists in the theory of solutions having molecules with different kinds of intermolecular forces. In both fields the first approach was to assume that all molecules interact by only a van der Waals or Lennard-Jones potential. Then in both fields hydrogen-bonding liquids were found to interact far more weakly with hydrocarbons than originally predicted[6,7]; we now agree that only part of the intermolecular potential (mainly the dispersion forces) in hydrogen-bonding liquids can interact with hydrocarbons. Later on in both fields there appeared proposals to predict the proportion of dispersion forces in liquids as exactly equal to the proportion predicted (by London in 1936) for pairs of gas molecules.[8,9] In these proposals it was assumed that the London dispersion forces, the Keesom dipole-dipole forces, and the Debye dipole-induced dipole forces were equally additive in bulk liquids and that the hydrogen bonds were only dipole interactions. The foregoing assumptions were proved quite inaccurate in 1966 by experiment[10]; dipole-dipole interactions in acetone were predicted by the equal additivity hypothesis to account for 69.5% of the intermolecular forces, but the experimental value is only 14%. More recent developments are found only in solution theory; these recognize the importance of hydrogen-bonds and of acid-base interactions[11,12], and generally ignore the rather minor role of dipole-dipole and dipole-induced dipole interaction. Furthermore both the acid-base and hydrogen-bonds are treated as donor-acceptor interactions[13].

Let us look into the concept of hydrogen-bonds and acid-base interactions as donor-acceptor interactions at liquid/solid interfaces. If the liquid is acidic and the solid is basic, a strong interaction may occur (such as chloroform on a polycarbonate surface), but there is no acid-base interaction within the chloroform or within the polycarbonate. Similarly water may form hydrogen-bonds with the π-orbitals of polystyrene, but there are no hydrogen-bonds within polystyrene. Therefore we cannot attribute any interaction energies within liquids or solids because of interaction energies observed between them. We therefore state that the work of adhesion resulting from hydrogen-bonds ($W_A{}^h$) or from acid-bonds ($W_A{}^{ab}$) often has no relation to the bonding within either material, expressed in terms of the surface free energy γ^h or γ^{ab}:

$$W_{A_{12}}^h \neq f(\gamma_1{}^h, \gamma_2{}^h)$$

$$W_{A_{12}}^{ab} \neq f(\gamma_1{}^{ab}, \gamma_2{}^{ab})$$

The dispersion force interactions (between two liquids or between a liquid and a solid) can be rather accurately predicted by the geometric mean of their internal forces:

$$W_{A_{12}}^d = 2\sqrt{\gamma_1{}^d \gamma_2{}^d}$$

While there are some small deviations from the predictions of the above equation, these have been resolved as to differences in structure or density of packing of the liquid at its surface and interface[14,15]. The success of the above equations has led investigators to propose that hydrogen-bonds and acid-base interactions could be estimated in the same mathematical form, but for reasons already given we see that

$$W^h_{A_{12}} \neq 2\sqrt{\gamma_1^h \gamma_2^h} \quad \text{and}$$

$$W^{ab}_{A_{12}} \neq 2\sqrt{\gamma_1^a \gamma_2^b}$$

Of course if the correlations are not intended to provide information about bonding, we cannot object to their usefulness.

The same situation exists in solubility theory where the solubility parameter δ (equal to $\sqrt{\Delta E_{\text{vap}}/V}$) has been used to determine intermolecular interactions by the geometric mean ($\sqrt{\delta_1 \delta_2}$); here again the dispersion force interactions are rather well predicted by the above expression, and for polyfunctional molecules one can use $\delta_1{}^d$ and $\delta_2{}^d$ very effectively. But hydrogen-bonding and acid-base interactions are not predictable by such a geometric mean, and δ^h and δ^{ab} have no consistent meaning. Some investigators (using δ^p values) even claim evidence that benzene has a large dipole moment.

Dann[4] has provided some contact angle data for liquid alcohols, glycols, and amides on a variety of polymers which allow us to look at the form of the relation between the work of adhesion and $\gamma_L - \gamma_L{}^d$. Values of $\gamma_L - \gamma_L{}^d$ shown in Table I were obtained by contact angle measurements on paraffin wax, using the relation $\gamma_L{}^d = (1 + \cos\theta)^2/4\gamma_s{}^d$ and $\gamma_s{}^d = 25.5$ ergs[7].

TABLE I

Surface properties of liquids (25°C.)[4]

Liquid	γ_L	θ	$\gamma_L{}^d$	$\gamma_L - \gamma_L{}^d$
Water	72.2	100°	22.0	50.2
Glycerol	64.0	96°	36.0	28.0
Formamide	58.3	91°	32.3	26.0
Ethylene glycol	48.3	83°	29.3	19.0
2-Ethoxyethanol	28.6	44°	23.6	5.0

The liquids in Table I have surface tensions in excess of the $\gamma_L{}^d$ values by virtue of other intermolecular interactions:

$$\gamma_L - \gamma_L^d = \gamma_L^h + \gamma_L^p + \gamma_L^i$$

where $\gamma_L{}^p$ (due to dipole-dipole interactions) and $\gamma_L{}^i$ (due to interactions between dipoles and induced dipoles) are almost negligibly small compared to γ_L^h (due to hydrogen-bonding interactions). Therefore $\gamma_L - \gamma_L^d$ for these liquids is considered a measure of hydrogen-bonding and useful for predicting the work of cohesion due to hydrogen bonding:

$$W_c^h \approx 2(\gamma_L - \gamma_L^d)$$

When these liquids are placed in contact with the plane surface of a solid polymer having some ability to form hydrogen bonds, the work of adhesion includes the following terms:

$$W_A = W_A^d + W_A^h + W_A^p + W_A^i + W_A^{ab}$$

so that:

$$W_A - W_A^d = W_A^h + W_A^p + W_A^i + W_A^{ab},$$

where superscript *ab* refers to acid-base interaction, and where W_A^h and W_A^i are again expected to be nearly negligibly small compared with W_A^h or W_A^d. The polymer surface can be a proton-accepting hydrogen-bonding site (such as an ester, ketone, or ether), or it can be a hydrogen-bonding site with both proton-donor and proton-acceptor capabilities (such as amides, alcohols, or amines). Figure 1 shows Dann's results with polyesters (acceptor-type

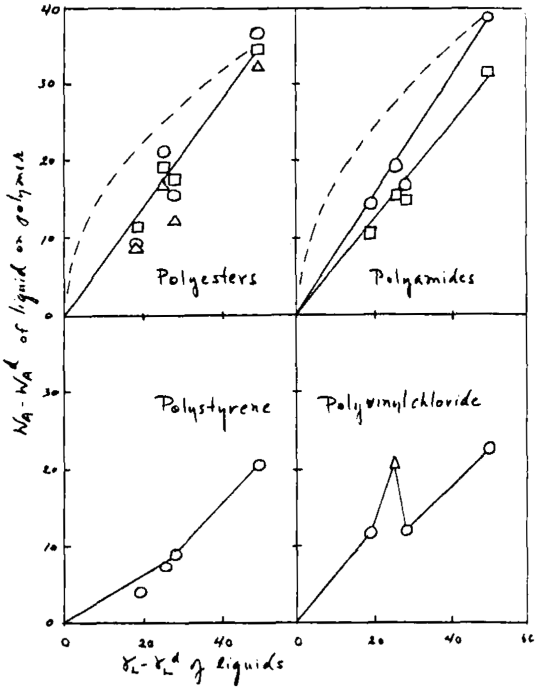

FIGURE 1 Hydrogen-bonding and acid-base interactions of water, glycerol, formamide, and ethylene glycol with seven polymer surfaces. Data by Dann[4].

hydrogen-bonding sites) and with polyamides (donor-and acceptor-type hydrogen-bonding sites). Here we see that $W_A - W_A{}^d$ is directly proportional to $\gamma_L - \gamma_L{}^d$; therefore $W_A{}^h$ is directly proportional to $\gamma_L{}^h$. The frequently suggested relation that $W_A{}^h$ is proportional to $(\gamma_L{}^h)^{1/2}$ is shown as a dashed curved line; clearly the straight lines are a much better fit.

The lower two graphs in Figure 1 are for interfaces where $W_A{}^{ab}$ may be of some importance so that

$$W_A - W_A^d \approx W_A^h + W_A^{ab}$$

Polystyrene can form hydrogen-bonds to proton-donors, but it has some slight basic character and should bond more strongly to the more acidic proton-donors. This may explain the strong adhesion of water. Polyvinylchloride has a definite acidic character associated with the hydrogen atom on the chlorine-carrying carbon, so it is no surprise to see that the slightly basic formamide (indicated by triangle) adheres more strongly than predicted by just its hydrogen-bonding ability. These interpretations of the role of $W_A{}^{ab}$ in adhesion to polymers suggest many obvious experiments which may throw further light on the subject.

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