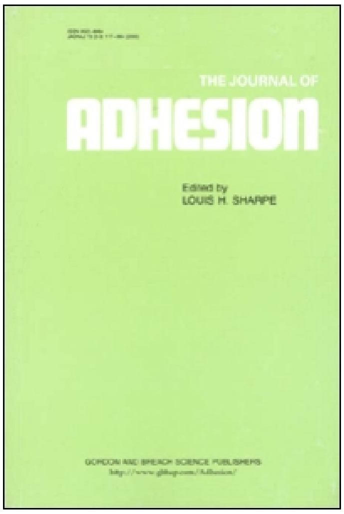

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# On the Calculation of Dispersion and Polar Force Components of the Surface Free Energy

A. J. Kinloch[a]; G. K. A. Kodokian[ab]
[a] Department of Mechanical Engineering, Imperial College of Science, Technology and Medicine, London, UK [b] E. I. Du Pont de Nemoursya, Wilmington, DE, USA

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# NOTE

# On the Calculation of Dispersion and Polar Force Components of the Surface Free Energy

A. J. KINLOCH and G. K. A. KODOKIAN†

*Department of Mechanical Engineering, Imperial College of Science, Technology and Medicine, Exhibition Rd., London, SW7 2BX, UK*

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Contact angle measurements have been widely used[1–6] to calculate the values of the dispersion force, $\gamma_s^d$, and polar force, $\gamma_s^p$, components to the total surface free energy of a material using a derivation originally proposed by Kaelble.[2] In this analysis a pair of simultaneous equations is derived which for two liquids, *i* and *j*, on a common solid surface may be written as:

$$\begin{aligned} 1+\cos\alpha_i &= \frac{2(\gamma_s^d)^{0.5}(\gamma_l^d)_i^{0.5}}{(\gamma_l)_i} + \frac{2(\gamma_s^p)^{0.5}(\gamma_l^p)_i^{0.5}}{(\gamma_l)_i} \\ 1+\cos\alpha_j &= \frac{2(\gamma_s^d)^{0.5}(\gamma_l^d)_j^{0.5}}{(\gamma_l)_j} + \frac{2(\gamma_s^p)^{0.5}(\gamma_l^p)_j^{0.5}}{(\gamma_l)_j} \end{aligned} \tag{1}$$

where $\alpha$ is the contact angle of the liquid on the solid surface. Thus, if the values of $\alpha$, $\gamma_l^d$, $\gamma_l^p$ and $\gamma_l$ (where $\gamma_l = \gamma_l^d + \gamma_l^p$) for the two liquids are known, these equations may be solved to yield the dispersion, $\gamma_s^d$, and the polar, $\gamma_s^p$, force components to the surface free energy of the solid surface. The total surface free energy, $\gamma_s$, is then simply the sum of these components.

Now, consider the schematic representation of $(\gamma_s^p)^{0.5}$ *versus* $(\gamma_s^d)^{0.5}$ shown in Figure 1 where the four linear relationships, obtained from employing four liquids, for example, are plotted using one of the simultaneous equations given in Equation 1. Previously reported work has solved for the two unknowns using one of the following techniques:

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† Present address: E. I. Du Pont de Nemours, Experimental Station, Wilmington, DE, 19880-0304, USA.

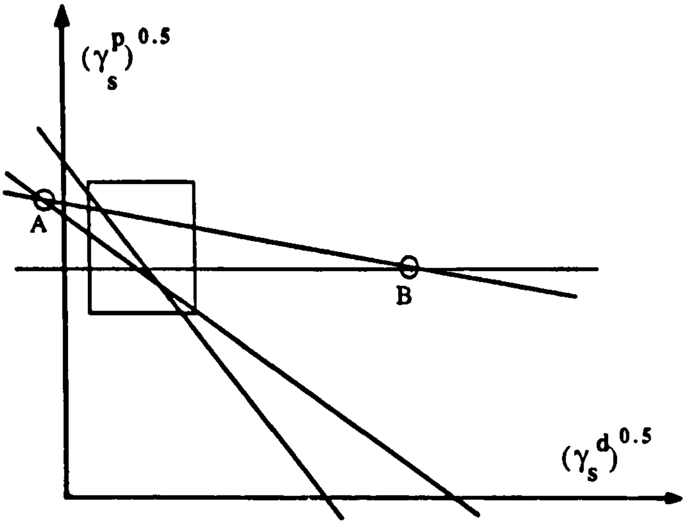

FIGURE 1 Schematic representation of typical individual relationships of $(\gamma_s^p)^{0.5}$ *versus* $(\gamma_s^d)^{0.5}$ deduced from one of the simultaneous equations (see Eq. (1)); results from using four liquids are illustrated.

(1) By solving for each individual pair of lines and then averaging the results, although this direct approach was found to lead to considerable scatter in the values of $\gamma_s^d$ and $\gamma_s^p$ which were obtained.

(2) As above, but ignoring results which are negative, *i.e.* point *A*, and values which are not close to the majority of intersections such as point *B*. Kaelble[2] examined the boundaries of the rectangle shown in Figure 1 and suggested that the pairs of lines which have a value of $D > 10\,\mathrm{mJ/m^2}$ should be ignored, where *D* is given by:

$$D = \{(\gamma_l^d)_i(\gamma_l^p)_j\}^{0.5} - \{(\gamma_l^d)_j(\gamma_l^p)_i\}^{0.5} \tag{2}$$

The condition that $D > 10\,\mathrm{mJ/m^2}$ was relatively successful at reducing the scatter, but it is an arbitrary condition.

The purpose of the present note is to describe a new method for analysing the contact angle data where it is possible not only to assess the surface energy values by accepting all the data, but also to obtain the least error when performing the calculations. This technique, known as the least squares method, does not depend on the individual intersections but instead on the slopes of the straight lines shown schematically in Figure 1. It should be noted that previous work by Sherriff[7] has attempted to calculate the surface free energies by minimising the errors. However, the method described by Sheriff is rather tedious. For example, the errors in the error matrix (see Eq. (3) below) had to be re-substituted and the surface energy values then re-calculated. This process had to be repeated many times until the error matrix was a minimum. The method proposed by the present authors is described below.

Now consider $m$ equations with two unknowns in matrix form:

$$[A]_{m\times 2}[X]_{2\times 1} = [B]_{m\times 1} + [e]_{m\times 1} \tag{3}$$

where matrix $A$ represents the constant coefficients of the two unknowns in matrix $X$, matrix $B$ is the constant values of the equations and matrix $e$ is the error involved in balancing the individual equations. Now, if matrix $B$ is taken to the left-hand side of the above equation, then:

$$\{[A]_{m\times 2}[X]_{2\times 1} - [B]_{m\times 1}\} = [e]_{m\times 1} \tag{4}$$

Multiplying both sides of the equality with the transpose of the left-hand side then:

$$\{[A]_{m\times 2}[X]_{2\times 1} - [B]_{m\times 1}\}^T\{[A]_{m\times 2}[X]_{2\times 1} - [B]_{m\times 1}\} = [E]_{1\times 1} \tag{5}$$

and expanding the above equation gives:

$$\begin{aligned} &\{[X]^T[A]^T[A][X]\}_{1\times 1} - \{[X]^T[A]^T[B]\}_{1\times 1} \\ &\qquad - \{[B]^T[A][X]\}_{1\times 1} + \{[B]^T[B]\}_{1\times 1} = [E]_{1\times 1} \end{aligned} \tag{6}$$

When the partial derivative of matrix $E$ is taken with respect to the two unknowns ($X_1$ and $X_2$) and equated to zero to minimise the error then:

$$\begin{aligned} &\partial[E]/\partial X_1 = [A]^T[A][X] + [X]^T[A]^T[A] - [A]^T[B] - [B]^T[A] = 0 \\ &\text{and:} \\ &\partial[E]/\partial X_2 = [A]^T[A][X] + [X]^T[A]^T[A] - [A]^T[B] - [B]^T[A] = 0 \end{aligned} \tag{7}$$

Since the above two equations are the same, then rearranging one of them gives:

$$\{[A]^T[A][X] - [A]^T[B]\}_{2\times 1} + \{[X]^T[A]^T[A] - [B]^T[A]\}_{1\times 2} = 0 \tag{8}$$

However, the above equation is in the form of: $[Z] + [Z]^T = 0$. Therefore, to satisfy the equality to zero then both matrix $[Z]_{2\times 1}$ and its transpose $[Z]^T_{1\times 2}$ should be individually equal to zero, therefore:

$$\{[A]^T[A][X]\}_{2\times 1} = \{[A]^T[B]\}_{2\times 1} \tag{9}$$

and:

$$\{[X]^T[A]^T[A]\}_{1\times 2} = \{[B]\}^T[A]\}_{1\times 2} \tag{10}$$

Equation 9 is the transpose of Eq. (10) and, therefore, only one of these two equations is required for analysis of the contact angle measurements. The benefits of the analysis are: (i) all the constant coefficients are known, (ii) it will give the minimum error, (iii) it will accept all the data and (iv) it is very simple to employ. (We would add that we have written a simple computer program (in "BASIC" for the "Apple Macintosh SE") which solves Eq. (9) and a print-out of the program may be obtained by writing to the authors.)

To illustrate the differences between the different methods for analysing the same contact angle data, then Table I shows the results from contact angle data obtained by Andrews and Kinloch.[3] They examined a fluorinated ethylene-propylene copolymer (Du Pont "FEPA") which had been chemically etched in a proprietary organic dispersion of sodium naphthalene for varying periods of time.

TABLE I
Comparison of the various methods for estimating surface free energies from contact angle data

| Material | All angles used in Eqn 1 | | Kaelble Method (Eqns 1 and 2) | | New method (Eqn 9) | |
|---|---|---|---|---|---|---|
| | $\gamma_s^d$ | $\gamma_s^p$ | $\gamma_s^d$ | $\gamma_s^p$ | $\gamma_s^d$ | $\gamma_s^p$ |
| FEPA etched: 10s | 38.0 ± 16.8 | 5.9 ± 6.5 | 35.4 ± 8.4 | 5.3 ± 4.3 | 40.0 ± 2.6 | 3.2 ± 0.7 |
| FEPA etched: 60s | 39.8 ± 46.0 | 14.3 ± 22.0 | 33.8 ± 13.7 | 13.4 ± 10.2 | 39.7 ± 4.6 | 6.1 ± 4.6 |
| FEPA etched: 120s | 34.9 ± 37.7 | 24.8 ± 27.5 | 34.4 ± 13.3 | 15.9 ± 13.4 | 37.8 ± 5.4 | 9.7 ± 2.9 |
| FEPA etched: 1000s | 29.2 ± 17.6 | 28.0 ± 26.1 | 35.5 ± 12.7 | 15.1 ± 12.3 | 38.5 ± 5.2 | 9.4 ± 2.8 |

Notes:
a. All values of surface free energies in $mJ/m^2$.
b. Condition that $D > 10\,mJ/m^2$ was used in Eq. (2).

From the results shown in Table I it is obvious that, as reported by Kaelble,[2] the use of the simultaneous equations (Eq. 1) to analyse the results from the various pairs of liquids together with Eq. (2) (which leads to excluding certain liquid pairs) does indeed greatly reduce the extent of scatter compared with simply using Eq. (1); *i.e.* compared with the case where all the various liquid pairs are included. However, the new method, which uses Eq. (9), has the obvious advantages of using all the data and giving even lower scatter. Thus, we would suggest that the new method outlined above for analysing the contact angle data to obtain values of the dispersion, $\gamma_s^d$, and the polar, $\gamma_s^p$, force components to the surface free energy of the solid surface appears to offer considerable benefits in this area of adhesion science.

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