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Polar and Dispersion Contributions to Solid Surface Tension— a Reconsideration of Their Mathematical Evaluation

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One technique for the experimental determination of the dispersion and polar contributions to solid tension, γ_s^d and γ_s^p , is to measure the contact angle θ of a set of m liquids of known dispersion and polar contributions to surface tension on the solid and then to calculate γ_s^d and γ_s^p . There are two common techniques for this calculation, graphically¹ or analytically.^{2, 3} The graphical technique is limited in that it only considers dispersion forces (i.e., nonpolar systems) and so only isolates γ_s^d . For this reason the analytical procedures which isolate both γ_s^d and γ_s^p are more commonly used, and they can be expressed in matrix notation as:

$$A\hat{x} = b \quad (1)$$

where A is a 2×2 matrix containing information about the characterizing liquids and their contact angles, and the vector \hat{x} is related to γ_s^d and γ_s^p . Equation (1) is solved for all mC_2 different liquid pairs to give a set of values for γ_s^d and γ_s^p which can then be subjected to statistical analysis.

Considerable scatter is found in the calculated values as is demonstrated in Figure 1 which is the feasibility diagram for Kaelble's data on PTFE.⁴ This scatter is primarily a function of errors in the determination of θ , a problem which has received a great deal of attention in the literature,⁵

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and its effect on the present situation can readily be demonstrated by a perturbation analysis of Eq. (1). To minimize the standard deviation of calculated values Kaelble solves Eq. (1) by standard determinant techniques and discards all liquid pairs for which the modulus of the determinant of coefficients is less than 10.0. There is no theoretical basis for this arbitrary discarding of results as it not only gives a false degree of accuracy to the calculated values, but ignores valuable experimental data.

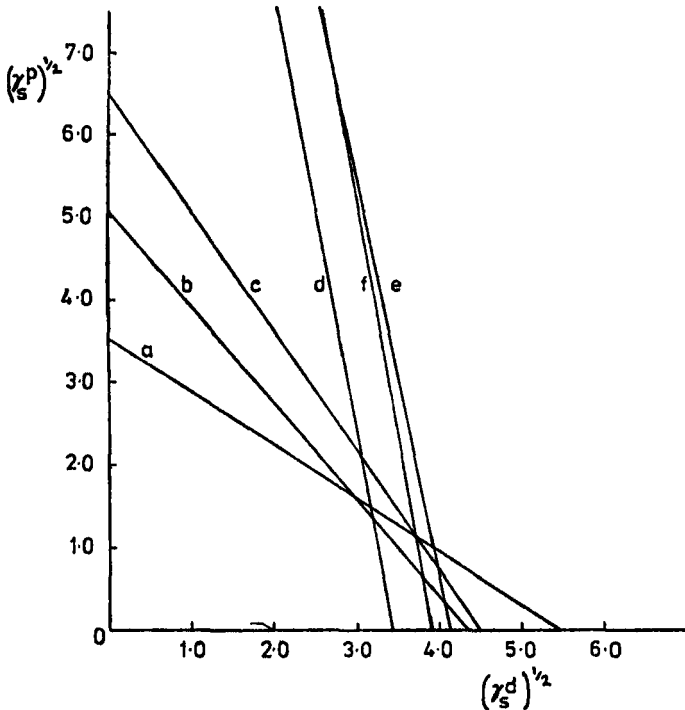


FIGURE 1 A feasibility diagram for PTFE (data from ref. 4). Liquids (a) water, (b) glycerol, (c) formamide, (d) methylene iodide, (e) trichlorobiphenyl, (f) tricresylphosphate.

What must be recognized is that the equations defined in (1) are not a 2×2 system of evenly determined equations which have an absolute solution but are an $m \times 2$ series of over determined equations for which no one vector \hat{x} can satisfy all the equations. It is possible to calculate a vector \hat{x} which minimizes the errors over the entire data set. One such method is the least squares solution in which the vector \hat{x} is selected such that the sum S of the residuals R is a minimum, i.e.

$$R = (A\hat{x} - \hat{b})$$

$$S = R^T R$$

It is possible, although tedious, to calculate the least squares \hat{x} by hand,⁶ but with the advent of computer subroutine libraries the problem is almost trivial. In the present work NAG subroutines† were used in conjunction with a CDC 6600 computer. Householder transformations were applied to A and b to form the upper right triangular form E and matrix C respectively. A first approximation to \hat{x} , \hat{x}_0 , is obtained by back substitution in $E\hat{x} = C$ and the residual R evaluated. A correction D to \hat{x} is calculated from $AD = R$, \hat{x}_0 is replaced by $\hat{x}_0 + D$ and the process repeated until D is negligible.⁷

To test this approach the data of Kaelble for PTFE were re-evaluated and the results for both methods are summarized in Table I. The root-mean-square error for the over determined analysis is less than that for the analysis in which fifteen liquid pairs were selected out of a possible twenty-one. Similar results were obtained for other low energy polymers justifying the applicability of this best fit analysis.

TABLE I

A comparison of γ_s^d and γ_s^p values for PTFE by the over determined and paired equation analysis (data from ref. 4)

Over determined analysis			Paired equation analysis		
γ_s^d	γ_s^p	r.m.s. error	γ_s^d	γ_s^p	r.m.s. error
14.82	0.68	1.686	14.54	1.02	1.781

units: mNm^{-1}

As experimental errors make it impossible to obtain "absolute" values for γ_s^d , γ_s^p from θ measurements, it is recommended that γ_s^d , γ_s^p be evaluated as the solution which minimizes the error over the whole data set of over determined equations. It also follows that as large a number of test liquids as possible should be used.

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