Estimation of Interfacial Tension Components for Liquid–Solid Systems from Contact Angle Measurements

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Synopsis

A technique has been developed for estimating the hydrogen bonding and London dispersion force components of liquid surface tension and solid surface free energy levels. The technique relies on (a) measuring contact angles generated by sessile drops of liquids on solids and (b) performing calculations based on theories of thermodynamic wetting of solids by liquids. The technique is used to estimate interfacial force components of certain liquids and papers typical of those used in xerographic processing.

INTRODUCTION

In applications where printing or imaging is performed by depositing liquid drops or pools on papers or other substrates, it is important to know how the liquid interacts with the paper. One type of interaction is the wettability properties between liquids and paper, which is addressed in this work. Another type of interaction is the rate of spreading and penetration of liquids into paper, which controls, to a large extent, print quality and paper deformation (e.g., curl, cockle) due to moisture gradients set up in the paper.

One parameter used as a measure of the wettability of paper by a liquid is the Zisman empirical parameter,[1] the critical surface tension of wetting. Liquids whose surface tension are less than the critical surface tension of wetting would be expected to spread easily on the paper.

Another parameter which is used in the surface characterization of polymers is the surface free energy. This quantity is the sum of the polar (dipole–hydrogen bonding) and the London dispersion components of surface-free energy. A method for estimating these quantities was reported by Owens and Wendt.[2] The method is based on the measurement of contact angles between a polymer and liquid drops of water and methylene iodide. In the present paper, an extension or modification of the Owens–Wendt method is described which determines the polar and dispersion components of the interfacial forces for both the liquid and the solid.

Estimates of interfacial tension components for certain liquids and papers, using the new method, are presented.

DESCRIPTION OF THE METHOD

The following steps are followed in order to estimate (a) the surface-tension components for liquid A and (b) the surface-free energy components for a solid (e.g., a polymer, paper, etc.). First, the contact angles generated by liquid drops

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of water, methylene iodide, and liquid A are measured on the surface of the solid or polymer. Normally, a low surface-free energy polymer would be used in order that the contact angle between methylene iodide and the surface can be measured.

The contact angle is measured as the tangent angle formed between the liquid drop and its supporting surface. The angle is measured fairly accurately on a Ramé–Hart° or NRL Contact Angle Goniometer, based on a design of W. Zisman of the Naval Research Laboratory.

Second, the surface-free energy and its components are calculated for the polymer according to the method of Owens and Wendt.[2] The method uses contact angle measurements between water, methylene iodide on a solid surface for estimating the surface-free energy components for the surface.

Finally, the contact angle measurements between (a) water and the solid, liquid A and the solid or (b) methylene iodide and the solid, liquid A and the solid are used to calculate the surface tension components for liquid A, as described in the next section.

Subsequently, by making contact angle measurements between water, liquid A and several papers or solid surfaces, the surface-free energy estimates for these surfaces are obtained by the method of Owens and Wendt.

CALCULATIONS

The formulae used in calculating interfacial tension components are based on the equation of thermodynamic wetting of a solid by a liquid, as described by the well-known Young's equation

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} - \pi_e, \tag{1}$$

where γ_{lv}, γ_{sv}, γ_{sl} are, respectively, the free energies of liquid, solid against their saturated vapor, and of the interface between the solid and liquid, and π_e is the equilibrium pressure of the adsorbed vapor of the liquid on the solid. Subscripts l, s, and v refer to liquid, solid, and vapor, respectively.

From eq. (1), Fowkes[3] derived the equation

$$\gamma_{lv} (1 + \cos\theta) = 2(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^h \gamma_l^h}), \tag{2}$$

based on the assumptions

$$\gamma = \gamma^d + \gamma^h \tag{3}$$

$$\pi_e \cong 0 \tag{4}$$

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\sqrt{\gamma_{sv}^d \, \gamma_{lv}^d} + \sqrt{\gamma_{sv}^h \, \gamma_{lv}^h}) \tag{5}$$

Equation (3) states that the interfacial tension (liquid or solid) consists of dispersion and hydrogen bonding components, and eq. (4) assumes that π_e is close to zero for most liquid–solid systems.

The superscripts h and d refer to hydrogen bonding and dispersion force components, respectively.

The calculation of γ_s^d, γ_s^h from contact angle measurements, described by Owens and Wendt,[2] follows from the relationships stated here without proof:

$$\gamma_s^d = (D/2)^2$$
$$\gamma_s^h = (H/2)^2 \tag{6}$$

where

$$D = (c_1 a_2 - c_2 a_1)/(b_1 a_2 - b_2 a_1)$$
$$H = (c_1 - b_1 D)/a_1$$
$$a_i = \{\sqrt{\gamma_l^h}/\gamma_{lv}\}_i$$
$$b_i = \{\sqrt{\gamma_l^d}/\gamma_{lv}\}_i \tag{7}$$
$$c_i = 1 + \cos\theta_i$$
$$i = 1, 2 \text{ for water, methylene iodide, respectively.}$$

Note that $\gamma_{sv} = \gamma_s$, $\gamma_{lv}^h = \gamma_l^h$, and $\gamma_{lv}^d = \gamma_l^d$ for the sake of brevity.

The calculation of γ_l^d, γ_l^h, for a liquid of known surface tension, on a solid surface with known γ_s components, is calculated from

$$\gamma_l^h = (\alpha\gamma_{lv})^2$$
$$\gamma_l^d = (\beta\gamma_{lv})^2 \tag{8}$$

where

$$\alpha = \left\{\frac{HC_I}{D^2} + \left[\frac{1}{\gamma_{lv}}\left(1 + \frac{H^2}{D^2}\right) - \left(\frac{C_I}{D}\right)^2\right]^{1/2}\right\}\left(1 + \frac{H^2}{D^2}\right)^{-1} \tag{9}$$

$$\beta = \frac{C_i - H\alpha}{D} \tag{9}$$

$$C_1 = 1 + \cos\theta_I$$
$$\theta_I = \text{contact angle of the liquid on the surface}$$

The formulae in eq. (8) are derived by solving the equations

$$H\alpha + D\beta = C_I$$
$$\alpha^2 + \beta^2 = 1/\gamma_{lv}. \tag{10}$$

RESULTS AND DISCUSSION

The method was used for estimating the surface tension components for three liquids (Table I), bleached glassine, and eight papers typical of those used in xerographic processing (Table II).

Liquids A and B are, respectively, 45% and 65% solutions of methanol and water and liquid C is a commercially available printing ink. A characterization of a typical xerographic paper is given in Table III.

TABLE I

Liquid	dynes/cm			Contact angle (°)
	γ_{lv}	γ_l^h	γ_l^d	
Water	72.8	51.0	21.8	90.0
Methylene iodide	50.8	1.3	49.5	44.2
Liquid A	45.4	24.5	20.9	60.7
Liquid B	62.3	16.5	45.8	61.4
Liquid C	42.0	27.2	14.8	65.9

Notes
1. Data for water and methylene iodide are taken from Ref. 2.
2. Contact angle measurements were performed on bleached glassine at 70°F, 18% RH (see Table II).

TABLE II

Surface	ergs/cm²			dynes/cm γ_c[a]
	γ_s	γ_s^h	γ_s^d	
Bleached glassine	42.1	2.6	39.5	—
Paper 1	64.2	2.6	61.6	42.0
Paper 2	46.2	11.2	35.0	40.5
Paper 3	58.5	1.5	57.0	35.0
Paper 4	39.2	18.0	21.2	38.0
Paper 5	35.5	0.5	35.0	39.0
Paper 6	33.0	0.1	32.9	49.0
Paper 7	25.8	20.9	4.9	39.0
Paper 8	52.1	0.0	52.1	40.0

[a] γ_c = Critical surface tension of wetting. Estimates of γ_c for cellulosic films have been reported in the 35.5–49.0 ergs/cm² range (Ref. 4).

The method described in this paper, which is an extension of the Owens and Wendt method, provides reasonably good estimates of interfacial tension components for liquid–solid systems. It was verified that fairly good agreement in the interfacial tension estimates are obtained, although data from different liquid combinations on one solid surface are used in performing the calculations.

Estimates for the surface-free energy levels for papers are variable, due to nonuniformity of the surface properties of paper introduced by the additives to the paper. Rough estimates of the surface-free energy of papers could be used, however, for identifying which paper-making additives create desirable wetting properties between liquid–paper systems.

Table IV illustrates the sensitivity of the surface free energy estimates to variability in the contact angle measurements. The sometimes large percent variations (up to 11%) in contact angle measurements on paper are not surprising, since the surface properties of uncoated papers are not usually homogeneous. The projected variability in the surface-free energy estimates is large, if the error due to variability in the contact angle measurement exceeds 5%.

Zisman plots[1] of the surface tension of a homologous series of liquids against the cosine of their contact angles on paper are useful for estimating the critical surface tension of wetting. It would be advisable to use estimates for the critical

TABLE III
A Typical Paper Characterization

Fiber	80% hardwood
	20% softwood
Internal additives	
(in varying amounts)	clay filler
	silica
	ti pigment
	rosin size
	alum
Surface size	5% ethylated corn starch
Basis weight	20 lb/1300 ft²
	(75 g/m²)
Caliper	4.0×10^{-3} in.
	(100 μm)
Tensile strength	5500 psi (37.9×10^3 Pa) (MD)
	3000 psi (20.7×10^3 Pa) (CD)

TABLE IV
Variability in Surface-Free Energy Estimates

| Surface | Contact angles (°) | | | Projected range for γ_s (ergs/cm^2) | Estimated value for γ_s (ergs/cm^2) |
	Mean	SD	Maximum % error		
Bleached glassine	88.7	0.58	1.62	41.7–42.5	42.1
Paper 1	71.4	0.55	1.92	57.2–78.0	63.7
Paper 2	64.1	0.69	2.67	42.9–51.3	46.2
Paper 3	69.6	3.19	11.38	43.5–63.6	58.5
Paper 4	48.6	0.49	2.51	38.5–41.5	39.2
Paper 5	117.2	5.27	11.17	26.7–52.2	35.5
Paper 6	108.3	2.80	6.43	26.7–40.5	33.0
Paper 7	105.2	0.96	2.26	23.7–28.3	25.8
Paper 8	95.4	1.00	2.60	35.3–75.2	52.1

1. Contact angles were measured between the surfaces and distilled water at 70°F, 53% RH.
2. Statistical estimates for the true mean contact angle were based on Student's t-distribution with a sample size of 3 (2 degrees of freedom) at the 95% confidence level.
3. Projected ranges for γ_s were calculated using the maximum percent errors measured for the contact angles.

surface tension of wetting to supplement those for the surface-free energy, since the two quantities are often of the same order of magnitude.

References

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