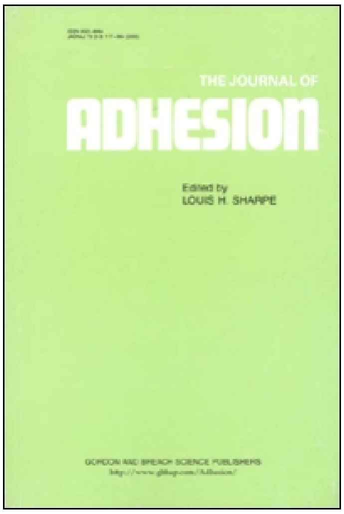

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Pauline N. Jacob[a]; John C. Berg[a]
[a] Department of Chemical Engineering, University of Washington, Seattle, WA, USA

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A Comparison of the Work of Adhesion Obtained from Wetting and Vapor Adsorption Measurements*

PAULINE N. JACOB and JOHN C. BERG**

Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA

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Some of the limitations to determining experimental values of the work of adhesion are discussed. Wetting measurements appear to provide the most direct means of assessing the work of adhesion for a solid-liquid system, but they require the formation of a finite contact angle by the liquid against the solid of interest, and the need for independent knowledge of the equilibrium spreading pressure of the liquid's vapor on the solid further limits their applicability. Vapor adsorption measurement using the technique of inverse gas chromatoraphy (IGC) provides a promising alternative means of determining the work of adhesion not subject to these limitations. The measurements are, furthermore, amenable to solids which are difficult to use with wetting measurements, *e.g.*, those which are porous or granular. An attempt is made here to compare values of the work of adhesion determined using both wetting and vapor adsorption measurements. Good agreement is attained between the two methods for diiodomethane in contact with poly (vinyl chloride), poly (methyl methacrylate), and chemi-thermo-mechanical wood pulp fibers, suggesting that the technique of IGC is particularly well-suited for rapid determination of the work of adhesion.

KEY WORDS Work of adhesion; wetting; contact angle; inverse gas chromatography; IGC; equilibrium spreading pressure; acid-base interactions.

INTRODUCTION

Many processes involving solids depend on the energetics of their surfaces. For example, adhesion, coating, wicking (absorbency), supported catalysis, and related phenomena, are governed by interactions between solid surfaces and some adjoining fluid phase. To understand, describe and ultimately predict such interactions requires, *inter alia*, knowledge of the surface energetics of the solid as well as of the liquid. Liquid surface energetics are relatively easily characterized in terms of surface tension and of interfacial tensions against a variety of second liquids. The simplicity of such characterization owes to the energetic and morphological homogeneity of fluid interfaces as well as to the accessibility of a mechanical (tension) measurement to determine the interfacial energy. Solid surfaces afford no such simplicity. They are, in general, both chemically and morphologically heterogeneous, and their surface energetics (or energy

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**Corresponding author.

distributions) are not accessible to direct measurement. The difficulty of obtaining solid surface characterization, however, in no way diminishes its importance.

In applications involving solid-liquid interfaces, it is not the solid "surface" energy in itself which is the determinant of a successful process, but rather its energy in the presence of the adjoining fluid phase. The "surface energy of a solid", terminology often used imprecisely, is strictly defined as its interfacial energy *in vacuo*. If the adjoining phase were dilute, inert gas, there would be no practical difference in the solid surface energy from that *in vacuo*, but the solid "surface" energy in the presence of an adjoining liquid phase depends on the properties of the liquid phase.

The solid surface energy may be quantified thermodynamically in terms of Dupré's work of adhesion, W_a, the reversible work required to disjoin a unit area of solid-liquid interface (*in vacuo*) from intimate molecular contact to infinite separation[1]:

$$W_a = \sigma_S + \sigma_L - \sigma_{SL} \tag{1}$$

where σ_S is the derivative of the solid surface free energy *in vacuo* with respect to its area (at constant system temperature and volume), σ_{SL} is the same derivative, but for the system energy when the surface area is that in contact with a liquid phase, and σ_L is the liquid surface tension *in vacuo*. The work of adhesion is numerically equivalent to the free energy of intermolecular interactions per unit area of solid-liquid interface.

The situation is complex because such interactions may be both physical and chemical in nature. The physical or Lifshitz-van der Waals forces of intermolecular attraction include London (dispersion), Keesom (dipole-dipole), and Debye (dipole-induced dipole) forces. The ubiquitous London forces play the most prominent role in determining the extent of physical interaction across the interface, because of the self-canceling effect of multi-body permanent dipole interactions.[2] The chemical or specific forces operating across most interfaces are present whenever there is the possibility of sharing a proton or an electron pair between neighboring molecules or functional groups, which leads to acid-base adduct formation. Fowkes and Mostafa asserted that nearly all chemical interactions of importance are Lewis acid-base interactions, including hydrogen bonding.[3] The work of adhesion can then be written as a sum of contributions from the Lifshitz-van der Waals (LW) and acid-base (AB) interactions:

$$W_a = W_a^{LW} + W_a^{AB} \tag{2}$$

The work of adhesion, therefore, reflects not only the extent, but also the nature of intermolecular interactions operative across an interface.

Wetting Measurements

Although not directly measurable itself, the work of adhesion is obtainable from a combination of surface tension and contact angle measurements. The contact angle is related to the free energies of the three interfaces meeting at the solid-liquid-gas interline by Young's equation:[4]

$$\cos\theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}, \tag{3}$$

where σ_{SG} and σ_{LG} are the solid-gas interfacial free energy and the liquid surface tension against the equilibrium vapor. Substitution of Young's equation into Eq. 1 gives

$$W_a = \sigma_{\mathrm{LG}}(1 + \cos\theta), \tag{4}$$

which suggests that the work of adhesion may be evaluated from measurements of the surface tension of the liquid and the contact angle of the liquid against the solid.

It is immediately evident, however, that the use of Eq. 4 is limited to situations in which the contact angle is finite, *i.e.*, $\theta > 0°$. This limitation is a serious one because conditions of zero contact angle may be the most important for processes like adhesion, coating, and wicking, in which they often correspond to desired behavior. If a liquid wets out a solid, modifiction of the solid surface to promote stronger interactions with the liquid will not be detectable as a change in the contact angle, since it will still be zero.

Secondly, the use of Eq. 4 for the work of adhesion tacitly assumes that $\sigma_{\mathrm{LG}} \approx \sigma_L$,and $\sigma_{\mathrm{SG}} \approx \sigma_S$, *i.e.*, that vapors from the solid do not adsorb at the liquid-gas interface and that vapors from the liquid do not adsorb at the solid-gas interface (Fig. 1a). While the former is generally a good assumption, the latter is not. In general, presence of adsorbed vapors of the liquid in equilibrium contact with the solid causes a reduction of the surface free energy of the solid, known as the equilibrium spreading pressure, *viz.*:

$$\Pi_e = \sigma_S - \sigma_{\mathrm{SG}} \tag{5}$$

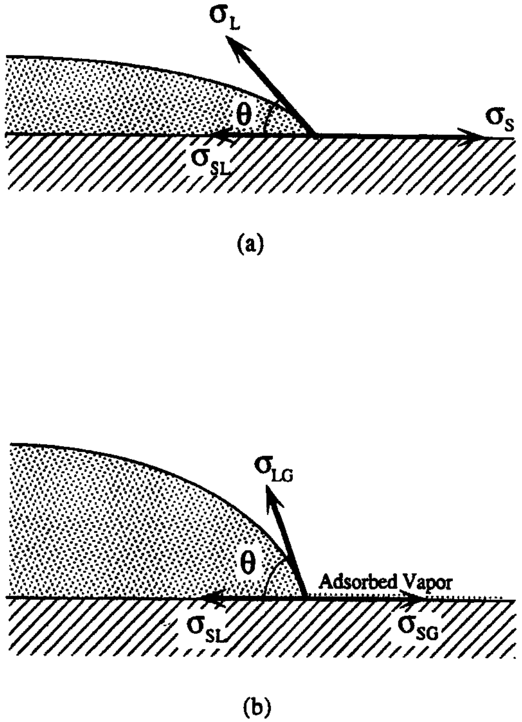

FIGURE 1 (a) Definition of the contact angle at the solid-liquid-gas interline, (b) Three-phase interline with liquid phase vapors adsorbed at the solid surface, where $\Pi_e = \sigma_S - \sigma_{\mathrm{SG}}$.

where σ_{SG} is the surface free energy per unit area of the solid surface in the presence of the vapor at its saturation pressure, P_0. This effect is shown schematically in Figure 1b, and is manifest in the Young-Dupré equation as:

$$W_a = \sigma_{LG}(1 + \cos\theta) + \Pi_e \tag{6}$$

The equilibrium spreading pressure is typically determined from integration of the adsorption isotherm of the vapor of the wetting liquid, $\Gamma(P)$, from zero to its saturation pressure, P_0, in accord with the Gibbs adsorption equation:[5]

$$\Pi_e = RT\int_0^{P_0} \Gamma\, d\ln P. \tag{7}$$

The equilibrium spreading pressure is an important parameter needed to relate direct energetic measurement of interactions (heats of immersion or wetting) to contact angle measurement,[6] but understanding its role in macroscopic wetting behavior has been at issue since the 1960's. Based on several cases for which a liquid yielding a finite contact angle against a "low energy" surface correlated with negligible spreading pressure, it has been common to argue that Π_e should be neglected for all cases in which the contact angle is finite.[7,8] There is a large and growing body of evidence, however, that this assumption may not be valid.[9-13] The main cause of the continued controversy over the importance of the equilibrium spreading pressure is the lack of convenient techniques for its determination.

Although the most common means of determining Π_e is the integration suggested in Eq. 7, this method is plagued with shortcomings. First, determination of an adsorption isotherm can be a cumbersome process, especially when the measurements are made gravimetrically. As discussed later, the technique of inverse gas chromatography (IGC) may provide some aid in expediting these experiments. Also, great care must be taken in measuring probe adsorption isotherms to avoid the effect of condensation at points of contact between particles or within a porous structure. Wade and Whalen[14] have proposed a model to account for condensation effects, but its applicability may be limited by the numerous assumptions required for the analysis, *e.g.*, the particles must be spherical and of known size distribution and known average number of contacts. Slight deviations in these parameters can lead to an order of magnitude difference in that apparent vapor adsorption. Condensation effects may be avoided by using flat plates to minimize the number of particle contacts, but this rules out the investigation of many solids of practical concern.

Condensation effects can usually be neglected below $P/P_0 \sim 0.7$,[14] but this creates a need to determine the most meaningful method to extrapolate the isotherm to P_0, the partial pressure to which the adsorption isotherm must be integrated for determination of Π_e. There have been some attempts at extrapolation of isotherms. Dorris and Gray[15] fit isotherms to a polynomial, or in some cases two polynomials, and extrapolated the fits to P_0. Schröder[10] linearly extrapolated the film pressure to Π_e from a log-log plot of Π_i *vs.* P. Others have simply not stated how they have extrapolated their abbreviated isotherms to saturation pressure[16,17] to determine Π_e.

An additional limitation to the use of an adsorption isotherm to compute Π_e is the effect of profound solid surface energetic heterogeneity on the adsorption isotherm. For an energetically heterogeneous surface, adsorption commences on the high energy sites with subsequent adsorption to the lower energy sites on the surface. It is possible to have a solid surface with disparate site energetics, such that adsorption occurs solely on a few patches of high energy sites,[18,19] even for partial pressures near the probe saturation pressure. In such cases, the adsorption characteristics are not representative of the entire surface and indeed may be indicative of interactions with only a minor portion of the solid surface. As an example, a synthetic polymer may be predominantly hydrophobic, but have a few hydrophilic patches of high energy. When measuring the adsorption of water, there may be appreciable adsorption on the hydrophilic sites, due to specific interactions, but no adsorption on the majority of the surface. Since the low energy sites are important in determining the magnitude of the advancing contact angle,[20] use of an equilibrium spreading pressure determined from adsorption to a small fraction of high energy sites may not be meaningful in the context of calculating the work of adhesion for the system.

There have been several attempts to provide an alternative to determining Π_e from an adsorption isotherm. Good[7] has proposed a model for direct calculation of Π_e, but it is useful only for homogeneous surfaces, a severely limiting criterion. Even for homogeneous surfaces, the model is confined to order-of-magnitude computations because of the many assumptions which need to be invoked. Bellon-Fontaine and Cerf[12] have proposed a technique using wetting measurements to determine Π_e. The spreading pressure is rather simply, but roughly, determined from the difference in the work of adhesion between a solid surface and mercury and the same solid surface with the probe liquid for which the spreading pressure is of interest. The system of interest must, therefore, exhibit a finite contact angle. This criterion limits use of the technique to "low energy" surfaces. Fowkes *et al.* have also proposed a technique for determining Π_e which employs wetting measurements.[8] The advancing contact angle of one liquid is used to measure the Π_e generated by the vapor of a second liquid, such that:

$$\Pi_e = \sigma_L \Delta \cos\theta, \tag{8}$$

where the contact angle of a liquid is measured in the absence and presence of the vapor of a second liquid. The benefit of this method's simplicity is offset by limitations as well. The vapor must be insoluble in the drop and the vapor's effect on the surface tension of the drop must be known. Thus, determination of the equilibrium spreading pressure is complicated by the lack of readily applicable techniques to measure it. Neither use of the probe adsorption isotherm nor wetting measurements provides a completely satisfactory method to determine the equilibrium spreading pressure.

While wetting measurements provide the most direct experimental link to the work of adhesion, there are, thus, two major shortcomings to their usage: the requirement of a finite contact angle for the system of interest, and even in these cases, the requirement of knowledge of the equilibrium spreading pressure. The limitations in the use of wetting measurements to determine experimental values of the work of adhesion provide motivation for developing other techniques to quantify it.

Vapor Adsorption Measurements (Inverse Gas Chromatography)

A particularly promising method to examine surface energetics is that of inverse gas chromatography. IGC is similar to conventional gas chromatography, except that the column is packed with the solid to be examined, and the vapors of probe liquids of known characteristics are passed through the column with a carrier gas. The resulting elution chromatogram is indicative of the extent of interaction between the probe and the solid surface. The method for obtaining the work of adhesion between a liquid and a solid surface by such measurements alone has been suggested by Gray *et al.*, *viz.*[15]

$$W_a = \frac{-\Delta G_{\mathrm{ads}}}{a_{\mathrm{mol}}}, \tag{9}$$

where ΔG_{ads} is the standard free energy change upon adsorption, and a_{mol} is the molar area of the adsorbate. The free energy change upon adsorption is obtained from chromatographic measurements (*i.e.*, inverse gas chromatography) as described below, while the adsorbate molar area is, in principle, obtainable from tabulated molecular dimensions or liquid molar volumes. Dorris and Gray[15] found success using

$$a_{\mathrm{mol}}(m^2/mol) = 1.33 \times 10^{-4}\left(\frac{M}{\rho_L}\right)^{2/3}(N_A)^{1/3}, \tag{10}$$

where M is the molecular weight of the probe liquid, ρ_L is its density, and N_A is Avagadro's number. The appropriate values for *n*-alkane molar areas were verified by Dorris and Gray in experiments with interfacial tension measurements between *n*-alkanes and water.[21]

In inverse gas chromatography, the quantity measured is the relative retention volume, V_N, defined as the amount of carrier gas required to elute the probe, and measured as:

$$V_N = J\,Q(t_R - t_{\mathrm{ref}}) \tag{11}$$

where j is the James-Martin compressibility factor[22] which corrects for changes in the carrier gas flowrate due to a significant pressure drop across the column, Q is the volumetric flowrate of the carrier gas, t_R is the retention time of the probe, and t_{ref} is the retention time of a non-adsorbing reference gas, such as methane. The measured retention volume is equated with probe adsorption onto the solid[23] as:

$$V_N = \left(\frac{\partial \Gamma}{\partial C}\right)_T A, \tag{12}$$

where Γ is the amount adsorbed, C is the concentration of the solute, T is the column temperature, and A is the surface area of the solid. Typically, IGC studies are performed in the region of "infinite dilution" along the adsorption isotherm,[24] as indicated by a symmetric chromatogram. Then,

$$V_N = K A, \tag{13}$$

where K is the adsorption equilibrium constant for the solute in the mobile gas phase relative to the amount adsorbed. From the adsorption equilibrium constant, the molar Gibbs free energy change upon adsorption of the probe can be determined:

$$\Delta G_{\mathrm{ads}} = -RT\ln K + C_1 = -RT\ln V_N + C_2, \tag{14}$$

where R is the gas constant, and C_1 and C_2 are constants dependent on the standard states of the gaseous and adsorbed states and the total solid surface area, respectively.

The direct use of Eq. 9 for the general evaluation of the work of adhesion is thus limited by uncertainty with respect to the appropriate choice of standard state for the adsorbed species. Dorris and Gray [21] used de Boer's standard state for the adsorbed species,[25] *viz.*, the surface concentration giving the average distance of separation between molecules equal to that in the standard gas state (taken to be ideal gas at 1 bar). Use of this standard state in connection with Eq. 9 may be appropriate only in the absence of cooperative effects during adsorption. It is of interest in the present work to test the usefulness of this standard state which, together with independently-measured adsorbent surface area, would permit the direct use of Eq. 9 for the work of adhesion. In this context, the results of using other standard states may also be investigated. Fortunately, however, present knowledge of Lifshitz-van der Waals interactions provides a situation in which the choice of standard state is *not* required. For the case in which only such interactions operate across the interface, *i.e.*, there are no specific (*i.e.*, acid-base) adsorbate-adsorbent interactions, the work of adhesion is given by:[26]

$$W_a = 2\sqrt{\sigma_L^{LW}\sigma_S^{LW}}, \tag{15}$$

where σ^{LW} is the Lifshitz-van der Waals component of the liquid (L) or solid (S) surface free energy quantity. Combining Eqs. 12, 13, and 15 results in the expression:

$$-\Delta G_{\mathrm{ads}} = RT\ln V_N = 2a_{\mathrm{mol}}\sqrt{\sigma_L^{LW}\sigma_S^{LW}} + C_2, \tag{16}$$

such that a plot of $RT\ln V_N$ *vs.* $a_{\mathrm{mol}}\sqrt{\sigma_L}$ for a series of non-specifically adsorbing probes, *e.g.*, *n*-alkanes, should result in a straight line, the slope of which is equal to $2\sqrt{\sigma_S^{LW}}$.

IGC thus provides a means for determining the work of adhesion through the agency of an "alkane line" in the case where only Lifshitz-van der Waals forces are operative across the interface. The present study, in which we seek to compare the results of wetting measurements to those obtained by IGC, thus limits itself to systems of this type. It should be mentioned that there have been several attempts to use IGC experiments to determine the acid-base contribution to the work of adhesion as well,[27–29] but such characterization is outside the scope of the present study. Investigations using IGC have been made to study the surfaces of a variety of materials, including carbons, silicas, and synthetic as well as natural polymers[30]. To the best of the author's knowledge, however, there has not yet been a thorough attempt to compare the values of the work of adhesion obtained from both wetting and vapor adsorption measurements. Some studies have come close to addressing the issue. Katz and Gray[31] have compared the values of σ_S^{LW}, as determined from IGC experiments according to Eq. 16, to values of σ_S^{LW} determined from Eq. 6, *assuming* exactly a 0° contact angle for *n*-alkanes against the surface. Good agreement was obtained, despite use of Young's equation under conditions in which it is not valid. In a separate study, the value of σ_S^{LW} was computed from the work of adhesion, as determined from both vapor adsorption and wetting measurements, *assuming negligible* Π_e. For the two solid surfaces investigated, one showed reasonable agreement between the values of σ_S^{LW} obtained from the two methods (~15% difference), but only marginal agreement (~50% difference in σ_S^{LW}) was achieved for the other surface[32]. The present work attempts to compare values of the work of adhesion determined by wetting and vapor adsorption measurements using systems in which the contact angle is finite and measurable and for which the equilibrium spreading pressures are independently evaluated.

The surfaces of two simple, synthetic polymers and one complex, natural polymer are investigated using both wetting and vapor adsorption experiments. A probe liquid of sufficiently large surface tension to yield a finite contact angle against these surfaces is a requirement for such a comparison. Furthermore, since the solid surfaces bear functional groups capable of specific interactions, the probe liquid must be inert. Diiodomethane was chosen to satisfy these criteria, since it is expected to engage only in Lifshitz-van der Waals interactions,[33] and it has a relatively large surface tension [$\sigma_L = 50.7$ dynes/cm at 23°C], such that it yields a finite contact angle against the tested solids.

The first specific objective of the present work is to obtain and compare W_a values from wetting measurements in accord with Eq. 6 and those from vapor adsorption measurements, employing an alkane line, in accord with Eq. 16, which does not require the specification of standard states for the adsorbate. The comparison is to be made for three systems which conform to all of the assumptions required by those equations, *viz.* the liquid of interest produces a finite contact angle against the solids but interacts with them only through Lifshitz-van der Waals interactions. Successful comparison of these values will suggest that wetting and vapor adsorption measurements yield equivalent evaluations of solid surface energies. Secondly, W_a values obtained from IGC measurements but computed directly from Eq. 9 will be examined. Numerical values will be obtained using both the de Boer standard state as well as a new "liquid adsorbate" standard state. Successful comparison of either of these results with those obtained from wetting measurements will suggest that the use of IGC may be made without the requirement of constructing an alkane line for the solid.

MATERIALS AND METHODS

Wetting Measurements

Wetting measurements for diiodomethane [Aldrich, 99 + % pure] against poly (vinylchloride) [PVC], poly (methyl methacrylate) [PMMA], and chemi-thermo-mechanical wood pulp [CTMP] fibers were performed using a dynamic tensiometer, as described elsewhere.[34] The sources of the solids are shown in Table 1. The CTMP fibers were separated from clumps of thousands of fibers using jeweller's forceps. Individual fibers were mounted and crimped in one end of an aluminum foil holder. A pin was used to pierce a hole in the opposite end of the foil, enabling the fiber to be suspended from the electrobalance. The CTMP fibers were then used without further

TABLE I
Specifications of solids investigated

Solid	Source	Form	Amount [g]	Σ [m^2/g]
PVC	Scientific Polymer Products, Inc.; lot#38	powder	0.34	2.0
PMMA	Scientific Polymer Products, Inc.; lot#20	powder	4.36	0.2
CTMP	James River Corporation	fibers	3.67	0.8

handling. The PMMA and PVC powders were dissolved into hot xylene or tetrahydrofuran, respectively, and cast onto glass slides to form flat plates. The results from wetting measurements for diiodomethane in contact with these two solids were part of earlier work from this laboratory.[35]

The downward force exerted on the solid partially immersed in the diiodomethane [DIM] was measured using the Wilhelmy technique, such that the difference in weight between the solid suspended in air and in the probe liquid is:

$$F\downarrow = \sigma_{LG} p \cos\theta - \rho_L g A h \tag{22}$$

where $F\downarrow$ is the force exerted on the solid, p is the wetted perimeter of the solid, g is the gravitational constant, A is the cross-sectional area of the solid, and h is the depth of immersion of the solid. The first term represents surface tension forces acting along the wetted perimeter of the solid and the second is the buoyancy of the displaced liquid.

Diiodomethane, contained in a small Teflon cup, was raised and lowered about the stationary solids at a constant speed of 10.4 μm/sec. For this velocity, the capillary number, a dimensionless ratio of viscous to surface tension forces, was less than 10^{-5}, indicating that viscous effects were negligible. The force on the solid as the DIM was advanced and subsequently receded over the solid surface was measured along a distance of 1.0 mm for the CTMP fibers and 2.0 mm for PVC and PMMA strips. For the smooth strips of PVC and PMMA, the DIM advancing and receding contact angles could be resolved from the force traces once the sample perimeters were independently-determined. Since *n*-octane yields a zero degree contact angle these surfaces, measurement of its force trace was to determine the sample perimeters.

CTMP fibers produced complex force traces, which are characteristic of the chemically and physically heterogeneous nature of the wood pulp fibers. The receding mode force trace represents only geometrical variations along the fiber surface, since it could be matched with that of *n*-octane ($\theta = 0°$) in contact with the fiber. The advancing mode force trace, however, reflects both the chemical and physical variations along the fiber surface. Therefore, the receding force was used to compute a perimeter template for the fiber, which could then be used with the advancing mode force trace to compute the advancing angle at each discrete sample of the fiber surface. These advancing angles were averaged to represent of the entire travel distance along the fiber surface. Contact angle measurements from twelve individual fibers were arithmetically averaged. All measurements were made under ambient conitions, $T = 23 \pm 0.5°$C, with a relative humidity of $55 \pm 10\%$.

Vapor Adsorption Experiments

PVC, PMMA, and CTMP fibers were packed into pre-cleaned stainless steel columns (O.D. = 0.25 in. for PMMA and CTMP, and O.D. = 0.125 in. for PVC). The amounts packed into the columns are shown in Table I. Specific surface areas for the three solids were determined from single-point BET nitrogen adsorption measurements using a Micromeritics Flowsorb 2300 apparatus. The measured values of Σ are shown in Table I. The probe liquids consisted of diiodomethane and a series of saturated *n*-alkanes (C_6–C_{10}) [Aldrich, 99+ % pure], which were stored over 8–12 mesh molecular sieve in vials capped with a septum.

Vapor adsorption measurements were performed using a Varian 3400 GC, equipped with flame ionization detectors sensitive to 10^{-12} g. Nitrogen carrier gas [General Welding Supply Co., 99.995% pure] was maintained at a constant flow rate of 10–20ml/min, depending on the column and temperature used. Flow rates were measured at room temperature using a soap bubble flowmeter, and were then corrected for the vapor pressure of the soap solution, as well as the temperature difference between the column and room temperatures. The injector and detector were operated at 185 and 205 °C, respectively. All vapor adsorption measurements were made at 23 °C.

Before vapor adsorption measurements were begun, the columns were conditioned 12 hours at 110 °C for the CTMP fibers, and 60 °C for the PVC and PMMA. Column temperatures were maintained below the polymers' glass transition temperatures, T_g, to avoid altering the surfaces, as well as to eliminate effects due to diffusion of small molecules into the softened polymer. For PVC and PMMA, however, diffusion of the methane into the bulk polymer was evident by a slight skew of the methane peaks, despite the fact that the column temperatures were below the glass transition temperature of the polymers. The skew was attributed to diffusion, because the higher alkanes, which are bigger and therefore less susceptible to diffusion, did not exhibit skewed peaks. Also, the degree of asymmetry of the methane chromatograms decreased with decreasing temperature, suggesting that the skew was not due to adsorption. According to Conder and Young,[22] the retention of a probe is unaffected by a small degree of mass transfer. In such cases, the peak broadening occurs about the retention volume. For PVC and PMMA, the effect of mass transfer on the chromatograms was considered negligible, since, for example, a methane chromatogram from the PVC column at 40 °C had a mean retention time of 0.45 min., with a variance of 0.002 min. Retention volumes for methane were, therefore, obtained from the peak maxima, *i.e.*, the volume corresponding to a superimposed, Gaussian peak. For the *n*-alkanes, retention volumes were obtained directly from the peak maxima of the symmetrical peaks. These data could then be used to compute σ_S^{LW} from Eq. 16.

In addition to the vapor adsorption measurements for *n*-alkanes on the three surfaces, such measurements were also necessary to determine adsorption isotherms for DIM on the surfaces, from which the equilibrium spreading pressure could be computed. Adsorption isotherms were determined using the "peak maxima method".[36] The concentration of the injected probe is assumed to be linearly proportional to the height of the elution chromatogram:

$$c(t) = k h(t) \tag{17}$$

where $c(t)$ is the concentration of the probe vapor, k is a detector calibration constant, and $h(t)$ is the height of the chromatogram. Since

$$n = Q \int_0^\infty c(t)\,dt \tag{18}$$

where n is the number of moles of injected probe, Eq. 17 can be substituted into Eq. 18, to express the calibration constant as:

$$k = \frac{n}{jQ \int_0^\infty h(t)\,dt} = \frac{n}{jQ A_h}, \tag{19}$$

where A_h is the area under the elution curve from an injection of a known number of moles. The calibration constant can then be used to determine the probe vapor concentration from measurement of the peak height. The adsorption isotherm can be determined from Eq. 12 after substitution of Eqs. 11 and 17:

$$\Gamma = \frac{jkQ}{A}\int_0^h (t_R - r_{\text{ref}})\,dh = \frac{jkQ}{m\Sigma}\int_0^h (t_R - t_{\text{ref}})\,dh, \tag{20}$$

where m is the mass of the column packing. The sorption effect on the isotherms was also considered, *i.e.*, the variation in gas flow rate due to the flux of solute molecules between phases.[22] When the sorption effect is considered, the expression for Γ becomes:

$$\Gamma = \frac{jkQ}{m\Sigma}\int_0^h \frac{(t_R - t_{\text{ref}})}{1 - 2y_{R_{max}}}\,dh, \tag{21}$$

where $y_{R_{mx}}$ is the maximum mole fraction of the solute at the exit of the column.

RESULTS AND DISCUSSION

The work of adhesion between DIM and the three solid surfaces was determined from the results of wetting measurements, according to Eq. 6. The average advancing contact angle of DIM against each of the three surfaces is shown in Table II. Π_e was determined using the classical technique of integration under the adsorption isotherm.[37] Adsorption isotherms for DIM on the three surfaces are shown in Figure 2. The isotherms were extrapolated to saturation pressure of DIM using the method proposed by Schröder,[10] as shown in Figure 3. The effects of condensation were neglected, since the extrapolations were made from $P/P_0 \sim 0.7$ to 1. The PVC isotherm was extrapolated from even lower partial pressure, because the small PVC column could not support liquid injections greater than 1 μl. A longer column with ten times as much packing was originally used, but chromatograms took nearly 10 hours to develop. A shorter column containing less material was used to expedite the data collection but, in so doing, the ability to accurately attain larger partial pressures was sacrificed due to flow rate alterations from larger liquid injections.

TABLE II

Comparison of W_a and related parameters from wetting and vapor adsorption measurements for diiodomethane on PVC, PMMA, and CTMP at 23°C [all units are mJ/m^2, except where otherwise noted]

Solid	θ_{DIM} [degrees]	Π_e	W_a [Eq. 6]	W_a [Eq. 15] σ_s^{LW} from IGC[ε]	W_a [Eq. 9] de Boer[l]	W_a [Eq. 9] liquid adsorbate[†]
PVC	57	26.9	105	93	150	109
PMMA	49	8.1	92	94	120	79
CTMP	44	11.0	98	97	131	89

[ε] denote the value of σ_s^{LW} obtained from infinite dilution adsorption of *n*-alkanes

[l] denotes the spreading pressure corresponding to de Boer's standard state (ideal gas configuration in the adsorbed state)

[†] denotes the spreading pressure corresponding to liquid density packing in the adsorbed state

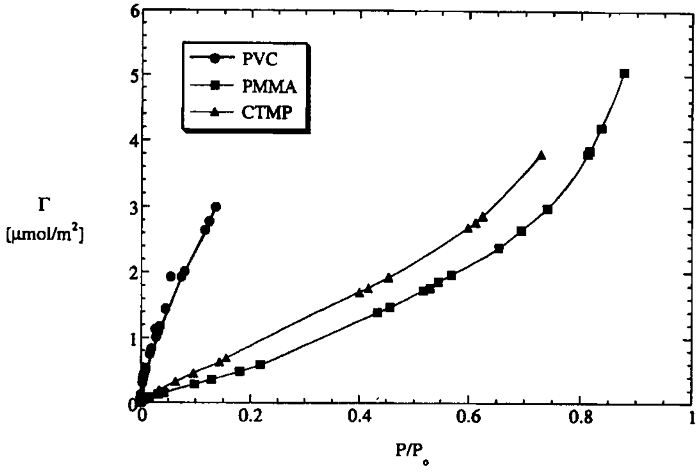

FIGURE 2 Adsorption isotherms for diiodomethane on PVC, PMMA and CTMP fibers [23 °C].

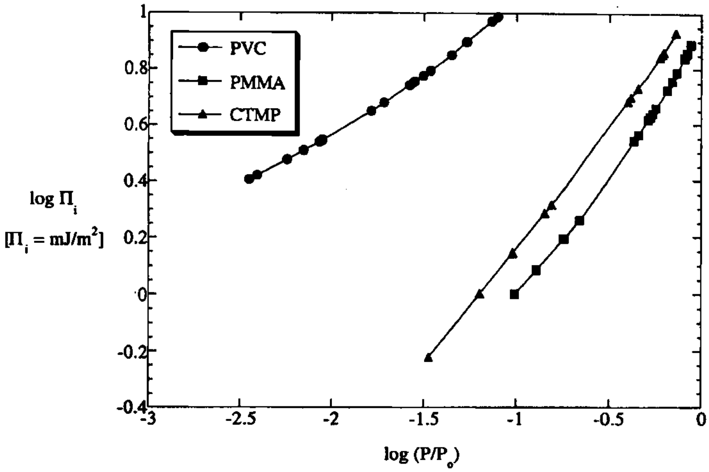

FIGURE 3 Variation of spreading pressure with partial pressure for diiodomethane on PVC, PMMA, and CTMP fibers [23 °C].

The effects due to profound energetic hetergeneity on the adsorption isotherms were also considered negligible. Earlier work involving the CTMP fibers indicated that the fiber surfaces were energetically homogeneous with respect to Lifshitz-van der Waals interactions.[38] PMMA and PVC were obtained as ultra-pure polymers, thereby permitting the safe assumption that their surfaces were free of sites of disparate Lifshitz-van der Waals interaction potential. Values for the work of adhesion, computed according Eq. 6, are listed in Table II. In all cases, the extrapolated values of Π_e are appreciable (~8–26% of W_a), verifying that it would have been erroneous to consider their values negligible.

The work of adhesion for *n*-alkanes with PVC, PMMA, and CTMP surfaces was determined from infinite dilution adsorption measurements using IGC. Normal-alkane molar areas were adapted from a model proposed by Dorris and Gray,[21] in which the alkane areas were computed from a constant methylene group area of 0.06 nm^2. The slightly larger area occupied by the methyl groups at the ends of the alkane chains was computed based on Dorris and Gray's reported lengths for carbon-carbon and carbon-hydrogen bonds.[38] The *n*-alkane retention volumes were plotted according to Eq. 16, as shown in Figure 4. The slopes of the lines were used to compute σ_S^{LW} for the three surfaces, the values of which are listed in the Table III. For comparison, also listed in Table III, are values of σ_S^{LW} computed from the work of adhesion as determined from wetting measurements. Values for σ_S^{LW} have also been computed assuming the equilibrium spreading pressure is negligible. These results show the importance of Π_e for these systems, for when it is included in the computations, the values of σ_S^{LW} determined from the results of wetting measurements are in close agreement with those detemined from *n*-alkane adsorption measurements.

The work of adhesion was also computed, according to Eq. 15, for DIM in contact with the surfaces, using the value of σ_S^{LW} determined from the *n*-alkane adsorption

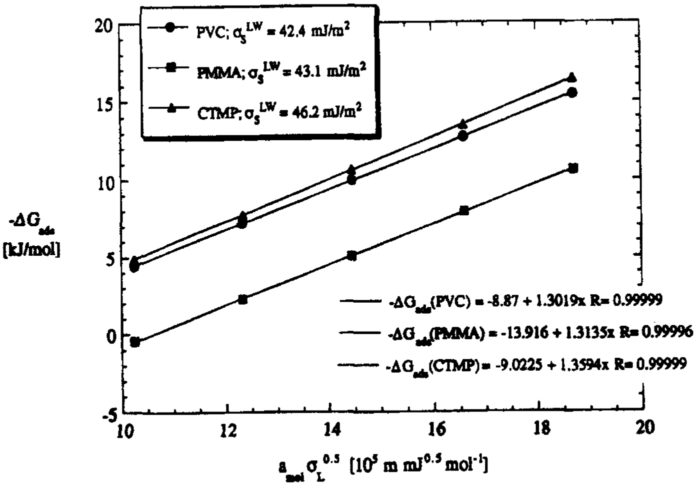

FIGURE 4 Gibbs free energy change upon adsorption correlated to the work of adhesion [23 °C].

TABLE III
Comparison of σ_S^{LW} values for PVC, PMMA and CTMP surfaces
[units are mJ/m^2]

Solid Surface	σ_S^{LW}(IGC) Eq. 16	$\sigma_S^{LW}(\theta, \Pi_e)$ Eq. 6	$\sigma_S^{LW}(\theta, \text{no } \Pi_e)$ Eq. 4
PVC	42.4	54.3	30.2
PMMA	43.1	43.4	34.8
CTMP	46.2	49.5	37.5

experiments. The results are shown in Table II, and are in good agreement with the values of the work of adhesion determined from wetting measurements. These results lend credence to the use of simple vapor adsorption measurements with *n*-alkanes on the solid surface to determine σ_S^{LW}, and to determine subsequently the Lifshitz-van der Waals contribution to the work of adhesion between the solid and a liquid of known σ_L^{LW}.

Vapor adsorption measurements using the technique of IGC were also used to determine directly the work of adhesion between diiodemethane and the three surfaces using Eq. 9. To determine the Gibbs free energy change upon adsorption from a measured retention volume requires information about the total adsorbate surface area, as well as the standard state of the adsorbed probe molecules. The first quantity was determined from knowledge of the solid specific surface areas and of the amount of material packed into the column. The latter quantity was first proposed by Dorris and Gray to be represented by de Boer's standard state, which arbitrarily defines the standard surface pressure as that pressure for which the average distance of separation between molecules in the adsorbed state equals that of the standard gas state[21]. Using this standard surface pressure, $\Pi_s = 0.338\,\mathrm{mJ/m^2}$, the following relationship can be made from the Gibbs adsorption equation in the Henry's law concentration region:

$$\frac{\Pi_s}{P_{s,s}} = \frac{RT\Gamma}{P_{s,s}} = K, \tag{23}$$

where $P_{s,s}$ is the adsorbate partial pressure in equilibrium with the standard adsorption state. Combining Eqs. 14 and 23, the Gibbs free energy change upon adsorption can be expressed as:

$$\Delta G_{ads} = -RT\ln V_N + RT\ln(m\Sigma) - RT\ln\left(\frac{P_{s,g}}{\Pi_s}\right), \tag{24}$$

where $P_{s,g}$ is the adsorbate partial pressure in the gaseous standard state (*i.e.*, 1 bar).

Since the distance of separation of adsorbate molecules is likely to be less than that of an ideal gas at $P_{s,g} = 1$ bar, another standard state, *viz.* the molecular separation corresponding to the molar volume of the *liquid* was considered, a "liquid adsorbate" standard state. Assuming and ideal, two-dimensional adsorbate, which may be reasonable for adsorption in the region of infinite dilution along the adsorption isotherm, the standard surface pressure can be computed from:

$$\Pi_s = \frac{RT}{a_{mol}}. \tag{25}$$

Using the molar area for DIM obtained from Eq. 10, $\Pi_e = 11.7\,\mathrm{nJ/m^2}$.

Values for ΔG_{ads} for DIM on the three solid surfaces were computed according to Eq. 24 using both the de Boer and the liquid adsorbate standard states. Since DIM exhibited concentration-dependent adsorption on the three surfaces, even at the limit of the detector sensitivity, the ΔG_{ads} corresponding to the region of infinite dilution along the adsorption isotherm was determined from a linear extrapolation to zero height, *i.e.*, zero concentration or infinite dilution, ΔG_{ads} from chromatograms of the most dilute concentrations. Using these values of ΔG_{ads}, and the molar area for DIM, computed from Eq. 10, the wor k of adhesion was then determined from Eq. 9. The results are represented in Table II. There is reasonable agreement between the valuesof the work of adhesion obtained from wetting measurements compared with the values obtained form vapor adsorption measurements. Use of the liquid density packing for the adsorbed state provides closer agreement with values of the work of adhesion obtained by wetting measurements. It appears that use of a standard state corresponding to a closer packing of molecules than that of a gas at standard pressure (1 bar) may be a reasonable choice.

CONCLUSIONS

Although wetting measurements are the most direct means of determining the work of adhesion for a system, they are not readily applicable to many systems of practical importance, *viz.*, "high energy" surfaces, which are "wet-out" by most convenient probe liquids, and porous or granular solids. In addition, since wetting measurements must be performed under conditions of adsorption equilibrium, the equilibrium spreading pressure for the system must be independently determined. There are several problems associated with its assessment. The most common method of determining Π_e, integration of the adsorption isotherm from zero pressure to saturation pressure of the probe, is subject to the effects of condensation and solid surface energetic heterogeneity. Also, adsorption isotherms are commonly determined for partial pressures below saturation pressure, thereby requiring an appropriate method of extrapolation. The technique of inverse gas chromatography is a convenient alternative to the use of wetting measurements to determine the work of adhesion. From retention volume measurements, the work of adhesion can be computed with knowledge of the adsorbate molar area. In general, however, this method requires the total area of the adsorbent and the assignment of an arbitrarily-chosen adsorbed standard state. For the special case in which there are only Lifshitz-van der Waals interactions across the adsorbate-adsorbent interface, however, determination of the work of adhesion is greatly simplified in that neither the adsorbent area nor the adsorbate standard state are required. The analysis requires instead the determination of an "alkane line", obtained by IGC experiments on the solid using a series of *n*-alkanes.

In this study, the work of adhesion was determined for systems involving Lifshitz-van der Waals interactions only, *viz.* diiodomethane in contact with PVC, PMMA and CTMP fibers using both the techniques of wetting and vapor adsorption measurements. Good agreement was attained between the values obtained from the two methods, with the following points to be emphasized:

- Π_e was determined from extrapolation by Schröder's method to saturation pressure for DIM on the three surfaces, and was found to be significant ($\sim$8–27% of W_a) in all cases. Only when the equilibrium spreading pressure was used in the computation of the work of adhesion, did the value obtained from wetting measurements agree well with that obtained from vapor adsorption measurements. These results add to the growing database of cases in which the equilibrium spreading pressure is appreciable, even though the liquid yields a finite contact angle against the solid surface. The equilibrium spreading pressure should evidently never be *assumed* to be negligible.

- Direct computation of the work of adhesion from vapor adsorption measurements depends on adsorption results from the region of infinite dilution along the adsorption isotherm. For the three surfaces investigated in this study, the Lifshitz-van der Waals interaction potential was either known or safely assumed to be relatively uniform across the surface. The sites probed by infinite dilution adsorption are, therefore, energetically equivalent to those filled at monolayer coverage of the surface. For systems in which specific interactions are operative across the adsorbate-adsorbent interface, the potential energy for adsorption of the sites filled under conditions of infinite dilution may be markedly different from those filled at higher surface coverages. Therefore, special care should be taken in extrapolating these results to systems for which acid-base interactions are possible.
- The Lifshitz-van der Waals contribution to the work of adhesion between a probe liquid and a solid surface can also be computed from the results of *n*-alkane adsorption to that surface. Using the value of σ_S^{LW} obtained from the IGC analysis, the work of adhesion can be computed for probe liquids of known σ_L^{LW}. The results obtained in this study are in very close agreement with those obtained from wetting measurements. Thus, for systems for which the equilibrium spreading pressure is unknown, vapor adsorption measurements using the technique of IGC may provide a quicker method for determining the work of adhesion.
- The work of adhesion was also computed directly, using Eq. 9, from the results of vapor adsorption measurements using both the de Boer and the "liquid adsorbate" standard states. Use of the de Boer standard led to consistently higher values of W_a than those given by wetting measurements, while the new "liquid adsorbate" standard state produced results in reasonable agreement with them. There are, of course, many possibilities for the configuration of the adsorbed standard state, and others may be better-suited for use with the phenomenon of adsorption.

The results obtained in this study represent, we believe, the first attempt to establish a connection between the results obtained from wetting and vapor adsorption measurements, and their good agreement with one another lends credence to values obtained by either method. In particular, one may have confidence in the validity of vapor adsorption measurements, which are in many cases easier to carry out and applicable to a wider range of material systems.

Acknowledgments

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