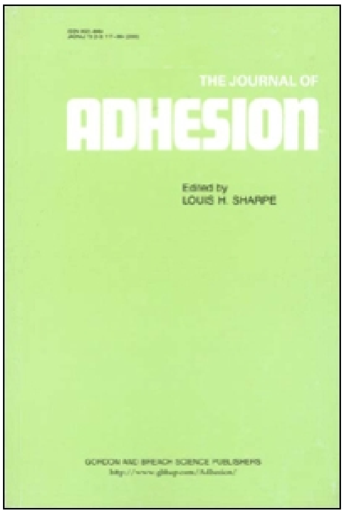

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G. Garnier[a]; W. G. Glasser[a]
[a] Department of Wood Science and Forest Products and Biobased Materials Center, Virginia Tech, Blacksburg, VA, U.S.A.

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Measurement of the Surface Free Energy of Amorphous Cellulose by Alkane Adsorption: A Critical Evaluation of Inverse Gas Chromatography (IGC)*

G. GARNIER and W. G. GLASSER**

Department of Wood Science and Forest Products and Biobased Materials Center, Virginia Tech, Blacksburg, VA 24061-0323, U.S.A.

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Surface energies of amorphous cellulose "beads" were measured by IGC at different temperatures (50 to 100°C) using n-alkane probes (pentane to undecane). The equation of Schultz and Lavielle was applied which relates the specific retention volume of the gas probe to the dispersive component of the surface energy of the solid and liquid, γ_S^d and γ_L^d, respectively, and a parameter ("a") which represents the surface area of the gas probe in contact with the solids. At 50°C, γ_S^d was determined to be 71.5 mJ/m^2, and its temperature dependence was 0.36 mJ m^{-2}K^{-1}. Compared with measurements obtained by contact angle, IGC results were found to yield higher values, and especially a higher temperature dependence, $d(\gamma_S^d)/dT$. Various potential explanations for these elevated values were examined. The surface energy, as determined by the Schultz and Lavielle equation, was found to depend mostly on the parameter "a". Two experimental conditions are known to affect the values of "a": the solid surface and the temperature. While the surface effect of the parameter "a" was ignored in this study, the dependence of the surface energy upon temperature and probe phase was demonstrated to be significant. Several optional treatments of the parameter "a" were modeled. It was observed that both experimental imprecision, but mostly the fundamental difference between the liquid-solid *vs* the gas-solid system (and the associated theoretical weakness of the model used), could explain the differences between γ_S^d and $d(\gamma_S^d)/dT$ measured by contact angle and IGC. It was concluded that the exaggerated temperature dependence of the IGC results is a consequence of limitations inherent in the definition of parameter "a".

KEY WORDS inverse gas chromatography (IGC); surface energy; amorphous cellulose beads; alkane adsorption; temperature dependence; modeling.

INTRODUCTION

The surface energy of polymers is an important property that controls many practical applications such as spinning of fibers, adhesion, dispersion stability and wetting of fibers[1] by liquids. The surface energy is a direct manifestation of intermolecular forces. The molecules at the surface of a liquid or a solid are influenced by

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**Corresponding author.

unbalanced molecular forces and, therefore, possess additional energy in excess of the bulk molecules of the solid or liquid phase.[1,2] Due to the lack of mobility at the solid surface, this free energy can not be measured directly, and indirect experimental methods must be used. The surface free energy can be estimated by extrapolating the surface tension of polymer melts to room temperature, or with methods that rely on the wettability of polymer surfaces by liquids of different surface tension, such as contact angle measurements and flotation techniques.[1,3–6] The contact angle methods are most widely used to characterize polymer surfaces. However, factors such as surface roughness, heterogeneity, and bulk penetration of the liquid often result in contact angle hysteresis.[6,7] The environment, the size of the drop, and the preparation of the surface also may affect the size of the angle. The thermodynamic significance of contact angle measurements is, therefore, often questionable.

The physical adsorption of gas molecules on solid surfaces provides an alternative concept of surface energy determination. Inverse Gas Chromatography (IGC) has recently become the technique of choice for quantifying the reversible gas/solid adsorption. Numerous relationships between various thermodynamic parameters and the basic experimental observation of IGC, the specific retention volume (V_g) of a probe molecule in the gaseous state, have been derived.[8] Unlike conventional techniques, IGC allows the detection of adsorption phenomena down to very low vapor concentrations (Henry's law region), where the surface coverage approaches zero and the lateral interactions are minute, if not negligible. This allows the thermodynamic functions to depend only on adsorbate-adsorbent interactions.[7–10] IGC provides a unique means of studying the adsorption characteristics of the surfaces in a controlled environment, over extended probe concentration and temperature ranges, and with a variety of organic probes.[11]

IGC has become a common surface characterization technique that is now widely used to distinguish a multitude of surfaces. It basically consists of measuring the adsorption behavior of volatile probes of known properties on the solid surface to be characterized. Two kinds of probes can be used: alkanes, to measure the dispersive component of adhesion and of the surface energy; and acid/base probes to quantify the specific polar component, the hydrogen bonds and the dipole moments. The enthalpy, the entropy and the free energy of adsorption between the probe and the surface can also be measured.[9,10,12]

Gray *et al.*[12,13] and Schultz and Lavielle[14,15] combined the thermodynamic relations of IGC with the concept of Fowkes on adhesion between hydrocarbons and a solid phase. They developed and formulated relations for measuring the dispersive component of the surface energy from the retention volume of a series of n-alkanes by IGC at constant temperature. The mathematical treatment by Schultz and Lavielle was further extended to quantify the acid/base interactions. This has created great interest in relating surface properties to adhesion.[16–19]

It was the objective of the present study to examine IGC as a quantitative method for determining the interfacial adhesion of thermoplastic polymers (especially polyolefins) to cellulose (fiber) surfaces. Since cellulose fibers exhibit complex chemistry (*i.e.* purity), complex morphology (*i.e.*, crystallinity, fibrillar orientation, etc.), complex anatomy (*i.e.*, wall thickness, lumen size, etc.), and complex geometry (*i.e.*, size, aspect ratio, size distribution, etc.), a model was adopted that consists of cellulose regenerated in the form of spherical "beads." Special attention was paid to the preparation of cellulose beads with uniform size useful for packing glass columns. Compared with cellulose in powder or fiber form, the regular spherical shape of the beads was expected to minimize surface heterogeneity and variability in terms of geometry and morphology. Chromatographic conditions could be optimized by ensuring a low pressure drop and a uniform flow rate of the carrier gas throughout the column. Channeling could be completely avoided.

Alkanes were chosen as probes because of their inert nature *vis-a-vis* cellulose surfaces, and because the adsorption mechanism is due only to dispersive types of forces.[9,10,12] It was the goal of this study to characterize the surface of amorphous cellulose by investigating the adsorption of a series of alkane probes over a wide range of temperature. The theoretical treatment of Schultz and Lavielle was used directly for determining the dispersive component of the surface energy of cellulose beads.

EXPERIMENTAL

I. Materials

Amorphous cellulose beads, without detectable X-ray diffraction, were prepared by dissolving[20] a partially crystalline (Whatman CF-11) cellulose in N,N-dimethylacetamide/lithium chloride (9% wt/v), and by subsequently precipitating the polymer by dropwise addition into a non-solvent. Using a pneumatic apparatus, droplets were regenerated as spherical gel beads.[21,22] The gel beads were thoroughly washed with water and then with acetone. The acetone treatment caused a drastic shrinkage of the beads. The beads were first dried for 4 days by free convection in a fume hood. They were then transferred into a vacuum oven kept at room temperature and under 20 mm Hg of vacuum for 2 days. Finally, they were heated to 55°C for another two days under 20 mm Hg of vacuum. In order to investigate the effect of various surface treatments the beads were exposed to the same environment but without the reactive agents. The beads were, therefore, mixed for 24 hr at 50°C in DMAc/LiCl with pyridine as a catalyst. This was followed by a 48-hr methanol extraction and by vacuum drying for 48 hr. The beads were then stored in an airtight container. At no time in the process were the beads touched by hand.

Surface analysis by X-ray Photoelectron Spectroscopy (XPS) showed no traces of lithium chloride or nitrogen resulting from the solvent system. The carbon and oxygen surface concentration were identical to the theoretical composition of cellulose. XPS also provided evidence that the post-treatment of the beads did not affect their surface composition. X-ray diffraction analysis revealed a completely amorphous structure. Scanning electron microscopy revealed a smooth and uniform glassy surface. Density was determined to be 1.35 g/mL using a density gradient column with a carbon tetrachloride/ethanol mixture. This was confirmed by a conventional technique (*i.e.* decane displaced).

II. Methods

Chromatographic Conditions Carefully-dried cellulose beads having a diameter ranging from 250 μm to 425 μm were weighed and packed into a glass column of 2 mm inside diameter. Uniform packing was achieved with 3.6740 g of beads per 1.2 m column length. Silane-treated glass wool was used to seal the ends of the column. The column was conditioned for 24 hr at 100°C under a flow of helium. No volume change was observed. Although below the glass transition temperature of cellulose (around 250°C[23]), this annealing treatment was intended to desorb all volatile molecules from the surface and to relax the beads from accessible stress and possible static charges. The carrier gas flow rate was accurately measured with a soap bubble flowmeter every day at the beginning and at the end of each series of experiments. Flow rates of 18 mL/min ± 0.5 mL/min were employed for each series of measurements. The cellulose beads were kept under a steady flow of helium to prevent any kind of oxidation.

The experiments were performed using a VARIAN 3700 Gas Chromatograph (GC) equipped with flame ionization detector and connected to a HP 3394A integrator. Detector and injector ports were both heated to 150°C; the measurements involved the temperature range from 50°C to 100°C. HPLC-grade n-alkane probes were purchased from Aldrich Chemical Co., and they were used as received. GC vials (2 mL), half filled with an alkane probe, were stored in a warm place close to the GC detector. Hamilton gas-tight syringes (10 μL) were used throughout the experiments. Typically, 1 μL of the alkane vapor was aspirated from the vial. The syringe was then flushed four times with 3 μL of air. Finally 1 μL of the methane marker was aspirated and injected in the GC. The same syringe, containing the residual molecules of the probes from the previous injection, was used for the subsequent injections, along with 1 μL of methane. Injections with the same (contaminated) syringe were performed until the peak totally vanished and could no longer be detected by GC. This was typically achieved after a minimum of 6 injections. Retention times were measured at the peak maximum, and the retention time at infinite dilution was obtained by extrapolation for a peak area of zero (zero coverage).

RESULTS AND DISCUSSION

1) Data Interpretation

The specific retention volume (V_g) is defined as the volume of carrier gas required to elute the probe molecules adsorbed by 1 g of packing material under normalized pressure and temperature conditions. V_g is defined as:

$$V_g = (t_r - t_m)\frac{1}{w}Q^* \tag{1}$$

where t_r and t_m are the retention times of the alkane probe and of the marker, respectively, and w is the weight of the polymer in the column. Q^* is the corrected carrier gas flow rate defined as:

$$Q^* = Q \frac{273.15}{T} JC \qquad (2)$$

where Q is the flow rate measured at the temperature T (K), and J and C are correction factors for the gas compressibility and the water tension of the soap solution of the flowmeter,[8,19] respectively.

For IGC at infinite dilution, the free energy of adsorption of one mole of solute from a reference state of adsorption (ΔG_A) leads to:[8,19]

$$\Delta G_A = -RT \ln\left(V_g \frac{P_o}{S\pi_o}\right) \qquad (3)$$

where S is the specific surface area, and π_o is the spreading pressure defined at the partial pressure P_o. The reference states of Rideal or De Boer are most commonly used to define π_o and P_o.[8] The free energy of adsorption is rigorously derived as:

$$\Delta G_A = -RT \ln(V_g K_1) = -[RT \ln V_g + RT \ln K_1] \qquad (4)$$

where $K_1 = P_o/S\pi_o$. Usually $RT \ln K_1$ is treated as a constant K_2, to yield:[14,15,17,19]

$$\Delta G_A = -RT \ln V_g + K_2 \qquad (5)$$

Gray *et al.* and Schultz *et al.* assumed the free energy of adsorption to be related to the work of adhesion, W_A, between the probe molecules and the solid, and to the surface area of the probe molecule, a, in contact with the solid:[9,14]

$$\Delta G_A = N\,a\,W_A \qquad (6)$$

where N is Avogadro's number. According to Fowkes, the work of adhesion between a solid (S) and a liquid (L), considering only dispersive interactions (d), can be described by the geometric mean of the surface free energy:[24]

$$W_A = 2(\gamma_S^d \gamma_L^d)^{1/2} \qquad (7)$$

where γ_S^d and γ_L^d are the dispersive components of the surface energy of the solid and the liquid, respectively. From equations 5, 6 and 7, Schultz and Lavielle derived the equation:[14,15]

$$RT \ln V_g = 2\,Na\,(\gamma_S^d)^{1/2} (\gamma_L^d)^{1/2} + K_3 \qquad (8)$$

where K_3 is a constant term. This equation is developed for liquid adsorption on a solid, although the molecules adsorbed at infinite dilution are not an adsorbed liquid film. Schultz *et al.* demonstrated, under certain conditions, the validity of equation (8) and of its assumptions by comparing the surface energies measured by contact angle with those determined by gas-solid adsorption.[14] For alkane adsorption on solid surfaces, the dispersive component of the surface energy of the liquid equals the surface tension of the alkane probe at the same temperature ($\gamma_L^d = \gamma_H$), and "a" represents the surface area that the probe covers when adsorbed onto the solid surface.

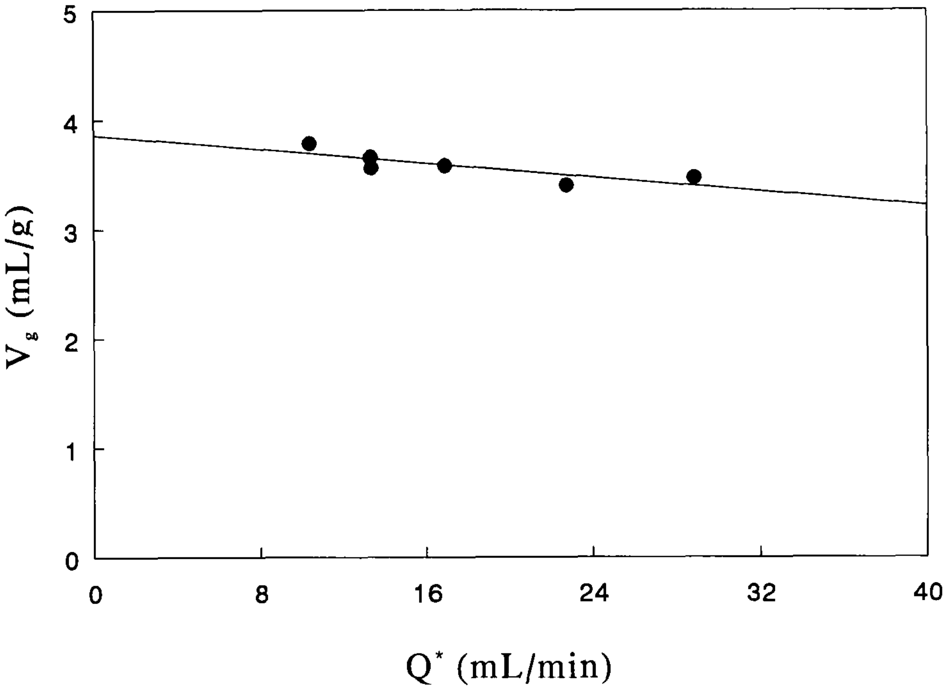

FIGURE 1 Effect of the corrected flow-rate (Q*) on the specific retention volume, V_g, measured at 60°C with octane on cellulose beads.

2) Experimental Results

Well-defined Gaussian peaks were recorded for each of the alkane probes over the entire range of temperature and concentration; there was no tailing. This suggests that kinetic factors were negligible, and that the experiments were performed under equilibrium adsorption conditions.[8,12]

Surface characterization relies on the premise that the mechanisms of probe retention are due only to surface phenomena; no bulk retention is involved. The bulk retention of the probe would be possible if 1) the polymer is porous; 2) the temperature is close to T_g; or 3) the probe is a solvent for the polymer.

If the polymer is porous, the retention volume is affected by the corrected carrier gas flow rate (Q*). Figure 1 represents the dependence of V_g on Q*. The experiments were performed at 60°C with octane as the probe. They cover a wide range of flow rates. A very small dependence of V_g on Q* was observed. This indicates a very weak dependence of diffusivity on flow rate. Since no pores were visible in the cellulose beads by SEM examination of the surface, only some micropores could possibly be responsible for this behavior. Tight control of the carrier gas flow rate (18 mL $\text{min}^{-1} \pm 0.5$) prevented any variance due to bulk diffusion.

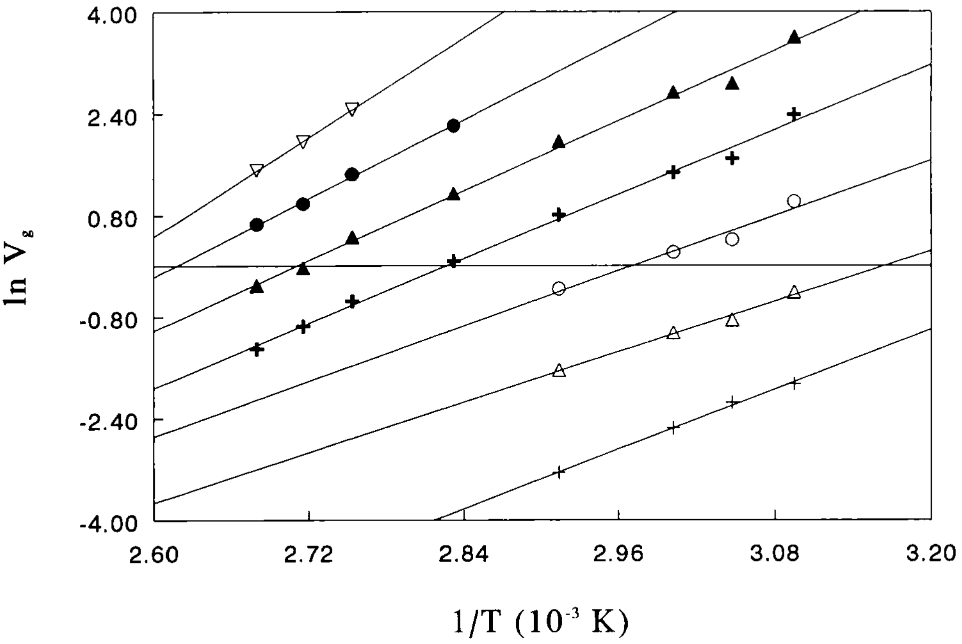

FIGURE 2 Adsorption behavior of alkane on cellulose beads for + pentane, △ hexane, ○ heptane, ✚ octane, ▲ nonane, ● decane, and ▽ undecane.

The relationship between ln V_g and 1/T for the seven alkane probes investigated, ranging from pentane to undecane and for temperatures from 50°C to 100°C (Figure 2), revealed linear behavior. Any change in slope with temperature would have indicated the appearance of a mixed surface and bulk mode of adsorption due to increased diffusion. This is often observed when approaching T_g.[25,26] No such change is detected for the experimental results recorded, suggesting that the retention of the probes is solely due to adsorption on the surface. Finally, none of the probes investigated can dissolve cellulose.

The differential and the isosteric enthalpy of adsorption can both be calculated from the slopes of Figure 2;[27] however, of prime interest is a measurement of the surface energy.

Because no bulk diffusion was detected, the formula of Schultz and Lavielle was confidently applied to the data of Figure 2. Equation (8) states that the slope of RT lnV_g as a function of $a(\gamma_H)^{1/2}$ is proportional to $(\gamma_S^d)^{1/2}$, the dispersive component of the surface energy. The values for parameter "a" are directly taken from the literature,[14] while the surface tension of the probes is corrected for temperature.[28] This relationship is illustrated for each of the temperatures investigated (Figure 3). A minimum of 3 alkane probes were used to produce each of the isotherms. These relationships are linear over the entire range of alkanes and for each of the isotherms. The slopes, the linearity coefficients and the resulting surface energies are calculated for each of the isotherms (Table I).

At 50°C a dispersive component of the surface energy of 71.5 mJ/m^2 was calculated, and this decreased to 52.3 mJ/m^2 at 100°C. A value of dγ/dT of -0.36 (mJ m^{-2} K^{-1}) was calculated. By comparison, the surface energy as measured by contact

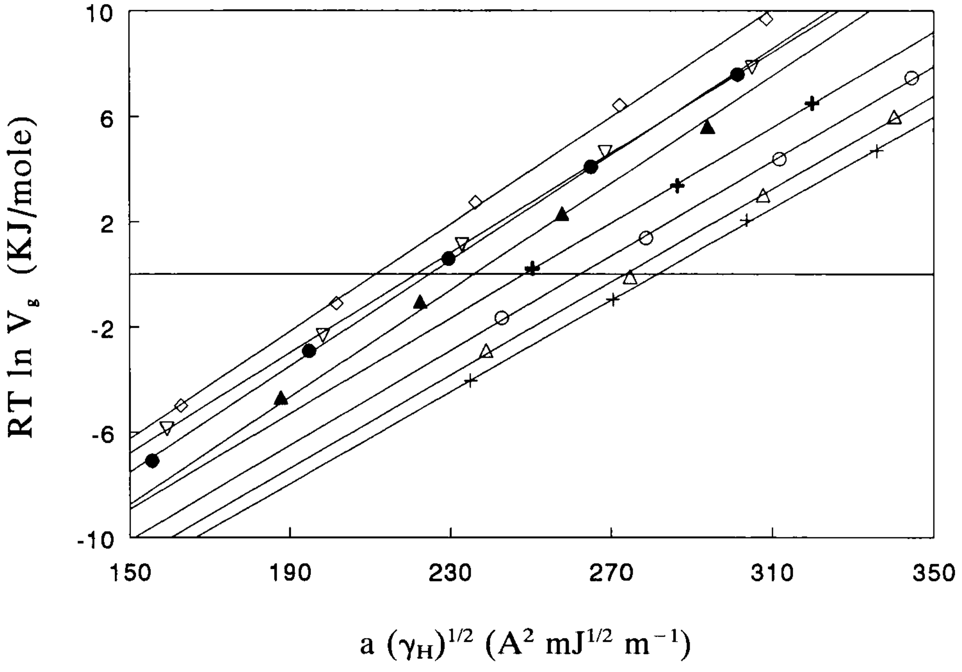

FIGURE 3 Adsorption energy plot of RT lnV$_g$ *vs* a(γ_H)$^{1/2}$ at + 100°C, △ 95°C, ○ 90°C, ✚ 80°C, ▲ 70°C, ● 60°C, ▽ 55°C, and ◇ 50°C.

TABLE I
Linearity coefficients of the slopes of RT lnV$_g$ *vs.* a(γ_H)$^{1/2}$ (Fig. 3), and dispersive component of the surface energy (γ_S^d) for each of the isotherms assuming a = constant

T	a = constant		
(°C)	slope	r^2	(γ_S^d)
50	0.10186	0.9994	71.5
55	0.09510	0.9998	62.3
60	0.10053	0.9998	69.7
70	0.10172	0.9987	71.3
80	0.09060	0.9999	56.6
90	0.08996	0.9997	55.8
95	0.08844	0.9992	53.9
100	0.08708	0.9998	52.3

angle of Cellophane®, another kind of (amorphous) regenerated cellulose, has been reported to be 45.4 mJ/m^2 at 20°C,[4] and 43.1 mJ/m^2 at 50°C. The temperature dependence of the surface energy as measured by contact angle or by the extrapolation of measurements in the melt usually range from -0.06 to -0.08 (mJ m^{-2} K^{-1}) for polymers.[4]

Both the surface energy value and its temperature dependence as measured by IGC appear to be excessive. $d\gamma/dT$ would be 4 to 6 times higher than with conventional techniques. Such a discrepancy might possibly be explained by (a) experimental factors; (b) unfounded assumptions underlying the theoretical model; or (c) the use of a non-representative reference. Cellophane might have a different surface from the cellulose beads. The following section examines the three possibilities.

3) Factors Affecting the Dispersive Component of the Surface Energy

The dispersive component of the surface energy, at temperature T, is obtained by plotting RT $\ln V_g$ as a function of the alkane properties, $a(\gamma_H)^{1/2}$. Good linearity and accurate determination of the slope are essential. The slope values are small (ranging between 0.05 and 0.1), and they are typically multiplied by a constant that is three orders of magnitude larger than the slope values. The product is raised to the second power. The slightest uncertainty regarding the slope is, therefore, greatly magnified. A change by 10% of the slope value results in a variation of 20% in the surface energy. It is, therefore, important to investigate the contribution of the variability of each parameter to the surface energy.

The values of the ordinate (T,V_g) come directly from experimental results. Temperature can easily be kept constant within a few tenths of a degree (°C) with a modern gas chromatograph, and the experimental error of the retention volume is typically less than 5%. Furthermore, the logarithmic function of V_g even decreases the significance of the experimental uncertainty. The effect of the possible experimental error margin on the ordinate parameters can, therefore, be considered as negligible (*i.e.* point (a) of discrepancy explanation, above).

Although both the abscissa values "a" (the surface area a probe molecule occupies on the solid) and "γ_H" (the surface tension of the liquid probe) can be determined experimentally, literature values are typically used for convenience. Accurate values for γ_H at different temperatures can be found in the literature.[28] However, the choice of "a" is much more problematic. The size of the adsorbed molecule is not constant but varies with the solid adsorbent, with temperature, and even with the reference substance (N_2, Krypton).[29] The semi-experimental technique used by Gray *et al.* can be applied to measure "a" of each probe on all different solid surfaces. However this is very tedious.[12] To overcome the effect of the solid surface on the probe molecule's diameter, Schultz and Lavielle determined the surface area of various alkane and acid/base molecules on neutral reference solids such as polytetrafluoroethylene (PTFE) and polyethylene (PE); and they adopted these values for calculating γ_S^d of unknown surfaces. The present study also adopted constant a-values as determined by Schultz and Lavielle. However, temperature is known to affect "a". Its influence on "a", and therefore on surface energy, can be tested by making assumptions regarding the physical state of the probe molecule. The choice of "a" has a major impact on the value of the surface energy, and it, therefore, deserves more attention.

4) Models for the Probe Surface Area Parameter "a"

Fairly low temperatures (below 100°C) are typically used for the surface characterization by IGC. One reason is that adsorption relies on reversible weak forces that decrease exponentially with temperature. For polymers, another reason is that adsorption must be measured well below (by at least 50°C) the glass transition temperature in order to avoid any diffusion of the probe molecules into the bulk of the material.[8,25,26] To investigate the dispersive forces, a series of 3 to 5 consecutive n-alkanes are typically used. In order to quantify the energetics of widely different surfaces, alkanes ranging from propane (C3) to hexadecane (C16) have been used over temperature ranges from 25 to 120°C.[27,30] Most of the probes were injected into a column kept below the boiling point of the probes. Sometimes even the detector and injector temperatures are below the boiling point of the respective probe in order to minimize the axial temperature gradient of the column.

To remain practical, IGC has to rely on a wide variety of probes and temperature ranges to characterize the various surface properties. Somehow, the results obtained under completely different conditions have to be compared using the same reference state. The question is whether theoretical corrections need to be added to the factor "a" in order to compare experimental results from a wide range of different conditions. The effect of the solid adsorbent on the probe molecule's surface can not be taken as constant without seriously questioning the interaction characteristics of each adsorbate-adsorbent pair. Although this is beyond the scope of the present article, temperature corrections can easily be made. The physical state of the probe can be assumed to be a liquid, a real gas or a perfect gas. These three states vary only in the magnitude of the probe molecule's intermolecular forces. The effect of temperature on the volume for these states is relatively easily tested using existing relationships.

Four hypotheses can be made to correct "a" for temperature. *Firstly,* no effect can be considered, and "a" remains constant. This can be justified by the recognition of "a" as a very complex function whose variables are not well understood. *Secondly,* the probe can be expected to behave as a perfect gas. If IGC is truly carried out at infinite dilution, the probe molecules will be diluted in the carrier gas flow, and they will be dissociated from each other. In the absence of any intermolecular interaction, the perfect gas state is obtained and, at a constant pressure in the column, the surface area of the probe is a function only of temperature. *Thirdly,* the probe can be considered to behave as a real gas. Since the adsorption behavior of many alkane probes is studied in a column kept at temperatures below the boiling point of the probes, molecular interactions affecting their expansion are probable. The surface area would not only be a function of the temperature, but also of a non-ideality factor best expressed by the compressibility factor, z. This factor is unity ($z=1$)

when no intermolecular interactions exist, such as in perfect gases, and this usually decreases when the non-ideality increases. Many models can be used to describe real gas behavior. Among them, the truncated virial equation well characterizes small deviations from the ideal-gas behavior of non-polar molecules.[31] For expanded ranges of temperature and pressure, and for the liquid phase, Benedict-Webb-Rubin (BWR) types of equations, such as the Lee-Kesler method, would be appropriate. However, these models have not been applied in the present study because the increase in complexity is not justified by the hypothetical considerations made. *Fourthly,* the probe can be assumed to remain liquid in the column. In this case, the correction of the surface area would be related to the change in density as a function of temperature. These relations are well-known.[32]

Any correction of the surface area of the probe implies that assumptions have to be made regarding the shape of the molecule. This study assumes spherical molecules. It may not be the best assumption for the longest alkane molecules, but it was successfully modeled for short alkanes.[12] Temperature and non-ideality corrections of the surface area of the probes considered as perfect or real gases are carried out using:

$$a_{(T,z)} = a_{REF}\left(\frac{T}{T_{REF}}\right)^{2/3}\left(\frac{z}{z_{REF}}\right)^{2/3} \qquad (9)$$

where a_{REF} is the reference surface area measured by Schultz;[14,15,33] T is the temperature (K); and z is the compressibility factor. For perfect gases, $z = z_{REF} = 1$, and the last term vanishes. For real gases, the truncated virial equation is used (Appendix A). When the probe is considered a liquid, the following correction is used:

$$a_{(T)} = a_{REF}\left(\frac{\rho}{\rho_{REF}}\right)^{2/3} \qquad (10)$$

where ρ is the density.

The adsorption energy plot of RT $\ln V_g$ *vs* $a(\gamma_H)^{1/2}$ for different alkanes (pentane to undecane), and at two temperature extremes (Figure 4), compares the data using a = constant, a = liquid, a = perfect gas, and a = real gas. The surface energies are calculated from the slopes. The results (slope, linearity correlation factor, and surface energy) obtained using the different hypothetical "a" values are summarized in Table II.

At low temperatures the four models gave good, linear relations, all supporting the hypothesis of equation (8). Values of γ_S^d (for $T_{REF} = 20°C$) ranging from 71.5 mJ/m^2 (a = constant) to 44.2 mJ/m^2 (a = real gas) were calculated at 50°C; these corresponded to 52.3 mJ/m^2 to 6.8 mJ/m^2 at 100°C. As the temperature rose, the difference between the models increased. Curvature effects appeared with the real gas model, and these increased with temperature (Figure 4B). Part of the curvature observed at high temperatures for the real gas model could be due to the limitation of the truncated virial equation, or to small gas non-ideality. At higher temperatures, a model such as that by Lee-Kesler could possibly produce better linearity.

The surface energy calculated with a = constant was the highest, at any temperature. The value further decreased with a = liquid and a = perfect gas; and a = real

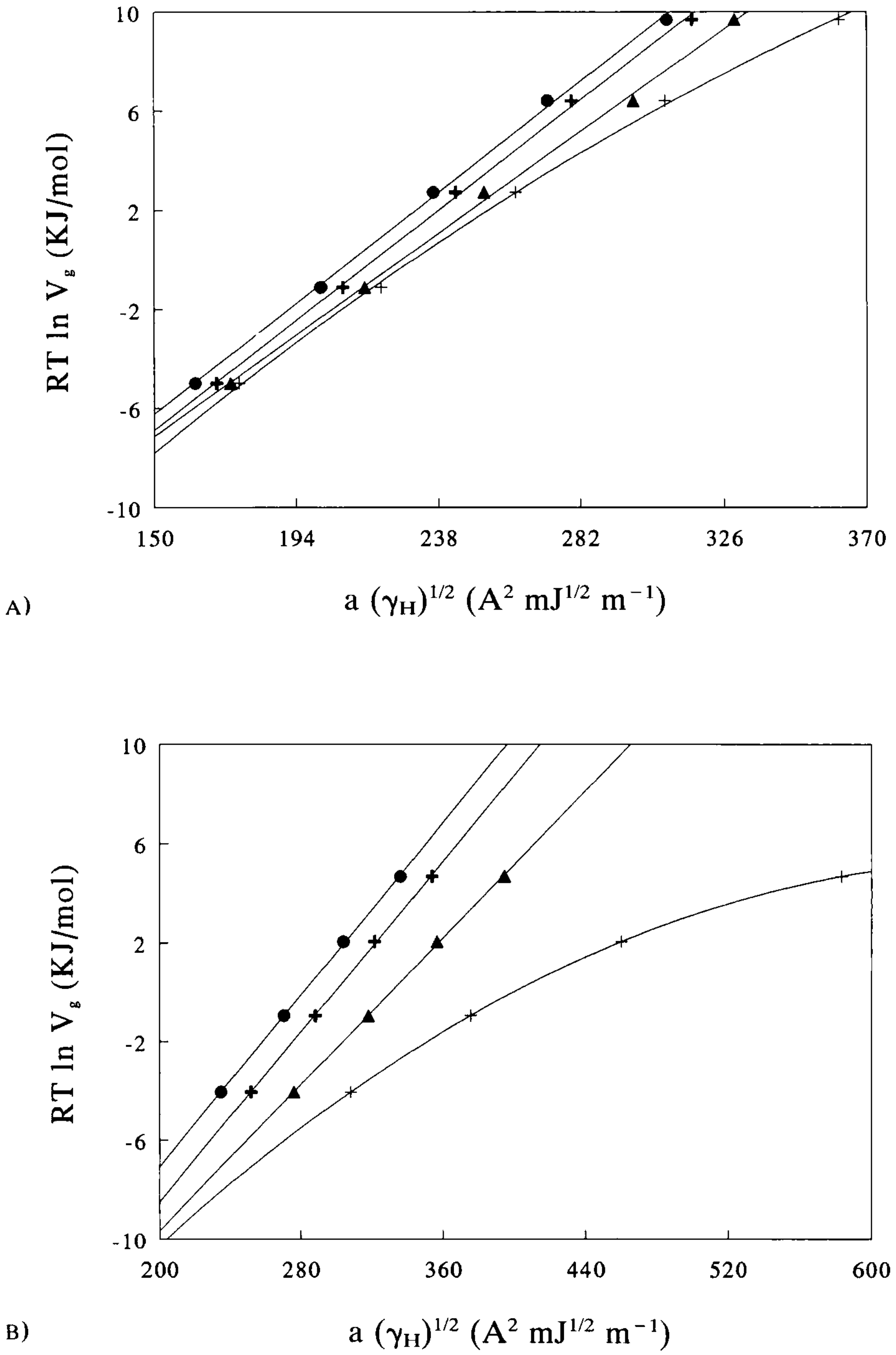

FIGURE 4 Adsorption energy plot of RT lnV_g *vs* a$(\gamma_H)^{1/2}$ for ● a = constant, ▲ a = perfect gas, + a = real gas, and ✚ a = liquid at A) 50°C and B) 100°C.

TABLE II
Linearity coefficients of the slopes of RT $\ln V_g$ *vs.* $a(\gamma_H)^{1/2}$ (Fig. 3), and dispersive component of the surface energy (γ_S^d) for each of the isotherms assuming a = perfect gas, a = real gas and a = liquid

T	a = liquid[1]			a = perfect gas[1]			a = real gas[1]		
(°C)	slope	r^2	(γ_S^d)	slope	r^2	(γ_S^d)	slope	r^2	(γ_S^d)
50	0.10144	0.9994	70.9	0.09546	0.9994	62.8	0.08010	0.9967	44.2
55	0.09429	0.9998	61.2	0.08820	0.9998	53.6	0.07282	0.9977	36.6
60	0.09962	0.9998	68.4	0.09231	0.9998	58.7	0.07498	0.9968	38.8
70	0.10034	0.9987	69.4	0.09158	0.9987	57.8	0.07245	0.9921	36.2
80	0.08972	0.9998	55.5	0.08001	0.9999	44.1	0.04432	0.9982	13.5
90	0.08917	0.9996	54.8	0.07799	0.9997	41.9	0.03404	0.9916	8.0
95	0.08754	0.9990	52.8	0.07598	0.9992	39.8	0.03273	0.9920	7.4
100	0.08616	0.9998	51.1	0.07415	0.9998	37.9	0.03133	0.9850	6.8

[1] Values corresponding to the condition representing a = constant are given in Table I.

gas gives the lowest value. Values of dγ/dT of −0.36 (mJ $m^{-2}K^{-1}$), −0.37 (mJ $m^{-2}K^{-1}$), −0.48 (mJ $m^{-2}K^{-1}$) and −0.82 (mJ $m^{-2}K^{-1}$) were found for conditions that considered "a" constant, liquid, perfect gas and real gas. The first two values (for a = constant and a = liquid) produced virtually identical results because the density of a liquid is a weak function of temperature. Treating "a" as a (perfect or real) gas further aggravates the dγ/dT-discrepancy between IGC and such conventional techniques as contact angle for which values of −0.06 to −0.08 mJ $m^{-2}K^{-1}$ have been reported (for cellophane[4]), and which agree with similar values for polymers in the melt state.[3,4] It must, therefore, be concluded that, while the temperature dependence of surface energy values on the probe surface area parameter "a" remains undisputed, there exists no justification in the classical theory for deriving an "a" value that would help reduce the dγ/dT-discrepancy between IGC and conventional methods. In fact, Luner and Sanders noticed that all dγ/dT values measured with cellulose by adsorption are 4 times as high as those determined conventionally.[35] This supports doubts about the assumptions underlying the Schultz-Lavielle model (*i.e.*, point (b) of the discrepancy explanation, above).

5) Surface Character Considerations

In addition to temperature, the nature and character of the solid surface and undetectable differences between the probe's surface and that of a reference material, may also be held responsible for the observed dγ/dT-discrepancy between IGC and conventional methods (*i.e.* point (c) of discrepancy explanation, above).

Both cellophane and the cellulose beads are composed of regenerated cellulose that can be regarded as chemically indistinct. However, the process of regeneration and the thermal histories of these materials are very different. Uniformity in surface smoothness and invariability of surface features with temperature do not necessarily ensure uniformity of surface energy. The chemistry of a cellulose surface may be more complex, and heterogeneities in surface site energies too varied, to permit the generation of surface energy values that remain constant irrespective of detection principle or temperature. Cellophane might not be an adequate reference with which to compare the surface energy of cellulose beads. IGC at infinite dilution will also measure the surface energy of those sites of highest energy, which are not detectable by contact angle; this could explain the high dγ/dT values reported.

However, the absolute experimental values of γ_S^d appear to be comparable with those in the literature. These minor differences can be justified by the uniqueness of the surface model, by the particular method of surface preparation, or by the geometry of the material being analyzed (*i.e.*, beads *vs* films). Cellulose surfaces have a unique way of interacting with polar, and especially water, molecules. This has been studied extensively by NMR and thermal analysis by Hatakeyama *et al.* and others.[39–41] Any type of surface irregularity due to sorbed H_2O molecules would be revealed with greater sensitivity by methods based on gas-solid adsorption, especially at elevated temperatures, than by experiments based on liquid-solid interaction. Gases are more affected by temperature than liquids. Surface energy determinations at different temperatures would be more accurate if they took into account not only the probe molecule's surface area in the adsorbed state, but also variations in the nature of the solid surface.

CONCLUSIONS

1. Alkane adsorption on surfaces measured by IGC was found to represent a sensitive technique for surface characterization.
2. The surface energy, as calculated by Schultz and Lavielle, was mostly dependent on a single parameter "a" representing the surface area of the gas probe in contact with the solid surface.
3. Unless measured experimentally, an assumption of the dependence of "a" on the energy of the solid surface and temperature must be made. This significantly influences the "a" value, which determines the surface energy calculation and the change in surface energy with temperature (*i.e.*, dγ/dT).
4. The temperature dependence of "a" using four models failed to produce agreement between contact angle and IGC results for amorphous cellulose surfaces. Advantages and disadvantages of each model are: (1) a = real gas gives similar surface energy values to those measured by contact angle at low temperature; (2) a = perfect gas best represents the Schultz-Lavielle model and the principles of IGC at infinite dilution; (3) a = constant is the easiest method, which produces good linearity and which requires no additional assumptions; however, it yields high values for surface energy, and it does not adequately describe gas behavior; and (4) a = liquid gives results very similar to a = constant.
5. The possible contribution of surface irregularities and inhomogeneities to dγ/dT-discrepancies between IGC and contact angle methods can not be ruled out.

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APPENDIX A

The compressibility factor is calculated with the generalized second virial coefficient and the theorem of corresponding states:[31,37]

$$z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r} \tag{A1}$$

where P_c and T_c are the critical pressure and temperature and P_r and T_r are the relative properties. B is the second virial coefficient. For nonpolar molecules:

$$\frac{BP_c}{RT_c} = B^{(0)} + wB^{(1)} \tag{A2}$$

where w is the Pitzer accentric factor, an indicator of the nonsphericity of a molecule's force field; (w = 0 for rare-gas spherical symmetry) and:

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{A3}$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{A4}$$

For polar molecules, an additional term $B^{(2)}$ can be added to equation (A2). The critical properties and the accentric factor can be found in References 31 and 37. If unavailable, critical properties can be estimated from Lydersen's correlation.[38]

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