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Surface Tension Obtained from Various Smectic Free-Standing Films: The Molecular Origin of Surface Tension

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High-resolution surface tension measurements have been carried out on the free-standing films of more than 30 selected liquid-crystal compounds in their smectic phases. Surface tension (γ) values falling into major categories of 27, 24, 21, 13, and 11.5 dyn/cm have been obtained. The dependence of γ on specific terminal groups or molecular structures will be discussed. Our results provide important information about the molecular origin of surface tension.

I. Introduction

The study of surfaces has for a long time attracted scientific effort, both theoretical and experimental.^{1–4} Experimentalists in particular have applied a wide range of methods in order to advance our understanding in this field. Recent examples include high-resolution synchrotron studies,⁵ scanning tunneling microscopy (STM) and atomic force microscopy (AFM) work,⁶ and characterization of Langmuir–Blodgett or self-assembled monolayers.^{7–9} There are many motivations for such a broad research undertaking, including the desire to characterize important surface physical properties, to probe surface

ordering and phase transitions, and to find reliable methods for creating technologically useful surfaces. Liquid crystals, which provide natural access to many fascinating physical behaviors, are a novel category of materials in which to seek answers to these important issues. Our goal in this report is to describe our use of liquid-crystal free-standing films as a highly favorable system for the detailed study of surface tension and for investigating molecular origin of surface tension.

Surface tension is a physical property about which accurate and detailed experimental information is of primary importance. Knowledge about surface tension, and the mechanisms underlying its origin, is critical in addressing such basic surface science issues as wetting, adhesion, friction, spreading, and detergency.^{10–12} Furthermore, relating macroscopic surface properties, such as surface tension, to the underlying microscopic structures, is not only intriguing from a fundamental physics point of view but also useful technologically for the efficient production of materials with properties that are “just right” for a given application. To obtain this kind of information about surface tension, in other words not only to reliably and reproducibly characterize γ for a wide range of surface compositions but also to link γ values to underlying molecular structures, clearly requires both a very favorable natural system to study and a correspondingly versatile measurement technique. We believe that our recent systematic studies of liquid-crystal free-standing films, utilizing our high-resolution, flexible string tensiometer to directly measure surface tension, represent such a powerful experimental combination. Our experimental

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results have revealed a significant "categorization" of surface tension into five different values, approximately 27, 24, 21, 13, and 11.5 dyn/cm, respectively, depending on the surface composition and molecular packing within the films studied. Moreover, we have identified specific, critical molecular subgroups we believe are responsible for these distinct surface tension categories.

We have also obtained very strong evidence indicating that the major contribution to surface tension is localized within a submolecular-group length scale from a fluidlike free surface. As early as 1916, Langmuir proposed that "each part of a molecule possesses a local surface free energy";¹³ therefore, a surface energy (or for liquids, a surface tension) should correspond quite sensitively to the type of "local" molecular parts making up the free surface. Our recent studies¹⁴ on free-standing films of specially selected liquid-crystal compounds have shown that a dramatic, nearly 25% increase in surface tension arises by replacing just a *single* fluorine atom with hydrogen in the submolecular ($-\text{CF}_3$) group populating the film/vapor interface. This finding represents a key advance in critically addressing Langmuir's principle of independent surface action for truly liquidlike surfaces.

II. Description of the Physical System Studied

Liquid crystals have been the subject of much experimental work in recent years.¹⁵ The intensive research has been sparked by a desire to test some fundamental physics concepts using the special characteristics of the liquid-crystal system. Additional incentive has come from the goal of exploiting liquid-crystal physical properties (such as large dielectric and optical anisotropy, and in some cases ferroelectric or antiferroelectric response) in technological applications, especially in the area of electrooptical switching devices.

As a function of temperature, liquid crystals exhibit mesophases with different degrees of ordering. A constituent molecule of such a material can be schematically pictured as an elongated rod or cigar, roughly 25 Å long and 5 Å in diameter. The molecular structure itself consists of a rigid core unit, with flexible tails extending off to either side. At high temperatures, these molecules will behave as an isotropic liquid, randomly oriented and distributed. As the temperature is lowered, the molecules may often form a so-called nematic phase, with the molecular center-of-masses still randomly distributed but with the long axes of the molecules aligned on average along a particular direction in space, called the director. At still lower temperatures, this orientation along the director is preserved, while a one-dimensional positional ordering sets in as the molecules' center-of-masses line up in planes. This arrangement is known as the smectic-A (Sm-A) phase, in which any local piece of the liquid crystal will look like a stack of molecular layers, with the director pointing perpendicular to the layer planes and with liquidlike center-of-mass ordering within the layers. In the Sm-A phase, the layer thickness is roughly equal to the molecular length. One other possible mesophase is the smectic-C (Sm-C), a tilted analogue of Sm-A, in which molecules within the layers have their long axis inclined on average with respect to the layer normal.

Many liquid-crystal compounds in the smectic phases can be spread into free-standing films. At an appropriate

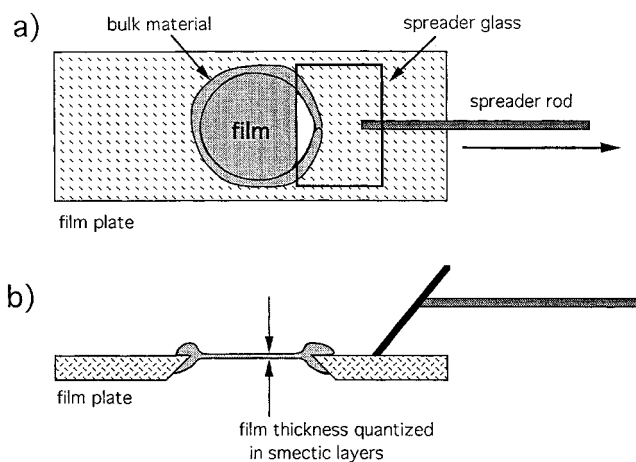


Figure 1. (a) A top view of a typical film plate on which a free-standing smectic film has been almost fully spread. (b) The same film after completion of spreading, shown in a cross section through the plate.

temperature, bulk material previously deposited around the edge of a knife-edged hole in a film plate is pulled across the opening with a glass spreader, in a "wiper"-like fashion. An illustration showing a cut through such a typical thin film is shown in Figure 1. The film thickness is quantized in units of smectic layers and is easily varied from more than several hundred down to only two layers. The film geometry has proven to be particularly fruitful for a wide variety of experimental studies.¹⁶ For example, the ability to create two molecular layer (approximately 25 Å/layer) films, together with the chance to probe phase transitions as a function of temperature in these unique, substrate-free systems, has motivated high-resolution heat capacity, optical ellipsometry, optical reflectivity, and electron diffraction studies in order to search for possible crossover from three-dimensional to effectively two-dimensional behavior.¹⁷

With respect to the unique suitability of free-standing films for surface tension studies, several facts can be emphasized. First, it is important to note the well-defined molecular orientation along the director. Within a Sm-A film, the molecules are oriented with their long axes aligned on average perpendicular to the layer plane. At the same time, the positional ordering of the molecules within the layers is fluidlike. This yields very uniform and homogeneous film free surfaces, populated by close-packed molecular groups. The nature of the chemical species exposed at the free surfaces is therefore strongly predefined over the entire area of the film. Second, in contrast with self-condensed monolayers, another system traditionally used in surface investigations, free-standing liquid-crystal films are substrate-free and, thus, eliminate any potentially complicating variable from consideration. Third, with creative chemical synthesis techniques, a wide range of submolecular groups can be incorporated into liquid crystals. Preserving a long, anisotropic molecular shape (and consequently anisotropic intermolecular interaction) is of great importance in promoting mesophase behavior. However, there is a large scope for variety in both the rigid core units (e.g., biphenyl groups, phenyl rings with carboxylate, azoxy, or Schiff base linkages,

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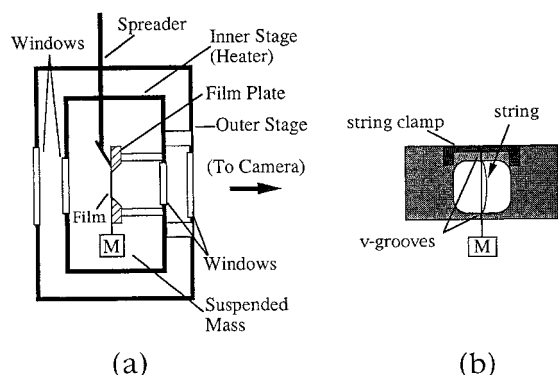


Figure 2. (a) Cross sectional, side view of the tensiometer sample chamber. (b) Top view of the film plate. The string is shown in two configurations: (1) suspended vertically downward with no film present; (2) deformed into an arc when a film is present in the right half of film plate opening.

pyrimidine, etc.) and the molecular tails (hydroalkyl, fluoroalkyl, mixed hydro/fluoroalkyl character, cyano-terminated, tails with ether linkages, etc.). Systematically introducing different chemical functionalities into molecules that order into the well-defined smectic layers offers great potential for investigating surface tension as a function of the type of molecular groups present at the film/vapor interface. Last, we should note that many previous studies on other close-packed organic surfaces were often based on contact angle measurements that relied upon extrapolation from Young's equation for three-phase coexistence.¹⁸ Using the novel method described below, we are able to measure the surface tension of free-standing liquid-crystal films *directly*, without any assumptions about the nature of the forces operative at the film/vapor interface. The combination of this experimental advantage, together with the physical and structural properties described above, makes Sm-A free-standing films a remarkably appropriate system for careful investigations of surface tension and its molecular origin.

III. Description of Experimental Design

The design we have developed to carry out our high-resolution surface tension measurements consists of a temperature- and pressure-regulated chamber. In this chamber we maintain our liquid-crystal sample under appropriate film spreading conditions at a desired temperature within the mesophase sequence (typically the Sm-A phase, with a few exceptions discussed below). The free-standing films are spread on a specially designed film plate mounted inside this apparatus. The chamber itself is shown in Figure 2a and is actually a two-stage oven. The outer stage provides a vacuum-tight seal, while the inner stage, which is wrapped in noninductive fashion with resistive wire, acts as the heat source. The oven temperature is computer-controlled via a PID feedback loop; in practice, the temperature of our oven is stable to within ± 5 mK. Both stages of the oven have windows built in to allow for optical access straight through the chamber. A glass spreader plate is mounted on the end of a rod that translates through a vacuum-tight fitting in the outer oven wall; it is the travel of this spreader across the film plate opening that draws out the free-standing films, as shown in Figure 1. A mechanical pump connected to the oven through a gas-handling assembly allows us to pump down the chamber. Between successive loadings of samples, the oven temperature is set into the isotropic

range of the liquid-crystal compound most recently studied in the chamber, and the oven is held at vacuum for at least several hours (or overnight). We have found this to be an important step in ensuring that there is no cross-contamination between successive loadings of different materials.

A more detailed view of the film plate itself is shown in Figure 2b. During the spreading of a film and subsequent data collection, the oven is mounted so as to orient the film plate vertically. The plate has a rectangular, knife-edged hole cut into it, with two very shallow V-grooves opposite one another on either side of this opening. A very thin, uniform, and flexible surgical suture (#8-0, approximately $40 \mu\text{m}$ in diameter) is suspended across the film opening, guided by the V-grooves, and clamped in place at its upper end. A known mass M is attached on the lower end of the string; in the absence of a film, the string hangs vertically downward, bisecting the film plate hole in a straight line as shown in Figure 2b. The straight-line distance of the opening between V-grooves is 1.76 cm ; the films we spread are approximately $1.76 \text{ cm} \times 0.65 \text{ cm}$ in area.

With the oven temperature is set to an appropriate value within the smectic phase window of the compound to be studied, bulk liquid-crystal material is loaded around half of the film plate opening, coating the edge from V-groove to V-groove. A small amount of material is also carefully deposited on the suture itself along its length across the hole. The oven is then resealed and again pumped down to full mechanical vacuum for approximately 1 h to remove any impurities introduced during loading, or any residual impurity (e.g., solvent) traces from the sample itself.¹⁹ Afterward, for the duration of data collection on the films, the oven chamber is held at one-half atmosphere pressure of argon or helium gas. The gas acts as an exchange medium that thermally connects the film plate with the heater wall, while at the same time providing an inert environment that minimizes sample degradation. The film temperature in our system is actually monitored by a type-E thermocouple mounted on the film plate itself, directly at the liquid-crystal film edge. We estimate that temperature difference between the film and thermocouple is less than 50 mK.

The idea behind our measurement of surface tension is as follows. A rectangular film of the liquid-crystal compound is spread across the opening, its boundary formed on three sides by the plate itself and on the remaining side by the suture. Surface tension causes the film to minimize its surface area. As a result, the originally undeflected and straight string is deformed into an arc, whose radius of curvature is dependent on the film's surface tension and the mass of the suspended weight. This before/after sequence is also indicated in Figure 2b. A typical set of corresponding photos with and without a film present is given in Figure 3.

Once equilibrium is attained, the film surface tension (γ) is related to the string's radius of curvature (R) and the mass (M) of the weight via

$$2\gamma R = Mg + f_f \quad (1)$$

We include the f_f term to account for any frictional force between the string and the lower V-groove, which would tend to irreproducibly affect the observed γ value. The factor of 2 in eq 1 arises from the fact that the film has

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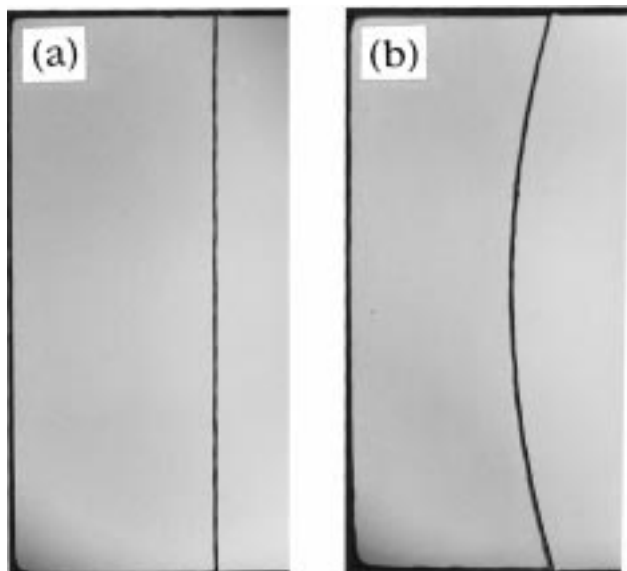


Figure 3. Typical photos showing the film plate without (a) and with (b) a film present in the right half of the opening. The film thickness is four layers. Due to strong interference effects, the film in (b) is transparent.

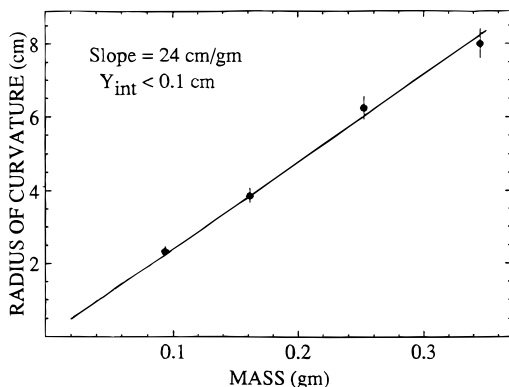


Figure 4. Linear relation between R and M , as per eq 1 in the text, the small intercept indicating negligible friction effects in the system.

two free surfaces. To evaluate the relative importance of the f_t term, we carried out measurements on four different four-layer films of the material 65OBC. The films were all spread at the same temperature of 74.5 °C in the Sm-A phase, but with a different suspended mass M in each case. The dependence of R on M was determined, and the results are given in Figure 4. A linear relation between R and M is obtained in accordance with our expectations; the fact that we obtain a zero intercept (within our experimental resolution) leads us to conclude that the friction term can be safely neglected. Similar results have been obtained in trials with three other compounds. As a result, the expression for surface tension reduces to simply

$$\gamma = Mg/2R \quad (2)$$

In our experimental approach, the ability to measure the radius of curvature R with good resolution is a critical factor in the accuracy of surface tension measurements. We have achieved our current high resolution of about 2% by implementing a careful imaging and data analysis procedure. Once a suitable film is spread, the film plate opening is photographed with a 35-mm camera. A teleconverter and macrolens assembly magnifies the image

by approximately a factor of 5. Backlighting gives a sharp, silhouetted image of the string in the black and white photos. The processed prints are subsequently scanned into a computer. Imaging software is used to "skeletonize" the string to a width of one pixel by a consistent algorithm. A series of points is then obtained from the shape of the deflected string. Distances are converted from pixels to real units by comparing the known span of the film plate to the same length in the scanned images. It is then straightforward to fit the points to an expression for a circular arc, which yields a value for the radius of curvature of the string. Equation 2 then allows us to determine the film surface tension from the measured values of R and M .

An important piece of information related to any given smectic liquid-crystal film is its thickness. We have implemented an optical reflectivity system as part of our experiment that allows us to determine the exact, integer layer thickness for sufficiently thin films (number of layers $N \leq 12$). The basic idea of the reflectivity measurement is simply to bounce a beam of laser light off the suspended film and measure the reflected intensity using a photodetector. Because of the anisotropy inherent in the liquid-crystal molecules, the Sm-A phase is not optically isotropic. However, to a good approximation, the film can be treated as a uniform uniaxial dielectric slab. Optical reflectivity at near normal incidence (the experimental setup) is given by²⁰

$$R = \frac{(n_o^2 - 1)^2 \sin^2(n_o h k)}{4n_o^2 + (n_o^2 - 1)^2 \sin^2(n_o h k)} \quad (3)$$

Here, n_o is the ordinary index of refraction, k the wavevector of the incident radiation, and h the thickness of the slab. Because of the layered nature of the film, $h = N\epsilon$, where ϵ is the layer spacing. We use an intensity-stabilized He-Ne laser ($\lambda = 633 \text{ nm}$) as our light source. The $n_o \approx 1.5$, the factor $n_o h k \ll 1$ for thin films ($N < 12$), and so in this limit eq 3 reduces to $R = cN^2$ with $c = [(1 - n_o^2)\epsilon k]^2/4$. Therefore, by measuring the relative reflectivity of a number of thin films, the constant c can be easily determined and the film thickness (in units of layers) can be easily determined. For films thicker than approximately 12 layers, this straightforward reflectivity measurement of thickness becomes less reliable. However, the thicker films show very characteristic colors due to interference effects, and with practice, film thicknesses in the 20 to 100 layer range can be estimated to within several molecular layers.²¹

Figure 5 gives an overall schematic of our experimental components. A series of mirrors is used to direct the laser light through the oven windows onto the film and likewise the reflected light into the photodetector. To maintain an appropriate light intensity upon our photodetector and avoid saturation for higher film thicknesses, a neutral density filter is used to attenuate the laser beam. To realize the cleanest possible reflectivity signal, a chopped laser light beam is used, with data acquisition through a lock-in amplifier. The beam incident on the film is polarized perpendicular to the plane of incidence, so that for Sm-A films we couple only to the ordinary index of refraction n_o , consistent with the above mathematical development. We have used this same versatile optical system to carry out high-resolution studies of smectic layer spacing versus temperature for a novel perfluorinated

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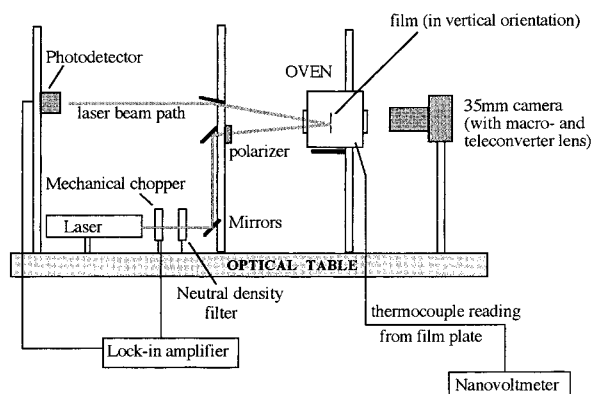


Figure 5. Overall schematic view of the experimental components. The incidence angle of the laser beam (with respect to the film normal) is roughly 10° .

material in the Sm-A and Sm-C phases²² and other materials in the vicinity of various phase transitions.²³

To date, several research groups have developed various innovative techniques to measure surface tension of liquid-crystal films.^{24–26} The flexible-string tensiometer²⁷ developed in our lab is fairly straightforward in design while offering sufficient resolution ($\pm 2\%$) to address important issues. Such an instrument enables us to conduct extensive surface tension measurements on numerous liquid-crystal compounds.

IV. Comparisons with Other Methods of Characterizing Surface Energy of Close-Packed Organic Surfaces

Whenever possible, we have sought to compare the values for γ obtained with our novel string tensiometer to other published data available on liquid-crystal compounds. Although we defer a more detailed discussion of our surface tension data to section V, we note here that our results consistently agree with data obtained by other methods.²⁸

It is important to discuss how our measurements on free-standing liquid-crystal films relate to previous experiments seeking to characterize the energies of various organic surfaces. There have traditionally been two general categories of systems extensively studied in this regard: substrate-anchored monolayers, often prepared by the Langmuir–Blodgett technique, and carefully prepared solid polymer surfaces. Knowing which molecular groups populate the free surface in question is a key issue in any systematic study. In the case of solid polymer surfaces, this information comes from the assumption that

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(28) For example, our $\gamma = 26.8$ dyn/cm value for the CBOOA compound in its Sm-A phase agrees well with measurements based on the bulk pendant drop method. (Krishnaswamy, S.; Shashidhar, R. *Mol. Cryst. Liq. Cryst.* **1977**, *38*, 353.) Light scattering studies on members of the *n*CB homologous series give values consistent with our $\gamma = 27.1$ dyn/cm for 12CB. (Böttger, A.; Joosten, J. G. H. *Europhys. Lett.* **1987**, *4*, 1297.) Our 12CB γ value is also in agreement with recent force balance studies on free-standing films of the analogous 8CB compound (ref 26). Additional data giving us confidence in our measurement technique come from X-ray studies and are cited above in the main text dealing with mixed fluoro- and hydroalkyl surfaces.

a high-molecular-weight polymer creates a surface populated almost entirely by the side chain groups attached to the polymer backbone. For substrate-anchored monolayers, one end of the monolayer molecules has a preference for attaching to the underlying substrate, thereby exposing the other terminal group at the monolayer-free surface.

Past studies measuring the surface energies of either self-assembled monolayers or solid polymer surfaces have often been based on contact angle methods. In such cases, use is made of the famous Young equation³ describing the equilibrium force balance in the coexistence of three phases: a liquid drop resting on an underlying solid surface, in equilibrium with the saturated vapor. The angle θ (with respect to the solid) made by the surface of the drop at the point where it meets the underlying substrate satisfies the relation:

$$\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{sl} \quad (4)$$

where γ_{lv} , γ_{sl} , and γ_{sv} are the surface energies per unit area of the liquid/vapor, solid/liquid, and solid/vapor interfaces, respectively. The inherent difficulty presented by Young's equation is that the quantities γ_{sl} and γ_{sv} are not usually accessible in a direct experimental measurement.²⁹ If one wishes to obtain a value, say, for the surface energy of particular chemical species, and uses a prepared series of solid polymer surfaces or oriented monolayers, it is precisely the quantity γ_{sv} that is of interest. To address this experimental difficulty, extrapolation methods have been used in order to provide meaningful surface energy numbers. Probably the most well-known of these is the idea of "critical surface tension", γ_c , pioneered by Zisman's group beginning in the 1940s.¹⁸ In this method, a series of nonwetting liquids is used, whose γ_{lv} is determined beforehand from standard liquid surface tension measurement techniques. The liquids are chosen to span a significant range in γ_{lv} and are deposited on the prepared polymer substrate or oriented monolayer containing a specific chemical functionality. The cosines of measured contact angles θ yield either a straight line or narrow rectilinear band when plotted against γ_{lv} . When extrapolated to $\cos(\theta) = 1$, which corresponds to the case of complete wetting by a liquid, the resulting γ_c intercept is an indicator of the underlying substrate's surface energy. On the basis of this method Zisman and his colleagues compiled an extensive tabulation of critical surface energies as a function of chemical functionality,¹⁸ for example, for $-\text{CH}_3$ containing surfaces, $-\text{CH}_2-$ containing surfaces, $-\text{CF}_3$ rich surfaces, etc. There exists a possible complication to this method that is difficult to address systematically. The presence of the vapor from the liquid may change the surface properties of the "solid" substrate and thus its intrinsic surface energy.

Although the γ_c extrapolation idea is intuitively very appealing, Young's equation in fact shows via

$$\gamma_{lv} \cos(\theta)|_{\cos(\theta)=1} \equiv \gamma_c = \gamma_{sv} - \gamma_{sl} \quad (5)$$

that the critical surface tension is not identical with the free energy of the solid/vapor interface but contains an additional dependence having to do with the interaction of the liquid and the underlying substrate. Zisman himself

(29) To our knowledge, only a few experiments have been reported where independent measurements or estimates of all the parameters in Young's equations could be made. Where such data are available, they are in agreement with the relation given by Young. A thorough description of one such recent study, along with additional references, is given in ref 30.

recognized the importance of such interactions. His reports note that using liquids which can hydrogen bond with the substrate causes deviations from the generally linear form of $\cos(\theta)$ vs γ_{lv} . In addition, when the nonwetting liquids used were not members of the same homologous series, the plotted $\cos(\theta)$ values tended to broaden into rectilinear bands, the scatter possibly arising from significant differences in the interaction energy γ_{sl} for liquids from different families. Other researchers addressing surface energy measurements³⁰ have shown that under an assumption of purely dispersive (i.e., van der Waals) force interactions at the relevant interfaces, γ_{sl} should approach zero as γ_{lv} heads to γ_{sv} (or, in Zisman's terminology, as γ_{lv} heads to γ_c). In fact, under this same dispersive force assumption, the so-called Good–Girifalco–Fowkes relation can be derived, in principle more accurately relating θ , γ_{sv} , and γ_{lv} :^{31,32}

$$\cos(\theta) = 2(\gamma_{sv}/\gamma_{lv})^{1/2} - 1 \quad (6)$$

Results for γ_{sv} obtained using eq 6 agreed with the general trend of Zisman's γ_c values (as a function of chemical species at the surface, characteristic energies of $-\text{CF}_3 < -\text{CF}_2- < -\text{CH}_3 < -\text{CH}_2-$, for example); however, while the surface energy value for close-packed $-\text{CH}_3$ surfaces differed hardly at all in these two alternate schemes, being around 21 dyn/cm, values for the other types of surfaces showed significant deviations, in the case of $-\text{CF}_3$ surface groups ranging from $\gamma_c \approx 6$ dyn/cm by Zisman's reports¹⁸ to approximately 11 dyn/cm from eq 6 results.³² Discrepancies of this sort suggest that while the assumption (inherent in both Zisman's γ_c interpretation and in eq 6) of dispersive interactions may be appropriate for some surfaces, and over some corresponding interval of surface energies, it may not be valid for all organic surface compositions. Using contact angle methods on some substrates may mask important γ_{sl} contributions, perhaps originating from the presence of either more polarizable groups at the free surface or some dipole contributions. Of course, a thorough tabulation of γ values covering a wide range of magnitudes, and as a function of many different chemical surfaces, has long been a fundamental goal in materials science.

Given this review of some previous studies, we feel that our measurement technique offers clear benefits. The underlying assumption of dispersive force interactions which allows contact angle measurements to be "converted" to surface energies remains to our knowledge to be fully justified; indeed, it may be distinctly inappropriate for surfaces such as those populated by $-\text{CF}_3$ groups, whose significant dipole moment³³ suggests possible interactions beyond purely van der Waals. The values of γ we obtain from the homogeneous surfaces of free-standing films come from direct measurements, involving no extrapolations or force assumptions. The only inherent limitation in the range of surface tensions (and corresponding surface chemical functionalities) we can explore with our method is the feasibility of chemical syntheses for creating smectic liquid-crystal molecules with various terminal groups that can be spread into free-standing films. These conditions have proven not to be unduly restrictive. Our results to date already cover a large variety of compounds with diverse surface tension values. There is no regime of surface tensions, or terminal

molecular structures, where the validity of our measurements might be questionable. This is an important advantage, for example, in the case of fluorinated surfaces. Our recent work providing data on many fluorinated liquid-crystal materials addresses an important area of surface science. This is especially true given the ever-growing interest in technological applications of fluorinated compounds, in areas ranging from dispersants, antistick coatings, pharmacological agents, etc.³⁴

The extensive work by Zisman and others characterizing substrate energies remains an important marker against which we can in many cases compare our own liquid-crystal surface tension values, bearing in mind that surface functional group densities may differ to some extent in these two situations. Our work is complementary in the sense that we probe surfaces with liquidlike in-plane ordering, in contrast to solid polymer substrates or anchored monolayers. This is not to say that our results, or indeed results from anchored monolayers, lack general relevance. For example, data gathered from both close-packed, organic monolayers containing $-(\text{CH}_2)_n\text{CH}_3$ groups and our free-standing films of hydroalkyl-tailed molecules give surface free energies in good agreement with a crystalline surface consisting of the same functionality (e.g., see our results on category C compounds below, compared with those in ref 18). However, our experimental access to free surfaces populated by well-defined chemical species but exhibiting *truly fluid positional order* at the same time is unique; this is a particular consequence of ordering within free-standing liquid-crystal films. Our system therefore offers another advantage with respect to traditional contact angle studies and their typical substrates. Namely, using our string tensiometer we can address Langmuir's principle of independent surface action *for truly fluid surfaces*. The fluidlike order within smectic layers may also more sensitively couple the packing arrangement of molecular cores to the nature of terminal groups exposed at the corresponding free surface, an effect that may be somewhat suppressed in monolayers of molecules firmly anchored to a substrate. Evidence for the effect of core packing upon surface tension can be seen, for example, in the values we have obtained for the materials of groups D(i) and D(ii), as discussed in more detail below. A direct probe for these kinds of information is not only intriguing on a fundamental level but is also important technologically, for example with regard to the more efficient use of liquid surfactants in many modern day applications.

V. Data and Results

To date, we have used our high-resolution string tensiometer to characterize the surface tension of over 30 liquid-crystal compounds. Table 1 gives a selected summary of our results, in which we have grouped the compounds into categories based on the surface tension values obtained. Also included in Table 1 are the temperatures at which the data were acquired, in all cases (except as noted below) corresponding to Sm-A phases of the materials. Structural formulas for the compounds are listed in Chart 1. For completeness, the ranges of uniform film thicknesses studied in the case of each material are also given in Table 1. In the course of our extensive measurements on compounds in all categories listed, we have to date shown surface tension to be independent of film thickness to within our experimental

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(31) Good, R. J.; Girifalco, L. A. *J. Phys. Chem.* **1960**, *64*, 561.

(32) Fowkes, F. M. *Adv. Chem. Ser.* **1964**, No. 43, 99.

(33) Gibbs, J. H.; Smyth, C. P. *J. Am. Chem. Soc.* **1951**, *73*, 5115.

(34) Kissa, E. In *Fluorinated Surfactants*. Marcel Dekker: New York, 1994; Chapter 8.

Table 1.

group	compound	surface tension ^a (dyn/cm)	temperature ^b (°C)	range of film thicknesses (layers)
A(i)	F3MOCPH11OB	14.6	78.1	4–10
	F4MOCPH11OB ^c	14.0	75.8	2–15
	H(10)F(5)MOPP	13.8	76.0	2–80
	H(7)F(6)EPP	12.5	83.8	3–12
	F7MOPH6OB	12.3	88.0	2–17
	H(8)F(7)MOPP	12.1	91.5	2–20
	H(8)F(4,2,1)MOPP	12.8	60.0	2–20
A(ii)	F4hMOCPH11OB	18.4	55.1	2–5
A(iii)	PMOMCF(2)EH(10)BC	16.7	127.9	2–20
	2F8OPF3H4OB	15.0	101.0	3–15
B(i)	F3MOCPF4H3OB	12.4	89.0	2–30
	F3MOCPF6H5OB	11.5	92.7	4–13
B(ii)	F(4)SB	12.7	54.3	2–6
	F(8)SB	11.1	90.2	4–6
	F(6)BBr	11.4	106.7	4–6
C	7O.7	20.2	72.5	2–20
	65OBC	20.8	75.0	3–25
	H5OCPH11OB	21.5	71.8	2–20
D(i)	12CB	27.1	54.0	2–80
	12OCB	25.8	82.7	2–60
	8OCB	25.9	56.5	2–60
	CBOOA	26.8	76.5	2–5
D(ii)	7AB	24.7	49.0	2–60
	8AB	24.3	57.0	2–9
	9AB	24.2	58.8	2–18
	10AB	23.5	63.7	4–9

^a The surface tension resolution for each individual compound listed is $\pm 2\%$. ^b Temperature at which the surface tension data were taken. ^c See ref 48.

resolution.³⁵ Corresponding data over a thickness range of 2 through 80 layers are given in Figure 6 for 12CB. These results indicate that the origin of surface tension is localized mainly to the outermost layers. In fact, it was our consistent observation of such thickness independence that prompted us to pursue in more detail our studies of surface tension localization and thereby attempt to critically address Langmuir's principle of independent surface action. We give below a more detailed discussion of these and other results according to categories of surface composition or particular submolecular group.

A. Surfaces with Mixed Fluoroalkyl and Hydroalkyl Content. Of all liquid-crystal materials, partially fluorinated compounds have attracted especially intense research effort in recent years. Much of the motivation for these studies has come from the novel physical properties of these materials, including larger bulk elastic modulus,³⁶ reduced optical birefringence,³⁷ unusually low surface tension,³⁸ and significant enhancement of the temperature ranges in which smectic phases are exhibited,³⁷ in comparison with typical, doubly hydroalkyl-tailed liquid-crystal molecules. Some special partially fluorinated compounds have been shown to exhibit a highly intriguing compression of smectic layer spacing as a function increasing temperature,²² lending themselves to inclusion in liquid-crystal mixtures that give a zero net thermal expansion coefficient in the Sm-C phase.³⁹ Many of these properties make partially fluorinated liquid crystals highly promising for applications in

display devices such as surface-stabilized ferroelectric cells.³⁹ As a consequence of this very broad interest, research groups have synthesized a large number of both fully and partially fluorinated liquid crystals;^{40–43} our listing of materials in categories A and B reflects this variety.

The seven different compounds listed as members of group A(i) in Table 1 possess one hydroalkyl and one fluoroalkyl tail in each case. From both an entropic and steric point of view, we argue that these materials give free-standing films whose film/vapor interface is populated by roughly equal numbers of $-\text{CF}_3$ and $-\text{CH}_3$ groups.⁴⁴ The liquidlike order within smectic layers strongly implies that there should be no systematic head or tail preference at a layer interface (and consequently at a film free surface). Here "head" and "tail" refer to the opposite terminal groups of the liquid-crystal molecules. In addition, there is a significant difference in size between the fluoro- and hydroalkyl tails. Published reports indicate that fluorine atoms are roughly as space-filling as oxygen atoms,⁴⁵ in comparison to the smaller excluded volume of covalently bonded hydrogen. Typical distances for covalent C–F (1.4 Å) and C–H (1.1 Å) bonds,² in addition to the relatively larger electron cloud of the fluorine atom (typical van der Waals radii for F and H of 1.45 and 1.2 Å, respectively^{2,45}), provide additional indications of the fluoroalkyl versus hydroalkyl steric difference (these values, along with other relevant hydrogen/fluorine comparisons, are summarized in Table 2). A significant

(35) Mach, P.; Huang, C. C.; Nguyen, H. T. *Langmuir* **1997**, *13*, 6357. This publication contains a brief discussion of our observed independence of surface tension on film thickness.

(36) Mol, E. A. L.; Shindler, J. D.; Shalaginov, A. N.; de Jeu, W. H. *Phys. Rev. E* **1996**, *54*, 536.

(37) Doi, T.; Takenaka, S.; Kusabayashi, S.; Nishihata, Y.; Terauchi, H. *Mol. Cryst. Liq. Cryst.* **1991**, *204*, 9. Liu, H.; Nohira, H. *Liq. Cryst.* **1996**, *20*, 581.

(38) Stoebe, T.; Mach, P.; Grantz, S.; Huang, C. C. *Phys. Rev. E* **1996**, *53*, 1662.

(39) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899. Epstein, K. A.; Keyes, M. P.; Radcliffe, M. D.; Snustad, D. C. US Patent No. 5417883, 1995.

(40) Lobko, T. A.; Ostrovskii, B. I.; Pavluchenko, A. I.; Sulianov, S. N. *Liq. Cryst.* **1993**, *15*, 361.

(41) Kromm, P.; Cotrait, M.; Rouillon, J. C.; Barois, P.; Nguyen, H. T. *Liq. Cryst.* **1996**, *21*, 121. Kromm, P.; Cotrait, M.; Nguyen, H. T. *Liq. Cryst.* **1996**, *21*, 95.

(42) Diele, S.; Lose, D.; Kruth, H.; Pelzl, G.; Guittard, F.; Cambon, A. *Liq. Cryst.* **1996**, *21*, 603.

(43) Liu, H.; Nohira, H. *Liq. Cryst.* **1997**, *22*, 217.

(44) A direct experimental confirmation of this assumption would be extremely valuable, yet is not available to date.

(45) Smart, B. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R. E., et al., Eds.; Plenum Press: New York, 1994; p 57 and references therein.

Chart 1. Molecular Structure of Liquid-Crystal Compounds Studied

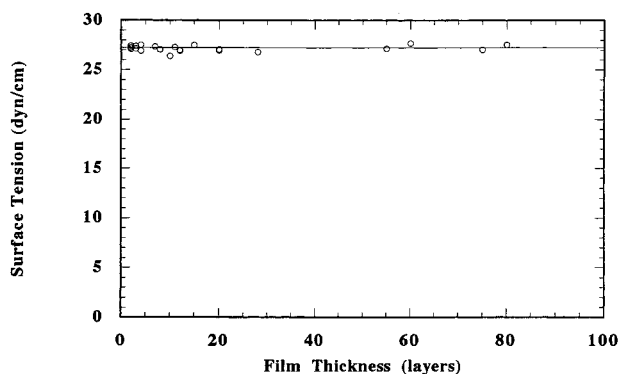
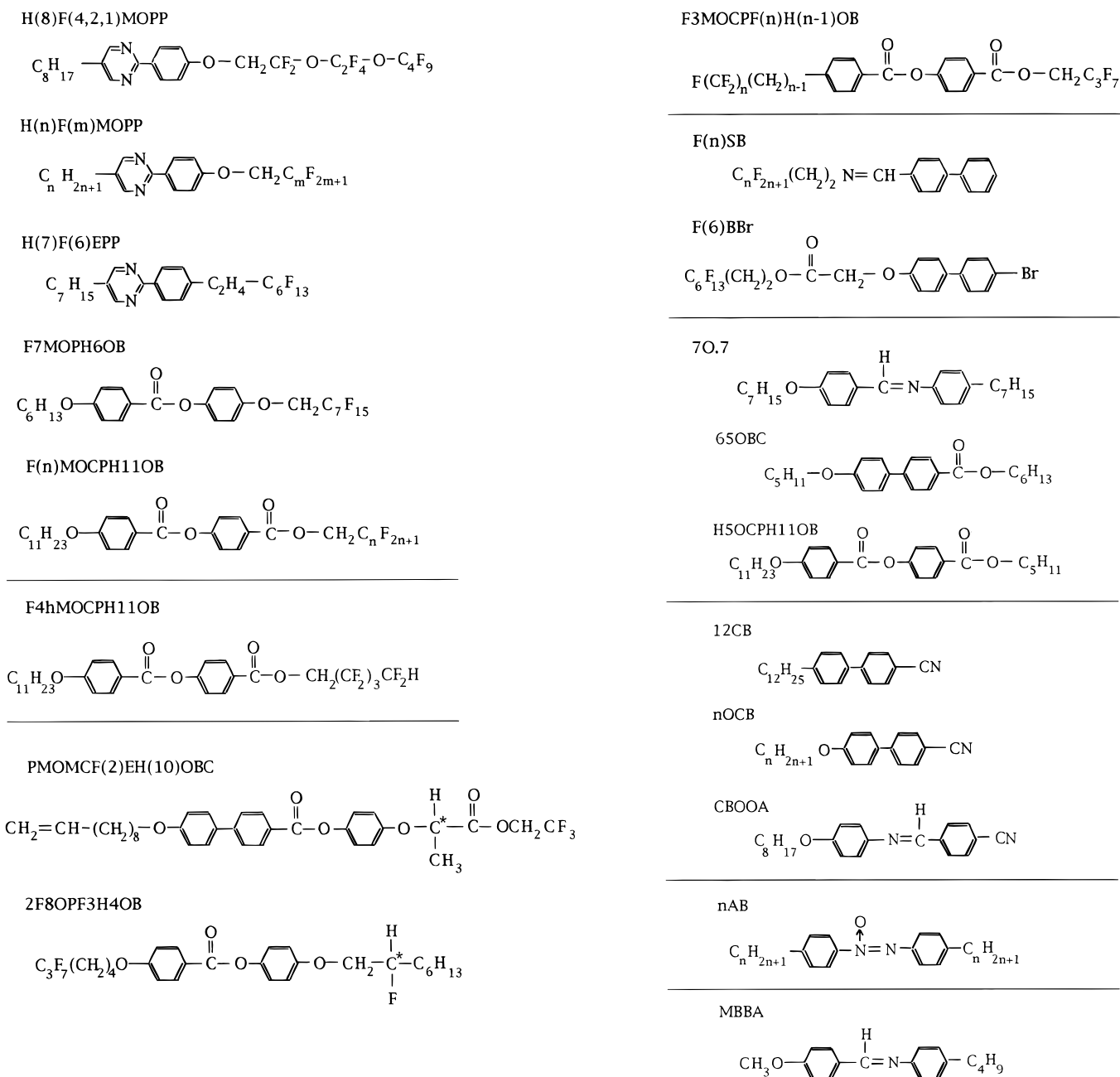


Figure 6. Data obtained from the 12CB compound in the Sm-Ad phase at 54 °C as a function of film thickness.

enhancement of either terminal species relative to the other at a layer interface would therefore be unfavorable,

Table 2

	X = F	X = H
covalent bond distance, C-X (Å)	1.4	1.1
van der Waals radius, X (Å)	1.45	1.2
difference between higher energy gauche and lower energy trans conformation within $-(\text{CX}_2)_n-$ chain (kcal/mol)	1.3	0.5
characteristic γ_c , $-\text{CX}_2-$ surface (dyn/cm)	18	31
characteristic γ_c , $-\text{CX}_3$ surface (dyn/cm)	6-12 ^a	22

^a The γ_c values quoted refer to the work of W. Zisman (refs 18 and 50). Our own measured values for $-\text{C}_n\text{F}_{2n+1}$ and $-\text{C}_n\text{H}_{2n+1}$ populated surfaces are 11.5 and 21 dyn/cm, respectively. A full discussion is given in the main text.

as it would lead to large deformation energy costs from locally "bowed" smectic layers. We have indicated schematically our picture of the hydro-/fluoroalkyl tail packing situation in Figure 7.⁴⁶

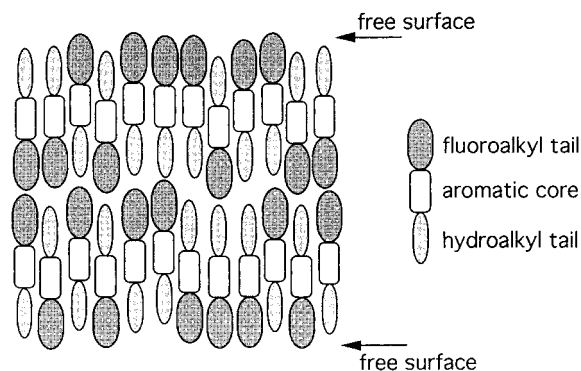


Figure 7. A model of molecular packing in a typical two-layer film in the Sm-A phase of a category A(i) material. The partial bilayer ordering, with offset molecular centers in a given film layer, is proposed due to the relatively similar surface tension values measured for category A(i) and B materials. A discussion is given in section VI.

Our measurements on category A(i) compounds give an average surface tension value of 13.2 ± 0.9 dyn/cm.⁴⁷ This value is significant in the context of previously published research efforts. First, to investigate the correlations in the thermal fluctuations of free-standing Sm-A films, de Jeu's group conducted high-resolution X-ray diffraction on the compound H7F6EPP; surface tension is one of the important parameters in characterizing the films' thermal fluctuations. Detailed X-ray data analyses³⁶ yield $\gamma = 13.0 \pm 0.5$ dyn/cm, in good agreement with our measured value for this same material and in keeping with the characteristic value for A(i). Although, to the best of our knowledge, no other surface tension data are available on this kind of "mixed" surface, the excellent agreement between the results from our direct measurement and the fitting to X-ray data gives us a high degree of confidence in applying our experimental technique to these materials. In addition, the consistence of the reported values, in light of the assumption of a symmetric form factor in the X-ray data analyses, strongly supports our picture of an antiparallel molecular arrangement within the smectic layers, with a roughly equal population of fluoro- and hydroalkyl tails present at the smectic layer surface. The good results obtained by considering a symmetric form factor hold even for films of only four-layer thickness, indicating that the approximately equal fluoro- and hydroalkyl interface character is true for the outermost film layers (and thus film free surfaces as well). Second, our γ value of 13 dyn/cm falls between values for close-packed $-\text{CH}_3$ and close-

packed $-\text{CF}_3$ surfaces, including both measurements on substrate-anchored monolayers,^{18,30} and values obtained in our free-standing film studies, again indicating a free-surface of mixed hydro-/fluoroalkyl character.

Making further use of category A materials, we have pursued an experimental scheme to shed light on the localized origin of surface tension. At the heart of our approach is the following consideration: Because Sm-A ordering always provides a homogeneous layer surface exposing molecular tails, and because the packing of the hydro- and fluoroalkyl tails is on average antiparallel, any change in the terminal submolecular group at either end of such a molecule should be consistently reflected in the resulting film's free surfaces. The compound F4hMOCPh11OB listed in A(ii) preserves the five-carbon length of the perfluorinated tail of F4MOCPh11OB but has a *single* fluorine atom in the terminal $-\text{CF}_3$ group replaced by hydrogen.⁴⁸ By reference to the reasoning given above, free-standing films of F4hMOCPh11OB will have fluidlike free surfaces with roughly equal populations of $-\text{CH}_3$ and $-\text{CF}_2\text{H}$ groups. These free surfaces can be further compared to those of H5OCPH11OB (a member of category C), which has molecular tails of the same length, but possesses a fully $-\text{CH}_3$ populated, liquidlike free surface. Taken together, this special set of three liquid crystals preserves molecular tail length while systematically incorporating a progression from fluoro- to hydroalkyl functionality at one terminal group. Of course, a series of fully symmetric liquid-crystal molecules showing similar hydroalkyl to fluoroalkyl functional evolution in their tails would be an ideal system to study and confirm our assumptions about the antiparallel packing. We are seeking such an appropriate set of materials for future study.

Our surface tension value for F4hMOCPh11OB is 18.4 dyn/cm, a dramatic increase over the $-\text{CF}_3$ terminated analogue, F4MOCPh11OB. In fact, this increase of nearly 25% already accounts for more than half the surface energy difference between the mixed CF_3/CH_3 surface typical of group A(i) and the fully CH_3 -containing surface of the corresponding member of group C. These results indicate that surface tension value is *already strongly determined within a submolecular group length scale from the free surface*. To our knowledge, *these measurements represent the first critical characterization of Langmuir's principle of independent surface action for truly fluid surfaces*.

We can say further, with regard to all of the materials listed in Table 1, that surface tension, a macroscopically measured quantity, is an indicator of the *submolecular groups* occupying the Sm-A/vapor interface. With this in mind, the $\gamma = 16.7$ dyn/cm value we observe for the A(iii) compound PMOMCF2EH(10)OBC is consistent with a surface populated by a mixture of $-\text{CH}_2$ and $-\text{CF}_3$ groups; characteristic surface energies of these two submolecular units are approximately 31¹⁸ and 11.5 dyn/cm (from our fully fluorinated surface data discussed in section B below). With regard to the $\gamma = 15.0$ dyn/cm value for material 2F8OPF3H4OB of group A(iii), we note that there is a

(46) For completeness, there is one additional difference between the two tail types that should be mentioned. Namely, the fluoroalkyl tails have been shown to be more "stiff" than their hydroalkyl counterparts, assuming (in a thermal average sense) a helical as opposed to planar-trans chain conformation (ref 49), in which the energy for gauche bond orientations is larger (by over a factor of 2 (Bates, T. W. In *Fluoropolymers*; Wall, L. A., Ed.; John Wiley & Sons: New York, 1972; p 451.), indicated also in Table 2). It is possible that the greater conformational flexibility of the hydroalkyl tails at a given temperature may "dynamically" reduce the excluded volume difference between the hydrogen- and fluorine-containing tails, which are otherwise of roughly equal length. Countering this idea, however, we can consider (as a first approximation) the roughly 30% larger "static" excluded volume for fluoroalkyl versus hydroalkyl tails, compared with only a 15% larger specific volume for alkanes in liquid as opposed to crystalline state (ref 50). This suggests that dynamical effects do not wash out the steric differences discussed above. Molecular conformation simulations addressing these more subtle dynamical issues would be extremely valuable in confirming this reasoning. We plan to pursue such studies in the course of our continuing research on partially fluorinated materials.

(47) The uncertainty reported here reflects the spread of γ values among the different liquid crystals in the group. The data shown in category A(i) exhibit a systematic variation with the length of the fluoroalkyl tail component.

(48) The F4MOCPh11OB compound actually shows no Sm-A phase, but rather the Sm-C phase. Using our tensiometer, we have performed several studies on the temperature dependence of surface tension, for example, over a 10 K interval in the Sm-A phase of H(10)F(5)MOPP (ref 38). No systematic variation in surface tension was seen within our experimental resolution. We have found the same to be true for several compounds in temperature windows encompassing a Sm-A to Sm-C transition. Thus, although even higher resolution studies of temperature effects on the surface tension of liquid-crystal films remain an intriguing goal, the categorization of surface tension values as described in this report, with the reported uncertainties, is unaffected by temperature considerations or any subtle differences in the packing of molecular tails arising across the Sm-A to Sm-C transition.

significant dipole moment on the chiral carbon atom located only five methylene units away from the terminal $-\text{CH}_3$ group. A strong transverse dipole (with a presumably "bulkier" local electron cloud) at such a position in the molecular tail may lead to less effective packing of the hydroalkyl component in the film's mixed surface, causing (as observed) an increase in surface energy relative to the approximately 13 dyn/cm typical of group A(i). Further studies on this and similar compounds are in progress to investigate this behavior in more detail.

B. Surfaces with Fully Fluoroalkyl Content. In category B are included liquid-crystal molecules that give film/vapor interfaces consisting entirely of fluoroalkyl tails. For instance, the compounds in group B(i) have molecular structures with typical rigid core units and fluoroalkyl tails extending off either side, exhibiting a Sm-A range in their mesophase sequence. The compounds in group B(ii) are somewhat different, in that they possess only one long tail. Thus, this group of molecules exhibits so-called partially bilayer smectic (Sm- A_d) phases.⁴¹ In a typical bilayer smectic phase, antiparallel overlap is favored between the significant, longitudinal dipole moments of the molecules. In the case of the F(6)BBr material, the lone, highly polarizable bromine atom on one side of the biphenyl core accounts for the longitudinal moment; the biphenyl core itself, with the highly asymmetric and likely electron-withdrawing fluoroalkyl tail extending off only one side, plays a similar role in the case of the F(n)SB materials. In a Sm- A_d phase, the typical layer spacing l is such that $l_0 < l < 2l_0$, where l_0 is the length of the molecule. The category B(ii) materials were spread and measured in their respective Sm- A_d phase windows.

The approximately 12 dyn/cm γ value obtained for the F3MOC PF4H3OB and F3MOC PF6H5OB compounds³⁵ represents, to our knowledge, the first directly measured surface energy value on a fully fluorinated, fluidlike surface. As discussed above, past attempts to characterize the surface energy of fully fluorinated surfaces, relying upon anchored monolayers,^{18,30,50} have given inconsistent results, with values reported from 6 to 13 dyn/cm. The corresponding 12 dyn/cm γ value for the Sm- A_d phases is highly intriguing. In contrast to the more or less close-packed fluoroalkyl tails of category B(i), each molecular tail pointing outward toward a bilayer interface is separated from its next nearest tail neighbor on average by an additional molecular core diameter. This increased free volume might be expected to give each molecular tail a larger probability of passing into gauche conformations that would expose $-\text{CF}_2-$ groups at the layer (and thus film) surface. The characteristic surface energy of $-\text{CF}_2-$ groups is significantly higher than that for $-\text{CF}_3$'s, as indicated in Table 2.¹⁸ Since surface tension is very sensitive to the type of submolecular groups present directly at a free surface, $\gamma \approx 12$ dyn/cm for the Sm- A_d phases of B(ii) materials indicates that the fluorinated tails most likely remain in their extended helical conformation, with at most a small amount of $-\text{CF}_2-$ exposed at the film/vapor interface. In fact, this interpretation of our γ values is consistent with the known stiffness of fluoroalkyl chains.^{45,49,50} These results provide a further indication that our surface tension values are reliable indicators for the nature and packing of submolecular groups at liquid-crystal film/vapor surfaces.

There is another subsidiary trend in our results, with a clearly resolvable decrease in surface tension from 12.4 to 11.5 dyn/cm as a function of a two $-\text{CF}_2-$ unit increase

in tail length for the materials of group B(i). This is consistent with our general observations of lower surface tension as a function of increasingly long fluorinated tails in category A(i) materials as well. Similarly for the bilayer materials in group B(ii), a systematic decrease in γ from 12.7 to 11.1 dyn/cm accompanies an increase in fluorinated tail length from four to eight carbons. An intuitive explanation for this behavior in the doubly fluoro-tailed B(i) materials might be improved molecular packing arising from greater attractive forces between tails of greater length. Such a decrease in surface energy due to better tail adhesion, along with supporting data, has been suggested in past literature.¹⁸ However, it is not immediately clear how to reconcile this idea with similar trends for the less closely packed tails of bilayer materials and the mixed fluoro/hydroalkyl tail surfaces of group A(i). Another factor to consider is the potential change in dipole moment and electronic redistribution within the fluoroalkyl tail as a function of adding more $-\text{CF}_2-$ units. Charge shifting effects due to replacement of hydrogen by fluorine in alkanes can be significant;³³ systematic dependence of surface tension arising from a dipole energy contribution, or through evolving molecular polarizabilities, might well contribute to the behavior we observe. More extensive work on homologous compound series with varying tail lengths and fluorine content is clearly important. As a means of addressing these issues, we emphasize again the importance of our *direct* measurement of surface tension on the free-standing films. No a priori assumptions about dispersive vs nondispersive forces operative at the free surface restrict the interpretation of our data.

C. Hydroalkyl Surfaces. The materials listed in category C have been found to possess $\gamma = 20.8 \pm 0.5$ dyn/cm. This value also follows logically from considerations of the molecular structure. In all cases, category C compounds are doubly hydroalkyl-tailed; no unusually "bulky" chemical groups are present to hinder close-packing within the liquidlike Sm-A layers (we discuss below the likely consequences of looser packing in section D). Therefore, the Sm-A film/vapor interface should be entirely populated by the hydroalkyl tails; more specifically, the film surface should contain the terminal $-\text{CH}_3$ groups. Critical surface tension values from contact angle studies¹⁸ indicate characteristic energies of ≈ 21 dyn/cm for close-packed $-(\text{CH}_2)_n\text{CH}_3$ surfaces, with a sufficiently large value of n , in good agreement with our results. Additional support comes from the work of Chaudhury and Whitesides, who have performed studies of close-packed $-(\text{CH}_2)_n\text{CH}_3$ surfaces by several methods, including adhesion force measurements³⁰ whose interpretation does not involve typical contact angle drawbacks. Their various techniques gave a self-consistent 21 dyn/cm surface energy.

There is one additional doubly hydroalkyl-tailed material we have studied which shows significantly different behavior. Our measured surface tension for MBBA films is 31.4 dyn/cm. The large difference between this number and the typical category C value is again a logical consequence of the relevant liquid-crystal ordering. MBBA exhibits not a Sm-A, but rather a nematic phase. The absence of the layered structure in nematics makes their free-standing films highly unstable and very difficult to spread. We successfully prepared several very thick, nonuniform MBBA films in our oven, at approximately 34 °C. The films lasted for approximately 2 min each before popping, which was adequate for obtaining surface tension measurements. However, this relatively short lifetime, during which we observed drainage of material

(49) Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549.

(50) Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1962**, *66*, 740.

in the films, suggests that the films may not have reached their minimum energy state. In a thick, nematic film, there is no strong orientational constraint on the molecules that would lead to a free surface populated selectively by the terminal $-\text{CH}_3$ groups of the molecules' tails. The director within such a film is likely nonuniform. A variety of molecular orientations are possible at the free surface, including alignment of the long axis parallel to the surface or at some slight angle to it. Consequently, the $-\text{CH}_2-$ units of the molecular tails, along with some phenyl edges from the core group, probably make up a significant proportion of the film/vapor interface. Characteristic surface energies of the $-\text{CH}_2-$ surface and even more polarizable phenyl surface are ≈ 31 and ≈ 35 dyn/cm, respectively.¹⁸ Our measured $\gamma = 31.4$ dyn/cm is in good agreement for a mixed surface with these higher energy submolecular groups.

D. Surfaces with Mixed $-\text{CH}_3$ and $-\text{CH}_2-$ Content. In category D we have indicated γ values for compounds with fully hydroalkyl tails, similar to those of group C. However, the materials of group D have structural pieces that affect the packing of the molecular tails and the nature of the submolecular groups exposed at the liquid-crystal film/vapor interface. The average value of $\gamma = 26.4 \pm 0.6$ dyn/cm for group D(i) compounds. The compounds of D(i) exhibit partial bilayer phases; in all cases, their reported γ values were measured in Sm-A_d phase windows. The salient feature of the bilayer phases with respect to molecular packing was already discussed above in the context of B(ii) compounds. Namely, due to the antiparallel overlap of the molecular cores, each hydroalkyl tail in a Sm-A_d bilayer has an additional amount of free volume to explore conformationally. In the case of all compounds listed in group D(i), the terminal cyano group, giving a large permanent dipole moment directed along the long axis of the molecule, is responsible for the partially bilayer overlap and ordering. Of course, even in the ordinary Sm-A phases of category C the hydroalkyl tails may occupy a lower cross-sectional area (when viewed "end on") than their associated biphenyl molecular cores. Some typical literature values for radii of excluded cylindrical volume are ≈ 2.6 Å for a biphenyl core and ≈ 2 Å for a hydroalkyl tail.² However, in the case of Sm-A_d bilayers, the packing of such hydroalkyl tails may become almost a factor of 2 less close, as each tail is now on average associated with a two-molecular-core overlapping unit. Unlike the behavior seen in fluorinated bilayers (category B(ii) materials), hydroalkyl tails are flexible enough for this increased available volume to lead to gauche conformations and consequent exposure of a significant number of $-\text{CH}_2-$ groups at the film free surface. As a result we observe a $\gamma \approx 27$ dyn/cm for such materials, a value intermediate between characteristic surface energies for fully $-\text{CH}_3$ and $-\text{CH}_2-$ containing interfaces;¹⁸ our value is in very good agreement with past measurements on hydroalkyl Sm-A_d materials using other experimental techniques.²⁸ We give in Figure 8 our picture of the plausible molecular packing in a 12CB partial bilayer, consistent with the measured γ .

The materials of group D(ii), with $\gamma = 24.2 \pm 0.5$ dyn/cm, represent an intermediate case between the hydroalkyl Sm-A_d bilayers and the close-packed $-\text{CH}_3$ terminated surfaces of category C. Interpreted in the context of a surface tension localized to very near the free surface, such a γ value is consistent with a less-well-packed $-\text{CH}_3$ surface, with molecular tails far enough apart to expose (on average) some $-\text{CH}_2-$ groups, but to a lesser degree than in bilayers. The molecular structure of the D(ii) compounds suggests such a packing arrangement is

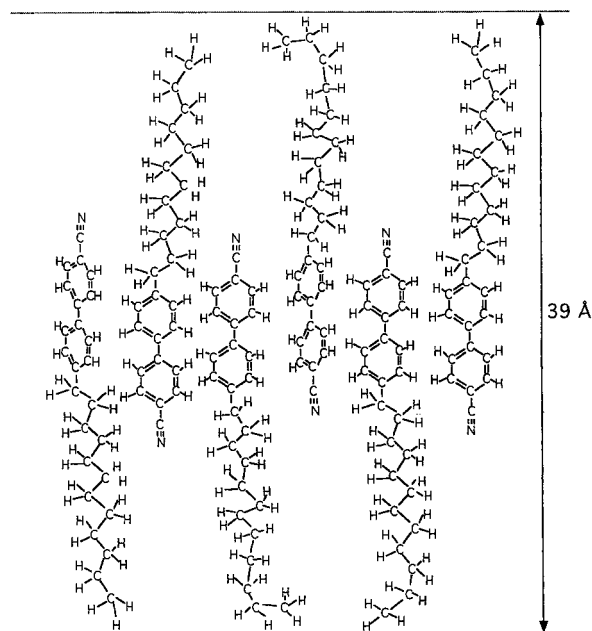


Figure 8. A schematic representation of the molecular arrangement within the partial bilayers of the 12CB compound. The bilayer thickness is indicated, as is the enhanced exposure of $-\text{CH}_2-$ submolecular groups at the layer interfaces (whose location is indicated by dashed lines).

plausible. The azoxy core of these materials has a significant transverse dipole moment. From a dynamical point of view, the transverse dipoles on adjacent molecules may form temporary antiparallel associations. Such an antiparallel offsetting of azoxy groups might effectively create a molecular packing less tight than that of group C materials. In addition, the sizable permanent charge separation on the azoxy group, and consequent enlarged electron cloud of the oxygen atom, may likely make the whole core unit more bulky, further inhibiting close molecular packing. Looser molecular packing within the Sm-A layers of the D(ii) compounds by either or both of these possible mechanisms would lead to an average enhancement of $-\text{CH}_2-$ population at the film/vapor interface, consistent with the γ value observed.

VI. Summary and Remarks

Before considering some intriguing directions for future research, we briefly summarize the results given above. Clearly, a distinct categorization of surface tension values exists among many different liquid-crystal materials. Although some of the more subtle features, such as evolution of surface tension magnitudes with fluorinated tail length (groups A(i) and B) remain to be more thoroughly investigated, a consideration of the various γ groupings is already highly informative. On the basis of our data, it seems possible to say that close-packed, fluidlike $-\text{CH}_3$ containing surfaces give rise to surface energies of approximately 21 dyn/cm; depending upon the amount of increased $-\text{CH}_2-$ content at the surface, $\gamma \approx 24$ dyn/cm and $\gamma \approx 27$ dyn/cm groupings result. On the side of smaller surface tensions, a roughly equal mixing of $-\text{C}_n\text{F}_{2n+1}$ and $-\text{C}_n\text{H}_{2n+1}$ surface functionality leads to an important category of $\gamma \approx 13$ dyn/cm materials, while purely $-\text{C}_n\text{F}_{2n+1}$ surfaces yield a γ asymptotically approaching 11 dyn/cm. Our results have also shown that even single atom replacements, when made upon groups located within a submolecular length scale from a fluidlike free surface, can lead to dramatic changes in measured surface tensions.

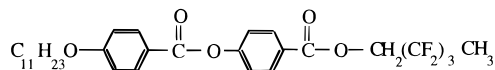
From a surface science point of view, it would be ideal to have a microscopic tool with which to probe directly the molecular structures in the liquid-crystal film/vapor interface. For example, X-ray photoemission spectroscopy (XPS) or optical second-harmonic generation⁵¹ might be valuable in providing additional characterization of surface packing and conformational structure in relation to such proposed arrangements as Figure 7. Unfortunately, to our knowledge, no tool has been successfully demonstrated to provide this kind of localized information in-situ on these truly fluidlike surfaces. However, even in the absence of such capabilities as XPS in our group, our surface tension results have so far already established a very useful template of reference values. Other measured surface tensions can be compared to this template, thereby giving a plausible indication of the underlying molecular arrangements at the surface. We hope that the intriguing categories of surface tension values we have measured will promote further direct investigations of the local structure at fluid/vapor interfaces.

VII. Future Study

Given the value of $\gamma \approx 11.5$ dyn/cm for the fully $-C_nF_{2n+1}$ surface-producing compounds of group B, and the 21 dyn/cm surface energy value characteristic of fully $-C_nH_{2n+1}$ populated surfaces, an important question to be addressed in future studies is the origin of $\gamma \approx 13$ dyn/cm for the category A(i) materials; this value is decidedly toward the lower end of the 12–21 dyn/cm range. As a matter of speculation, and keeping in mind the on-average anti-parallel packing discussed above, any tendency in group A(i) materials for overlap of the fluorinated tails across an interior layer interface would result in an effective distancing of hydroalkyl end groups from the films' free-surfaces. A similar effect could arise from an "inflation" of single-layer spacing, with the molecules; centers alternately offset in an average sense from the layer middle. X-ray data from both free-standing films and aligned bulk samples of materials provide support for this latter idea. The smectic layer spacing for several materials having one fluoro- and one hydroalkyl tail has been shown to exceed the extended molecular length by a factor of 1.05 to 1.10;^{36,40} the layers have, in effect, a partial Sm-A_d character. In such cases, the contribution of the group A(i) compounds' fluorinated tails to the measured surface

tension might be enhanced, especially if one could argue that the surface energy is strongly defined already within a distance from the free surface on the order of, say, a $-CF_3$ group size. Intriguingly, this is precisely the conclusion supported by our surface tension results on compounds with single-atom fluorine to hydrogen replacement. According to this line of thought, fluorination of the second molecular tail might cause a smaller reduction in surface tension than that initially expected, in accord with our observation of a characteristic $\gamma \approx 11.5$ dyn/cm for category B compounds. We are hopeful that our continuing research into carefully selected liquid crystals will shed additional light on the question of how much fluorination is necessary to achieve a particular reduction in surface energy, an issue of significant technological importance.

With further creative chemical synthesis, the work on atomic replacements in liquid crystals can be naturally extended. For instance, given our striking results for γ of F4MOCPh11OB, F4hMOCPh11OB, and H5OCPh11OB, a logical question to pose is: What would be the surface tension of the compound whose structure is given by



Our results suggest a γ somewhat less than 21 dyn/cm. Continuing the fluorine replacement inward by substituting methylene units for $-CF_2-$ would also be highly valuable. We hope that this systematic research effort will help to quantitatively pin down the length scale implied by the phrase "local part of a molecule" in Langmuir's principle of independent surface action.

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