Dramatic Effect of Single-Atom Replacement on the Surface Tension of Liquid-Crystal Compounds

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High-resolution surface tension measurements have been conducted on free-standing films of a specially selected series of liquid-crystal compounds. We have discovered a dramatic change in the surface tension of liquid-crystal compounds by replacing a single fluorine atom in the molecular tail with a hydrogen atom. The implication of this finding will be discussed. [S0031-9007(97)05062-X]

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A fundamental goal of surface science is to correlate macroscopic surface phenomena, such as adhesion, detergency, friction, and spreading, with the molecular structure of the surface involved. To meaningfully address this issue, knowledge about surface tension is of prime importance. In turn, characterizing the molecular origin of surface tension will yield both physically interesting and technologically important results. For instance, it is a very intriguing physics question as to how deeply below a free surface the mechanisms extend which give rise to surface tension. Such knowledge would also be extremely useful in designing the most chemically "efficient" materials to exhibit desired surface properties. As early as 1916, Langmuir [1] proposed the "principle of independent surface action." Qualitatively, this principle asserts that each part of a molecule possesses a local surface free energy, which is equivalent to a surface tension. Fifty years later, Fowkes [2] stated: "It is normal to consider that the [surface] tension resides in the surface monolayer, although in some systems it has been demonstrated to have contributions from second or third layers." Much experimental effort has been expended to investigate these somewhat different ideas. To the best of our knowledge, no definitive experimental conclusion has been reported which would resolve the issue of how localized the origin of surface tension is in a *truly fluid system*. We have recently measured surface tension of free-standing films of four specially selected liquid-crystal compounds. Our results demonstrate that the terminal molecular group exhibits an extremely large effect on the surface tension. In a partially perfluorinated liquid-crystal compound, by replacing just one terminal fluorine atom with a hydrogen atom, we obtain an increase of more than 20% in surface tension. As a matter of fact, such an increase already accounts for more than 50% of the difference in surface tension between the compounds with fully hydroalkyl versus partially perfluoroalkyl tails.

To obtain essential information related to the surface free energy, many research groups have established facilities employing different experimental techniques to characterize a variety of organic close-packed monolayer films [3–5]. Data gathered from this special class of systems are, in fact, of important general relevance, since the surface free energy obtained from these films is usually in good agreement with that of a crystalline surface consisting of the same functional "terminal" group.

Liquid crystals represent one category of materials from which close-packed organic surfaces may be formed. The liquid-crystal molecules themselves are often pictured schematically as rodlike or cigar shaped, having rigid core structures with flexible tails extending off either side, giving a typical overall length of roughly 30 Å. Under appropriate conditions, one can prepare uniform free-standing films from the smectic-*A* (Sm-*A*) phase of liquid-crystal compounds. These films possess a layered structure, with the film thickness quantized to a discrete number of layers. Within the layers, the molecules are oriented so as to have their long axis aligned on average with the layer normal, leading to a layer (and film) surface composed of close-packed molecular tails. The center of mass order within any given Sm-*A* layer is liquidlike, with the layer thickness approximately equal to the molecular length. These metastable substrate-free films can last for weeks, and have proven to be a rich system on which to conduct a variety of high-resolution experiments for studying substrate-free two-dimensional systems, the effect of surface-enhanced ordering, etc. [6]. For our investigations, a typical film area is about 1 cm^2, with film thicknesses ranging from two to a few hundred molecular layers. Because of its liquidlike in-plane molecular arrangement, the Sm-*A* free-standing-film/vapor interface is very uniform and homogeneous; the well-defined orientation of the molecules within the layers strongly predefines the nature of the molecular groups exposed at the surface. With appropriate experimental techniques, such as the one we describe in this Letter, the surface tension of Sm-*A* free-standing films is directly determinable; this is in contrast to studies of condensed monolayers anchored on substrates, where extrapolation methods based on Young's contact angle equation or assumptions about the

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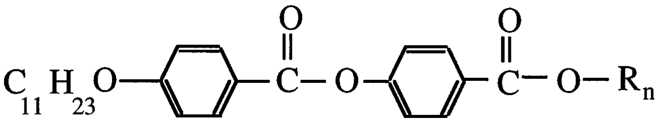
dispersive nature of the forces at the interface are necessary [3,4]. Along with the physical properties cited above, this experimental advantage makes the Sm-*A* film a unique system for investigating the effect of the terminal functional group on the surface tension. Different experimental facilities have been constructed to measure the surface tension of free-standing liquid-crystal films [7–13].

Employing our flexible-string tensiometer [8,9], we have obtained the surface tension from free-standing films of various liquid-crystal compounds. The principle idea behind our tensiometer is the following. An extremely flexible, uniform surgical silk suture ($\approx 40\ \mu$m in diameter) is suspended between two small V grooves spaced 1.76 cm apart across a knife-edged hole cut into the center of a vertically oriented film plate. The top end of the string is fixed to the plate and a known mass (M) is attached to the other end (see Fig. 1). Thus, when no film is present the string is straight and divides the hole into two parts [see Fig. 2(a)]. All of these elements are placed inside a controlled environment within a temperature-regulated oven. The free-standing films are created in one half of the hole, with the film boundary completed by the string. The action of surface tension tends to minimize the size of the film surface area. Therefore the string is under a film tension which is balanced by the tension from the mass (M). Geometrically, the resultant string deformation is part of a circle of radius R [see Fig. 2(b)]. The measured value of R is inversely proportional to the film-vapor surface tension (γ), i.e., $R = Mg/2\gamma$, provided that the friction due to the lower V groove is negligible, an assumption which we have tested experimentally [12]. Here $g = 980\ \mathrm{cm/sec}^2$ and the factor of 2 comes from the fact that there are two film-vapor interfaces for a given free-standing film. This remarkable, straightforward tensiometer allows us to measure surface tension with a resolution of better than 2% [9]. Surface tension data of liquid-crystal compounds obtained from our flexible-string tensiometer are in excellent agreement with the available data acquired from different experimental techniques [11,14–16].

Of all liquid-crystal materials, partially perfluorinated compounds are a class upon which particularly intense research effort has been directed. Motivated by the discovery of many novel physical properties [17] and potential applications in electro-optical switching devices [18], various research groups have synthesized several unique perfluorinated liquid crystals. Recently, we have completed systematic surface tension measurements on the following three such compounds:



where $R_1 = C_5H_{11}$, $R_2 = CH_2(CF_2)_3CF_2H$, and $R_3 = CH_2C_4F_9$.

The synthesis processes and initial characterization of this homologous series have been reported in Ref. [19]. This series was chosen to give a consistent five-carbon tail length on one end of the molecules, while at the same time providing an evolution from hydroalkyl to partially perfluoroalkyl character at this tail end. In keeping with the liquidlike character of a Sm-*A* layer, there is generally no preferential ordering of molecular "heads" or "tails" (meaning here the two opposite terminal chains). In other words, one can assume that for a molecule having two different terminal groups, both species will be present in equal populations at a layer or free surface. Thus, a systematic evolution of one tail's chemical structure, as we have achieved in our series of compounds, will be consistently reflected in the makeup of the surfaces formed in films of these materials. On the basis of steric and entropic considerations, such molecules also favor an average antiparallel arrangement throughout the film [8]. Additional experimental evidence supporting this assumption comes from x-ray studies, where a model assuming no head/tail preference at a Sm-*A* layer surface gives an excellent fit to observed data [16]. Any significant enhancement at the film surface in the population of one tail species at the expense of the other

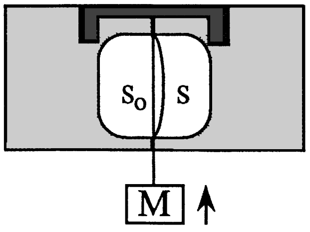


FIG. 1. Schematic of the film plate. When a film is present in the right half of the opening, the string is deformed from its straight configuration (s_0) into the arc (s), thereby elevating the mass (M).

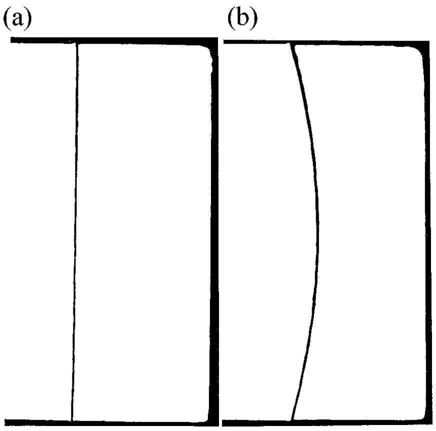


FIG. 2. Silhouette of the film plate without (a) and with (b) a film present. The film is approximately 1.76 cm by 0.65 cm of a 6-layer film of R_3' compound at 78.1 °C. Because of the strong interference effects, the film in (b) is invisible.

seems therefore to be unlikely, especially as the reported x-ray model was found to hold well even for films of only four-layer thickness, where the influence of the surface layers on the observed signal is correspondingly very significant [20].

In our series of materials, the R_3 compound exhibits a direct isotropic (I) smectic-C (Sm-C) transition. We have in the past conducted experiments using our string tensiometer on other materials that exhibit both Sm-A and Sm-C phases in free-standing films [21]. These studies were carried out over a temperature window (ranging from 10 to 25 K in width) chosen to include the Sm-A–Sm-C transition, both with and without an azimuthal aligning electric field applied. We did not observe any conclusive surface tension changes significantly greater than our experimental resolution; thus, we conclude that any variation in surface tension due to molecular orientation or packing changes across a Sm-A–Sm-C transition is small compared to the dramatic atomic replacement effects discussed below. However, in order to be sure of our arguments in this report, we have also measured the surface tension of the compound with $R_3' = \mathrm{CH_2C_3F_7}$, which has a Sm-$A$ phase. The relevant bulk transition sequences for our series are Sm-A (75.5 °C) I, Sm-C (51.7 °C) Sm-A (58.6 °C) I, Sm-C (88 °C) I, and Sm-C (77 °C) Sm-A (79 °C) I, for compounds with R_1, R_2, R_3, and R_3', respectively.

Our measured values of surface tension (in dyn/cm) are 21.3 ± 0.3, 18.3 ± 0.3, and 14.6 ± 0.2 for compounds with R_1, R_2, and R_3', respectively, in their Sm-A temperature range [22,23] and 14.0 ± 0.2 for the R_3 compound in its Sm-C temperature range. Within our resolution, the surface tension is independent of film thickness $(2 \leq N \leq 10)$ [24]. The surface tension of the compounds with R_3 and R_3' is in good agreement with other compounds having one partially perfluoroalkyl tail [8,16]. The small difference between the R_3 and R_3' compounds is most likely due to the additional $\mathrm{CF_2}$ group in R_3 [25,26]. The most striking and important aspect of the data is this: Replacing just one fluorine atom in the terminal $\mathrm{CF_3}$ group by a hydrogen atom results in an increase of about 25% in surface tension. In fact, such an increase accounts for more than 50% of the difference in surface tension between the compounds with the hydroalkyl (R_1) and partially perfluoroalkyl (R_3 or R_3') tails. Such a dramatic change clearly demonstrates the strong effect on surface tension exerted by the submolecular functional group present at the film-vapor interface. It should be noted that with some creativity in chemical synthesis, one can continue the systematic replacement of fluorine atoms in the R_2 compound by hydrogen atoms. Intriguing questions then logically follow, such as: What will be the surface tension of the compounds with $R_4 = \mathrm{CH_2(CF_2)_3CH_3}$? The above results suggest it should be in the vicinity of 20 dyn/cm. Furthermore, systematic studies of the compounds with $R_m = \mathrm{CH_2(CF_2)_{3-m}(CH_2)_mCH_3}$ $(m = 1$ and $2)$ would be extremely valuable. Measurements of both layer spacing and the surface tension are critical in future studies. Layer spacing information will enable us to see if there is any discernible change in the molecular packing which may change the terminal functional group at the film-vapor interface. The systematic variation of surface tension will allow us to give a critical answer to the size scale implied by the phrase "each part of a molecule" as cited in the principle of independent surface action. In addition, one could speculate that the atomic replacement of hydrogen by more electronegative fluorine might lead to some electronic redistribution within a molecule; an experimental probe to look for such an effect, and any consequent influence on surface tension via altered packing or conformation, would also be highly intriguing. These important experimental objectives are a natural extension of our current results, which clearly establish the large effect on surface tension by replacing just one atom at the film-vapor interface.

In summary, spreading a liquid-crystal free-standing film in the Sm-A phase with a homogeneous and uniform molecular arrangement represents an excellent method of forming an organic surface that has at the same time very well-defined chemical functionality and truly *fluid positional order*. Experimentally, we have demonstrated that such a film is a unique physical system for direct, systematic investigations of the effect on surface tension due to differences in molecular functional groups. Our results have established that *Langmuir's principle of independent surface action* can apply on a very small submolecular length scale, with even *single-atom replacements at a fluid free-surface* causing dramatic shifts in surface tension. Our extensive effort to investigate the molecular origin of the surface tension should also provide us with a much better understanding of the anchoring and wetting behavior of liquid-crystal molecules on various solid substrate surfaces [27].

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[21] The materials studied were p-(n-decyloxybenzylidene)-p-amino-(2-methylbutyl) cinnamate (DOBAMBC) and 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxy-biphenyl (A7).

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[24] Our previous measurements on other compounds give thickness-independent surface tension over film thicknesses ranging from 2 to 80 layers [9].

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