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SURFACE TENSION OBTAINED FROM VARIOUS SMECTIC-A LIQUID-CRYSTAL FREE-STANDING FILMS

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Abstract Employing a straightforward experimental technique, we have investigated the surface tension of various liquid crystal compounds in the smectic-A and smectic-A_d phases. The results clearly demonstrate the significant role of molecular packing in determining the surface tension.

The label "smectic", coined by G. Friedel, means soap in Greek. Much like a soap film on a ring, one can prepare free-standing, smectic films suspended over a hole cut into a film plate, provided that appropriate liquid-crystal compounds are chosen [1]. These substrate-free films are extremely intriguing and may be characterized as a stack of two-dimensional layers separated by roughly the length of the highly anisotropic liquid-crystal molecules (≈ 25 Å long and ≈ 5 Å in diameter). In free-standing films, the layer normal is parallel to the film normal. Because uniform substrate-free films can be created from two to several hundred layers in thickness, they are uniquely suited to study the evolution from three-dimensional to two-dimensional behavior, the nature of two-dimensional systems without substrate, the behavior of layer-by-layer transitions, the properties and effect of free surfaces and reduced dimensionality, etc. To date more than 15 different smectic phases have been identified. The free-standing film offers a unique physical system to study a variety of phase transitions in single smectic domain samples employing a number of experimental probes.

Because of the asymmetry in the binding at virtually all solid/vapor interfaces, the particles or molecules in the vicinity of the interface tend to be less ordered. A similar situation is encountered in ordinary liquid/vapor interfaces. In contrast, because of the lack of long-range smectic order in the bulk, at a liquid-crystal/vapor interface the ordering of the orientationally-aligned molecules is further enhanced due to the action of the surface tension. Thus the molecules at the surface layer tend to be more ordered than those in the bulk. It is this surface-enhanced ordering which is mainly responsible for an unusual phenomenon observed in liquid-crystal free-standing films. Upon heating, the melting of most materials starts at free surfaces. *However, in the case of liquid-crystal films, the melting originates in the interior layers* [2]. This novel behavior is manifest in a detailed surface tension measurement. As temperature increases, the surface tension of most materials decreases. In contrast, Gannon and Faber reported in 1978 an increase of surface tension in the nematic phase of 5CB and 8CB [3].

Surface tension is clearly an important quantity necessary to characterize the surface-enhanced ordering, and also many other physical phenomena related to the liquid-crystal/vapor interface. For example: 1) de Gennes [4] discussed the lenticular fracture of a smectic liquid crystal in which knowledge of the surface tension is critical; 2) Lejcek and Oswald [5] presented theoretical calculations to illustrate the influence of surface tension on the stability of edge dislocations in SmA liquid crystals; 3) The surface tension constitutes an important fitting parameter for the x-ray scattering profile from thin SmA free-standing films [6]. 4) The surface tension is an important paramerter in determing the stability of one and two layers free-standing films. Thus numerous methods have been designed or utilized to measure the surface tension of liquid crystals [3, 7-9].

In an effort to gain much better understanding of the films and their free surfaces, Pieranski *et al.* [7] and Stoebe *et al.* [8] have independently established straightforward methods to determine the surface tension of free-standing films. Details of our measurement technique have been reported previously. Its principal idea is the following. An extremely flexible uniform surgical silk suture is suspended between two small v-grooves spaced 1.76 cm apart across a knife-edged hole cut into the center of the film plate. The top end of the string is fixed to the plate and a mass is attached to the other end. Thus, when no film is present the string is straight and divides the hole into two parts. 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. 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 two v-grooves is negligible. Here $g = 980$ cm/sec^2 and the factor of two comes from the fact that there are two film-vapor interfaces for a given free-standing film. One of the major limitations on experimental resolution is due to the finite width of the string (40 μm in diameter). To achieve much better resolution in measuring surface tension, we are currently establishing a new system.

To date, employing our existing system, we have measured the surface tension of more than 20 different liquid-crystal compounds exhibiting smectic-A (SmA) or smectic-A_d (SmA_d) phases. In the SmA phase, the layer spacing (*d*) is approximately equal to the length of the molecule (*l*). In the SmA_d phase, the molecules form a bilayer structure and $l < d < 2l$. Unexpectedly, a more than 25 % variation of surface tension has been discovered among the alkyl-tailed molecules, with the values depending on the molecular structure.

Table 1 gives a partial list of our measured results. Some commonly found SmA materials are given in group C, and their surface tension is determined to be 21 dyn/cm. This value is in good agreement with critical surface tension (22 dyn/cm) of a surface consisting of CH_3 groups [10]. The result strongly suggests that the molecular group residing at the film-vapor interface of these ordinary liquid-crystal compounds is mainly CH_3. In contrast, the molecules listed in the first group possess a strong longitudinal dipole moment from the cyano-group. These materials form a bi-layered SmA_d phase. As with all the liquid crystal compounds studied, the surface tension remains constant [11] for $2 \leq N \leq 100$ within our experimental resolution of about ±1%. Here N is the number of layers. The results obtained from the 12CB compound are shown in Fig. 1.

Table I. Surface tension of various liquid crystal compounds measured at the given temperature

Group	Compound	Surface Tension (dyn/cm)	Temperature (°C)
A	12CB(a)	27.1	54.0
	CBOOA(b)	26.8	76.5
	8OCB(c)	25.9	56.5
	12OCB(c)	25.8	82.7
B	7AB(d)	24.7	49.0
	8AB(d)	24.3	57.0
	9AB(d)	24.2	58.8
	10AB(d)	23.5	63.7
C	4O.8(e)	20	61.9

	7O.7(e)	20	72.5
	65OBC(f)	20.8	75.0
	3(10)OBC(f)	21.0	76.0
D	FPP(g)	12.5	83.8
	H8F7MOPP(h)	12.1	91.5
	H10F5MOPP(h)	14.0	76.0

(a)12CB: 4-cyano-4'-n-dodecylbiphenyl,
(b)CBOOA: p-cyano-benzylidene p'-n-octyloxyaniline,
(c)*n*OCB: 4-cyano-4'-n-*alky*loxy-biphenyl,
(d)*n*AB: p,p'-di-n-*alkyl*azoxybenzene,
(e)*n*O.*m* : 4-n-*alkyl*oxybenzylidene-4-n-*alkyl*aniline,
(f)*nm*OBC: n-*alkyl*-4'-n-*alkyl*oxybiphenyl-4-carboxylate,
(g)FPP: 5-n-heptyl-2-(n-(tridecafluorooctyl) phenyl) pyrimidine,
(h)H*n*F*m*MOPP: 5-n-*alkyl*-2-(4-n-(*perfluoroalkyl*-metheleneoxy) phenyl) pyrimidine.

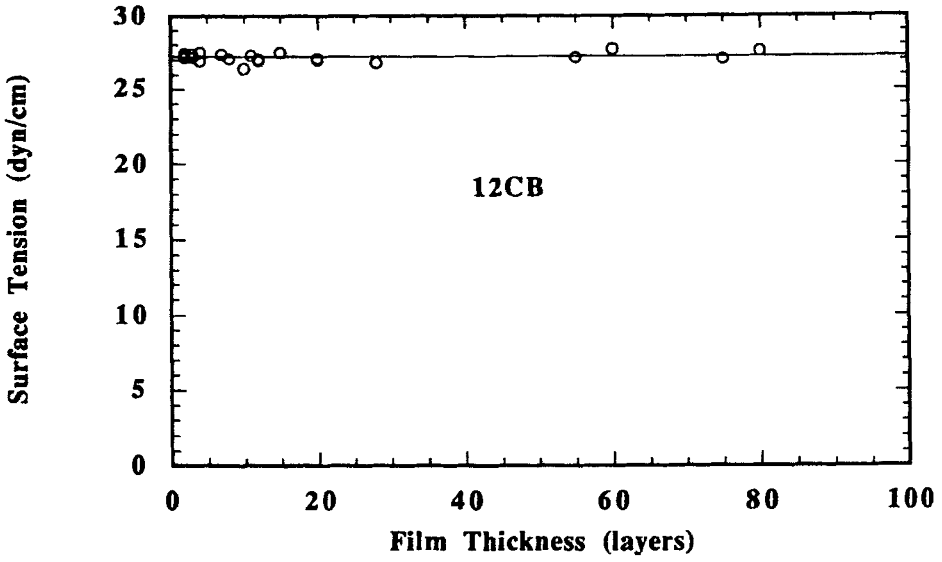

Fig. 1 Surface tension as a function of film thickness for 12CB free-standing films. The sample temperature was 54 °C in the SmA_d phase.

Although the group of smectic A_d molecules possesses a strong longitudinal dipole moment, the anti-parallel molecular arrangement yields a negligible molecular polarizability contribution to the surface tension [12]. On the other hand, from a steric point of view, the anti-parallel molecular arrangement results in more space available for each flexible alkyl tail [13]. Consequently, the molecular group at the film-vapor interface may consist of a higher percentage of CH_2 groups. It has been experimentally demonstrated that a surface of CH_2 possesses a higher critical surface tension (31 dyn/cm) than that of CH_3 [10]. This may be the primary origin of the high surface tension (26 dyn/cm) of the smectic A_d liquid crystals listed. The materials in group B have an azoxy unit in the core part of the molecule. In comparison with the structures of category C compounds, the azoxy group may require more space in packing the center part of the molecules. This will leave more space for the flexible alkyl tails. Again, the enhancement of the surface tension is most likely due to the presence of the CH_2 group at the film-vapor interface.

In the case of partially perfluorinated compounds, both entropic and steric effects favor approximately equal proportions of CH_3 and CF_3 terminal groups. This combination yields a predicted surface tension of 13.5 dyn/cm [14]. This is in good agreement with our measured results. Finally, we have successfully prepared several thick films of MBBA (N-(*p*-methoxybenzylidene)-*p*-butylaniline), a room temperature nematic material. In MBBA, there exists no layer structure. The film-vapor interface should consist of CH_2 units, or other molecular groups, with a very small percentage of CH_3 groups. As expected, a high value of surface tension (31.4 dyn/cm) is obtained.

In summary, our measured results of CBOOA, 7O.7 and FPP are in excellent agreement with the surface tension determined by the other methods [9a, 6a, 6c]. Furthermore, the *salient* features found in our experimental studies are the following: (1) Within our experimental resolution (± 1%), the surface tension is independent of film thickness (see Fig. 1). If, however, the surface tension is assumed to be linearly dependent on the film thickness, then the coefficient (α) of the linear term *obtained from our free-standing films* is $< 3 \times 10^{-3}$ dyn/cm-molecular layer [11], consistent with the previously reported results of Pieranski *et al.* [7]. (2) Our experimental results strongly indicate that the origin of the surface tension is well localized at the film-vapor interface. Its value depends on the available space for the alkyl tail(s). To obtain direct experimental confirmation of this important observation, we are establishing a new experimental setup.

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11. In our laboratory, without the proper apparatus necessary to measure film thicknesses greater than roughly 200 layers, our current resolution in determining the linear coefficient α in the relation $\gamma(N) = \gamma(0) + \alpha N$ is about 3 x 10^{-3} dyn/cm-layer. Here $\gamma(N)$ is the thickness dependent surface tension. However, the agreement between our value of surface tension of 2-, 3-, 4-, and 5-layer CBOOA films and that of the pendant drop (bulk sample) method [9 a] leads us to conclude that the linear coefficient is practically zero, unless one can convincingly argue that the surface tension of thick smectic free-standing films differs from that of bulk samples without well-organized layer structure in the interior.
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