

Anisotropic Interactions across the Interface Liquid Crystals–Glass with Adsorbed Monolayers of Polysoaps

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The interfacial orientations of liquid crystal molecules deposited on different anisotropic solid substrates have been studied. The free energy of adhesion, critical surface tension, and polarity of these systems have been found. The polar contributions to the adhesion free energy of liquid crystal–solid systems have been calculated taking into account the liquid crystal orientation. We have also evaluated the order of magnitude of the anisotropy for the dispersion forces.

I. INTRODUCTION

The role of permanent dipoles in orientational order (1) and interfacial structuring (2) of a liquid crystal has already been reported. The effect of sterical and dispersion force interactions on the orientational order of liquid crystal in bulk (3) has been widely studied, but the influence of these forces on the interfacial structuring remains unclear.

The orientation of liquid crystal molecules at the interface with another phase or “anchorage” depends on each interaction anisotropy. This anchorage anisotropy can be considered in terms of polar and dispersion force interactions (2, 5). Using the approach proposed by Fowkes (6), Girifalco and Good (5), and Zisman (7), one can calculate dispersion force interactions between two phases. However the theory of Fowkes–Girifalco–Good established for spherical molecules does not allow the evaluation of the anisotropy effect.

Indeed recently Fowkes (8) showed that the dispersion energy involved in the total energy of adhesion had to be completed by a correlated molecular orientation term (CMO), which may be important when the liquid molecules are anisotropic.

Since 1943, when Chatelain (9) dis-

covered that rubbing a glass slide could produce a planar alignment of liquid crystal molecules near the interface, a number of various techniques have been used to obtain this effect. These techniques consist in the deposition of organic or inorganic layers on the solid surface. To obtain different liquid crystal interfacial orientations, the system of glass slides covered with polysoap monolayers has been used. Some preliminary results of this work have already been reported (10).

The purpose of this work is to evaluate the dispersion force contribution to the liquid crystal/solid free energy of adhesion from data concerning the: anchorage of liquid crystal molecules at a solid plane; liquid crystal/solid free energy of adhesion; and surface polarity.

II. THEORETICAL CONSIDERATIONS

It is possible to determine the liquid/solid free energy of adhesion W_a

$$W_a = \gamma_l + \gamma_s - \gamma_{sl} \quad [1]$$

using the Young–Dupre equation (1):

$$W_a = \gamma_l(1 + \cos \theta) \quad [1 \text{ bis}]$$

where θ is the contact angle of a drop of

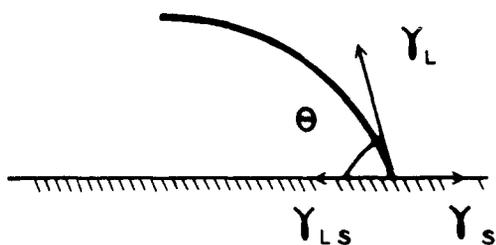


FIG. 1. Equilibrium of a liquid drop on a solid.

liquid on a solid. The subscripts *s* and *l* refer to a solid and a liquid. γ refers to a surface free energy (see Fig. 1).

Following the theory of Fowkes, Girifalco, and Good:

$$W_a = W_a^d + W_a^p \quad [2]$$

$$W_a^d = 2(\gamma_s^d \gamma_l^d)^{1/2} \quad [3]$$

where the superscripts *d* and *p* are respectively the dispersion and polar force interactions.

Fowkes (6) has shown that Zisman's concept (7) of critical surface tension, γ_c , may be used to estimate the γ_s value of the solid. It should, thus, be possible to use γ_c in solving Eq. [3]. On the other hand the polar force contribution W_a^p to the total liquid/solid free energy of adhesion may be calculated from the expression proposed by Zettlemoyer and Chassic (12):

$$W_a^p = F\delta\mu_{\text{eff}} \quad [4]$$

where F = mean electrostatic surface field of a solid; δ = close packed layer of liquid molecules at the solid-liquid interface; μ_{eff} = effective dipole moment of liquid molecules.

Nevertheless Eq. [4] could not be directly applied to the liquid crystals. It may be considered as a first approximation in estimating W_a^p for the complex systems.

In their recent study of adsorption of a mixture of two polar liquids on a surface which displays a surface electrostatic field F , Levine *et al.* (13) have related the orientation of the liquid molecule dipoles and their distribution to the superficial electro-

static energy E_{el} of the monolayer. They assume that the monolayer has a two-dimensional hexagonal lattice with a coordination number $c = 6$. The nearest neighbor distance, d , is related to the density of liquid molecules, δ , in the monolayer by:

$$d^2 = \frac{2}{\delta(3^{1/2})} \quad [5]$$

The excess λ of dipole molecules parallel to the surface field may be defined as the following ratio:

$$\lambda = (\delta_+ - \delta_-)/\delta \quad [6]$$

where δ_+ = density of electric dipoles parallel to the surface field F ; δ_- = density of electric dipoles antiparallel to the surface field F .

The superficial electrostatic energy, E_{el} , is expressed by

$$E_{\text{el}} = \frac{c\delta(\lambda\mu + \alpha F)^2}{2(d^3 + c\alpha)} - \delta F\mu\lambda - \frac{1}{2}\delta\alpha F^2 \quad [7]$$

where μ is the parallel dipole and α the polarizability of liquid molecules. The calculation takes into account the nearest neighbor interactions between permanent and induced dipoles, the energy involved in the creation of induced dipoles, and the dipole field interaction.

E_{el} is the polar interaction energy between the first layer of a liquid and a solid. If we assume that the range of solid/liquid polar interactions is limited to this layer, we can write:

$$W_a^p = -E_{\text{el}} + T\Delta S_{\text{el}} \quad [8]$$

where ΔS_{el} is the entropy change of the interfacial liquid layer induced by the field F and may be defined as:

$$\begin{aligned} \Delta S_{\text{el}} &= S(\lambda) - S(\lambda = 0) \\ &= k(\ln C_\delta^{\delta+} - \ln C_\delta^{\delta/2}) \end{aligned}$$

with

$$C_n^m = \frac{n!}{(n-m)!m!}$$

and

$$\Delta S_{el} \approx \frac{k\delta}{2} \left[-\ln(1 - \lambda^2) + \lambda \ln \frac{1 - \lambda}{1 + \lambda} \right] \quad [9]$$

in the case where λ is different from unity.

We can write [8] using [7] and [9]:

$$W_a^p = - \frac{c\delta(\lambda\mu + \alpha F)^2}{2(d^3 + c\alpha)} + \delta F\mu\lambda + \frac{1}{2}\delta\alpha F^2 + \frac{kT\delta}{2} \times \left[\lambda \ln \frac{1 - \lambda}{1 + \lambda} - \ln(1 - \lambda^2) \right]. \quad [10]$$

Equation [10] requires the thermodynamic equilibrium condition for any variation of λ .

$$\frac{kT}{2} \ln \frac{1 + \lambda}{1 - \lambda} = \mu F - \frac{c\mu(\lambda\mu + \alpha F)}{d^3 + c\alpha}. \quad [11]$$

We can then write [10] and [11] using [5] and [6]:

$$W_a^p = - \frac{2.45\delta^{5/2}}{1 + 4.9\alpha\delta^{3/2}} (\lambda\mu + \alpha F)^2 + \delta F\mu\lambda + \frac{1}{2}\delta\alpha F^2 + \frac{kT\delta}{2} \times \left[-\ln(1 - \lambda^2) + \lambda \ln \frac{1 - \lambda}{1 + \lambda} \right] \quad [12]$$

$$F\mu = (1 + 4.9\alpha\delta^{3/2}) \frac{kT}{2} \times \ln \frac{1 + \lambda}{1 - \lambda} + 4.9\mu^2\delta^{3/2}\lambda. \quad [13]$$

In the case when λ is different from 0 and 1, we can eliminate F in [12] using [13]:

$$W_a^p = 2.45\lambda^2\mu^2\delta^{5/2} + 2.45\alpha\delta^{5/2}kT\lambda \times \ln \frac{1 + \lambda}{1 - \lambda} + \left(\ln \frac{1 + \lambda}{1 - \lambda} \right)^2 \times (1 + 4.9\alpha\delta^{3/2}) \frac{k^2T^2\delta\alpha}{8\mu^2} - \frac{kT\delta}{2} \ln(1 - \lambda^2). \quad [14]$$

When $\lambda < 0.5$, it is possible to develop [11] and [12] up to the second order which yields the final result with a 2% accuracy.

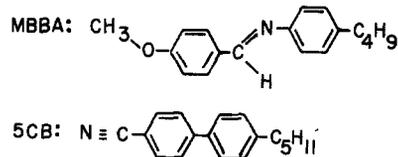
$$F\mu = \lambda[(1 + 4.9\alpha\delta^{3/2})kT + 4.9\mu^2\delta^{3/2}] + O(\lambda^3) \quad [13 \text{ bis}]$$

$$W_a^p = \lambda^2 \left[2.45\mu^2\delta^{5/2} + 4.9\alpha\delta^{5/2}kT + \frac{k^2T^2\delta\alpha}{2\mu^2} \times (1 + 4.9\alpha\delta^{3/2}) + \frac{kT\delta}{2} \right] + O(\lambda^4). \quad [14 \text{ bis}]$$

III. EXPERIMENTAL

1. Materials

Liquid crystals. *p-n*-Methoxybenzilidene-*p*-butylaniline (MBBA) obtained from Vari Light Corporation and 4-4'-pentylcyanobiphenyl (5CB) obtained from B.D.H. Chemicals Ltd are used as received. Their formulas are:



Polysoaps. A series of polysoaps, poly(2 methyl/5 vinyl pyridinium) bromide quaternized by alkyl radicals such as C_4H_9 , C_8H_{17} , and $C_{16}H_{33}$, with the quaternization rate of 100, 54, and 38% (respectively, PVPC4, PVPC8, and PVPC16), were used for deposition on the glass slides. These polysoaps were kindly prepared for us by C. Loucheux.

Liquids used for contact angle measurements. Methylene iodide and formamide were Merck reagent grade products; decaline was purified on silica gel and tri-distilled; water was distilled from permanganate solution in Pyrex apparatus.

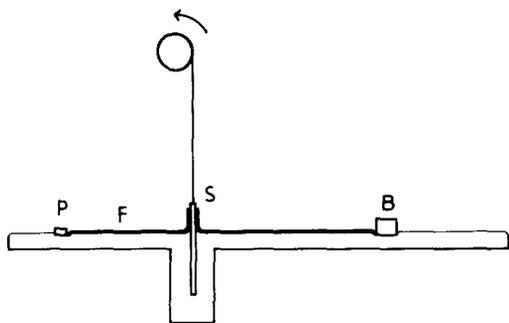


Fig. 2. Deposition of a polysoap monolayer on glass.

2. Methods

a. Adsorption of polysoaps on glass slides. The deposition of polysoaps on glass surfaces is realized by a Blodgett method at constant surface pressure (Fig. 2) (14). The glass slides are cleaned with sulfochromic mixture. The rates of glass slide retraction were experimentally chosen to find the best conditions for a uniform and homogeneous alignment of the liquid crystal. For PVPC4 and PVPC8 this rate is 10^{-2} cm sec $^{-1}$ and for PVPC16 2.10^{-3} cm sec $^{-1}$.

b. Surface pressure. Polysoaps, in methylic alcohol and chloroform mixture 50–50, is spread at the surface of 0.1 M KCl aqueous solutions; water was distilled from permanganate solution in Pyrex apparatus and solutions were foamed. Surface pressure measurements of polysoaps were made on a MGW LAUDA Langmuir film balance pressure. The variation of the film area at constant pressure shows that the surface density at the liquid/air interface is the same as that of the deposited layers of polysoaps at the glass slides.

c. Microscopic studies of anchorage.

TABLE I

Collapse Pressure of Polysoaps

Polysoap	π_c (dyn·cm $^{-1}$)	a_c (Å 2 monomere $^{-1}$)
PVPC4	1	50
PVPC8	27	26
PVPC16	40	16

The observation of the orientation of molecules of liquid crystals is performed by means of a usual optical method. The liquid crystal is placed in a cell made of two parallel glass slides having adsorbed the same amount of polysoap. They are observed with a polarizing microscope.

d. Contact angles. The contact angles of liquids on polysoap-covered glass slides are measured by the drop-on-plate method (15). Contact angles were observed 1 min after the drop deposition. The accuracy of measurement is $\pm 1^\circ$. The values of contact angles of decaline–methylene iodide mixture on polysoap-covered glass slides were used to construct Zisman's plots (7) to determine the γ_c values.

e. Surface tension. A Wilhelmy type microelectrobalance was used to measure the surface tension of all liquid and liquid mixtures used in this study.

IV. RESULTS

1. Polysoaps at the Liquid/Air Interface

The properties of polysoap monolayers adsorbed at the surface of water have already been studied for PVPC4 and PVPC8 (16). These measurements have been completed for PVPC16.

The surface pressures Π_c and molecular areas a_c at the collapse point of the adsorption isotherms are represented in Table I.

2. Anchorage of Liquid Crystals on Polysoap-Covered Glass Slides

We have examined the liquid crystal orientation for various densities of polysoap adsorbed on glass. These orientations are represented in Table II.

As it can be seen from Table II different orientation of liquid crystals are possible. They are called:

—“planar” when the axis of molecules are parallel to the substrate;

—“planar uniaxial” when all molecules have their axis planar to the substrate and

when their alignment is in one direction only;

—“planar multidomain” when all molecules have their axis parallel to the substrate but their alignment is in all directions possible;

—“homeotropic” when the molecules have their axis perpendicular to the substrate.

When the liquid crystal has an uniaxial planar structure the molecule long axis is always parallel to the direction of retraction of polysoap-covered glass slides.

MBBA and 5CB in contact with PVPC4 produce only planar orientation. This orientation is uniaxial except for MBBA and PVPC4 with a high surface density (surface area, 50 Å²).

The PVPC8 produces an uniaxial planar anchorage of 5CB at low surface density, and a homeotropic anchorage at high surface density. On the other hand, this soap produced multidomain planar structures of MBBA for all densities.

For PVPC16 the only observed orientation is homeotropic. These results confirm that the structure of polymer and the distribution of its main and side chains play an important role in structuring of a liquid crystal. The shorter the side chain, the more important is the effect of the main chain. When the main polymer chain is exposed to the solid/liquid crystal interface, the orientation is planar; but when the main chain is screened by a long side chain, the obtained orientation is homeotropic.

3. Free Energy of Adhesion for MBBA, 5CB, and Formamide on Polysoap-Covered Glass Slides

To calculate these energies we have used the surface tensions values listed in Table III and Eq. [1 bis].

These results are represented in Table IV.

The results obtained with mixtures of methylene iodide and decalin are plotted in Fig. 3. Methylene iodide has a very low

TABLE II

Orientation of Liquid Crystal on Polysoaps-Covered Glass Slides^a

Substrates (Å ²)	MBBA orientation	5CB orientation
PVPC4		
200	↔	↔
50	↔	↔
	x	↔
PVPC8		
200	↔	↔
	x	↔
50	↔	⊥
	x	⊥
PVPC16		
75	⊥	⊥
60	⊥	⊥
40	⊥	⊥
16	⊥	⊥

^a ↔, planar uniaxial orientation; x, planar multidomain orientation; ⊥, homeotropic orientation.

polarity. Decalin is a saturated hydrocarbon and thus nonpolar (Table III). The mixture may be considered as nonpolar. Its surface tension varies between 31.6 and 50.8 ergs/cm² (17).

From Eqs. [1 bis], [2], and [3] we obtain:

$$\cos \theta = \frac{-\gamma_1 + 2(\gamma_s^d \gamma_1^d)^{1/2}}{\gamma_1} \quad [15]$$

The γ_s^d calculated from [15] and the data of Table III and Fig. 3 are similar to γ_c values extrapolated in Fig. 3.

Surprisingly, we have obtained for all solid substrates the same value:

$$\gamma_c \approx \gamma_s^d \approx 32 \pm 2 \text{ dyn} \cdot \text{cm}^{-1}.$$

TABLE III

Dispersion and Polar Contributions of Surface Tensions

Liquid	γ_1	γ_1^d	γ_1^p
MBBA (2)	38	29	9
5CB (22)	40	40	0
Formamide (27)	58	32	26
Decaline (17)	31.6	31.6	0
Methylene iodide (27)	50.8	48.5	2.3

TABLE IV

Adhesion Free Energy and Contact Angle of MBBA, 5CB, and Formamide on Glass Covered with Polysoap

Solid substrate and area per residue (\AA^2)	MBBA/solid		5CB/solid		Formamide/solid	
	W_a (ergs \cdot cm $^{-2}$)	Contact angle	W_a (ergs \cdot cm $^{-2}$)	Contact angle	W_a (ergs \cdot cm $^{-2}$)	Contact angle
PVPC4						
200	74.7	15.5	77.5	20	109	28.5
50	72.5	25	75	28.5	102	37.5
PVPC8						
200	67	40	70	41.5	103	39
26	71	29	74	32	103	39.5
PVPC16						
75	72	27	75	29.5	97.5	47.5
60	73.5	20	77	22.5	92.5	54
40	72.5	25	76.3	25	88.5	59
16	73.5	21.5	77	22.5	79	69

V. INTERPRETATION

We shall assume in this paper that polar and dispersion force interactions are independent and one can deduce them separately when the other contribution is known. We shall thus calculate the W_a^p term for our systems using Eq. [12].

Determination of the Electrostatic Surface Field of the Solid

In order to evaluate the polarity of the solid, we use the wettability results obtained with formamide (Table IV). The formamide molecules are small and we assume that their anisotropy is negligible as

regards dispersion force interactions with the solid, and that the Fowkes–Girifalco–Good formalism can be applied (Eqs. [2] and [3]). The W_a^p values are listed in Table V.

Table V also contains the values for λ and F calculated from Eqs. [13 bis] and [14 bis]. This calculation implies the knowledge of the polarizability of formamide molecule α , which may be found using Onsager's expression (18):

$$\alpha = \frac{n^2 - 1}{n^2 + 2} \frac{3M}{4\pi Nd}$$

where n = refractive index (1.445); d

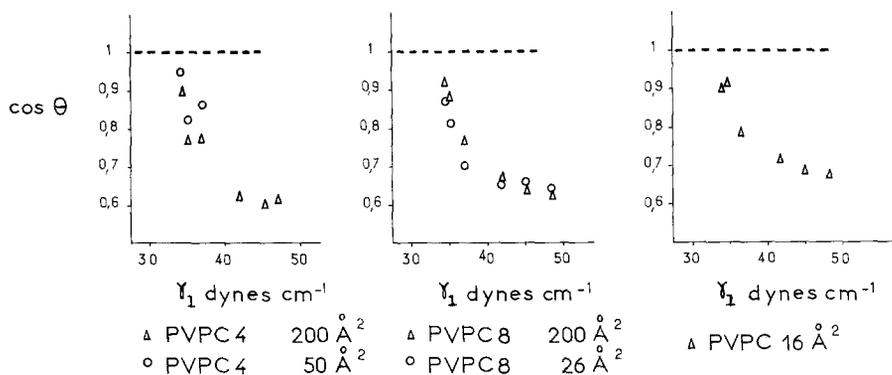


FIG. 3. Wettability of methylene iodide/decaline mixtures on various substrates. γ_1 , surface tension of the mixture; θ , contact angle.

TABLE V
Electrostatic Field of Solid Substrates

Substrate (Å ²)	W_a^p formamide (ergs/cm ²)	λ formamide	F solid (c.g.s.u.e.s)
PVPC4			
200	45	0.43	1.07 10 ⁵
50	36.5	0.38	0.95 10 ⁵
PVPC8			
200	39	0.40	10 ⁵
26	39	0.40	10 ⁵
PVPC16			
75	33.5	0.37	0.92 10 ⁵
60	28.5	0.34	0.85 10 ⁵
40	24.5	0.31	0.77 10 ⁵
16	15	0.25	0.62 10 ⁵

= density (1.134); M = molecular weight (45). It is obtained $\alpha = 4.19 \cdot 10^{-24}$ c.g.s.u.e.s.

Taking for formamide $\mu = 3.25 \cdot 10^{-18}$ c.g.s.u.e.s and $\delta = 6 \cdot 10^{14}$ molecules/cm² (closed packed layer of formamide molecules), one obtains:

$$F = 2.5 \cdot 10^5 \lambda + O(\lambda^3)$$

$$W_a^p = 248.04 \lambda^2 + O(\lambda^4).$$

Polar and Dispersion Forces for 5CB/Solid

Knowing F , we calculate the polar interactions between the liquid crystal and polysoap-covered glass.

We use Eqs. [13 bis] and [14 bis] in which the parameters α , μ , and δ are different and depend on the orientation of liquid crystal molecules. For each liquid crystal we have to distinguish between longitudinal (L) and transversal (T) quantities. The data from Ref. (19) give for 5CB the mean polarizability $\bar{\alpha} = 3.26 \cdot 10^{-23}$ cm³ and the anisotropic polarizability $\Delta\alpha = \alpha_L - \alpha_T = 2.72 \cdot 10^{-23}$ cm³. Thus from equation: $\bar{\alpha} = \frac{1}{3}\alpha_L + \frac{2}{3}\alpha_T$ we have $\alpha_L = 5.07 \cdot 10^{-23}$ cm³ and $\alpha_T = 2.35 \cdot 10^{-23}$ cm³.

The relation between the main polarizabilities of the fluctuating molecule (α_L and α_T) and the polarizabilities of the motionless 5CB molecule (α_L' and α_T') is (21):

$$\alpha_L = \bar{\alpha}_L' + \frac{2}{3}S(\alpha_L' - \alpha_T')$$

$$\alpha_T = \bar{\alpha}_T' - \frac{1}{3}S(\alpha_L' - \alpha_T') \quad [16]$$

where the order parameter S of the liquid crystal is equal to 0.46 in the bulk (24). We suppose that $S = 1$ at the interface with the solid.

We can deduce α_L' and α_T' and taking $S = 0.46$ we find:

$$\alpha_L' = 7.18 \cdot 10^{-23} \text{ c.g.s.u.e.s}$$

$$\alpha_T' = 1.3 \cdot 10^{-23} \text{ c.g.s.u.e.s.}$$

We take the dipole moment value chosen from Ref. (22) and the surface densities of the first layer of 5CB in contact with the solid in two orientations, planar (δ_{\parallel}) and homeotropic (δ_{\perp}), as follows:

$$\mu = \mu_L = 4.45 \cdot 10^{-18} \text{ c.g.s.u.e.s}$$

$$\delta_{\perp} = 4 \cdot 10^{14} \text{ molecules/cm}^2$$

$$\delta_{\parallel} = 10^{14} \text{ molecules/cm}^2.$$

Thus to calculate F and λ for the homeotropic structure from Eqs. [13 bis] and [14 bis], using the data or the longitudinal polarisability we have:

$$F = 2.09 \cdot 10^5 \lambda + O(\lambda^3)$$

$$W_a^p_{\perp} = 213.81 \lambda^2 + O(\lambda^4).$$

For the planar structure, the situation is different. It is possible to avoid the nearest neighbor approximation (Eq. [7]). Here all the induced dipoles have the same orientation and the permanent dipole contribution is zero. The interaction between an induced dipole and its nearest neighbor is equal to $c\mu_{\text{ind}}^2/d^3$. The interaction energy of the lattice is then:

$$\sum_{\text{lattice}} \frac{\mu_{\text{ind}}^2}{r^3} = \frac{\mu_{\text{ind}}^2}{d^3} \times 10.3 \quad [17]$$

¹ In the case of PVPC16, if we introduce the real density of liquid crystal molecules: $\delta_{\perp} = \delta_{\text{lattice}} - \delta_{\text{hexadecyl}}$, instead of the density of the lattice sites: ($\delta_{\text{lattice}} = 4 \cdot 10^{14}$ sites · cm⁻²), the correction factor is then within the limits of the experimental error.

where r is the distance between a dipole and one of its neighbors. Thus Eq. [6] becomes:

$$E_{el} = \frac{10.3\delta\alpha^2F^2}{(2d^3 + 10.3\alpha)} - \frac{1}{2}\delta\alpha F^2$$

$$= -\frac{1}{2} \frac{\delta\alpha F^2}{(1 + 8.44\alpha\delta^{3/2})} \quad [18]$$

and Eq. [10] gives: $W_{a^p} = 5.86 \cdot 10^{-10} F^2$. The results of this calculation for all polysoaps studied are reported in Table VI.

Polar and Dispersion Forces MBBA/Solid

The polarizability of MBBA molecule is obtained using Vuks equation (23):

$$\frac{n_e^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{\rho N}{M} \alpha_L \quad \overline{n^2} = \frac{2}{3}n_o^2 + \frac{1}{3}n_e^2.$$

$$\frac{n_o^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{\rho N}{M} \alpha_T$$

We obtain the main polarizabilities α_T and α_L of MBBA molecule as a function of the ordinary n_o and extraordinary n_e refractive index, of the density ρ , and of molecular weight M . At room temperature, we have (24):

$$n_e = 1.8; \quad n_o = 1.56; \quad \rho = 1.088 \text{ g/cm}^3;$$

$$S = 0.64; \quad M = 267$$

which yields the values of α_L and α_T equal to:

$$\alpha_L = 4.64 \cdot 10^{-23} \text{ cm}^3$$

$$\alpha_T = 2.97 \cdot 10^{-23} \text{ cm}^3.$$

Using Eq. [16], we obtain the main polarizabilities for the motionless molecule:

$$\alpha_L' = 5.26 \cdot 10^{-23} \text{ cm}^3$$

$$\alpha_T' = 2.65 \cdot 10^{-23} \text{ cm}^3.$$

To calculate F and W_{a^p} we use the longitudinal (μ_L) and transverse (μ_T) dipole moments, and the surface densities of MBBA molecules in their planar $\delta_{||}$ and homeotropic δ_{\perp} structures:

$$\mu_L = 0.4 \cdot 10^{-18} \text{ c.g.s.u.e.s.} \quad (25)$$

$$\mu_T = 1.9 \cdot 10^{-18} \text{ c.g.s.u.e.s.} \quad (25)$$

$$\delta_{\perp} = 4 \cdot 10^{14} \text{ molecules} \cdot \text{cm}^{-2}$$

$$\delta_{||} = 10^{14} \text{ molecules} \cdot \text{cm}^{-2}.$$

For the planar structure, Eqs. [12] and [13] become:

$$F = 1.21 \cdot 10^{-4} \ln \frac{1 + \lambda}{1 - \lambda} + 0.931 \cdot 10^4 \lambda$$

$$W_{a^p} = 16.8 \cdot 10^{-5} F \lambda - 0.783 \lambda^2 + 1.17 \cdot 10^{-3} F^2$$

$$+ 2.04 \left[-\ln(1 - \lambda^2) + \lambda \ln \frac{1 - \lambda}{1 + \lambda} \right].$$

The $T\Delta S_{el}$ term in Eq. [9] is not correct when $\lambda = 1$; in this case, we have: $T\Delta S_{el} = kT\delta \ln 2$.

For the homeotropic structure, λ is small and we can use Eqs. [13 bis] and [14 bis] which yield:

$$F = 3.27 \cdot 10^5 \lambda$$

$$W_{a^p} = 3 \cdot 76.62 \lambda^2.$$

The results of these calculations for all polysoaps are reported in Table VII.

VI. DISCUSSION

We can define the anisotropy ΔW_{a^i} of i interactions as the difference between the i contributions to the interfacial energies of the planar and homeotropic anchorages. Using [1], we obtain:

$$\Delta W_{a^i} = W_{a||}^i - W_{a\perp}^i \quad i = p, d.$$

When two different interactions tend to produce opposing orientations, the strongest anisotropy imposes its orientation. Then, it is possible to deduce from the values of W_{a^d} which correspond to the observed orientation and from W_{a^p} , calculated, the maximum value that W_{a^d} would take if the orientation changes. These maximum values are reported in the last columns of Tables VI and VII.

The values of W_{a^d} for the planar orientation show that MBBA would have a weaker interaction with the main polysoap chains

² See note on previous page.

TABLE VI

5CB: Calculation of Polar Contribution of the Adhesion Free Energy for Planar and Homeotropic Orientation^a

	Area per residue (Å ²)	Quater-nised area per residue (Å ²)	<i>F</i> (c.g.s.u.c.s.)	λ		W_a^p (ergs·cm ⁻²)	W_a^p (ergs·cm ⁻²)	W_a (ergs·cm ⁻²)	exp.	$W_a^d = W_a - W_a^p$ (ergs·cm ⁻²)	Remarks
				homeo-tropic case							
PVPC4	200	200	1.07 10 ⁵	6.7	0.51	55.6	77.5	↔	70.8	$W_a^d \perp < 21.9$	
	50	50	0.95 10 ⁵	5.3	0.45	43.3	75	↔	69.7	$W_a^d \perp < 31.7$	
PVPC8	200	370	10 ⁵	5.9	0.48	49.3	70	↔	64.1	$W_a^d \perp < 20.7$	
	26	48	10 ⁵	5.9	0.48	49.3	74	⊥	24.7	$W_a^d \parallel < 68.1$	
PVPC16	75	197	0.92 10 ⁵	5	0.44	41.4	75	⊥	33.6		
	60	158	0.85 10 ⁵	4.2	0.41	35.9	77	⊥	41.1		
	40	105	0.77 10 ⁵	3.5	0.37	29.3	76.3	⊥	47		
	16	42	0.62 10 ⁵	2.3	0.30	19.2	77	⊥	57.8		

^a The values in italics of W_a^p and λ (calculated) correspond to the effectively observed structure (in the planar case, $\lambda = 1$). The contribution of dispersion forces is deduced in that case.

than 5CB; this is verified by the orientation observations: when 5CB has uniaxial planar structure, MBBA has a multidomain planar structure (see Table I).

The anisotropy value of dispersion force interactions is considerable and its value may be as high as 50 ergs·cm⁻². We can understand this in considering that for PVPC4 and PVPC8 the solid faces two dif-

ferent liquids in their planar and homeotropic structure: In the former case, there are about 4 10¹⁴ atoms in contact with 1 cm² area of solid, and in the latter about 20 10¹⁴.

These results show that to describe the liquid crystal/solid adhesion it is necessary to take into account the anisotropy of liquid molecule.

One can notice that in the cases where

TABLE VII

MBBA: Calculation of Polar Contribution of the Adhesion Free Energy for Planar and Homeotropic Orientation^a

	Area per residue (Å ²)	Quater-nised area per residue (Å ²)	<i>F</i> (c.g.s.u.c.s.)	λ		W_a^p (ergs·cm ⁻²)	W_a^p (ergs·cm ⁻²)	W_a (ergs·cm ⁻²)	exp.	$W_a^d = W_a - W_a^p$ (ergs·cm ⁻²)	Remarks
				↔	⊥						
PVPC4	200	200	1.07 10 ⁵	1	0.33	27.8	41	74.7	↔	46.9	$W_a^d \perp < 33.7$
	50	50	0.95 10 ⁵	1	0.29	23	31.7	72.5	↔ X	49.5	$W_a^d \perp < 40.8$
PVPC8	200	370	10 ⁵	1	0.31	24.9	36.2	67	↔ X	42.1	$W_a^d \perp < 30.8$
	26	48	10 ⁵	1	0.31	24.9	36.2	71	↔ X	46.1	$W_a^d \perp < 34.8$
PVPC16	75	197	0.92 10 ⁵	1	0.28	21.8	29.5	72	⊥	42.5	
	60	158	0.85 10 ⁵	1	0.26	19.2	25.5	73.5	⊥	48	
	40	105	0.77 10 ⁵	0.99	0.24	16.4	21.7	72.5	⊥	50.8	
	16	42	0.62 10 ⁵	0.97	0.19	11.4	13.6	73.5	⊥	59.9	

^a The values in italics correspond to the effectively observed structures. The contribution of dispersion forces is deduced in that case.

the liquid crystal molecules are parallel to the main polysoap chains (PVPC4, PVPC8, 200 Å²), the value of W_a^d has the same order of magnitude as the one obtained with Fowkes-Girifalco-Good formalism, i.e., using Eqs. [2] and [3], and taking for γ_l^d the values from Refs. (2) and (22):

$$\text{MBBA: } \gamma_l^d = 29 \text{ dyn cm}^{-1}$$

$$5\text{CB: } \gamma_l^d = 40 \text{ dyn cm}^{-1}.$$

One finds for 5CB $W_a^d = 70 \text{ ergs} \cdot \text{cm}^{-2}$ quite similar to the values of Table VI, for MBBA one finds $W_a^d = 60 \text{ ergs} \cdot \text{cm}^{-2}$. The difference is explicable if one remarks that, for the planar orientation, the interactions between MBBA and the main chains of polysoap are much worse than between 5CB main chain interactions.

The dispersion force contribution to the adhesion free energy of MBBA and 5CB on glass covered with PVPC16 increases with the density of hexadecyl chains. To analyze the change of W_a^d with the density of hexadecyl chain we shall consider the interface as a mixed layer of liquid crystal molecules and hexadecyl chains. In this two-dimensional lattice each site is occupied either by a hexadecyl chain or by a liquid crystal molecule. W_a^d can be expressed by the following equation:

$$W_a^d = W_a^{d0} - N_{ab}\epsilon_{ab} + (N_{aa}^0 - N_{aa})\epsilon_{aa}$$

ϵ_{ab} (resp. ϵ_{aa}) is the dispersion force interaction between a liquid crystal molecule and a hexadecyl chain (resp. liquid crystal molecule) and N_{ab} (resp. N_{aa}) the number of such interactions in the layer. The superscript 0 refers to the situation when there are no hexadecyl chains.

We can write W_a^d versus the density δ_{C16} of hexadecyl chains:

$$W_a^d = W_a^{d0} + \frac{3\delta_{C16}}{\delta_{\text{sites}}} (2\epsilon_{ab} - \epsilon_{aa}) - 6\delta_{C16}(\epsilon_{ab} - \epsilon_{aa}). \quad [19]$$

In Fig. 4 are represented the theoretical curves for MBBA and 5CB calculated using Eq. [16] and also the experimental data from Table V and Table VI.

The shape of the curve in Fig. 4 shows that:

$$|\epsilon_{ab}| > |\epsilon_{aa}|.$$

The experimental values did not allow us to determine the values of ϵ_{ab} and ϵ_{aa} accurately enough.

Remarks

Contrary to other studies (26), we have obtained only planar and homeotropic anchorages, and the critical surface tension

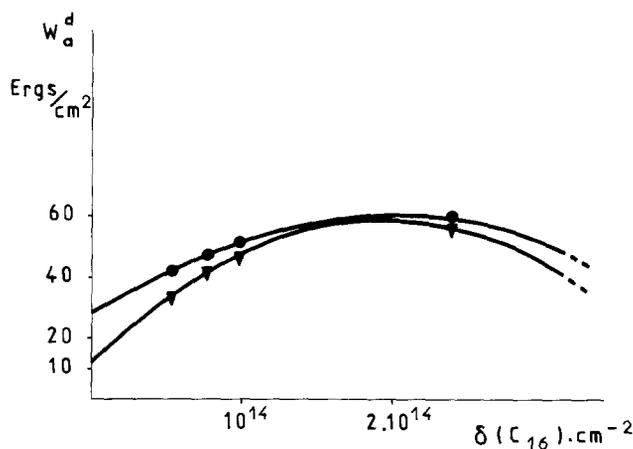


FIG. 4. Variation of the dispersion term of the free energy of adhesion, (W_a^d), with the density (δ) of hexadecyl chain.

seems independent of the parafinic side chain length of the polysoap.

The observed orientations allow the structure of the adsorbed polysoap layer to be revealed. In the cases of planar orientations for PVPC4 and PVPC8, at least one of the liquid crystals could display a good uniaxial orientation. We can deduce that on the average the polysoap chains adsorbed on glass lie flat on the surface.

CONCLUSION

The usual way to evaluate polar and dispersion force interactions between two phases is the application of Fowkes-Girifalco-Good formalism: Polar interactions are deduced from the calculated dispersion forces and from the experimental value of the free energy of adhesion.

When the method of inverse calculation is applied, i.e., deducing dispersion forces from the calculated polar interactions and from the value of the adhesion free energy, the anisotropy of dispersion force interactions between a liquid crystal and a solid can be evaluated. We have shown that such energy anisotropies can be large. It would be interesting to compare these results for a nonpolar liquid crystal and solid.

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