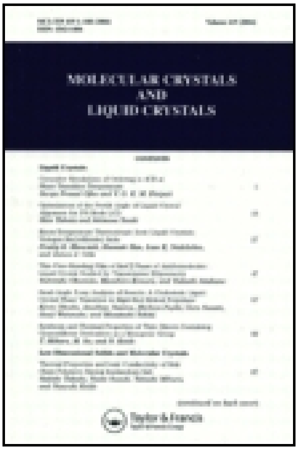

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Interfacial Origin of Liquid Crystal Anchorage

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Interfacial Origin of Liquid Crystal Anchorage

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We have tried to find criteria for liquid crystal orientation by solid surfaces physico-chemical concepts. The solid surface is glass with a soap or polysoap monolayer on it or without such a monolayer.

We consider the liquid/solid interaction anisotropies mainly for polar and dispersion forces, and steric interactions.

INTRODUCTION

The orientation of ordinary liquid molecules at interfaces is hardly detectable. The use of liquid crystals allows an easy detection of this orientation.

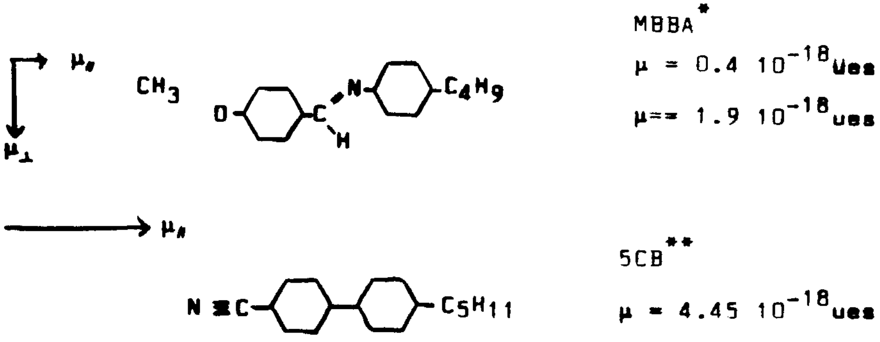
In a first paper,[1] results have been reported using a nematic liquid crystal with negative dielectric anisotropy. In this paper, we compare qualitively liquid crystals with positive and negative dielectric anisotropies oriented by macromolecules.

EXPERIMENTAL

We deposit a soap monolayer on a solid surface and determine the liquid–solid interaction energy.

The orientation was determined by enclosing liquid crystal within cells made of two parallel glass slides, and observing them with a microscope between crossed polarisers.

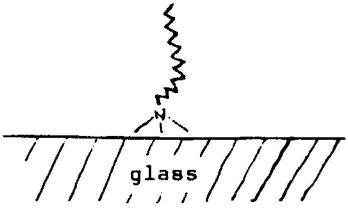
Used systems We have been using two liquid crystals, MBBA and 5CB shown in Figure 1.



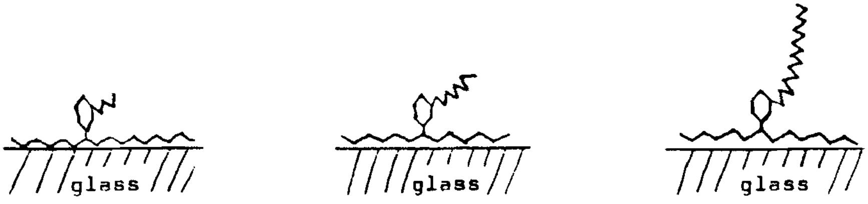
* Maurel, P. and Price, H., *J. Chem. Soc. Faraday Trans.*, **11**, 1953.

** Minkin, Osipov, Zhdanov, *Dipole Moments in Organic Chemistry*, 1970, Plenum Press, New York.

FIGURE 1 Structure of MBBA and 5CB



soap CTAB : hexadecyltrimethylammonium bromide



n=4 n=8 n=16

polysoaps : poly (2methyl-5vinyl-piridinium-C_nH_{2n+1})Br^-

FIGURE 2 Used detergents

MBBA has a negative dielectric anisotropy constant its main electric dipole moment is perpendicular to the long axis of the molecule.

Pentylcyanobiphenyl: 5CB has a positive dielectric anisotropy constant: its dipole moment has only one component parallel to the long axis of the molecule.

We have been using two detergents shown in Figure 2.

One is the well known CTAB with a 16 carbon paraffinic chain.

The others are a homologous series of polymerised soaps with different side chains: poly-(vinyl pyridinium) bromide with a 4, 8 or 16 CH_2 lateral chain.

We call them respectively PVPC 4, 8, 16.

Technique of deposition

The technique of deposition is slightly different for a soluble soap than for an insoluble soap.

CTAB is soluble in water. At the free surface of a solution of CTAB, the molecules form a monomolecular layer, the density of which varies with the solution concentration. We immerse a clean glass slide, we wait for equilibrium and we withdraw it by the method Ter-Minassian-Saraga used in 1960. The molecular surface density is measured using ^{14}C labelled molecules.

In the case of polysoaps, we have been using the film balance shown in Figure 3.

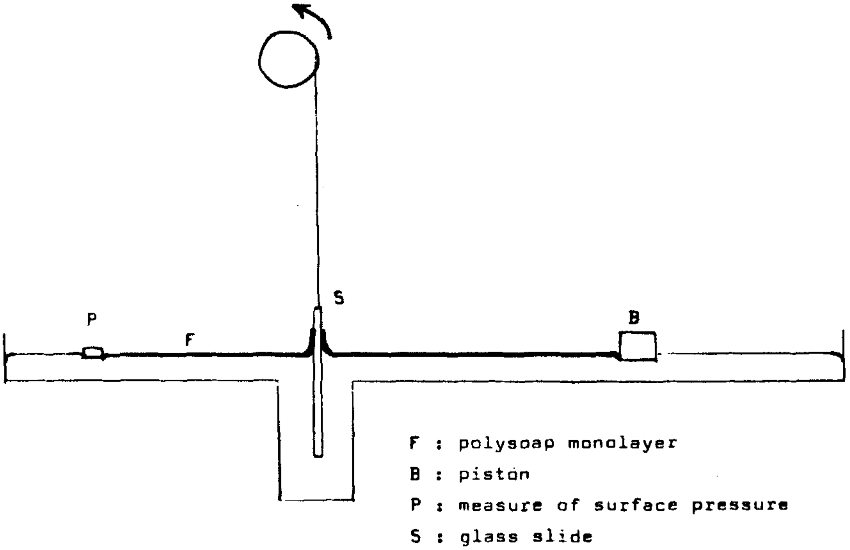


FIGURE 3 Deposition of a polysoap monolayer on glass.

The glass slide is first immersed in water, then we spread a known number of polysoaps residues on water. We maintain the pressure or residue area constant with the piston *B* and pressure gauge *P* while withdrawing the slide.

Liquid/solid interaction

In order to determine the liquid/solid interaction energy, the critical surface tension γ_c and polar contribution to the surface energy of the solid substrate γ_S^p, we measure the contact angle of a drop of liquid on the solid.

Figure 4 shows a drop of liquid on solid at equilibrium determined by the different surface tensions.

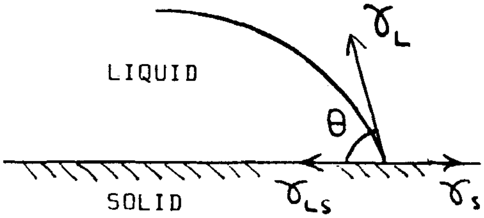


FIGURE 4 Equilibrium of a liquid drop on a solid.

WETTABILITY

Adhesion free energy

The adhesion free energy is the work necessary to separate two surfaces:

$$W_a = \gamma_L + \gamma_S - \gamma_{SL}.$$

Combining it with the equilibrium between surface tensions, the Young equation, we get the Young–Dupré equation relating the measurable parameters γ_L, liquid surface tension and θ contact angle, to the adhesion free energy W_a:

$$W_a = \gamma_L(\cos\theta + 1).$$

According to Fowkes' formalism,[2] we separate dispersion forces (1st term) and polar (2nd term) contributions to the adhesion free energy and get:

$$W_a = W_a^d + W_a^p = 2\sqrt{\gamma_L^d \gamma_S^d} + F\delta\lambda\mu$$

where F is the electrostatic surface field of the solid, $\lambda\mu$ is the efficient dipole moment depending on the liquid crystal molecules orientation; δ is the liquid crystal molecular density at the interface, dependent on the orientation.

The superscripts d and p refer respectively to dispersions forces and polar interactions.

In order to obtain the polar contribution to the liquid/solid interaction energy, Wu[3] uses the empirical equation:

$$W_a^p = \frac{4\gamma_S^p \gamma_L^p}{\gamma_L^p + \gamma_S^p}$$

Critical surface tension

We have been determining the critical surface tension of the solid surfaces according to the Zisman method:[4] plotting the cosine of the contact angle θ of drops of different liquids on the solid versus the liquid surface tension, and extrapolating the curve to $\cos \theta = 1$, we get the critical surface tension γ_c. Fowkes[2] has shown that γ_c is approximately equal to γ_S^d.

RESULTS

We have measured the critical surface tension γ_c of the solid by Zisman's method. From the measurements of the contact angle of drops of MBBA, 5CB, formamid on the substrates, we have applied Fowkes' formalism to separate W_a^d and W_a^p, taking from Refs. 1, 5 and 6 the values of γ_L^d:

MBBA: $\gamma_L^d = 29$ ergs · cm^{-2}
5CB: $\gamma_L^d = 40$ ergs · cm^{-2}
formamid: $\gamma_L^d = 32$ ergs · cm^{-2}; $\gamma_L^p = 26$ ergs · cm^{-2}

The values of W_a^p relative to measurements with formamid make it possible to characterize the polarity of the solid substrates, and we have used Wu's equation to evaluate γ_S^p.

We will only give here the results concerning PVPC8 (see Table III).

In the systems we have been studying, the interaction anisotropies are either polar originating in the electrostatic surface field of the glass which is normal to the surface or steric and due to dispersion forces, as in soap monolayers adsorbed on the glass. We have seen that the organic soap chains are either parallel or normal to the surface. The liquid crystal molecules orientation is such that the liquid/solid interfacial energy is minimum, i.e. that W_a is maximal.[1]

Clean glass

The results of orientation and polar contribution to adhesion free energy on clean glass are shown in Table I.

TABLE I

Liquid crystal on clean glass

Liquid crystal	L.C. orientation	W_a^p ergs · cm^{-2}
MBBA	⇆	27(1)
5CB	⊥	21(4)

⇆ planar monodomain; ⊥ homeotropic.

We suppose that the dispersion forces interactions are isotropic at the glass interface, so that only W_a^p is important here. We can thus foresee the anchorage with the relative value of polar contribution to W_a^p in the planar and homeotropic case:

$$\mu_T\delta_{\parallel} - \mu_L\delta_{\perp}\begin{cases} > 0\text{: planar} \\ < 0\text{: homeotropic} \end{cases}$$

for MBBA, the experimental results are agreeing with the Eq. (2), and for 5CB, they are not; a possible explanation of this discrepancy is that the value of μ_L of 5CB is so important, and the distance between nearest-neighbours 5CB molecules is so small that we cannot neglect dipole–dipole interactions between 5CB molecules comparatively to 5CB/glass polar interaction as we did in the case of MBBA; in the latter case, the planar structure imposes a larger nearest-neighbours distance between MBBA molecules which makes negligible the MBBA molecules polar interaction within the first layer, comparatively to the MBBA/glass polar interaction.

Glass covered with an organic monolayer

a) In simple cases shown in Table II, there is one anisotropy feature of the monolayers dominating all the others:
—PVPC16 and dense CTAB favour homeotropic anchorage; their paraffinic C16 chains allow strong anisotropic sterical interactions.

TABLE II

Glass covered with an organic monolayer

Substrate L.C.	PVPC4	PVPC16	CTAB
MBBA	⇄	⊥	⊥
5CB	⇆	⊥	⊥

TABLE III

Glass covered with PVPC8

PVPC8	γ_s^d ergs/cm^2	γ_s^p ergs/cm^2	MBBA	5CB
$\delta = 0.5 \cdot 10^{14}$ residues cm^{-2}	32	15.5	$\rightleftharpoons$ $W_a^p = 6$	$\overset{x}{\rightleftharpoons}$ $W_a^p = 0$
$\delta = 4 \cdot 10^{14}$ residues cm^{-2}	32	15.5	$\overset{x}{\rightleftharpoons}$ $W_a^p = 10$	$\perp$ $W_a^p = 4$

$\perp$ homeotropic; $\rightleftharpoons$ planar monodomain;
$\overset{x}{\rightleftharpoons}$ planar multidomain.

—PVPC4 has very short side chains which do not contribute to the orientation process. The main chain of PVPC4 has very strong anisotropic sterical interactions, and favours planar orientations.

b) There are other cases where several anisotropies are competing; no one being really preponderant.

For example, PVPC8 (see Table III) is more complicated.
—There is an anisotropy due to main chains.
—Side C8 chains have a weak effect but may not be negligible.
—There is also a polar effect.

The orientation of 5CB resulting from these different anisotropic interactions shows that:
—at low surface density, the dispersion forces and steric interactions with the main chain of the polysoap is predominant.
—at high surface density, polar, dispersion and steric interactions between the side chains and 5CB are more important than interactions with the main chain.

The results concerning MBBA orientation show that anisotropies of polar interactions are the most important.

CONCLUSION

It is well known that the general criterion for liquid crystal anchorage is the relative value of adhesion free energy in planar case and homeotropic case:

$$W_{a\parallel} - W_{a\perp} \begin{cases} > 0 \Rightarrow \parallel \\ < 0 \Rightarrow \perp \end{cases}$$

If the solid substrate anisotropy originates only in a surface electrostatic field (as for clean glass) the general criterion reduces to:

$$W^p_{a\parallel} - W^p_{a\perp} \begin{cases} > 0 \Rightarrow \parallel \\ < 0 \Rightarrow \perp \end{cases}$$

We can predict it using the expression giving polar contribution to adhesion free energy.

If the substrate gives strong sterical and dispersion forces anisotropies (long organic chains), without electrostatic field, the criterion becomes:

$$W^d_{a\parallel} - W^d_{a\perp} \begin{cases} > 0 \Rightarrow \parallel \\ < 0 \Rightarrow \perp \end{cases}$$

In this case, the anisotropy of W^d_a is not directly measurable, the critical surface tension measure gives only an average value of γ^d_s; on the other hand, we have evaluated the surface tension anisotropy of 5CB; it is very small:[7]

$$\gamma_\parallel - \gamma_\perp \simeq 4 \cdot 10^{-3} \text{ ergs/cm}^2.$$

Furthermore, the use of liquid crystals which could have anisotropic intermolecular interactions allowed us to compare qualitatively the force of different types of interactions at the interface: polar, sterical and dispersion forces interactions 5CB and the main or lateral chains of polysoaps.

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