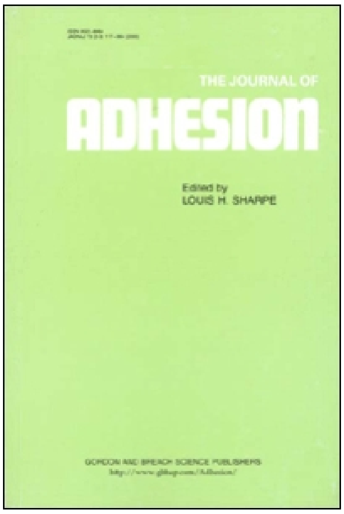

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The Anisotropy of the Surface Tension of Polar Liquids: The Case of Liquid Crystals

J. Cognard[a]
[a] Asulab S.A., neucha, Switzerland

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The Anisotropy of the Surface Tension of Polar Liquids: The Case of Liquid Crystals

J. COGNARD

Asulab S.A., 2000 Neuchatel, Switzerland

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The contact angle of the liquid crystal (LC) 4-phentyl, 4′-cyano biphenyl (5CB) on glass or polyethylene does not correspond to the value expected from its surface tension measured by the "du Nouy" method (29×10^{-3} JM^{-2}). The value deduced from the Young–Dupré law is 40×10^{-3} JM^{-2}.

Both these values have already been reported in the literature. Their apparent discrepancy is explained by the LC surface tension anisotropy. We show that 5CB as many other LCs orient perpendicular to the free surface but parallel to glass or polyethylene Thus both values of the surface tension correspond to two different molecular orientations.

The LC oriented perpendicularly has a surface tension of 29×10^{-3} JM^{-2} and 40×10^{-3} JM when it lies parallel to the surface. We suggest that the anisotropy between the perpendicular and parallel state of LCs also exists between two perpendicular orientations. Furthermore, such anisotropy associated with any polar molecules explains the difference of the interfacial energy of similar polar or non polar (*i.e.*, octanol–octane) compounds and water.

INTRODUCTION

For quite some time it has been considered that polar molecules could be oriented at the surface of a liquid. Such orientation may, in the case of anisotropic molecules, modify the value of the surface tension. For instance, the fact that the interfacial free energy of the *n*-Octane–Water interface is $\gamma_{12} = 50.6$ m Jm^{-2} while that of the *n*-Octanol–Water interface is $\gamma_{12} = 8.8$ m Jm^{-2} is attributed to the orientation of the hydroxyl group of the alcohol toward the water surface.[1] At the free surface, an orientation of all hydroxyl groups outwards would give a surface energy γ_{OH} of 190 m Jm^{-2} [2] which is diminished to the experimental $\gamma_{Octanol} = 22$ m Jm^{-2} by the orientation of the alkyl chains at the liquid free surface. We suggest that the anisotropy of the surface tension is a general property of polar liquids. This proposal will be exemplified in the case of nematic liquid crystals as liquid crystals (LCs) extend the interfacial interactions over large distances (some microns) which allow the visual observation of their direction of alignment. Nematic LC are, in most cases, made up of long, polar cylindrical molecules as schematically represented on Fig. 1. The interactions of the LC with surfaces lead to an orientation of the molecules parallel to one direction described by the "nematic director" $\vec{n}$. Namely the nematic director may be oriented parallel or perpendicular to a given surface. The surface tension of the LC has two values $\gamma_{CL}^{\parallel}$ and $\gamma_{CL}^{\perp}$, respectively, corresponding to these two orientations. The existence of these two surface-tension values has been invoked[3] to describe the orientation of the liquid crystal 4-methoxy benzylidene, 4-butylaniline (MBBA) on a glass surface treated with fatty amines of different alkyl chain length. It was argued that when the solid surface-tension, γ_s, is higher than $\gamma_{CL}^{\parallel}$ a parallel orientation is observed whereas the LC molecules are oriented perpendicularly to the solid surface if γ_s is lower than $\gamma_{CL}^{\perp}$.[4] For intermediate values a tilted orientation is predicted. Porte's results are relative to MBBA whose surface anisotropy $\Delta\gamma = \gamma_{CL}^{\parallel} - \gamma_{CL}^{\perp}$ is positive (*i.e.* $\gamma_{CL}^{\parallel} > \gamma_{CL}^{\perp}$). It has been recently proposed[5] that in the case of LCs of negative surface tension anisotropy the above conclusions would be reversed.

The verification of both Porte's and Warenghem's hypothesis lacks experimental values. We will define the LC surface tension anisotropy and after discussion of the experimental measurements of LC surface tension, present the first values of LC surface tension anisotropy obtained by direct measurements. The concept of surface tension anisotropy is easily extended to other polar molecules.

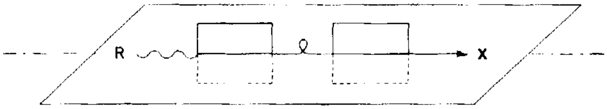


FIGURE 1 A schematic representation of a liquid crystal molecule. At least two organic rings are bound together and bear at one end an alkyl chain and at the other end a polar group. In general the molecule has only one symmetry plane.

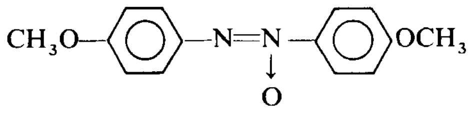
1) Liquid crystal surface tension anisotropy

The orientation of molecules in the nematic phase leads to an anisotropy of the surface tension which has been calculated in the case of non polar molecules.[6] The result is expressed as a function of the isotropic surface tension γ_{iso} and the order parameter $S = \frac{1}{3}(\cos^2\alpha - 1)$ where α is the mean angular variation of the LC molecules relative to $\vec{n}$, by equations (1) and (2)†

$$\gamma_\perp = \gamma_{\text{iso}}\left(1 + S + \frac{S^2}{4}\right) \tag{1}$$

$$\gamma_\parallel = \gamma_{\text{iso}}\left(1 - \frac{2S}{3} + \frac{43}{96}S^2\right) \tag{2}$$

A typical LC has[7] $\gamma_{\text{iso}} \sim 30$ m Jm^{-2} and $S = 0.6$ which yields $\gamma_\perp \sim 48$ m Jm^{-2}, $\gamma_\parallel \sim 18$ m Jm^{-2} and a negative value of the LC surface tension anisotropy: $\Delta\gamma = 0.89\,\gamma_{\text{iso}} \sim 27$ m Jm^{-2}. The calculation applies to non polar molecules such as para-azoxy-anisole (PAA) with the formula:



which is symmetrical and slightly polar. For PAA, $\gamma_{\text{CL}}^{\parallel}$ is effectively lower than $\gamma_{\text{CL}}^{\perp}$ as shown by its orientation parallel to the free surface.[8]

In general LC molecules are polar and all commercial LC mixtures designed for display applications (which are electrically operated) use highly polar compounds in which the polar substituent of Fig. 1 is a cyano group while the alkyl chain bears more than four methylene groups. One conceives that the molecules can take three orientations at an interface either parallel or with its polar group outward or with the alkyl chain outward as shown in Fig. 2. As molecular groups have independent contributions to the surface tension,[2] the presence of three different molecular entities at the surface due to the three orientations

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† We give the Gannon's equation, as the original work of J. D. Parsons, *J. Phys.* **37**, 1187–1195 (1976) contained a mistake.

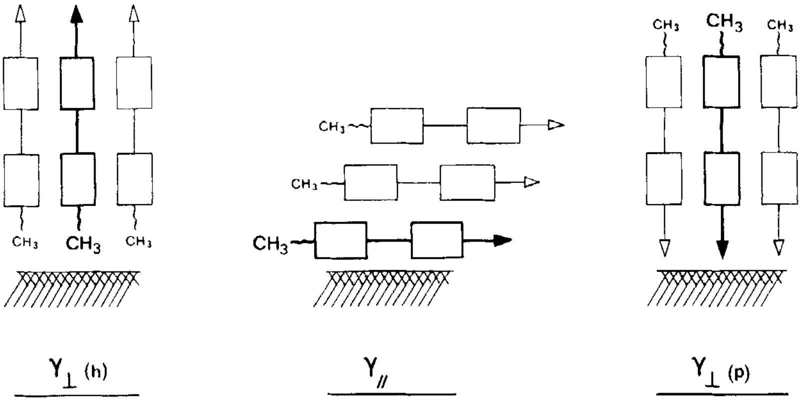

FIGURE 2 Surface tension of liquid crystal molecules may have three different values as the molecules have different orientations at the interface.

of the LCs results in three surface tension values that we denote $\gamma^{\parallel}$, $\gamma^{\perp}_{(p)}$ (p for polar) and $\gamma^{\perp}_{(h)}$ (h for hydrocarbon), respectively.

From the values known for organic compounds[1] one will expect for $\gamma^{\perp}_{(p)}$ a value over 100 m Jm^{-2} as in the case of OH groups, for $\gamma^{\perp}_{(h)}$ the usual hydrocarbon value of 25 m Jm^{-2} and for $\gamma^{\parallel}$, a value somewhat higher than the isotropic value of such molecules (about 40 m Jm^{-2}). Therefore the surface tension anisotropy $\Delta\gamma$ may be either positive or negative. Some LC molecules contain the same substituents at both ends (as PAA), and will have only one $\gamma^{\perp}$ value either $\gamma^{\perp}_{(p)}$ if both substituents are polar or $\gamma^{\perp}_{(h)}$ if both are alkyl chains. We suggest that LC anisotropy results from either the nematic order (non polar molecules) or from the orientation of the end groups at the free surface. In the latter case the molecular orientation normal to the surface homeotropic with the alkyl chain pointing outward has the lower surface energy $\gamma^{(h)}_{\mathrm{CL}}$.

2) Measurement of the surface tension of liquid crystals

There are many experimental methods to obtain the surface tension of isotropic liquids (see Ref. 1). These have been applied to liquid crystals in both their isotropic and nematic state, in the latter case the interfacial orientation has to be taken into account. Whereas with the hanging drop method the surface orientation is ill-defined, Wilhelmy or the du Nouy methods relate to the ordered free surface. At the free surface, liquids orient in such a way as to have the lower surface energy. For

LCs this will be in a direction perpendicular to the free surface with the alkyl chain pointing outward.

All cyano-biphenyls LCs have such an orientation with a surface tension between 26 and 29 m Jm^{-2}. This has been observed for the pentyl cyanobiphenyls[6] and octyl cyano-biphenyl[9] derivatives. We have checked it for many 4-alkyl and 4-alkoxy, 4-cyano-biphenyls (Table I).

Then the value of the surface tension obtained by a detachment method is that corresponding to the orientation at the free surface. With most

TABLE I
Orientation of Liquid Crystals at the free surface as determined by conoscopic observation of a suspended film of LC. M_p: Melting Point; T_{NI}: Nematic to isotropic transition temperature

Code	Name	*n*	M_p°C	T_{NI}°C
Single compounds				
K15	Pentyl-Cyano-Biphenyl	Per	23	35
K18	Hexyl-Cyano-Biphenyl	Per	14.5	29.4
K24	Octyl-Cyano-Biphenyl	Per	21.5	40.5
K30	Decyl-Cyano-Biphenyl	Per	44	50.5
K33	Undecyl-Cyano-Biphenyl	Per†	53	57.5
K36	Dodecyl-Cyano-Biphenyl	Per†	48	58.5
M12	Butyloxy-Cyano-Biphenyl	Per†	78	75.5
M15	Pentyloxy-Cyano-Biphenyl	Per†	53.5	67.5
M18	Hexyloxy-Cyano-Biphenyl	Per†	57	75.5
M21	Heptyloxy-Cyano-Biphenyl	Per†	54.7	74
M24	Octyloxy-Cyano-Biphenyl	Per†	55	80
M30	Decyloxy-Cyano-Biphenyl	Per†	59.5	84
M36	Dodecyloxy-Cyano-Biphenyl	Per†	71.5	87.5
S1185	Pentyl-Cyano-Bicyclohexyl	Per	62	85
S1186	Heptyl-Cyano-Bicyclohexyl	Per†	71	83
S1222	Propylcyclohexyl-Benzoic acid-Propylphenyl ester	Per	89	186
S1476	Propylcyclohexyl-Ethoxybenzene	Par	41	37
S1477	Propylcyclohexyl-Butoxybenzene	Par	36	32
S1014	2-Cyano-Heptylphenyl Pentyl-Biphenyl-Carboxylate	Par	47	102
S1461	Propyl 2-Cyanophenyl-Propyl cyclohexyl-Benzoate	Par	56	113
PAA	P Azoxyanisol	Par	116	134
Mixtures				
ALN51	Mixture of Alkyl Penyl Cyclohexane	Per	20	81·3
Zli1275	Mixture of Esters	Per	00	80
Zli1132	Mixture of Cyanophenyl Cyclohexane	Per	−6	70
E7	Mixture of Cyanobiphenyls	Per	−10	59.8
E8	Mixture of Cyanobiphenyls		−12	70.5

† The dagger indicates a slight angle to the normal.

of the commercial compounds made for display application, this will be $\gamma_{\mathrm{CL}}^{\perp}(h)$. As LCs shear at a distance from the surface[10] the initial orientation on the plate (or the ring) has no importance. In the shear plane the molecular orientation is that of the free surface. Knowing the surface tension of a liquid γ_L, the surface tension γ_S of a solid substrate may be calculated from the value of the contact angle, θ, of a drop of that liquid deposited on the solid surface by the equation of state[11]

$$\cos\theta = \frac{\gamma_L + (0.015\,\gamma_S - 2.00)\sqrt{(\gamma_S + \gamma_L)^{\frac{1}{2}}}}{\gamma_L(0.015\,\sqrt{(\gamma_S\gamma_L)^{\frac{1}{2}}} - 1)} \tag{3}$$

These values have been tabulated.[12] We have used that table to obtain γ_{CL} from the γ_S value experimentally determined. We have, already, seen that practical LCs orient normally to the free surface. As liquid crystals orient parallel to solid surfaces which have a critical surface tension γ_c higher than that of the LC[4] they lie parallel to most surfaces.[7] In a drop of LC deposited on a solid surface of surface tension above 29 m Jm^{-2}, the molecules at the free surface are oriented normal to

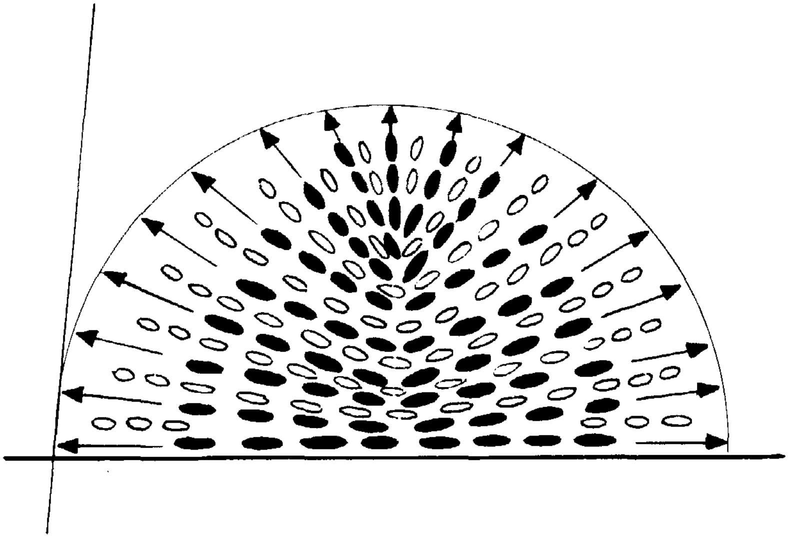

FIGURE 3 In a drop of a polar liquid crystal which orients normally to the free surface and parallel to the solid surface there is no elastic deformation at the point of contact of the three phases.

that surface while those at the solid LC interface lie in the solid surface plane (Fig. 3) and there is no elastic deformation at the point of contact of the three (Air, LC Solid) phases (Fig. 3). Then the value of $\gamma_{CL}^{\parallel}$ which is obtained through equation (3) will be γ_{CL}. The preceeding considerations allow the determination of the experimental conditions for the measurements of LCs surface tension anisotropy that we may summarise as follows:

1) determine the free surface orientation

2) measure the lower surface tension by a detachment (Wilhemy or du Nouy) method—this generally gives $\gamma_{CL}^{\parallel}$ (*h*).

3) Measure the contact angle on a known surface which gives generally γ_{CL}. The values of the dispersive and polar components of γ_{CL} will, as usual, be obtained on a polar surface of known polar and dispersive contribution to the surface tension.[13] We have not been able to get the $\gamma_{CL}^{\perp}$ (*p*) value. This should be obtainable by a two liquid method[14] where a second polar liquid would orient the poar end of the LC at the interface.

3) Anisotropy of some LC surface free energies obtained by direct (surface tension) and indirect (contact angle) measurements

3.1. *Orientation at the free surface.* Thin films of liquid crystals are suspended in a hole 0.5 mm in diameter drilled in a 10 μm thick Mylar film which is supported on a ring made of brass 1 cm large. The orientation of the film is observed by a conoscopic method.[15] An homeotropic orientation is indicated by the presence of a Maltese cross. Among all the 27 single compounds studied (Table I) only 5 do not align

TABLE II

Values of surface tension of LCs measured by the Du Nouy ring method. The liquid crystals studied orient perpendicular to the free surface, *i.e.*, $\gamma_{CL} = \gamma_{CL}^{\perp}$

LC	γ (m Jm^{-2})	LC	γ (m Jm^{-2})
E7	32.2 (22°C) 29.3	Zli 1275	26.7 (19°C)
E8	27.9 (19°C) 30.6	Zli 1132	29.30 (22°C) 31 ± 05
K15	29 (20°C)(1)	ALN 51	26.9 (22°C)
K24	26 (41°C)(1)		

(1) values equal to those of Gannon.

perpendicular to the free surface and consequently have $\Delta\gamma = \gamma^{\parallel}_{\mathrm{CL}} - \gamma^{\perp}_{\mathrm{CL}} < 0$. Beside PAA, two bear a polar substituent in the direction perpendicular to the molecular axis and two are non polar compounds. Mixtures orient as their components.

3.2 *Surface tension measurements of Liquid Crystals.* For all the LCs orienting normal to the free surface, the du Nouy ring method gives $\gamma^{\perp}$ (h). The values measured by this method on a "Kruss" tensiometer† with electronic correction for the liquid meniscus below the ring, are reported in Table 2.

3.3 *Measurement of the contact angle of LCs on solid surfaces.*

3.3a) Characterisation of some surfaces of reference.

We consider some flat surfaces as: toughened glass, cast paraffin wax, paraffin wax spread on a flat glass and polyethylene‡ film cast between two flat glasses one of which was removed afterwards. We obtained the value of the surface tension from equation (3) with the contact angle values of water, formamide and triethylene glycol and the dispersive part of the solid surface free energy from the contact angle of methylene iodide.[16]

The polar contribution is calculated using the equations:[13]

$$W_a = \gamma_L(1 + \cos\theta) = W_a^p + W_a^d \tag{4}$$

and

$$W_a^p = 2(\gamma_L^p \gamma_S^p)^{\frac{1}{2}}$$

from the measured contact angle values for liquids of known surface tension. The corresponding values for the surface free energy of our reference samples are gathered in Table 3.

3.3b) Contact angle of 4-pentyl, 4′-cyanobiphenyl (K15).

The liquid crystal K15 aligns perpendicularly to the paraffin and polymethyl siloxane surfaces. Observation of a film enclosed between two plates with polarized light shows no variation as the cell rotates. On

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† A. Kruss D 2000 Hambourg 60, Postfach 60265.

‡ Abifor 1200 $T = 65$, $p = 0.91$. Billeter Kunstoff pulver A.G. 8033 Zürich.

TABLE III
Surface energies of reference surfaces

Surface	γ_s m Jm^{-2}	γ_s^d(CH$_2$I$_2$) m Jm^{-2}	γ_s^p m Jm^{-2}
Paraffin wax cast	23.8 ± 0.3	23.5 – 24.1	0
Paraffin spread over glass	26.5 ± 1	25.6 – 27.4	0
Polyethylene (low density)	32 ± 1	32 ± 1	0
Toughened glass	36	31 ± 0.5	5.4 ± 0.3†
Silicone 991 (Polymethylphenylsiloxane)	29	27 ± 3	4.4 ± 0.3‡

† From the contact angle of different solvent one obtains: Water 5.7, Formamide 5.1, Triethylene glycol 5.08 m Jm^{-2}.

‡ There is a distinct polar contribution as seen from the contact angle of pyridine.

glass and polyethylene the alignment of the LC molecules is parallel to the walls. That may be seen by visual inspection, in polarized light, of a K15 film enclosed between a P.E. coated glass and a plate covered with polyimide and rubbed (the latter is known to induce uniform alignment parallel to the substrate). The contact angle of a drop of K15 on the P.E. coated glass is $\theta = 32 \pm 1°$ (average of seven drops). From Neumann's table one obtains for $\theta = 32 \pm 1°$ and $\gamma_s = 32$ m Jm^{-2} the surface tension of K15 in its parallel orientation: $\gamma^{\|} = 37.5 \pm 1.5$. As polyethylene gives only dispersive interactions the value obtained is $\gamma_{\mathrm{CL}}^{d\|}$.

The energy of adhesion $\gamma_L\,(1 + \cos\theta)$ is nearly equal to the geometric mean $(\gamma_S\gamma_L)^{\frac{1}{2}}$ confirming that the LC interactions are exclusively dispersive. On glass the contact angle value $\theta = 13 \pm 1$ (average of seven drops) confirms the very weak polar interactions of cyanobiphenyls and the glass surface. The corresponding energy of adhesion is $W_a = 74$ m Jm^{-2}. The glass plates we used have a dispersive component of their surface energy equal to that of polyethylene, then $W_a^d = 69.3$ m Jm^{-2}. The difference $W_a - W_a^d$ may be attributed to polar interactions which correspond to a polar component of the liquid crystal tension $\gamma_{\mathrm{CL}}^{P\|} = 4$ m Jm^{-2}. In conclusion, the liquid crystal K15 has in is parallel orientation at 25°C a surface tension

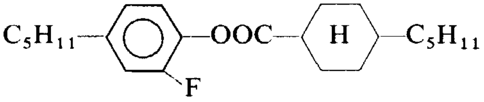
$$\gamma_{\mathrm{CL}}^{\|} = 41.5 \text{ m Jm}^{-2}$$

the part due to dispersive interactions is $\gamma_{\mathrm{CL}}^{\|;d} = 37.5 \pm 1.5$ m Jm^{-2} and the polar interactions amount to $\gamma_{\mathrm{CL}}^{\|;P} = 4$ m Jm^{-2}. These values are comparable to those obtained by Proust[21] who found $\gamma^d = 40$ m Jm^{-2} and $\gamma^P = 0$. Taking in account the value $\gamma_L^{\perp} = 29$ m Jm^{-2} of Table II, the surface tension anisotropy of K15 is found at 25°C:

$$\Delta\gamma = 12 \pm 2.5 \text{ m Jm}^{-2}$$

3.3.c) Contact angle of 2-fluoro, 4-n-pentylphenyl, trans 4-pentylcyclohexane carboxylate.†

The title compound (2F ester)



does not easily align uniformly and homeotropically on glass plates treated with either D.M.O.A.P.‡ or Lecithin‡; better orientation is observed on glass plates treated with chromium stearate complexes.‡[17]

The molecular alignment at the free surface is homeotropic. The surface tension measured by the Nouy-ring method is $\gamma_L = \gamma_L^{\perp}(h) = 24.5$ at 27°C.

The LC aligns perpendicularly to the paraffin surface ($\gamma_S =$ 25 m Jm^{-2}) and parallel to polyethylene ($\gamma_S = 33 \pm 3$ m Jm^{-2}). Contact angle over glass is higher ($\theta = 18.7 \pm 3°$) than over polyethylene ($\theta = 9.5 \pm 3°$), indicating the absence of polar interactions between glass and LC, *i.e.*, $\gamma_L \sim \gamma_L^d$.

From the contact angle over polyethylene one gets,

$$\gamma_L \sim 33.7 \text{ m Jm}^{-2}$$

which results in a surface tension anisotropy,

$$\Delta\gamma = 9 \text{ m Jm}^{-2}.$$

The particular behaviour of that compound cannot be interpreted from its surface tension properties. The difficulties of obtaining a uniform alignment results, probably, due to the shorter-range effects through the nematic medium which are observed with LCs of low permittivity or of negative dielectric anisotropy.[18]

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† Kindly supplied by I. C. Sage from B.D.H. Chemicals Ltd, Broom Road, U.K. Poole BH12 4NN.

‡ For information concerning these products and their use see J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl. 1*, 1982.

3.3.d) Mixtures of liquid crystals.

It is not certain that the above procedure may be applied to mixtures, as some compounds may segregate at the surface. The following values are tentative but illustrate the procedure. On alkylphenylcyclohexane mixture, ALN 51, which orients near the surfaces, as K15 does, the experimental results are:

$$\gamma^{\|} = 33.8 \pm 2 \text{ m Jm}^{-2} \quad \text{and} \quad \gamma^{\perp} = 26.9 \text{ m Jm}^{-2}$$

The commercial mixture of dialkylphenyl-benzoate, Zli 1275, which orients parallel to both P.E. and paraffin wax, has $\gamma^{\|} = 32.5\ 2.5$ m Jm^{-2} and $\gamma^{\perp} = 26.7$ m Jm^{-2}. In light of the preceeding discussion, one understands the reason for the wide discrepancies between the experimental values of LC surface tension found in the literature.[7] For instance, the surface tension of MBBA is found to be between 28.8 and 38. The first value[19] is obtained by the du Nouy ring method—that we consider as $\gamma^{\perp}$ while the other[20] is obtained from contact angle measurement. In our present understanding we would say $\gamma^{\perp}_{\text{MBBA}} = 28.8$, $\gamma^{\|}_{\text{MBBA}} = 36 \pm 2$. In the same fashion, the K15 surface tension was found between 29[6] and 40 m Jm^{-2}.[21]

4) CONCLUSIONS

Orientation of polar molecules at an interface is an old idea although often forgotten in modern theories of surface chemistry. In liquid crystals, the interfacial orientation extends over some ten microns and becomes visible. From known values[1] one may consider that the difference in the surface tension of a polar alkyl derivative C_nH_{2n+1}—X oriented with its alkyl chain ($\gamma^{\downarrow}$) or its polar (X) group, ($\gamma^{\uparrow}$) outwards is of the order of 100 m Jm^{-2}. The energy of water/polar organic liquid interactions shows a high excess, *i.e.*, 40 m Jm^{-2} over the calculable dispersion force interactions.[16] This is generally attributed to polar interactions as shown in equation (4). The consideration of two surface tension values $\gamma^{\uparrow}$ and $\gamma^{\downarrow}$ for the upward and downward orientation of a polar molecule would explain equally well the results. In the introduction we mentioned that a γ_{octanol} value of 130 m Jm^{-2} would account for the measured water-octanol surface energy. The values of interfacial energy given[16] for butyronitrile, dinbutylamine and octanoic acid correspond to surface energies $\gamma_{\text{butyronitrile}} = 137$ m Jm^{-2}; $\gamma_{\text{dinbutylamine}} =$

136.7 m Jm^{-2}; $\gamma_{\text{octanoic acid}} = 130$ m Jm^{-2} with an anisotropy $\Delta\gamma_c = \gamma^{\uparrow} - \gamma^{\downarrow}$ value of some 110 m Jm^{-2}.

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