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Contact Angles and Alignment of Liquid Crystals on Lecithin Monolayers

K. Hiltrop [a] & H. Stegemeyer [a]
[a] Department of Physical Chemistry, University of Paderborn, 4790, Paderborn, Germany

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CONTACT ANGLES AND ALIGNMENT OF LIQUID CRYSTALS ON LECITHIN MONOLAYERS

K. HILTROP AND H. STEGEMEYER
Department of Physical Chemistry, University of Paderborn, 4790 Paderborn, Germany

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Abstract: The mechanism of aligning liquid crystals by surface action of solid substrates was explained in literature among others by a thermodynamical model. This model claims the difference of surface energies of the solid substrate and the liquid crystal to determine the orientation of the liquid crystal. In this letter, contact angle measurements found with two different nematics on different lecithin monolayer coated substrates are reported. Decreasing area per molecule of the lecithin monolayer from 0,8 nm^2 to 0,4 nm^2 resulted in an increase of contact angle and simultaneously in a loss of homeotropic orientation, which is contradictious to the proposed thermodynamical arguments.

Much work has been done in the last few years to understand the mechanisms of aligning liquid crystals (LC) by surface action of suitably prepared solid substrates. The induction of homogenous planar alignment by micro grooves is well understood in detail[1].

To explain the homeotropic orientation of nematic LC different models have been proposed. Particularly, thermodynamical and sterical arguments were used[2,3]. The thermodynamical treatment of the problem was simplified by Creagh and Kmetz[3], who claimed the orientation of a given LC on a given solid substrate to be determined by the surface energy γ_L of the LC and the critical surface energy γ_C of the solid[4]. In detail they assumed the difference of surface energies

$$\Delta\gamma \equiv \gamma_L - \gamma_C \qquad (1)$$

to be characteristic for the kind of orientation:

$$\Delta\gamma > 0 \rightarrow \text{homeotropic alignment} \qquad (2)$$

$$\Delta\gamma < 0 \rightarrow \text{planar alignment} \qquad (3)$$

In a later paper[5] these ideas were extended to the assumption, that the strength of anchoring should increase with increasing absolute value $|\Delta\gamma|$. The authors[3] reported experimental data with 4'-methoxybenzylidene--4-butylaniline (MBBA) on very clean as well as on lecithin coated glass plates which fulfilled condition (2).

The predicting power of the relative surface energies was contradicted experimentally by Haller[6]. In our own experimental work on the mechanism of homeotropic alignment[7], we found contradictions to the general thermodynamical statements, too. As shown in detail[7] in a recent paper the orientation of a LC on a solid substrate coated with an amphiphilic monolayer strongly depends on the following parameters:

1. Molecular structure of the amphiphilic molecule
2. Molecular structure of the LC molecule
3. Packing density of the amphiphilic monolayer
4. Temperature of the system LC/substrate

Keeping the molecular structures (par. 1 and 2) as well as the temperature (par. 4) constant we found the following result by polarizing microscopy: The orienting power of all examined amphiphilic films decreases with increasing packing density A^{-1} in a range of $A \sim 0{,}6\ \mathrm{nm}^2$ per amphiphilic molecule to $A \sim 0{,}4\ \mathrm{nm}^2$ per molecule[7]. (Remember that the cross section of one dialkyl-lecithin molecule amounts to about $0{,}4\ \mathrm{nm}^2$). Additionally to polarizing microscopy we measured contact angles of nematics on coated solid surfaces. (Contact Angle Meter Erma, Tokyo). The nematic LCs used were MBBA and 4-n-pentyl-(4-cyanophenyl)-cyclohexane (PCH 5). As amphiphilic compounds we used DL-γ-palmitoyl-lyso-lecithin and DL-β,γ-dilauroyl-α-lecithin but the results are very similar for several other lecithins. We observed a great difference between the contact angles of advancing and receding drops. The results given in fig. 1 and 2 refer to advancing drops. Generally, it has been found the contact angle not to depend on temperature in the region of $25^\circ C$ to $50^\circ C$ within the accuracy of the angle measurement of $\pm 1^\circ$. Anyway the temperature was constant for all measurements with MBBA and PCH 5 within $\pm 0{,}2^\circ C$.

The diagrams show that the contact angle θ decreases with increasing area per molecule A. Thus from the Young-Dupré-equation[8]

$$W_{ad} = \gamma_L(\cos\theta + 1) \qquad (4)$$

the work of adhesion W_{ad} is derived to increase with increasing area per amphiphilic molecule. The critical surface energy γ_C may be assumed to increase with the work of adhesion W_{ad} if the LC surface energy γ_L is kept constant. We conclude the value of $\Delta\gamma$ (1) to increase with decreasing area per molecule that means with increasing packing density. Following condition (2) the homeotropic alignment should become stronger with increasing packing density; our experiments give just the opposite result. Exceeding a characteristic packing density the value of which depends strongly on the structure of the amphiphilic[7], the homeotropic orientation is distorted or vanishes completely. Therefore, the value of $\Delta\gamma$ does not characterize the orientation of a LC on a solid substrate universally. Possibly, the thermodynamical effects are superposed and overcompensated by other mechanisms, e.g. a sterical one which we believe to be the dominant orienting mechanism of amphiphilic compounds such as lecithin[7].

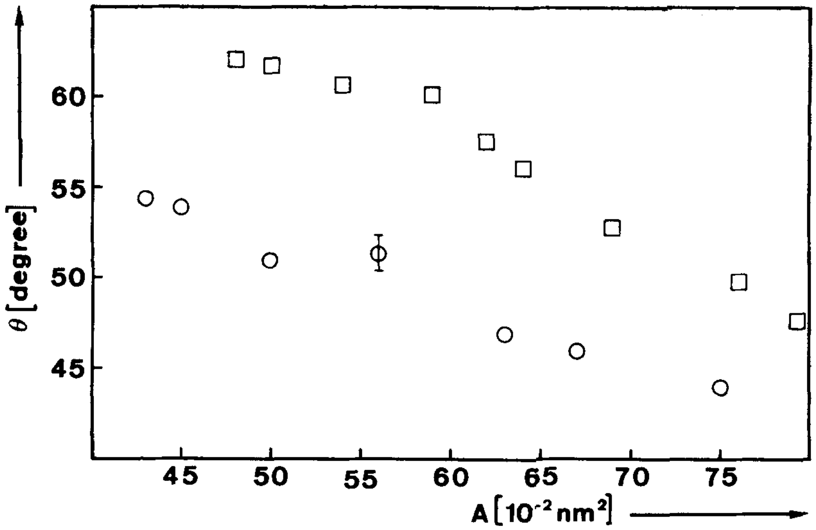

Fig.1: 4'-methoxybenzylidene-4-butylaniline (MBBA)

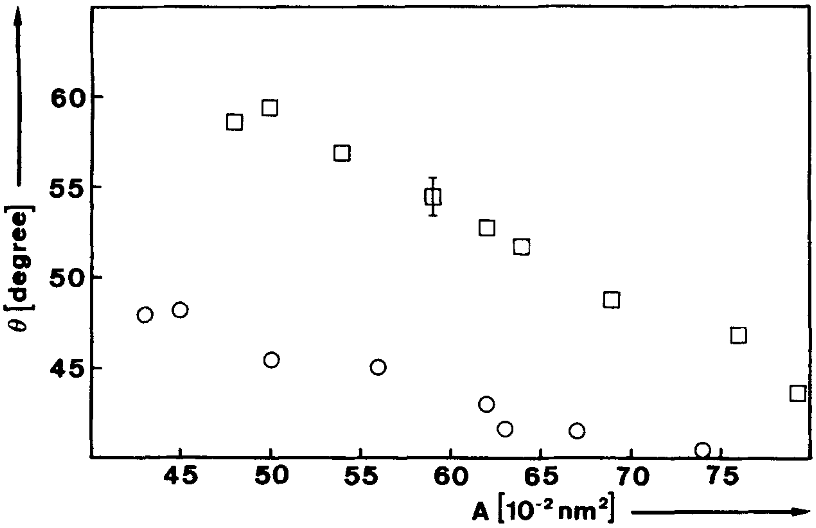

Fig.2: 4-n-pentyl-(4-cyanophenyl)-cyclohexane (PCH 5)

Fig.1 and 2: Contact angle θ of LC drops on lecithin coated glass plates versus area A per lecithin molecule, T = 35 °C

□ DL-β,γ-dilauroyl-α-lecithin

○ DL-γ-palmitoyl-lyso-α-lecithin

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