

Chapter 3

INTERFACE ROUGHNESS AND ORDERING IN ULTRATHIN LIQUID CRYSTAL FILMS

3.1 Introduction

In Chapter 2, we described our studies on monolayer and multilayer films of 8CB at the air-water interface. Using reflection and polarising microscopy, we were able to determine the phases of the D_2 and D_3 domains. We can also probe the ordering of the LE phase and the D_1 domains using X-ray reflectivity. For this, we transferred the films onto a glass substrate using a new transfer technique where the substrate is placed horizontally. It must be remarked that there already existed in the literature another transfer technique [1] where the substrate is kept horizontally. It is important to stress that the study of ultrathin films of organic molecules is gaining importance because of their applications [2] in optical and opto-electronic devices, biosensors, lubricants etc. Langmuir Blodgett (LB) films are suitable model systems for studies of ultrathin organic films at solid - gas interfaces because their thickness can be precisely controlled and their properties can be changed by chemical engineering. Such studies become even more important for films made of liquid crystal forming compounds. In this case, an understanding of the surface roughness, structure and ordering of the films has a bearing on liquid crystal science and technology.

In the previous studies [3, 4, 5, 6] of thin liquid crystal films on solid substrates, the films were prepared on the substrate by conventional techniques like spin coating, surface treatment, vapour deposition etc, which may not preserve the liquid crystalline order. On the other hand, our technique preserves the order, as indicated by our microscopy studies.

In these films, the absorbate (8CB) – substrate (glass) interaction is through an intermediate absorbate – water interaction which involves hydrophobic forces. This makes the study of the roughness and ordering of these films interesting. In this chapter, we describe our X - ray studies on these transferred films.

3.2 Experimental Techniques

3.2.1 Formation of the Films

Here we describe the technique used by us to transfer the monolayer onto the glass substrate. All the transfers were performed at room temperature. The glass substrates used were 4cm by 5cm glass rectangles cut out of float glass. They were cleaned with a detergent and then left overnight in chromic acid. They were washed repeatedly with millipore water and then with N/10 sodium hydroxide solution to remove all traces of the acid.

The monolayer transferring was done on a specially designed Langmuir trough. A schematic diagram of the trough is shown in Fig 3.1. The trough used here was deeper (9 mm) than the one used in studies described in the previous Chapter. The trough walls had a step at a depth of 4 mm. We used two barriers which could be moved on this step. The two barriers were used for symmetric compression of the monolayer. The substrate was placed under water on glass supports of length 5mm, to ensure that the upper surface of the substrate was at a level higher than the lower end of the barriers. The monolayer was spread at the interface between the two barriers in the usual manner and allowed to stabilise for 15 minutes. Then the monolayer was compressed very slowly (compression rate $\sim 0.01 \text{ \AA}^2$ per molecule per sec) to obtain either a monolayer in the LE phase, a film almost

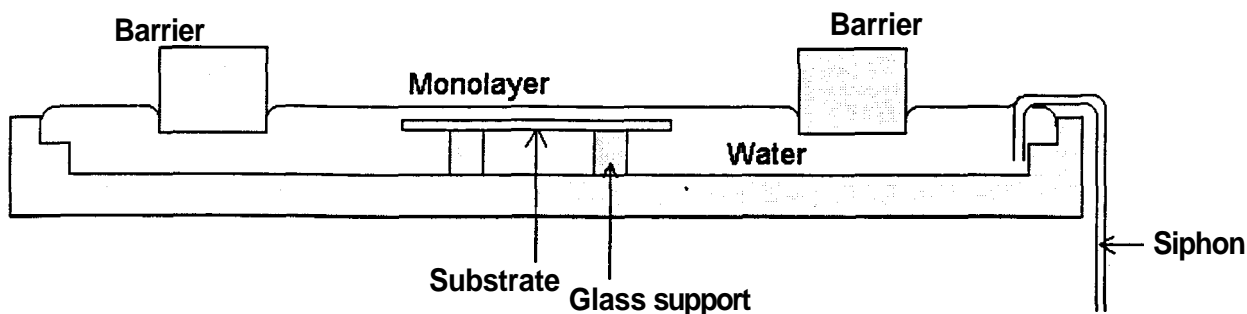


Figure 3.1 A schematic diagram of the experimental setup used to transfer the films on glass substrates.

wholly consisting of D_1 domains or a film with co-existing LE phase, D_1 and D_2 domains. The monolayer was compressed slowly to allow for the growth of large D_1 and D_2 domains. The points on the $\pi - A_c$ isotherms where the transfer was carried out are shown in Fig 3.2 by arrows. The location on the isotherm was determined by monitoring A_c , which in turn yielded π , and also by observing under the fluorescence and reflection microscopes.

The water was removed from the trough drop by drop using a narrow glass siphon. The removal of water lowered the air - water interface very slowly. This facilitated the transfer of the film onto the substrate (Fig 3.1). Faithful transfer was confirmed by observing the films on the glass substrate under fluorescence and polarising microscopes. Also, we could actually observe the whole process of transfer under the microscope. We found that factors like slight vibrations of the film at the air-water interface, contamination of the glass plate, non - horizontal placement of the substrate etc. resulted in deformation of the surface topography of the transferred film.

We used this transfer technique in preference to the conventional Langmuir Blodgett (LB) technique due to the following reason. The D_1 and D_2 domains,

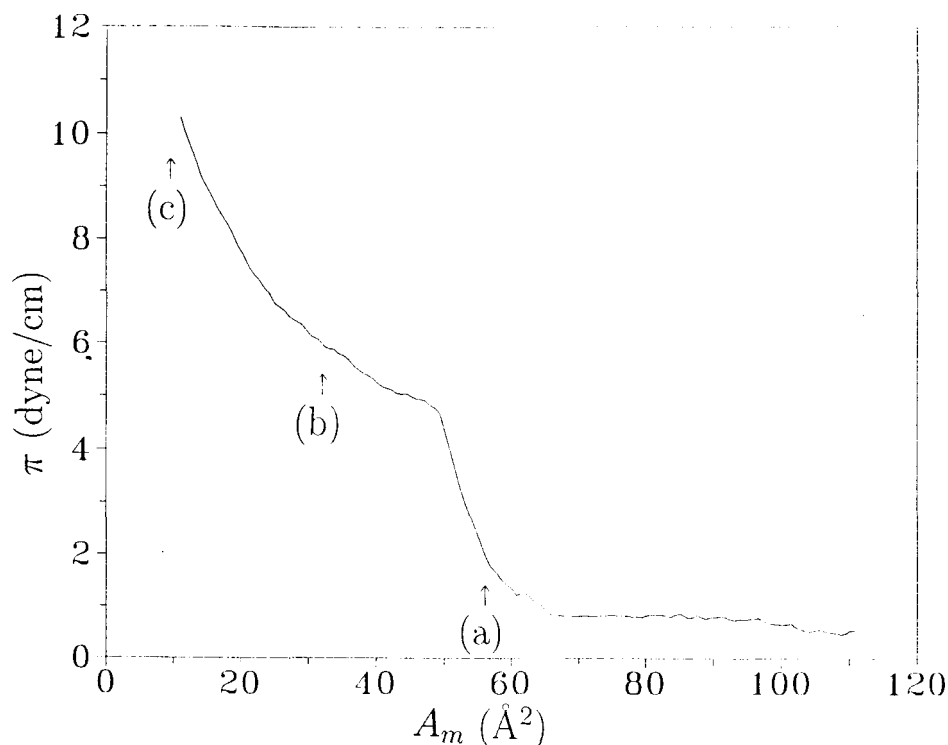


Figure 3.2 A $\pi - A_m$ isotherm of 8CB at 25°C showing the points at which the transfer was carried out. (a) monolayer film, (b) 3 layer (D_1) film and (c) multilayer (D_2) film.

which we were interested in studying, are 3D structures. Hence they are likely to be destroyed during LB transfer, since in this process, the monolayer is curved at the point of transfer. There may also be distortion due to action of gravity. In our technique, the films remained in a horizontal position, so such possibilities were minimised. Moreover, this technique is extremely simple and could be done easily on home made equipment, without resorting to sophisticated LB equipment.

In the other transfer technique [1] where again the substrate is placed horizontally, the monolayer is spread on water contained in a conical trough. The substrate is placed under water. After the monolayer has stabilised, the water is drained out through a tap at the bottom of the trough.

3.2.2 X - Ray Studies

We employed high resolution x-ray studies to investigate the ordering in these films. The measurements were carried out using the Cu-K, doublet of an 18KW

rotating anode x-ray source. (These experiments were performed at Liquid crystal Institute, Kent State university, Kent, USA in collaboration with Yushin shi and Satyendra Kumar.) A pair of Ge (111) single crystals served as monochromator and analyzer [7]. Specular and diffuse scatterings of these films were studied as a function of temperature.

X - ray specular reflection measurements were carried out on the films transferred to glass plates at various Λ_s . The points on the $\pi - A_s$ diagram where the transfers were carried out were:

a) *Monolayer film*: The monolayer was transferred in the pure LE phase. This corresponded to $\Lambda_s = 55 \text{ \AA}^2$,

b) *D₁ film*: A film consisting predominantly of D₁ domains, with co-existing LE and D₁. It was transferred at $\Lambda_s = 30 \text{ \AA}^2$,

c) *Dense D₁ film*: Three three - layer films transferred one after the other on the same substrate,

d) *Multilayer film*: A film consisting of D₂ domains with D₁ and LE phases. This was transferred at $\Lambda_s = 10 \text{ \AA}^2$, and

e) *Dense multilayer film*: Three multilayer films transferred one after the other on the same substrate.

The presence of the different phases in the film was always checked under the epifluorescence or reflection microscope.

3.3 Results

Using epifluorescence microscopy, we observed that the LE - D₁ co-existence pattern was faithfully reproduced on the transferred film. This pattern was stable over a period of a few days.

The transfer of the D₂ domains was observed both in epifluorescence and reflection. The transferred D₂ domains also showed uniform interference colours under reflection, showing that their surface topography was not disturbed. The

circular shape of the domains was retained during the transfer.

The X - ray reflectivity recordings against scattering angle are shown in Fig 3.3. We obtained the thickness of the monolayer film to be 14 Å and that of the D₁ film to be 44 Å. The fitting of the reflectivity profile for the D₁ film indicated a coverage of 60%. This was considerably higher for the dense D₁ films. This is indicated by the depth of the first minimum beyond the critical angle (Fig 3.3). The specular reflectivity of the D₁ film as a function of temperature is shown in Fig 3.4. The profile of the specular reflectivity remained the same as the film was heated from room temperature to 41°C through the smectic A, nematic and isotropic phases. The reflection characteristic of the film disappeared on heating to 51°C, and was not recovered on cooling (Fig 3.4, curve (e)).

In the multilayer film, the coverage of D₂ domains, as determined from X - ray reflectivity was less than 3%. This could be due to smearing out of the signal by different thicknesses of the D₂ domains. The specular reflectivity of dense multilayer films is given in Fig 3.5. The coverage of D₂ domains was estimated to be about 25% in this film. The intensity profiles corresponding to the D₁ structure of the D₁ domains also appeared in the smectic and nematic phases. In addition to these there was an additional Bragg peak due to the D₂ domains. On cooling the film to the crystal phase (below the smectic A phase), the reflection features of the D₁ structure were lost. The features were partially recovered on heating to the smectic A phase. The recovery improved on heating to the nematic phase, but was not complete. In order to get complete recovery, we had to heat the film to the isotropic phase.

Diffuse scattering studies (non - specular longitudinal scattering) of the films were undertaken to determine the conformality transition in D₁ films. We found that in the isotropic phase (at 41°C), the diffuse scattering had a similar profile as the specular reflectivity. In the smectic A phase (at 30°C), the profile of the diffuse scattering did not show the features of the specular reflection.

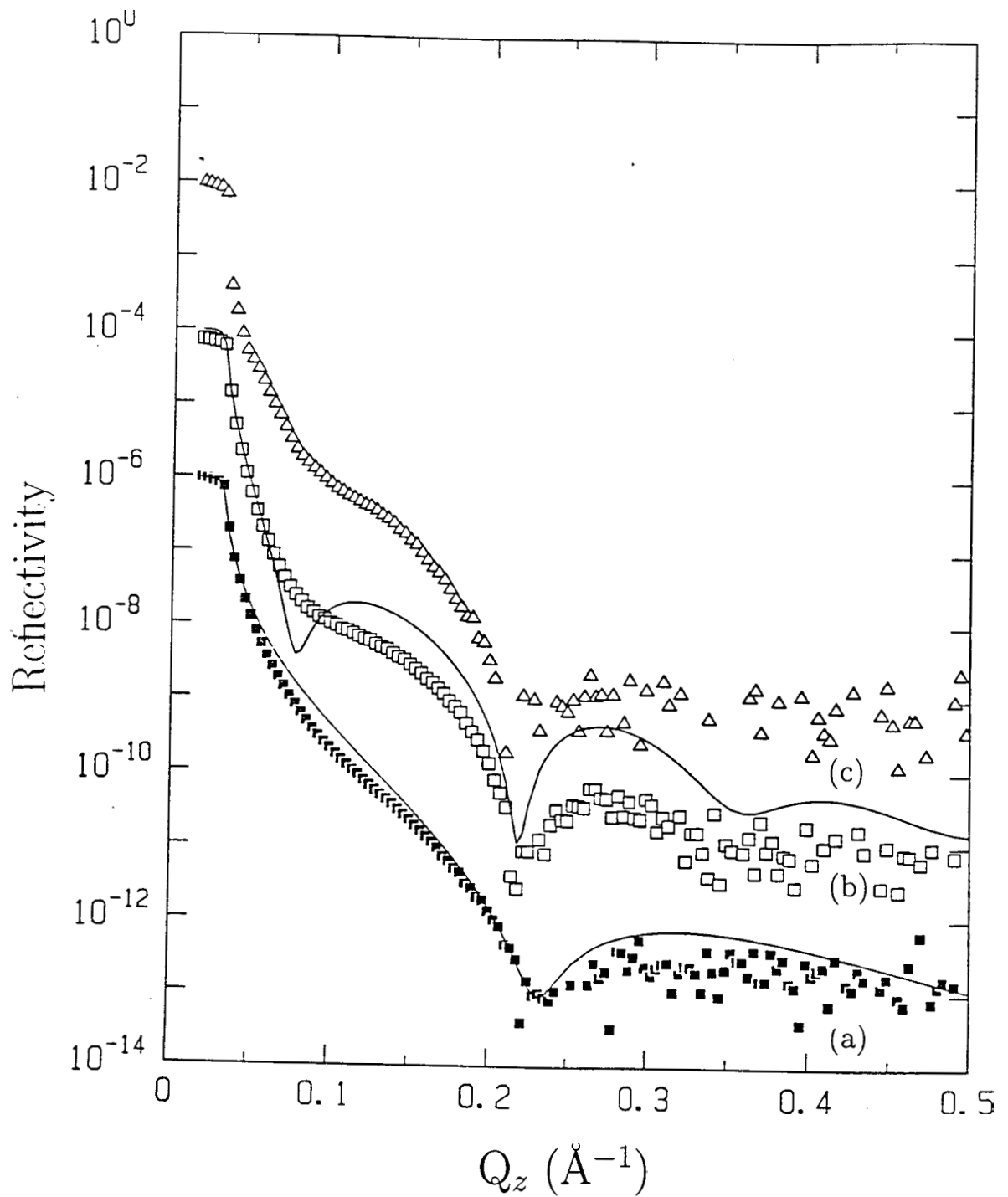


Figure 3.3 X-ray reflectivity as a function of the wave vector (Q_z) for different films at 25°C. (a) Monolayer film, (b) D_1 film and (c) dense D_1 film. The films are the actual experimental data points. The continuous lines denote the calculated reflectivity for the corresponding thicknesses.

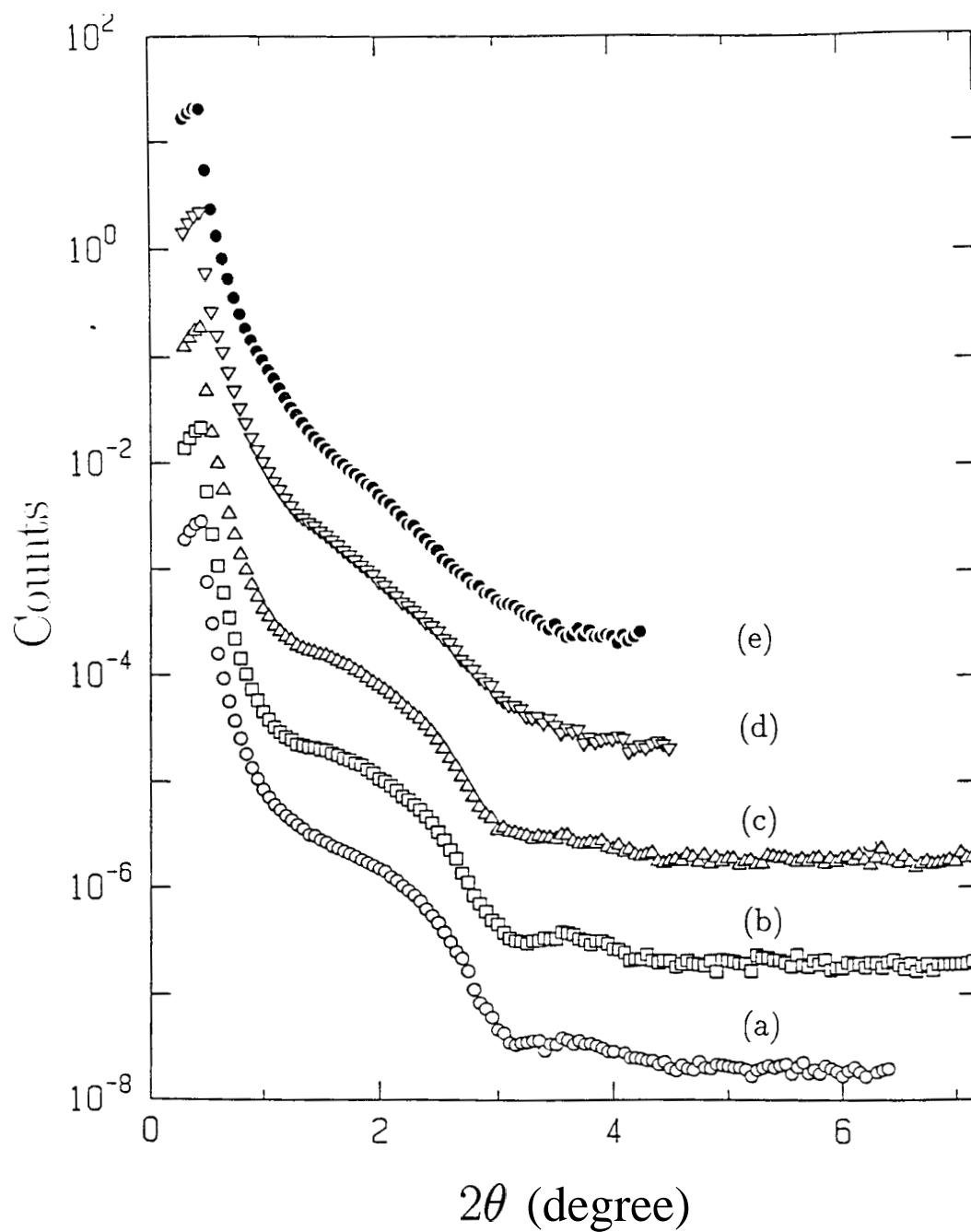


Figure 3.4 Specular reflectivity (counts) of D_1 film of 8CB as a function of Bragg angle (θ) at different temperatures. (a) 23.55°C , (b) 35.5°C , (c) 41.0°C , (d) 51.0°C and (e) 23.5°C after cooling from 51.0°C . As can be seen, the shoulder to the left disappears on heating and is not recovered on cooling.

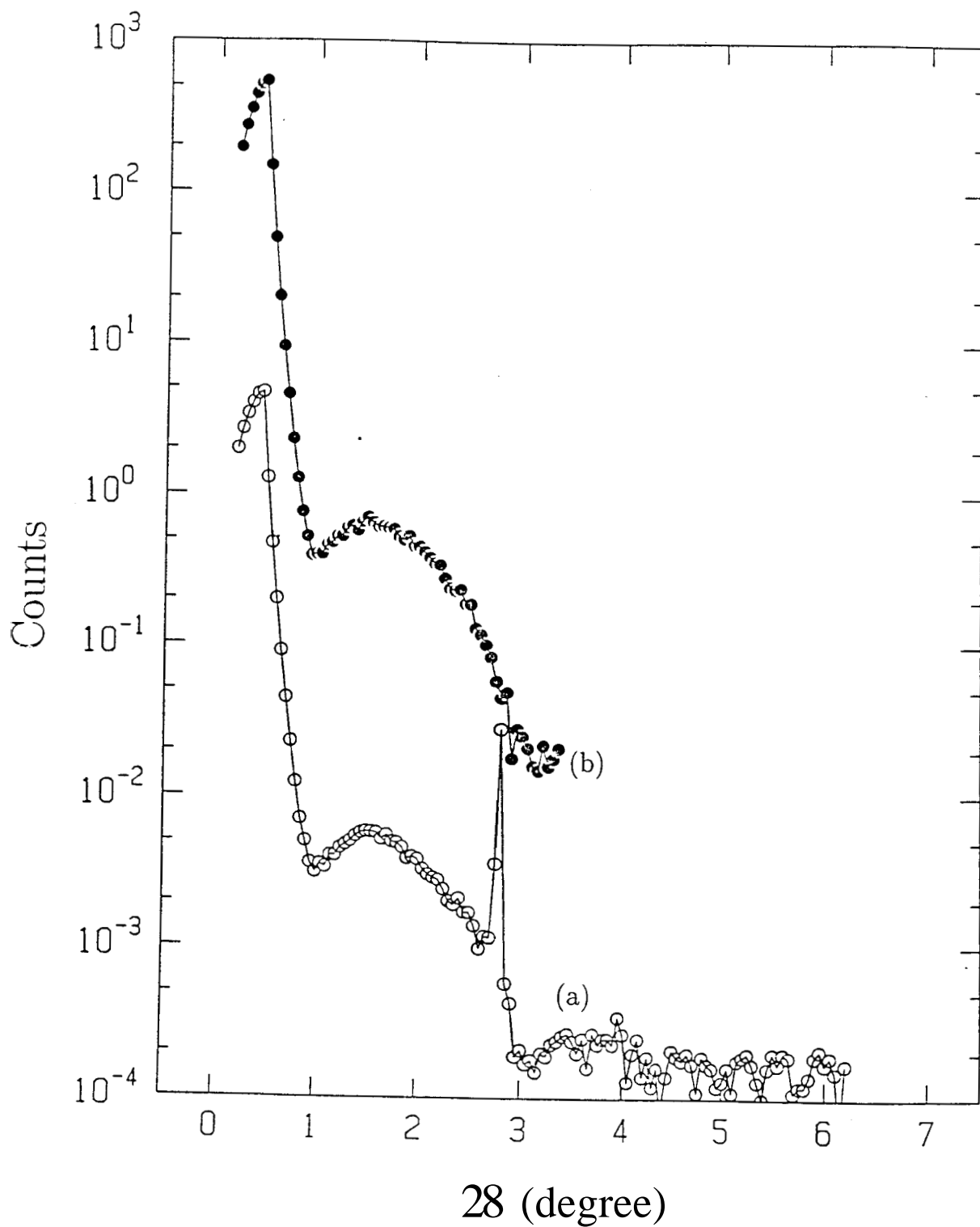


Figure 3.5 Specular reflectivity (counts) of dense multilayer film of 8CB as a function of Bragg angle (θ) at two temperatures. (a) 23.55°C and (b) 39.5°C.

3.4 Discussions

We find that the D_1 films have a thickness of 44 \AA while the monolayer has a thickness of 14 \AA . Thus the thickness of the D_1 film is almost three times that of the monolayer. This is a direct proof of the model suggested by Xue *et.al.* [8]. In a recent work, Sakamoto *et.al* [9] report that the D_1 domains on the water surface are twice as thick as the monolayer in the LE phase. Our studies indicate a much higher relative thickness for the D_1 domains. This might be the result of a change in the orientation of the molecules during transfer.

Another important result is that the reflection characteristics of the D_1 film disappear when the temperature is increased to 51°C , and are not recovered on cooling. This indicates an irreversible breakdown of the D_1 structure on heating. Riegler *et.al.* [10] have studied LB films of behenic acid. They report an irreversible breakdown of the multilayer films into islands of much higher thickness on heating. These islands are separated by areas of a bare monolayer. They attribute this phenomenon to a competition between interfacial tension and van der Waal's energy. The irreversible breaking of the D_1 structure of the 8CB film seen here may be due to a similar reason.

Another interesting observation is the disappearance of the D_1 reflection features on cooling to the solid phase. This is an indication of dewetting. The wetting of the substrate is recovered only partially on heating the substrate to the smectic A temperature. To get complete recovery, the substrate has to be heated to the isotropic temperature, when the restructuring of the D_1 film is complete.

The results from diffuse scattering experiment are interesting. In the isotropic phase, the roughness at the film - glass and air - film interfaces are conformal. On the other hand, in the smectic A phase, the conformality of the two roughnesses decreases exponentially on cooling as the crystallisation temperature is approached.

3.5 Conclusions

The D_1 and D_2 domains in the 8CB film are deposited on glass substrate by a transfer technique where the substrate is placed horizontally. The transfer preserves the order and surface topography of the domains, as confirmed by microscopic observations.

X - ray studies on the transferred films indicate that the D_1 domains are thrice as thick as the monolayer. This is a direct evidence of their **3** layer structure.

The reflection characteristic of the D_1 structure disappear irreversibly on heating the film to 51°C . This indicates a breakdown of the **3** layer structure on heating, and could be due to island formation.

The reflection features also disappear on cooling to the crystal phase. This process is reversible on heating to the isotropic temperature and is due to dewetting.

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