

Reflection–absorption FT–IR spectroscopy of vinyl octadecanoate at the air/water interface

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Abstract

Reflection–absorption Fourier transform infrared (RA FT–IR) spectra of spread monolayers of vinyl octadecanoate have been obtained for a range of surface pressures at 292 K. Unpolarised and s- and p-polarised radiation at 30° angle of incidence have been used. Results in the C–H stretching region show that even at very low surface pressures the monolayer appears to consist of condensed domains where the acyl chains are highly ordered and densely packed. At higher surface pressures the average packing density is higher, but otherwise the spectra are unaltered, showing that the acyl chains remain highly ordered with few *gauche* bonds throughout the accessible range of surface pressure (0.1 to 18 mN m⁻¹). There was no appreciable change in the spectrum when the monolayer passed through the LC to S phase transition. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fragility of floating monolayers used for water evaporation control [1,2] and of Langmuir–Blodgett films in such potential applications as sensors and microelectronic devices [3,4] could possibly be improved by the use of polymeric amphiphiles or of monomeric amphiphiles that could be polymerised in situ. There have been few studies of polymerisation in monolayers and one

important reason for this is the difficulty of detecting and measuring the polymerisation process. Changes in such physical properties as molecular area and surface viscosity can be detected in floating monolayers but their interpretation in terms of the extent of polymerisation is difficult. The problem is exacerbated by the high viscosity and non-uniformity of many polymer monolayers [5,6]. Properties that are less reliant on mechanical effects thus offer better prospects for studying polymerisation in monolayers.

This report is the first stage in such a study. Reflection–absorption infra-red (RA FT–IR) spectroscopy was used to investigate the confor-

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mation of the acyl chains in monolayers of vinyl octadecanoate (VO) at the air/water (A/W) interface as a function of the monolayer surface pressure. Qualitative information for the average molecular orientation of the hydrocarbon chain relative to the substrate normal was also obtained. However, the RA FT-IR bands arising from the polar group were largely obscured by the absorption bands of water vapour despite attempts to minimise the problem.

2. Experimental section

2.1. Materials

Vinyl octadecanoate (VO) was purchased from the Tokyo Chemical Industry Company Ltd., Tokyo, Japan. Its melting point was 36–37°C in agreement with published literature values [7]. The sample of VO was established by high resolution (400 MHz) ^{13}C NMR to be at least 99.0% pure and probably better than 99.5% pure and was therefore used without any further purification. Water for the subphase was from a Barnstead purification system and had a resistivity of $18.3 \pm 0.2 \text{ M}\Omega \text{ cm}$. The subphase pH was adjusted to 6.8 (0.75 mM potassium bicarbonate, Fisher Scientific Co., New Jersey, USA) to minimise the possibility of ester hydrolysis [8]. All experiments were performed at $292 \pm 1 \text{ K}$. The spreading solvent was *n*-hexane ('Baker analysed' HPLC grade) and the concentration of VO was 3.3 mg ml^{-1} .

2.2. Equipment

A description of the Langmuir film balance, FT-IR spectrometer and associated optical equipment has been given in a previous publication [9]. The film balance (Joyce-Loebl, Ltd.) uses a constant perimeter belt for symmetrical compression of the monolayer. Compression speeds of either 1.63 or $3.26 \text{ pm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ were used. Because of the stability of the monolayers no adjustments to the area were required during the recording of spectra.

For the IR spectra, angles of incidence of 30 and 60° (with respect to the surface normal) were used. However most experiments were performed at 30° as theoretical reflectance-absorbance calculations [10,11] predict a relatively high value of 0.002–0.003 absorbance units for the intensities of RA bands obtained with both s- and p-polarised IR radiation compared to the intensities expected at a 60° angle of incidence. Indeed the signal-to-noise ratios in the spectra at 60° angle of incidence were so poor that these spectra have not been included in this report. In all cases spectra were obtained for the region from 4000 to 800 cm^{-1} .

2.3. Treatment of data

For all spectra 1024 interferograms were coadded at 4 cm^{-1} optical resolution, except those for p-polarised IR radiation at 60° angle of incidence where 4096 scans were coadded and averaged to compensate for the very low energy throughput (i.e. low reflectivity from the surface). The coadded interferograms were apodised with a Triangular function and Fourier transformed with one level of zero filling to give data encoded at approximately 2 cm^{-1} intervals. The method of data analysis has been described in a previous publication [9].

The spectra have been plotted as absorbance ($-\log_{10}(R/R_0)$) against wavenumber ($\bar{\nu}/\text{cm}^{-1}$), where R and R_0 represent the single-beam reflectances of the film and of the aqueous substrate respectively.

3. Results

3.1. Surface pressure-molecular area isotherms

A typical surface pressure-molecular area (Π - $\hat{\text{A}}$) isotherm obtained from a monolayer of VO at the A/W interface is presented in Fig. 1. It shows that on compression the monolayer forms the liquid-condensed (LC) phase at a very low surface pressure with a rapid rise to $5.0 \pm 0.5 \text{ mN m}^{-1}$ where it undergoes a second-order phase transition to the S phase. Monolayers of VO exhibit

negligible surface pressure relaxation at all surface pressures up to 16 mN m^{-1} , but become insufficiently stable for RA FT-IR examination at higher pressures, and fracture at $22 \pm 1 \text{ mN m}^{-1}$. The isotherms obtained in expansion were identical to those obtained in compression and did not change over several cycles. There is no evidence for a liquid-expanded (LE) state.

3.2. RA FT-IR spectra in the C-H stretching region

Representative RA FT-IR spectra of the hydrocarbon stretching vibration region obtained at a 30° angle of incidence are shown in Figs. 2 and 3. They demonstrate that a high signal-to-noise ratio can be obtained even at relatively low surface pressures although it is important to recognise that the absorbance values are extremely low.

The strongest bands in these spectra occur at ≈ 2920 and 2850 cm^{-1} and originate respectively from the methylene antisymmetric and symmetric stretch vibrations, $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$. The methyl antisymmetric stretching band ($\nu_a(\text{CH}_3)$) is also visible at $\approx 2956 \text{ cm}^{-1}$ although of lesser

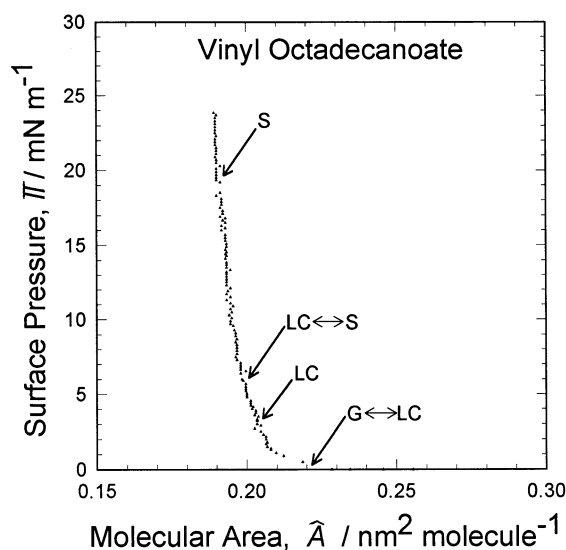


Fig. 1. Representative surface pressure-molecular area isotherm for a monolayer of VO at the A/W interface at 292 K. Compression speed: $3.26 \text{ pm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$. Labels indicate the phases and phase transitions.

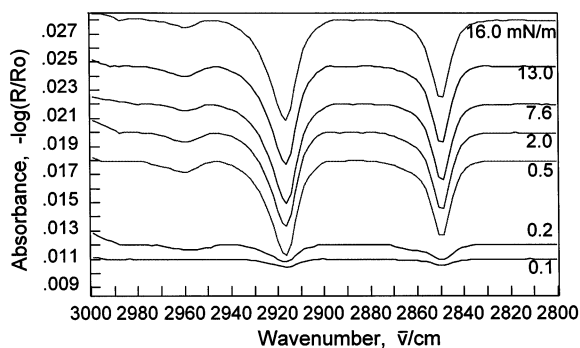


Fig. 2. Unpolarised RA FT-IR spectra in the C-H stretching vibration region for a monolayer of VO at the A/W interface at 292 K. For clarity, some spectra have been shifted on the absorbance scale. Monolayer surface pressures were as shown in the figure. Angle of incidence, 30° .

intensity. An interesting feature evident in Fig. 2 is the presence of both methylene stretching vibrations at very low monolayer surface pressures.

A small number of RA FT-IR spectra were obtained at a 60° angle of incidence, but are not presented. The methylene stretching bands are evident at $\approx 2920 \text{ cm}^{-1}$ ($\nu_a(\text{CH}_2)$) and $\approx 2850 \text{ cm}^{-1}$ ($\nu_s(\text{CH}_2)$), and the methyl antisymmetric stretching vibration ($\nu_a(\text{CH}_3)$) can also be seen in the spectra with s-polarised radiation as a very weak broad band at $\approx 2960 \text{ cm}^{-1}$. This band cannot be observed with p-polarised radiation because of the low signal-to-noise ratio.

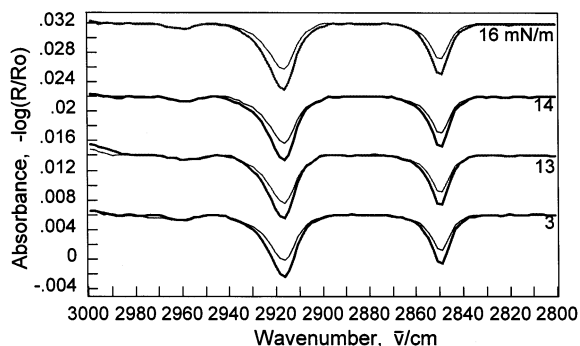


Fig. 3. Polarised RA FT-IR spectra in the C-H stretching vibration region for a monolayer of VO at the A/W interface at 292 K. Surface pressures were as shown. Angle of incidence, 30° . Heavy lines, p-polarised; light lines, s-polarised radiation.

Negative absorbance bands are usually observed in RA FT–IR spectra from floating monolayers [10,12,13]. In the present study, negative absorbance bands were mostly found, but with p-polarised radiation at a 60° angle of incidence positive absorbance peaks were observed for both $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$. Theoretical calculations predict positive absorbance bands in spectra obtained with p-polarised radiation at incidence angles above 54.73°, the Brewster angle for water [10,14].

3.3. RA FT–IR spectra in the 1900–1300-cm⁻¹ region

Spectra obtained in this region were complicated by the presence of water vapour rotation–vibration bands of sufficient intensity to preclude the identification of many of the bands from the particular subgroups within the monolayer. To minimise this problem residual water vapour bands were subtracted from the original absorbance spectrum using an appropriate reference spectrum and GRAMS/386 software. However complete subtraction of the water vapour rotation–vibration bands could not be achieved and consequently only a brief discussion of these results is given.

4. Discussion

4.1. RA FT–IR spectra in the C–H stretching region

In the 3100–2800-cm⁻¹ region, decreases in the observed peak frequencies for the conformation sensitive methylene stretching vibrations of long-chain hydrocarbon molecules have been empirically correlated with an increase in order, i.e. an increase in the relative number of *trans* conformers with a consequent reduction in the *gauche* defect concentration within the acyl chains of the monolayer [15–22]. A reduction in the number of *gauche* conformers results in a decrease in the average cross-sectional area of the acyl chains and an increase in their overall length [23]. The width of the bands has been used to obtain information on the mobility of the acyl chains [16,19,24–26].

The peak heights and integrated peak areas provide additional information about the packing density of the chains and can also be used to determine the chain orientation through the calculation of dichroic ratios from s- and p-polarised reflectance spectra [12,13,27,28].

4.1.1. Wavenumber dependence of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ on surface pressure

IR spectra from monolayers of VO reveal an approximately constant peak frequency for both methylene stretching vibrations as the monolayer is compressed from a low to a high surface pressure. This is illustrated in Fig. 4.

Values of 2917 and 2849 cm⁻¹ for the measured frequencies of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$, respectively were obtained with both unpolarised and polarised IR radiation and indicate a highly ordered all-*trans* conformation for the acyl chains. This conformation is found at surface pressures ranging from the G↔LC coexistence region (< 0.1 mN m⁻¹) up to 17 mN m⁻¹. However in the G↔LC coexistence region only the domains of LC phase are expected to contribute to the observed peak intensities as the gaseous matrix is probably too dilute to contribute.

The absence of *gauche* conformations even at very low surface pressures indicates close-packing of the acyl chains and requires the headgroup cross-sectional area to be no larger than the area of surface per chain. It follows that the vinyl group must be oriented in a direction more-or-less parallel to the chain axis. The monolayer area data (Fig. 1) also support this model. Furthermore, reflection–absorption FT–IR spectra obtained from an LB multilayer film of VO at the air–metal (A/M) interface (where the spectrum is not masked by absorption bands from water vapour) have confirmed that the vinyl group is oriented perpendicular to the substrate plane after deposition from a floating monolayer at 15.1 mN m⁻¹ [29].

4.1.2. Dependence of the peak width of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ on surface pressure

A decrease in peak width upon monolayer compression is indicative of a reduction in the rotational motion and flexibility of the methylene

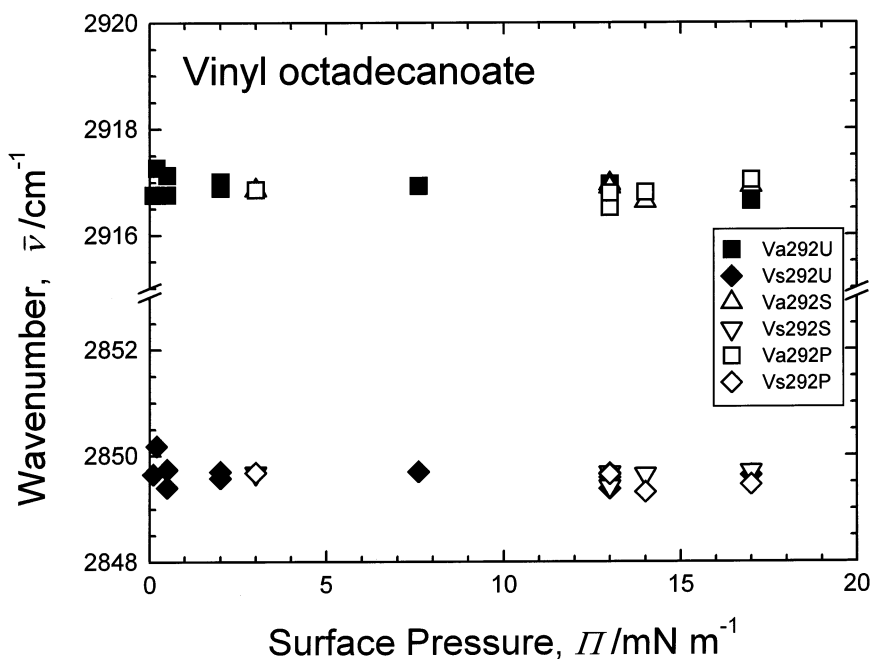


Fig. 4. Dependence of wavenumber of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ on the surface pressure of a VO monolayer at the A/W interface. Symbol codes are: Va, $\nu_a(\text{CH}_2)$; Vs, $\nu_s(\text{CH}_2)$; 292, temperature; U, unpolarised; S, s-polarised; P, p-polarised.

chain and indicates the transition to a more highly ordered, densely packed arrangement [16,19].

With the VO monolayers, values for the peak width (Fig. 5) are approximately constant at surface pressures from 0.5 to 16.0 mN m^{-1} , and indicate limited rotational motion and flexibility of the acyl chains with a reasonable expectation of similar behaviour up to the fracture pressure.

The greater widths observed for $\nu_s(\text{CH}_2)$ at surface pressures of 0.1 and 0.2 mN m^{-1} could indicate that the acyl chains are disordered and therefore possess a significant concentration of *gauche* rotamers, but the wavenumber values for both $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ suggest that the methylene units at these very low surface pressures adopt the *trans* conformation. For $\nu_a(\text{CH}_2)$ the values of the peak width at 0.1 and 0.2 mN m^{-1} are lower and higher, respectively, than the values at higher surface pressures. These observations illustrate the inaccuracy of the peak widths at low surface pressure where the bands are less intense and generally less clearly defined than at higher surface pressures. With such weak and

distorted band shapes the COG algorithm has difficulty in performing an accurate and reproducible baseline correction.

4.1.3. Dependence of the peak height and peak area of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ on surface pressure

The values of the peak height and integrated peak area for the two methylene stretching modes are dependent on the surface concentration of film molecules in the focal point of the IR beam, but may also be indicative of a change in the direction of the dipole moment for the stretching vibration and a change in the tilt angle of the ordered acyl chains [30–32].

Fig. 6 shows that once the surface pressure was increased to 0.5 mN m^{-1} the integrated peak areas of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ remained effectively constant. The peak height data are similar, but are not presented. These results suggest that the concentration of film molecules on the surface and the direction of the transition dipole moment (and therefore the tilt angle of the hydrocarbon chain) do not change appreciably as the surface

pressure is increased, even though the Π - \hat{A} isotherm (Fig. 1) indicates a transition from the LC to the S phase at 5 mN m^{-1} . However the scatter in the FT-IR data is such that the approximately 10% reduction in molecular area on compression from 0.5 to 16 mN m^{-1} would not necessarily be observed.

The observed increases in peak height and integrated peak area for both $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ as the surface pressure was increased from 0.2 to 0.5 mN m^{-1} could, in principle, arise from a decrease in the average tilt angle of the acyl chains from the surface normal and/or from an increase in surface concentration. The latter certainly occurs as domains of the LC phase are pushed together by the compression, even though the packing within the domains is unchanged, as discussed above. It is therefore unlikely that any small change in tilt angle could be observed.

The limited data obtained with polarised radiation show constant values of peak height (not presented) and peak area (Fig. 6) at surface pressures from 3 to 17 mN m^{-1} , with the values for p-polarised radiation being significantly higher

than those for s-polarised radiation. The dichroic ratios have an average value of about 1.35 and show no dependence on surface pressure. The dichroic ratio, D , is equal to A_p/A_s , where A_p and A_s refer respectively to the absorbances obtained with parallel polarised (p-polarised) radiation and perpendicularly polarised (s-polarised) radiation.

Buontempo and Rice [27,28] have claimed that an observed insensitivity of the dichroic ratio to a decrease in the monolayer surface area implies that there is no change in the collective tilt of the hydrocarbon chains. This appears to be the situation with VO monolayers.

4.2. RA FT-IR spectra in the 1900 – 1300-cm^{-1} region

The only spectral band attributable to VO visible in this region of the spectrum is the carbonyl stretching vibration ($\nu(\text{C=O})$) at $\approx 1748 \text{ cm}^{-1}$ which is clearly evident amongst the water vapour rotation–vibration bands. The band is broad and non-symmetrical. The stretching vibration of the vinyl group ($\nu(\text{C=C})$), expected at $\approx 1645 \text{ cm}^{-1}$, could not be observed.

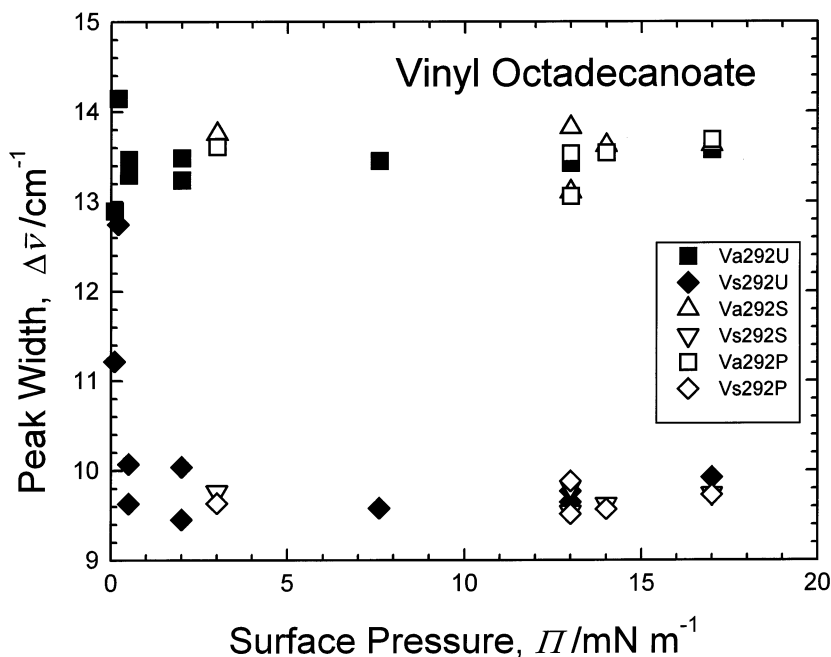


Fig. 5. Dependence of the peak width of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ on the surface pressure of a VO monolayer at the A/W interface.

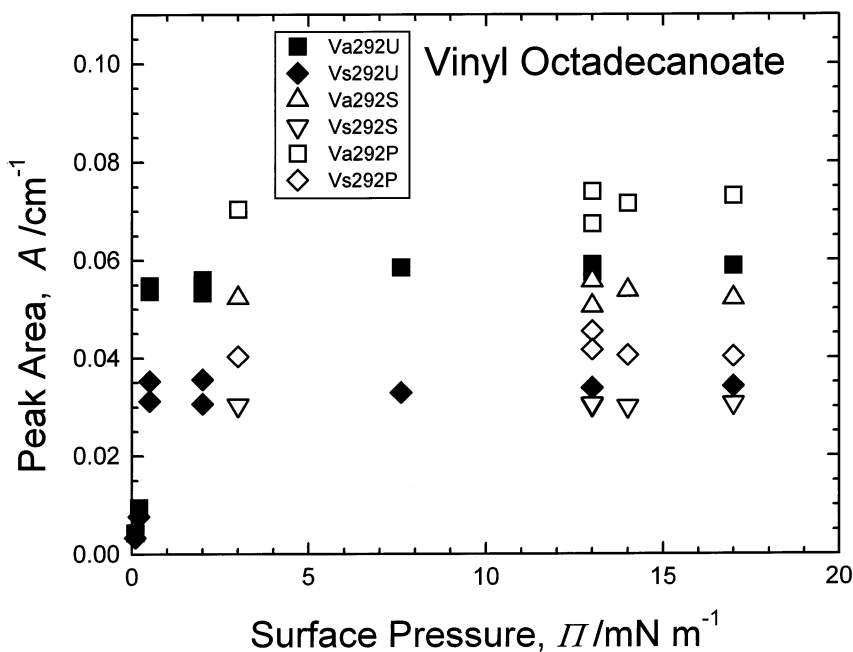


Fig. 6. Dependence of integrated peak area of $v_a(\text{CH}_2)$ and $v_s(\text{CH}_2)$ on the surface pressure of the VO monolayer at the A/W interface.

5. Conclusions

The RA FT-IR spectra of monolayers of VO at the A/W interface show that the conformational order within the acyl chains is nearly independent of the compressional status of the monolayer. Even at very low surface pressures the monolayer appears to consist of condensed domains where the acyl chains are highly ordered and densely packed. As the film is compressed the decrease in the monolayer area leads to a reduction in the distances between domains and possibly an increase in domain size. When the compression reaches the stage where the surface pressure-molecular area isotherm indicates that the monolayer has entered the condensed phases (LC and S) there are no further changes to the methylene antisymmetric and symmetric stretching bands on compression. Thus any changes in monolayer structure in this region, such as the LC \leftrightarrow S transition, are too small to be seen in the RA FT-IR spectra. The Π - \hat{A} isotherm also indicates a highly condensed monolayer from low

surface pressures up to fracture, but does show the LC \leftrightarrow S phase transition.

For investigating polymerisation in VO monolayers it would be useful to be able to observe changes in the head-group spectrum, particularly the band arising from the C=C stretching vibration. This was not possible in the present experiments because of water vapour absorption bands so further progress depends on the elimination of these bands. Two approaches will be tried: the use of polarisation modulation to identify and remove the water vapour bands, and removal of water from the system by studying films deposited on a solid surface by the Langmuir-Blodgett technique.

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