SYNOPSIS

Brewster angle microscopy, interfacial stress rheometry are powerful methods to investigate the quiescent and transient structure of air/water and oil/water interfaces. During the past ten years mostly simple fatty acids at the air-water interface were investigated. In recent time more complex samples are investigated experimental and by numerical methods [1-4]. Of interest are materials of technical relevance and increasingly the structure and rheology at the oil/water interface. Here emulsification processes and the manyfold interaction among interfacial rheology and interfacial structure together with dispersing effects in deformable interfaces, that includes time-dependent concentration gradients in planar (e.g. Marangoni effect) and three dimensional phases, transport phenomena, and adsorption kinetics are of interest.

1 INTRODUCTION

The adsorption of surfactants at interfaces is well-known. Amphiphilic molecules significantly lower the surface free energy by adopting orientations in which the hydrophilic part is orientated towards the aqueous phase while the hydrophobic part typically points towards the air or an oily phase. When amphiphiles are studied as monolayers at the air/water interface, the reduction in surface energy is expressed as the surface pressure, \( \Pi = \gamma_0 - \gamma \), where \( \gamma_0 \) and \( \gamma \) are the surface tensions of the clean and covered surfaces, respectively. As the accessible surface area is reduced, the monolayer can undergo several phase transitions as gaseous, liquid and solid phases, analogous to the familiar phase behaviour of three-dimensional systems [5]. In both cases interfacial films typically exhibit a high degree of orientational order that is induced by the geometrical restriction in two dimensions. Other monolayer properties, including phase behaviour, domain structures and viscoelasticity, are also influenced by the molecular organisation of the films. Furthermore, during layer deposition (air/water) or emulsification (oil/water), the film experiences shear and extensional flow that can imprint additional orientational properties on the sample or can influence the drop deformation and break-up, respectively. For example, anisotropy in deposited films, due to velocity gradients in the film during vertical deposition, has been demonstrated [6].

Consequently, knowledge of the structural and rheological properties as a function of strain, frequency, and temperature, can provide insight into molecular interactions and organisation at the interface and, therefore on deposition and emulsification processes. In this study, surface rheometric measurements, in conjunction with morphology characterisation by Brewster Angle Microscopy (BAM), are used to study monolayers formed from cellulose derivatives.

2 EXPERIMENTAL

2.1 Samples

All samples investigated are rigid rod polymer molecules of cellulose derivatives modified by the addition of flexible sidechains in order to be suitable for monolayer formation (short name HPC) [7, 8]. Monolayers were spread from dilute chloroform solutions on deionized water in two different Langmuir troughs. Subphase temperatures were varied from 15-35°C in increments of 5°C and a Wilhelmy plate was used to monitor the surface pressure. The compression speed for all samples investigated was 0.25–1 mm/s. Surface pressure
area-isotherms recorded for monolayers of HPC-C18 are presented in Fig. 1.

![Surface pressure-area isotherms recorded for HPC-C18 as a function of temperature: (a) 10°C, (b) 15°C, (c) 20°C, (d) 25°C, (e) 30°C, (f) 35°C](image1.png)

The isotherm shape exhibits a striking temperature dependence as observed generally for rigid rod monolayers. Also, upon compression, a characteristic constant pressure plateau is observed in the monolayer surface pressure-area isotherms.

2.2 Brewster Angle Microscopy (BAM)

Brewster angle microscopy was carried out with a laboratory-built microscope [3, 9-11]. The set-up consists out of a laser light source-polarizer unit and a lens-analyser-camera unit as shown in Fig. 2.

![Set-up of the BAM](image2.png)

The laser light is p-polarized (electric field vector perpendicular to the interface) before hitting the interface. Under Brewster angle conditions, p-polarized light is fully transmitted and no reflection is observed from a pure interface. In the presence of an interface active material, sufficiently dense to alter the refractive index, the Brewster angle condition is no longer met and reflection occurs. The resulting contrast permits the observation of film structures and domains. The reflected light passes through the lens-analyser unit and is detected by a CCD camera.

2.3 Interfacial Rheology

An interfacial stress rheometer (ISR) was used to investigate the rheological properties of monolayers at the air-water interface. The rheometer is equipped with a Minitrough, enabling the variation of surface concentration and the simultaneous monitoring of surface pressure [2]. A schematic of the set-up is shown in Fig. 3.

![Top view of the interfacial stress rheometer showing glass barriers, magnetic needle, Helmholtz coils, flow field, and detection of needle position](image3.png)

A magnetized rod is used to probe the interface’s resistance to deformation. A set of Helmholtz coils is used to create a magnetic field gradient that generates a force to induce the motion of the rod. The current through the coils is generated by a function generator to create an oscillatory magnetic field. The rod’s position is determined by monitoring the motion of the rod’s edge at the interface. The shadow is imaged with an inverted microscope and detected with a microscope-position sensor unit and monitored with a computer via a data acquisition board. From the rod’s position (strain) in relation to the applied current (stress), one is able to detect both the delay in phase between the strain and the stress and the ratio of their amplitudes. With these values, the complex surface modulus, $G_s^*$, can be determined.
3 RESULTS AND DISCUSSION

3.1 Phase Behavior and BAM Images at Rest and under Flow

Spread monolayers of HPC-C18 were examined by BAM and typical images obtained at 15°C at several surface pressures are presented in Fig. 4.

The monolayers exhibit rich phase behaviour at low surface pressure (Fig. 4a) where a concentrated liquid phase (bright areas) is observed in co-existence with a dilute, presumably gaseous, phase (dark areas). The bright areas are clearly fluid and are easily deformed as discussed later in this section. The elongated non-circular shape is indicative of a relatively low line tension between the two phases. Upon further compression, the two phases co-exist until a surface pressure of 5-6 mN/m is reached (Fig. 4b). The transition to a homogenous liquid monolayer occurs at the same surface pressure for each of the investigated temperatures (Fig. 4c). The important temperature dependence of the surface pressure-area isotherms is not reflected in the BAM images. Additional compression of the films eventually leads to collapse to three-dimensional aggregates (Fig. 4d). These structures appear in the BAM images at surface pressures exceeding 40 mN/m. Comparison with the isotherms of Fig. 1 illustrates that the observed monolayer collapse is not accompanied by a detectable change in surface pressure. The structural changes of the monolayer generated by an extensional flow field are depict in Fig. 5.

3.2 Rheo-Morphological Phase Diagram

Rheological properties as the surface storage modulus, \( G_s' \), and the surface loss modulus, \( G_s'' \), were investigated as a function of both strain and frequency. Representative strain sweeps at various surface pressures are shown in Fig. 6 where both moduli are plotted as a function of strain.

In general, the linear viscoelastic plateau, where the rheological properties are not a function of the applied strain, is quite pronounced and no non-linear effects have to be taken into account. Only at low surface pressures (2.5 and 5 mN/m) strain-thinning is observed, implying a structural breakdown of the sample at that particular surface pressure. From the corresponding BAM image (Fig. 4a), one can easily suggest that the inhomogeneous domain structure is responsible for the non-linear behaviour.

The dynamic moduli, represented by the loss angle, \( \tan \delta = \frac{G_s''}{G_s'} \), are plotted in Fig. 7 as a function of surface pressures for various temperatures between 20 and 35°C.
The rheological properties exhibit a strong temperature dependence as discussed in the following section. At 20°C, the loss modulus initially exceeds the storage module ($\tan \delta > 1$) at low surface pressure where domains are freely swimming in a gaseous phase, and thus respond to the imposed stress like a fluid. Under these conditions the monolayer is morphologically non-homogeneous (as concluded from the BAM image of Fig. 4a) and viscous; therefore we label this phase as $NH, viscous$. Upon compression, $G_s'$ increases more rapidly than does $G_s''$, with the two curves crossing at a surface pressure of 6 mN/m ($\tan \delta = 1$), above which the storage modulus is larger the loss modulus ($\tan \delta < 1$). The rheological properties of the monolayer change from a more viscous to a more elastic behaviour. From the BAM images it is known that $\Pi = 6$ mN/m corresponds to the surface pressure at which a homogeneous phase is achieved. Therefore this phase is referred as $H, elastic$. The crossover point of $G_s''/G_s'$, ($\tan \delta = 1$) shifts to higher surface pressures with increasing temperatures. For temperatures higher than 20°C, again a homogeneous monolayer is observed for surface pressures exceeding 6 mN/m (Fig. 4c) but the films are not elastic. Here a third phase, called homogeneous viscous ($H, viscous$) is observed. Upon further compression the monolayer can, however, form a continuous molecular network with pronounced elastic properties. This information is summarised in a schematic rheo-morphological phase diagram shown in Figure 6. Phases labelled as $H, elastic$ and $H, viscous$ are the homogeneous/elastic and the homogeneous/viscous phases, respectively. The borderline between $H, elastic$ and $H, viscous$ is given by the crossover of $G_s'$ and $G_s''$ obtained from the rheological measurements.

### 3.3 Time-dependent flow behaviour

The dependence of the complexe modulus, $G_s^*$, on frequency reveals information about the elasticity and viscosity of the monolayer on different time scales. The frequency dependence of the dynamic moduli are plotted in Fig. 8, at two different temperatures and surface pressures, all within the domain of homogeneous film formation.
expected for a rubber-like material. However, for higher temperature and lower pressure (e.g. 25°C and 10 mN/m), a more viscous behaviour is found with $G''_s$ exceeding $G'_s$. The observed frequency dependence of the moduli is not, however, that of a typical fluid. For a fluid-like sample, the Maxwell model predicts slopes of 2 and 1 for the frequency dependence of $G'_s$ and $G''_s$, respectively. Therefore one is not dealing with a pure two-dimensional liquid but with an already interacting two-dimensional network. Since the dynamic moduli are not found to be a function of frequency, the rheo-morphological phase diagram presented in Figure 7 is valid not only for the probed frequency of the strain sweeps of 0.92 rad/s but also for a wider regime of frequencies ($0.1 < \omega < 10$ rad/s).

4 SUMMARY AND CONCLUSIONS

We have investigated the formation of monolayer structures of surface active cellulose derivatives by BAM. At a high surface area per molecule, the liquid phase co-exists with a dilute gas phase. Monolayer compression eventually leads to complete coalescence to yield a uniform liquid phase. BAM images reveal only uniform surface films at molecular areas within the transition region.

Surface rheological measurements indicate important changes in monolayer mechanical properties during compression. Importantly, these changes can be correlated with isotherm shape. This observation is interpreted as an indication of the partial crystallisation of interdigitated side-chains. Sidechain crystallisation, postulated to be possible only below 30°C, creates cross-links between chains in neighbouring layers, which in turn render the surface film elastic.

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