Microarticle

Experimental investigation of a flowing superspreader solution using Reflection Anisotropy Spectroscopy

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A B S T R A C T

Superspreading is the phenomenon where a drop of trisiloxane surfactant solution rapidly spreads on a moderately hydrophobic substrate over a very large area. However the mechanism of superspreading is unknown to date. In this work Reflection Anisotropy Spectroscopy (RAS) is used for the first time in order to investigate the causes of superspreading. An aqueous solution of the superspreader Evonik S240 (0.1%) is compared with the chemically similar but non superspreading solution of Evonik S233 (0.1%), on a polycarbonate (pcp) substrate. This study is aimed at finding evidence of organised structures, such as micelles, at the contact line of the receding film which could be part of the mechanism of superspreading. The RA signal is monitored as the solutions recede from vertically aligned pcp substrates. The results are then analysed for evidence of anisotropy on the surface arising from any micelle structures located at the contact line of the film.

Introduction

When a drop of water is put on a moderately hydrophobic surface, such as a polycarbonate sheet, it takes the shape of a spherical cap with hardly any wetting of the surface; however, when small amounts of certain trisiloxane surfactants are added to water, spreading is greatly enhanced, which is commonly referred to as "superspreading". To date, the mechanism governing this phenomenon is poorly understood; in particular, there is little direct experimental evidence for the state of the superspreader/substrate interface at the molecular scale. Models have been proposed which try to explain the different behaviours of non superspreading and superspreading surfactants, even though they may have similar chemical structures. These models relate micelle crystallisation and mono/bi layer formation to their effect on superspreading [1,2]. Currently there is no experimental evidence for these models, although macromolecular structures near a moving contact line have been shown to affect the wetting behaviour of systems such as dilute solutions of flexible polymers [3].

Here, Reflection Anisotropy Spectroscopy (RAS) is used to investigate whether superspreaders generate ordered macromolecular structures (e.g. micelles or bi-layers) on surfaces, which could help to understand the mechanism of superspreading. RAS is a non-destructive optical technique where reflected light yields data on the anisotropy of a surface, or a process occurring at a surface. RAS [4,5] measures the difference in reflectance (Δr) of normal incidence plane-polarised light between two orthogonal directions in the surface plane (x, y), normalised to the mean reflectance (r):

$$\frac{\Delta r}{r} = \frac{(r_x - r_y)}{(r_x + r_y)/2} \tag{1}$$

where $\Delta r/r$ represents the measured complex reflectance anisotropy and r_x and r_y are the complex Fresnel reflection coefficients in the x and y directions of the surface plane. Fig. 1 shows the reflection anisotropy (RA) spectrometer setup and the geometry of the substrate: the y direction was chosen to be vertical and aligned to the direction of the fluid flow, with x orthogonal. RAS can measure anisotropy in many different systems [5]. Here, we use RAS to search for anisotropic entities that may be aligned in a preferred direction resulting from the flow of fluid across an isotropic substrate – a polycarbonate plastic sheet (pcp).

Experimental procedure

To perform the RA measurements, polarised light at near-normal (<5°) incidence is shone onto the sample surface such that the direction of the incident plane of polarisation is at 45° to the x and y axes (Fig. 1) enabling both axes to be evenly illuminated. If the structures of the surface along the x- and y-directions are different the Fresnel reflection coefficients along the two directions will also be different. As a result the x and y components of the

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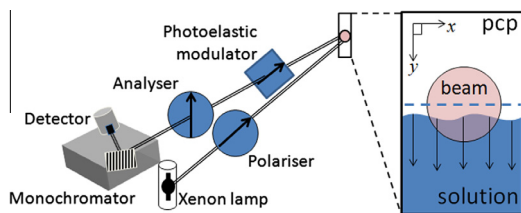
Fig. 1. Schematic layout of the RAS setup and sample orientation. The solution is shown receding, primarily due to gravity, down the pcp substrate and through the RAS beam.

polarisation vector of the reflected light are unequal, leading to elliptically polarised light. The polarisation of the reflected light is analysed to yield the anisotropy of the system according to Eq. (1). To monitor fluid flow over the substrates, dynamic RA measurements are performed at a fixed wavelength and the anisotropy measured as a function of time. We monitor (i) the RA signal (the real part of Eq. (1)) and (ii) the DC signal (directly related to the denominator of Eq. (1) and the reflectivity [6]) at a single wavelength of 414 nm (3 eV photon energy). This wavelength is found to give an optimum RAS signal on a horizontal pcp substrate covered with a thin film of S240 (0.1%) (aq) solution.

Dynamic RA experiments were performed to follow the receding contact line of (i) S240 (0.1%) (aq), (ii) S233 (0.1%) (aq), both supplied by Evonik Industries (Germany), and (iii) water. S240 and S233 surfactants have a similar molecular structure, however only S240 exhibits superspreading features. The pcp substrate was aligned vertical and submerged in a beaker containing the solution to a level bisecting by half the position of the RAS beam incident on the pcp substrate (dashed line, Fig. 1). The RAS beam has a diameter of 8 mm and the rectangular pcp substrates had dimensions of 25 mm × 60 mm × 1 mm. The beaker was removed downwards and as soon as it was clear of the optical path, the RA time scan was started. The RA time scan monitored the solution receding down the pcp substrate and across the lower half of the RAS beam (Fig. 1). Care was taken not to move the substrate which would change the position and direction of the reflected beam. Ultrapure water (Milli-Q) was used in all solutions.

Results and discussion

The results for two different experiments using S240 (0.1%) are shown in Fig. 2. Over several experiments we found that there was
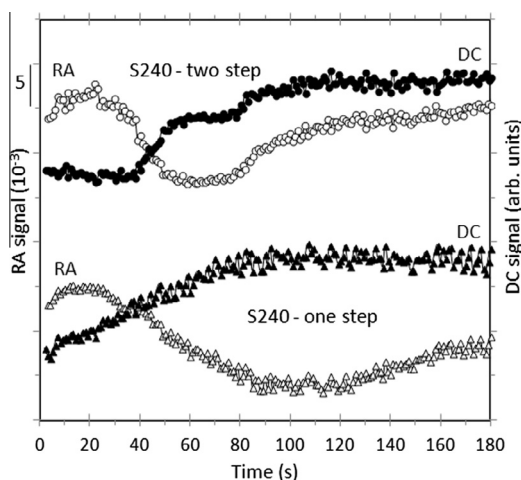
Fig. 2. RA signal [open symbols] and DC signal [filled symbols] at 414 nm versus time for the moving contact line of S240 (0.1%) (aq) on a pcp substrate. Results of two experiments are shown [circles and triangles] depicting a two-step and a one-step process, shifted in the *y* axis for clarity.
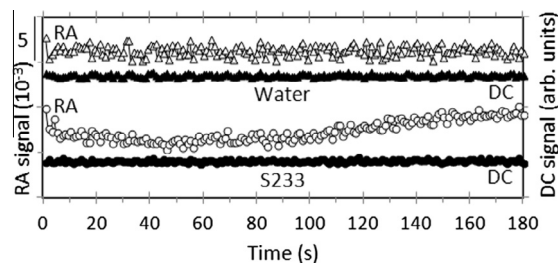
Fig. 3. RA signal [open symbols] and DC signal [filled symbols] at 414 nm versus time for water [triangles] and S233 (0.1%) (aq) [circles]. Scans are shifted in the *y* axis for clarity.

some variability in the occurrence in time when features appeared in the RA and DC scans, however, there were in general two types of behaviour, characterised by either a one step or a two-step change in the DC signal (Fig. 2). The upper curves in Fig. 2 show a two-step process: the DC signal increases after 40 s and again at approximately 80 s. The gradient of the trace at these two times is similar, highlighting a similar rate of change in the reflectivity. The two step behaviour could be explained by the presence of a 'bulk' film receding first, followed by a thinner 'interfacial' film. The second experiment (lower curves of Fig. 2) shows a single gradual change in both DC and RA signals. The reason for two types of behaviour is not clear. Further experiments with full control over all parameters are necessary, for example, the removal speed of the beaker, and controlling the exact electrostatic charge on the pcp substrate [7] are expected to influence the results.

For both behaviours of S240 on pcp (Fig. 2) the RA signal exhibits an initial small increase followed by a decrease to a minimum and a recovery towards its initial value. If we assume that during the experiment there is no change in r_x (orthogonal to the flow), then r_y (in the direction of flow) would decrease initially (first 20 s) then increase to a maximum, followed by a decrease towards the initial value. For the two-step behaviour, the maximum anisotropy lies between the first and second step changes in the DC signal (Fig. 2). This could indicate that an anisotropic thin surface layer exists on the substrate during this time period. Similarly the largest anisotropy signal observed for the one-step results could indicate a temporal anisotropic surface layer. This layer may be subsequently lost due to evaporation.

The results for S233 (0.1%) (aq) and water are shown in Fig. 3. In contrast to the superspreading S240 solution, the S233 solution exhibits a featureless time scan for RA and DC signals. These results indicate no pronounced anisotropy at the contact line of the descending S233 film or anywhere else. Only a relatively small decrease and gradual recovery to the initial level is observed. RA signal versus time graphs for a descending film of water are, as expected, flat and featureless indicating that the water film is isotropic. Reflectivity scans for descending films of S233 and water are flat and featureless indicating light is reflected in a uniform constant way as the films descend.

Conclusions

The results support the theory that the descending film of S240 (0.1%) (aq) contains anisotropic structures and/or a preferred directional alignment of structures in the solution. The descending films of S233 (0.1%) (aq) and water had featureless RA time scans, indicating isotropic behaviour. We conclude that the anisotropic RA signals are related to superspreading, however, it is not possible to say if this is at the contact line or to assign the anisotropy to a specific structure, e.g. micelles or bilayers. Further work is needed to conclude these details definitively and indeed how such a superspreading mechanism might operate.

Acknowledgement

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