

# Surface Quasi-elastic Light Scattering (SQELS): A Probe of Interfacial Rheology

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## 1. Abstract

Light is scattered quasi-elastically from thermally driven capillary waves found at all fluid interfaces. The power spectrum of this quasi-elastically scattered light provides information on the interfacial properties of the fluid interface. These measurements complement those made using conventional methods since they measure the interfacial properties at high frequencies (ca. 20 kHz), in addition sensitivity is improved as the interfacial tension is reduced. We outline the construction of an apparatus to measure this quasi-elastically scattered light and give some preliminary results on the behaviour of  $\beta$  - casein spread at an air-buffer interface, as a function of pH. At high surface pressures the dilational modulus measured by SQELS is markedly higher than the static modulus, this can be attributed exchange mechanisms between the surface layer and subphase. These results are analysed in terms of the Aguié-Béghin model and indicate that the 'solvent quality' of the buffer varies with pH from being close to a  $\theta$  solvent at the isoelectric point to a good solvent at pH9.8.

## 2. Introduction

Interfacial rheological properties can be probed using a wide range of techniques, including a range of direct mechanical surface viscometers, pendant droplet and oscillating bubble methods and mechanically excited wave methods<sup>1</sup>. A further member of this family of techniques is surface quasi-elastic light scattering (SQELS), Langevin<sup>2</sup> provides an excellent review of this technique. Capillary waves with amplitudes of a few angstroms and wavelengths of the order of 100 $\mu$ m are found at all fluid interfaces and they scatter light very efficiently. The majority of this light is scattered elastically but a component of it is scattered inelastically, through an exchange of momentum between photons and the interfacial waves. This inelastically scattered light is found in a cone surrounding the specular reflection, this cone represents inelastically scattered light with a range of  $q$  values. The power spectrum of this inelastically scattered light contains information on the interfacial properties. SQELS complements other interfacial analysis techniques in a number of ways, perhaps the key feature is that it becomes *more* sensitive as the interfacial tension is reduced because the amplitude of the thermal fluctuations in the interface is increased. The capillary wave

frequency is of order 10-100kHz and so the interfacial properties are probed at a much higher frequency than is usual, this corresponds to short time scales and may be significant when applying results to the understanding of fast industrial processes such as emulsification.

Data are normally analysed in terms of a model treating the interfacially layer as a thin flat elastic sheet at the interface<sup>3</sup>, more recently Buzza et al.<sup>4</sup> have proposed a model that explicitly incorporates features of a polymer brush into the model of the interfacial layer.

The dispersion relation  $D(\omega)$  for waves at an air-liquid interface is given by:

$$D(\omega) = [\varepsilon q^2 + i\omega\eta(q + m)] \left[ \gamma q^2 + i\omega\eta(q + m) - \frac{\rho\omega^2}{q} \right] - (i\omega\eta(m - q))^2 \quad (1)$$

where  $m$  is:

$$m = \sqrt{q^2 + i\frac{\omega\rho}{\eta}}, \text{Re}(m) > 0 \quad (2)$$

$\eta$  is the subphase viscosity and  $\rho$  is the subphase density.  $\gamma$  is the surface tension (or transverse modulus) and  $\varepsilon$  is the dilational modulus. Solving this equation for  $D(\omega) = 0$  gives us an expression for the wave frequency,  $\omega$ , as a function of the scattering vector  $q$ . The solutions describe both dilational and transverse waves, in a light scattering experiment it is only the transverse waves that scatter light and their power spectrum  $P_q(\omega)$  is given by:

$$P_q(\omega) = \frac{kT}{\pi\omega} \text{Im} \left[ \frac{i\omega\eta(m + q) + \varepsilon q^2}{D(\omega)} \right] \quad (3)$$

The behaviour of the dilational waves can be inferred because there is coupling between dilational and transverse waves. A fluid - fluid interface can be modelled using a trivial modification of (1). In the experiments carried out here a photon correlation spectrum is acquired and this is simply the Fourier transform of the power spectrum,  $P_q(\omega)$ . The surface moduli can be expanded to take into account viscous effects:

$$\begin{aligned} \gamma &= \gamma_o + i\omega\gamma' \\ \varepsilon &= \varepsilon_o + i\omega\varepsilon' \end{aligned} \quad (4)$$

In this work data is analysed by directly fitting the correlation function with a theoretical curve calculated from the interfacial properties. An alternative is to fit the correlation function with a damped cosine and either work directly with the frequency and damping thus obtained or finding values of the interfacial properties which are consistent with the values of

frequency and damping. Since there are four interfacial properties and only two parameters it is necessary to make some assumptions.

$\beta$  - casein is an important milk protein and has been extensively studied<sup>5</sup>, the key features that make it of particular interest here are that it has a substantially random coil structure making it, in many respects, comparable to synthetic polymers. An interesting feature of  $\beta$  - casein is that its well defined sequence should lead to a well defined polyelectrolyte behaviour and a well defined molecular weight, these features are difficult to obtain in a synthetic polyelectrolyte. Here we will look at  $\beta$  - casein spread at air-buffer interfaces and in addition to doing SQELS experiments at pH7.0 we will measure the conventional surface pressure - area isotherms at a range of pH.

In addition to making SQELS measurements on  $\beta$  - casein spread at air - buffer interfaces, we also make use of the Aguié-Béghin model<sup>6, 7</sup> to analyse conventional isotherm data. This model treats the protein as a multiblock copolymer and calculates the scaling exponent,  $\gamma$ , (where  $\Pi \sim \Gamma^\gamma$ ) using conventional methods of polymer scaling theory. The scaling exponent varies with the solvent quality. Solvent quality is a 'formal' concept in polymer physics; if, in a particular solvent, a polymer chain obeys the scaling relationship between radius of gyration and monomer number predicted by the Flory-Huggins model then the polymer is described as being ideal and the solvent as being a  $\theta$  solvent. A solvent which leads to a more compact configuration is known as a poor solvent and one that produces a more expanded configuration is known as a good solvent.

### 3. Experimental Method

A surface quasi-elastic light scattering apparatus has been constructed based on a design proposed by Earnshaw<sup>8</sup> and Hård<sup>9</sup>, this is illustrated schematically in figure 1. The goal of such an apparatus is to measure the power spectrum of light scattered inelastically from the capillary waves at the fluid interface as a function of scattering vector,  $q$ , from the elastically scattered light. Photon correlation spectroscopy (PCS) is a convenient means by which to measure the small shifts in frequency that this entails. The photon correlation is done in heterodyne mode and so it is necessary to provide a coherent source of light of the original frequency at the appropriate  $q$  value. This light is provided using a weak diffraction grating. In order for the heterodyne signal to dominate the correlation function the ratio of the intensity of the inelastically scattered light to the 'reference' light must be adjusted to a value

of the order of  $10^{-3}$ . Turning to figure 1: Light, with wavelength 532nm, is provided by a 150mW single mode diode pumped solid state laser (Laser Quantum, Manchester). Polarisation and intensity are controlled using the combination of the half wave plate ( $\lambda/2$ ) and prism polariser (P). The beam size, profile and collimation are controlled using the spatial filter, S. The grating (G) provides a fan of diffracted 'reference' beams. The lenses L1 (f=150mm) and L2 (f=350mm) perform two tasks; they converge the reference beams and the main beam to a single point at the fluid interface and they focus the reference beams and the main beam at the front of the photomultiplier. The relative intensity of the reference beams is adjusted by moving the neutral density filter (NDF) such that it intercepts the diffracted spots but not the main beam. The mirrors M1-M4 direct light from the laser onto the surface and from there into the detector. The light is detected using a photomultiplier (PMT) and processed using a PC - card based photon correlator (Brookhaven Instruments, Worcester), the pulse discriminator used in the PMT is modified to allow the use of the 'multi-photon' mode originally described by Earnshaw<sup>10</sup>. At the detector the laser light appears as a bright central spot with a series of focussed reference spots at 2-3mm intervals away from the central spot. Each of these spots is composed of the reference beam originating from the diffraction grating and inelastically scattered light from the main beam. The reference beams are sufficiently weak that inelastic scatter from the reference beams can be ignored. Each spot corresponds to light being scattered to a different q value, the mirror M4 is adjusted in order that the appropriate reference beam falls on the detector.

The liquid surface is maintained in a Langmuir trough (Nima Technology, Coventry) mounted on an active anti-vibration table (Halycion, Germany), both of which are enclosed in a draft proof enclosure. These steps are necessary because the liquid interface is highly sensitive to perturbation by drafts and vibration. Conventional isotherm data were acquired simultaneously with the light scattering data, using a Wilhelmy plate.

The SQELS data presented here were collected at a range of surface concentrations for a layer of  $\beta$  - casein spread at the surface of a 0.01 M phosphate buffer of pH7.0 at a temperature of 23°C. The data were all collected at scattering vector, q, of  $34654\text{m}^{-1}$  from the specular reflection, at each point a set of 10 correlation functions were acquired each of which was the accumulated data for one minute.

$\beta$  - casein (Sigma, C-6905, 90% pure) was used as supplied, a  $1\text{ mg ml}^{-1}$  solution in water was prepared and then the appropriate volume (typically  $50\text{ }\mu\text{L}$ ) of this solution was dispensed

dropwise onto the buffer surface using a micropipette. In addition to data collected on a pH7.0 buffer, conventional isotherms were acquired for pH5.8 and pH8.5 (phosphate buffer), pH4.8 (citrate buffer) and pH10.0 (tris-HCl buffer)<sup>11</sup>.

#### 4. Results and Discussion

Figure 2 shows an example of a typical correlation function, along with a fit using the full spectral expression, the inset shows the residuals between experimental data and fitted curve scaled by a factor of 10.

Figure 3 shows a comparison between the surface pressure as a function surface concentration as measured by Wilhelmy plate and the surface pressure derived from the SQELS data. The SQELS data are consistently slightly lower (by about 1 mN m<sup>-1</sup>) than those measured conventionally, a non-zero value for the transverse viscosity,  $\gamma'$ , could lead to an *increase* in the value of the SQELS determined  $\Pi$  but not a decrease. The most likely explanation for this discrepancy is an error in the measured  $q$  value, an approximate solution for the capillary wave is:

$$\gamma = \frac{\rho\omega^2}{q^3} \quad (5)$$

Therefore the uncertainty in  $\gamma$  and hence the surface pressure is around three times the uncertainty in the  $q$  value, to account for the discrepancy of 1 mN m<sup>-1</sup> an error in  $q$  of only 0.6% is required.

The dilation modulus,  $\epsilon$ , can be calculated from the conventionally measured surface pressure ( $\Pi$ ) - area ( $A$ ) isotherm using the expression:

$$\epsilon = -\frac{d\Pi}{d \ln A} \quad (6)$$

This was done by interpolating the isotherm data to uniform increments in area then carrying out a numerical differentiation using an 11 point second order Savitsky-Golay filter. It is this data which is compared with the values of the dilational modulus obtained using SQELS in Figure 4. At surface concentrations below 1 mg m<sup>-2</sup> there is good agreement between the moduli measured using SQELS and that measured conventionally, however at higher surface pressures the SQELS measured  $\epsilon$  is somewhat higher than that measured conventionally. This type of behaviour has been observed previously and the discrepancy can be attributed to the exchange of the  $\beta$  - casein between surface and bulk, this process has the effect of reducing

the dilational modulus at low frequencies (i.e. conventional measurement) but not at the high frequencies used in the SQELS experiment. The variation of  $\epsilon$  with the frequency of measurement has been modelled by Lucassen and van den Tempel<sup>12</sup>.

Figure 5 shows the variation of the dilational viscosity  $\epsilon'$  as a function of surface concentration. At low surface concentrations  $\epsilon'$  is small and positive whilst at higher concentrations  $\epsilon'$  is negative. This type of behaviour has been observed in a number of other systems<sup>13, 14</sup>, in a literal sense negative values of  $\epsilon'$  are unphysical, they occur because the dispersion relation does not accurately describe the behaviour of the interfacial layer. The values of the interfacial parameters are therefore those which best describe the behaviour resulting from a different physical model. This idea has been tested quantitatively by Buzza et al, who have proposed a new model for an interfacial polymer layer which correctly incorporates details of the layer. They found that fitting simulated data from this new model using the old model produced negative values of  $\epsilon'$ . Alternatively Earnshaw<sup>15</sup> has suggested that there is a coupling between transverse and dilational waves that has not previously been considered and this too can lead to the observation of  $\epsilon' < 0$ . As can the presence of diffusive exchange between surface layer and subphase with a potential barrier, as described by Hennenberg et al<sup>16</sup>. Identifying which of these explanations is correct is the subject of ongoing work.

At low surface pressures Aguié-Béghin et al have shown that the scaling exponent,  $y$ , where  $\Pi \sim \Gamma^y$ , can be calculated from:

$$y = \frac{\epsilon}{\Pi} \quad (7)$$

For the data presented here this relationship is linear up to a surface pressure of around 4 mN m<sup>-1</sup>. Figure 5 shows a plot of the scaling exponent obtained, from the conventional surface pressure - area isotherm, for a range of buffers with pH from 4.8 to 10. The exponent exhibits a linear variation as a function of pH with a value of around 6.6 at the lowest value of pH to a value of 4.0 for the highest value. This change in exponent corresponds to a change in the solvent quality from approaching  $\theta$  conditions at low pH to a good solvent at high pH. The limiting values of  $y$  quoted by Aguié-Béghin are 8 for the  $\theta$  solvent and 3 for a good solvent. The probable cause for this variation is the change in charge of  $\beta$  - casein as a function of pH, the isoelectric point is at approximately pH 5.0 and as the pH is increased the charge increases. This causes an expansion of the polypeptide chain, most probably because the

interior of the protein is more hydrophilic when the charge is increased rather than the charges on the chain causing expansion by electrostatic repulsion.

It is also possible to derive scaling exponents from log-log plots of the surface pressure - area isotherm, the scaling exponents are found from the slope of the linear regions of the plot. It is found that all the isotherms exhibit a region at high  $\Gamma$ , where  $y = 1/2$ , this is consistent with an elastic layer which is able to reorganise under strain such that the stress is uniformly distributed.

## 5. Conclusions

We have shown that SQELS is a useful tool in probing the interfacial rheology of biopolymers at liquid interfaces. At high surface pressures the high frequency dilational modulus measured by SQELS is found to be considerably larger than the static value, this can be attributed to exchange of  $\beta$  - casein between the surface and bulk. It is found that as the pH and hence charge on the protein is increased the scaling exponent,  $y$ , varies from 6.6 at pH4.8 to 4.0 at pH9.8. This suggests that the solvent quality has moved from close to  $\theta$  conditions at low pH to good conditions at high pH. In the future we intend to extend the SQELS measurements over a range of  $q$  values in order to establish the origin of the negative *effective* dilational viscosities and also to look at liquid - liquid interfaces, where the interfacial tension is much lower than at the air - liquid interface.

## 6. Acknowledgments

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## 7. References

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## Figures

**Figure 1:** Schematic diagram of the SQELS apparatus, ( $\lambda/2$ ) - half wave plate, P - prism polariser, S - spatial filter, G - diffraction grating, NDF - neutral density filter, M1-4 - mirrors, L1 - biconvex lens ( $f = 150\text{mm}$ ), L2 - biconvex lens ( $f = 350\text{mm}$ ). Inset: isometric view.

**Figure 2:** Example of a correlation function fitted with a 'full spectral form', inset shows residuals  $\times 10$

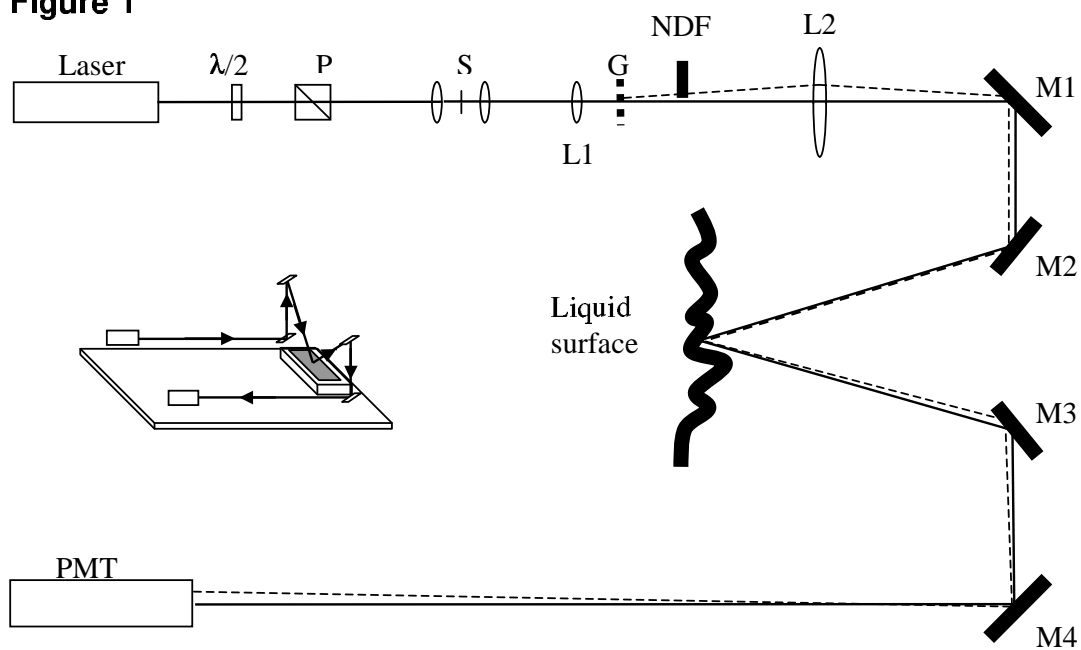
**Figure 3:** Surface pressure,  $\Pi$ , as a function of surface concentration,  $\Gamma$ , for  $\beta$  - casein spread on a phosphate buffer (pH 7.0) measured using SQELS and Wilhelmy plate.

**Figure 4:** Dilational modulus,  $\epsilon_0$ , as a function of surface concentration,  $\Gamma$ , for  $\beta$  - casein spread on a phosphate buffer (pH 7.0) measured using SQELS and Wilhelmy plate.

**Figure 5:** Dilational viscosity,  $\epsilon'$ , as a function of surface concentration,  $\Gamma$ , for  $\beta$  - casein spread on a phosphate buffer (pH 7.0), measured using SQELS.

**Figure 6:** Variation of the scaling exponent,  $y$ ,  $\Pi \sim \Gamma^y$ , of the  $\beta$  - casein surface concentration vs pressure isotherm as a function of buffer pH.

**Figure 1**



**Figure 2**

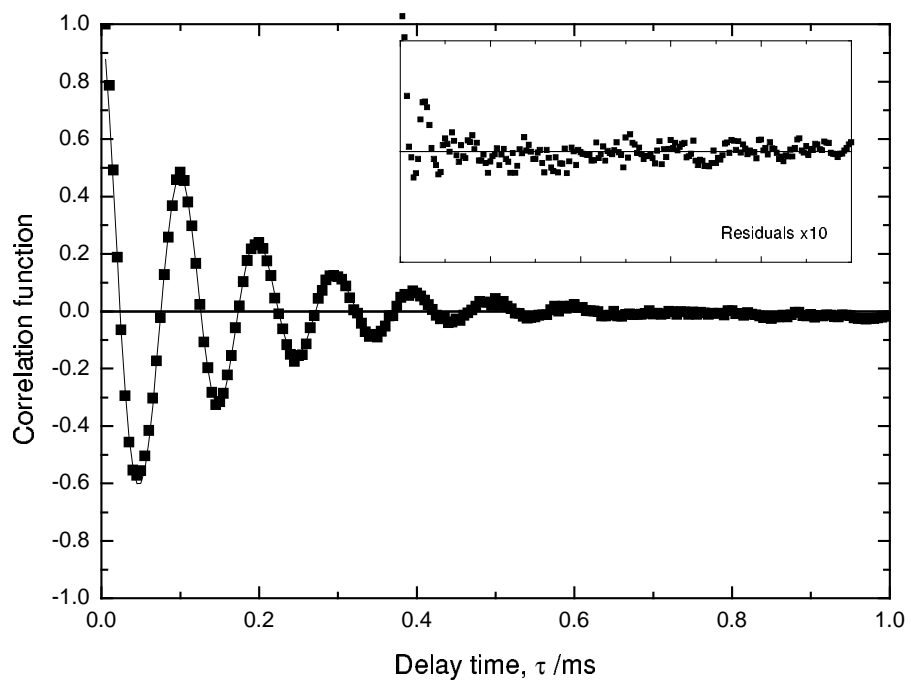


Figure 3

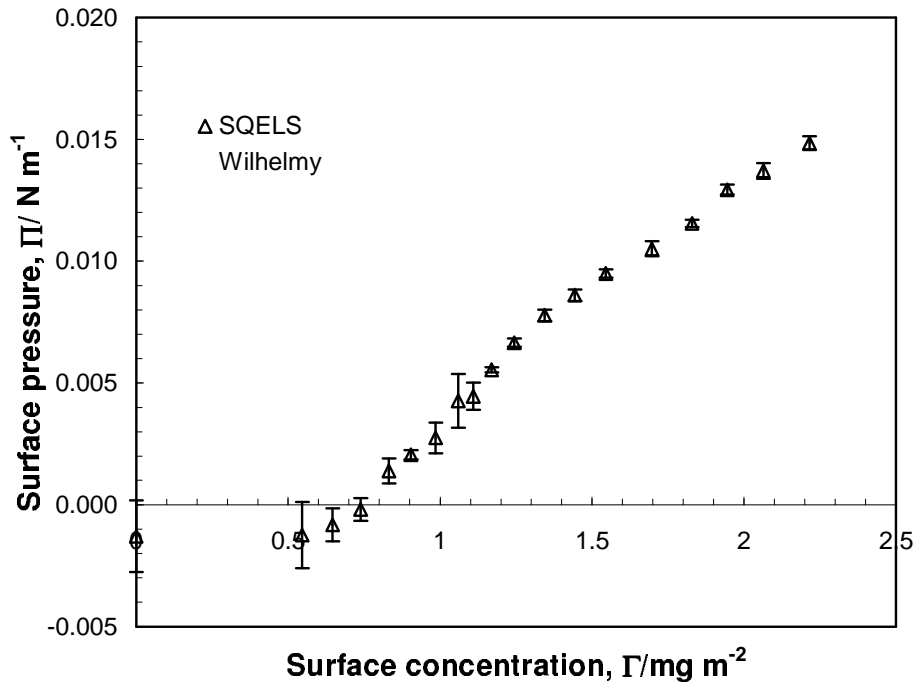


Figure 4

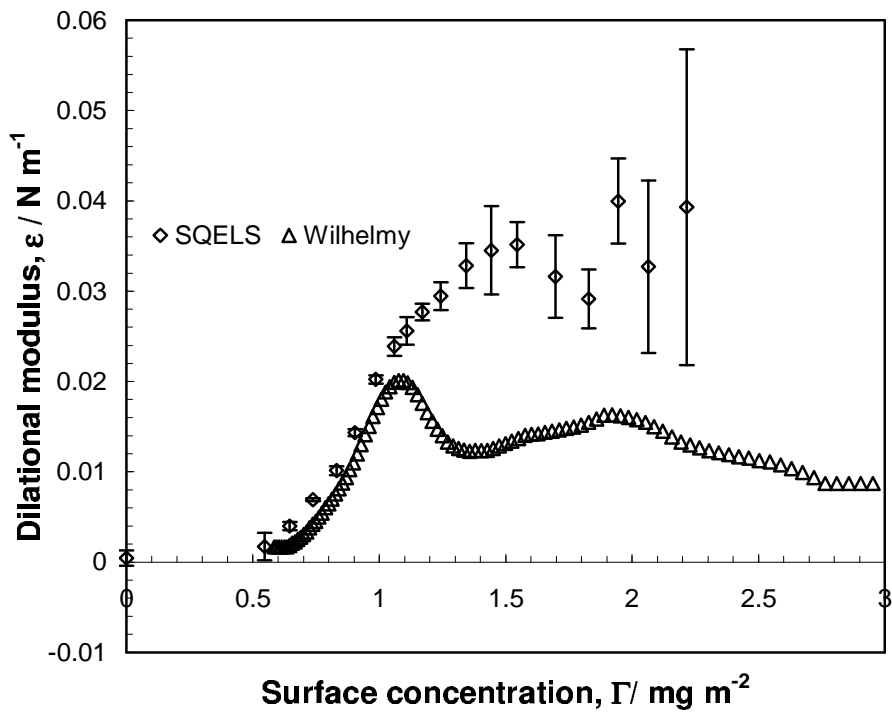


Figure 5

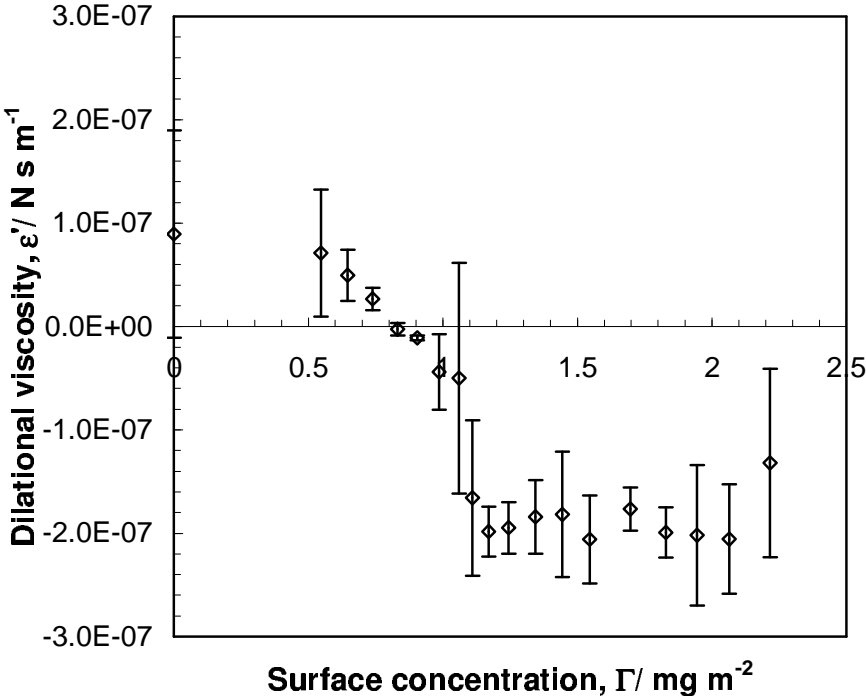


Figure 6

