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Capillary wave fluctuations of spread films of an amphiphilic graft copolymer at the air-water interface

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A graft copolymer with a polymethyl methacrylate backbone and polyethylene oxide grafts was spread at the air-water interface. The polyethylene oxide grafts contained 54 monomer units and were randomly distributed along the backbone. Surface quasi-elastic light scattering was used to determine the frequency and damping of the thermally drive surface waves. Surface visco-elastic moduli were also obtained at the air-water interface from spectral analysis of the correlation functions. The dependence of these parameters on surface concentration of graft copolymer and surface wave frequency exhibits features which are not commensurate with current theory. Dilational waves appear to be destabilized whilst capillary waves become strongly damped. A mixing of the two modes occurs and the frequency behaviour of the damping is symptomatic of this mixing. A qualitative molecular explanation has been attempted using the Alexander-de Gennes brush theory as a model for the organization of the graft copolymer at the air-water interface. It is evident that quantitative description requires development of relevant theory. Copyright © 1996 Elsevier Science Ltd.

(Keywords: capillary waves; polymer film; interfacial dynamics)

INTRODUCTION

More than 120 years ago Lord Kelvin[1] demonstrated that the surface of a liquid was continually roughened by thermal fluctuations. This roughening, known as capillary waves, is mainly determined by the surface (or interfacial) tension of the liquid surface. Mandelstam[2] predicted over 80 years ago these surface waves would scatter light, a suggestion that was verified by Raman[3] in the mid 1920s. It was some 40 years before further developments were made with the advent of the laser as a light source and expressions for the spectral distribution of light scattered from a liquid surface being derived[4,5].

The spectral surface scattering responds to the time evolution of the liquid surface fluctuations. For a pure liquid this spectral distribution can be interpreted in terms of the bulk viscosity and surface tension. When a film is present the evolution of the surface waves is modified and can be interpreted to provide surface visco-elastic parameters of the interfacial layer. Additionally, since there is a range of surface wave frequencies present, suitable experimental design enables the frequency dependence of the surface visco-elastic parameters to be obtained. Although mechanical generation of surface waves has been often used[6,7], the frequency range is not so large as that available by observation of the naturally occurring capillary waves. Moreover, the application of the light scattering techniques is a non-perturbative method and this may be highly desirable for some systems.

Evidently, a knowledge of the interfacial visco-elastic properties is relevant to surfactants. Equally, microemulsions, liquid-liquid interfaces and bio-membranes are all dependent on the behaviour of the surface visco-elastic parameters for their stability, and discussions of these systems are to be found in the literature[8]. Investigations of the surface visco-elastic properties of polymers at fluid interfaces are much more sparse but recent developments in theory[9-11] and a widening of studies[12-16] clearly demonstrates that quite different behaviour is observed for different polymer systems. A correlation with the surface organization of the polymer appears to be the cause of the differences.

The basis of the surface quasi-electric light scattering (SQELS) method will be set out here and the analysis of the data for surface visco-elastic properties outlined. This analysis is then applied to SQELS data obtained for a graft copolymer of polymethyl methacrylate and polyethylene oxide. We emphasize here that the surface visco-elastic properties obtained are not able to be exhaustively discussed at a molecular level at present because the data clearly display shortcomings in currently available theories for these parameters. A qualitative discussion of the cause of the distinctive behaviour of the visco-elastic parameters is set out which may form the basis for a more quantitative theoretical description. We stress here that these data are preliminary and the subject is developing continuously.

THEORETICAL BACKGROUND

A full exposition of the theory and properties of capillary

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waves and their subsequent analysis by surface quasi-elastic light scattering will not be presented here. Detailed treatments of both aspects are available elsewhere[17,18]. Surface fluctuations of the liquid surface lead to a departure of the liquid level from the equilibrium plane. These deviations have an r.m.s. amplitude of *ca* 2 Å and can be decomposed into a set of Fourier modes characterized by a surface wave number, q ($=2\pi/\Lambda$, Λ is the capillary wave length). The fluctuating surface acts as a diffraction grating and scatters incident light from which can be obtained (for a given q value) the capillary wave frequency (ω_0) and damping (Γ). The observed capillary wave frequency is a complex quantity;

$$\omega = \omega_0 + \mathrm{i}\Gamma \tag{1}$$

where the damping arises from energy dissipation processes due to the viscosity of the liquid.

When a surface layer is present (either as a film or as a surface excess), additional dissipation processes contribute to the damping. As the layer is perturbed by the capillary wave the local concentration at the surface will vary and there will be a relaxation process to the equilibrium surface concentration. Since the time dependence of the surface concentration will depend on the capillary wave frequency, other surface parameters will also show a frequency dependence. Of special relevance here are the shear modulus normal to the surface and the in plane compressional modulus, the surface tension, γ, and dilational modulus, ϵ, respectively. The surface tension quantifies the resistance to change in shape of the surface, the dilational modulus is a measure of the resistance to change in surface area. These two surface moduli are visco-elastic parameters and are complex quantities.

$$\gamma = \gamma_0 + \mathrm{i}\gamma'\omega_0 \tag{2}$$

$$\epsilon = \epsilon_0 + \mathrm{i}\epsilon'\omega_0 \tag{3}$$

where γ_0 and ϵ_0 are the surface tension and dilational modulus at the frequency, ω_0, of the capillary wave. The primed terms γ' and ϵ' are the transverse shear viscosity and dilational viscosity, respectively. In principle, the transverse capillary waves and the longitudinal dilational waves are independent of each other and only the capillary waves scatter light to a significant extent. However, there is a weak coupling between the two modes which results in dilational properties being accessible from light scattering by the capillary waves.

The relation between q and surface wave frequency is given by a dispersion equation, $D(\omega)$. Various forms have been given for the dispersion equation, many of them more or less equivalent when particular conditions are imposed. The power spectrum of the light scattered by the surface is then[4]

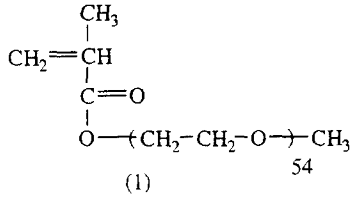
$$P(\omega) = -\left(\frac{k_\mathrm{B}T}{\pi\omega}\right)\mathrm{Im}\left[\frac{\mathrm{i}\omega\eta(q+m)+\epsilon q^2}{D(\omega)}\right] \tag{4}$$

The Fourier transform of this expression is the correlation function of the light scattered by the liquid surface, i.e. the temporal evolution of the scattered light intensity. The scattered light has a wider frequency distribution than the incident light and it is this broadening which is analysable for the frequency (ω_0), damping (Γ) and surface visco-elastic parameters of the system. The broadening is small and an optical mixing method is used to obtain the heterodyne correlation function. Measurable frequency shifts of the scattered light from incident light frequency obtainable by this technique are in the range from 1 Hz to 1 MHz. To obtain such data, the scattered light is mixed at the detector with a weak reference beam of light which has the same frequency as the incident light. The correlation function is observed as a 'beat' pattern resulting from the two slightly different frequencies. Surface wave frequency and damping are easily obtainable from such correlation functions.

EXPERIMENTAL

Polymer

A graft copolymer of polymethyl methacrylate (PMMA) and polyethylene oxide (PEO) was prepared by free radical polymerization of methyl methacrylate and a macromer of methoxy polyethylene glycol methacrylate (**1**) in refluxing ethanol using AIBN (0.5 mol%) as initiator.



(1)

After isolation the resulting copolymer had a composition of 49.1 mol% ethylene oxide (weight fraction 0.3) and relative molar masses obtained by size exclusion chromatography were $\bar{M}_\mathrm{w} = 83\,600$, $\bar{M}_\mathrm{n} = 55\,400$.

Surface quasi-elastic light scattering

SQELS experiments were carried out on apparatus constructed in our laboratory. The design is essentially identical to equipment used by others[19] and has been described elsewhere[14]. Reference beams are obtained by passing the incident laser beam (wavelength 633 nm, power 35 mW) through a transmission grating. The different diffraction orders are incident on the liquid surface at different angles and observing each of these different orders allows us to explore the q (and hence frequency) dependence of the surface waves. Spread films of the graft copolymer were obtained by deposition of small volume (~30 μl) of a solution of the copolymer in chloroform (~0.5 mg ml^{-1}) on to the surface of water (at 298 K) contained in a Langmuir trough (surface area 900 cm^2). The Langmuir trough (NIMA, Warwick Science Park, Coventry, UK) was placed on an active vibration isolation table (JRS, Afolltern, Switzerland) which in turn rested on a large, heavy optical table. The scattered light and reference beam was focused on to the photocathode of a photmulitiplier through a pinhole (~1 mm diameter) and the signal generated collected by a digital correlator (Malvern, K7025) with 128 time channels.

Two types of experiments are reported here. In the first of these a fixed value of q was selected (220 cm^{-1}) and SQELS correlation functions collected as a function of the surface concentration of the graft copolymer. This latter parameter was varied by compression of the surface film by controlled closing of the barriers of the Langmuir trough. The surface concentration range explored was 0.1 mg m^{-2} to *ca* 1.7 mg m^{-2}. In the second series of experiments, discrete surface concentrations of 0.2, 0.7 and 1.25 mg m^{-2} were investigated over the range of q accessible on our apparatus (approximately 200–1100 cm^{-1}). For all correlation functions the contents of the first delay channel were disregarded since after pulsing and 'dead time' effects may influence this channel. Consequently, the correlation functions are normalized to the contents of the second delay channel and thus the correlation functions appear asymmetric about zero.

RESULTS

A typical correlation function is shown in *Figure 1*. To obtain the surface wave frequency and damping, correlation functions were fitted by a damped cosine function which included correction terms for instrumental broadening, low frequency vibrations and a phase shift term to account for the non-Lorentzian nature of the power spectrum of the scattered light. *Figure 2* shows the frequency (ω_0) and damping (Γ) of the surface waves as a function of the surface concentration (Γ_s) of graft copolymer. We draw attention to the maximum in the surface wave frequency at a surface concentration of 0.4–0.5 mg m^{-2}. Maxima in surface wave frequency are due to resonances between the capillary and dilational waves and one condition where such resonance occurs is when the ratio of dilational modulus (ϵ_0) to surface tension (γ_0) is 0.16.

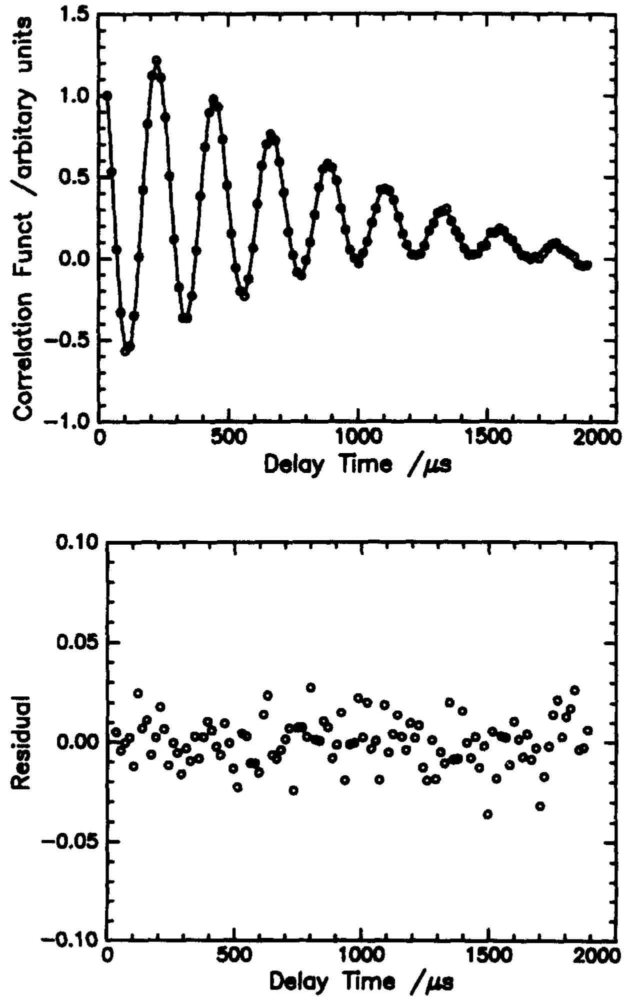


Figure 1 Typical correlation function. Surface concentration of graft copolymer 0.4 mg m^{-2} solid line is a spectral fit to the data. The residuals displayed are those pertaining to the spectral fit to the data (solid line, see text for details)

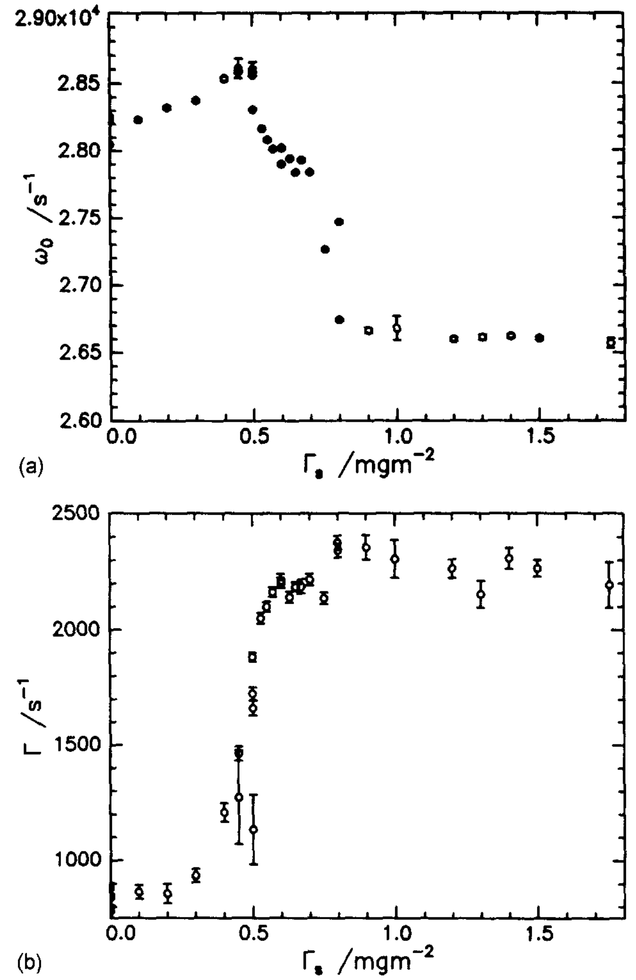


Figure 2 (a) Frequency (ω_0) and (b) damping (Γ) of surface waves as a function of surface concentration (Γ_s) of graft copolymer. Value of q is 220 cm^{-1}

To obtain further insight into the surface visco-elastic properties requires values of γ_0, $\gamma'\epsilon_0$ and ϵ'. Spectral fitting to the correlation function data was used to obtain these. This method has been developed by Earnshaw[9] and its applicability to spread films of low molecular weight materials and surfactant solutions has been extensively discussed[20]. Applications to polymer systems are still scant[14,15,21]. The essential feature of the process is the non-linear least squares fitting of the Fourier transform of the power spectrum (equation (4)) to the correlation function data with incorporation of instrumental effects as outlined for the cosine fitting. The fitting variables are the four surface visco-elastic parameters set out earlier and these can be subject to boundary conditions within which the search for optimum values is made. For γ_0 and ϵ_0 the search was made in the range 0–100 mN m^{-1}. For γ' and ϵ' the boundary conditions were -1×10^6 to $+1 \times 10^6$ mN s m^{-1} since there are no priori reasons or precedents for restriction of these parameters to a narrower range. The quality of the spectral fits to the correlation function data is demonstrated by the solid line in *Figure 1*. *Figure 3* shows the values of γ_0, γ', ϵ_0 and ϵ' obtained and their variation with surface concentration of graft copolymer. For comparison, the surface tension obtained from the surface pressure isotherm for this polymer is included in *Figure 3a*.

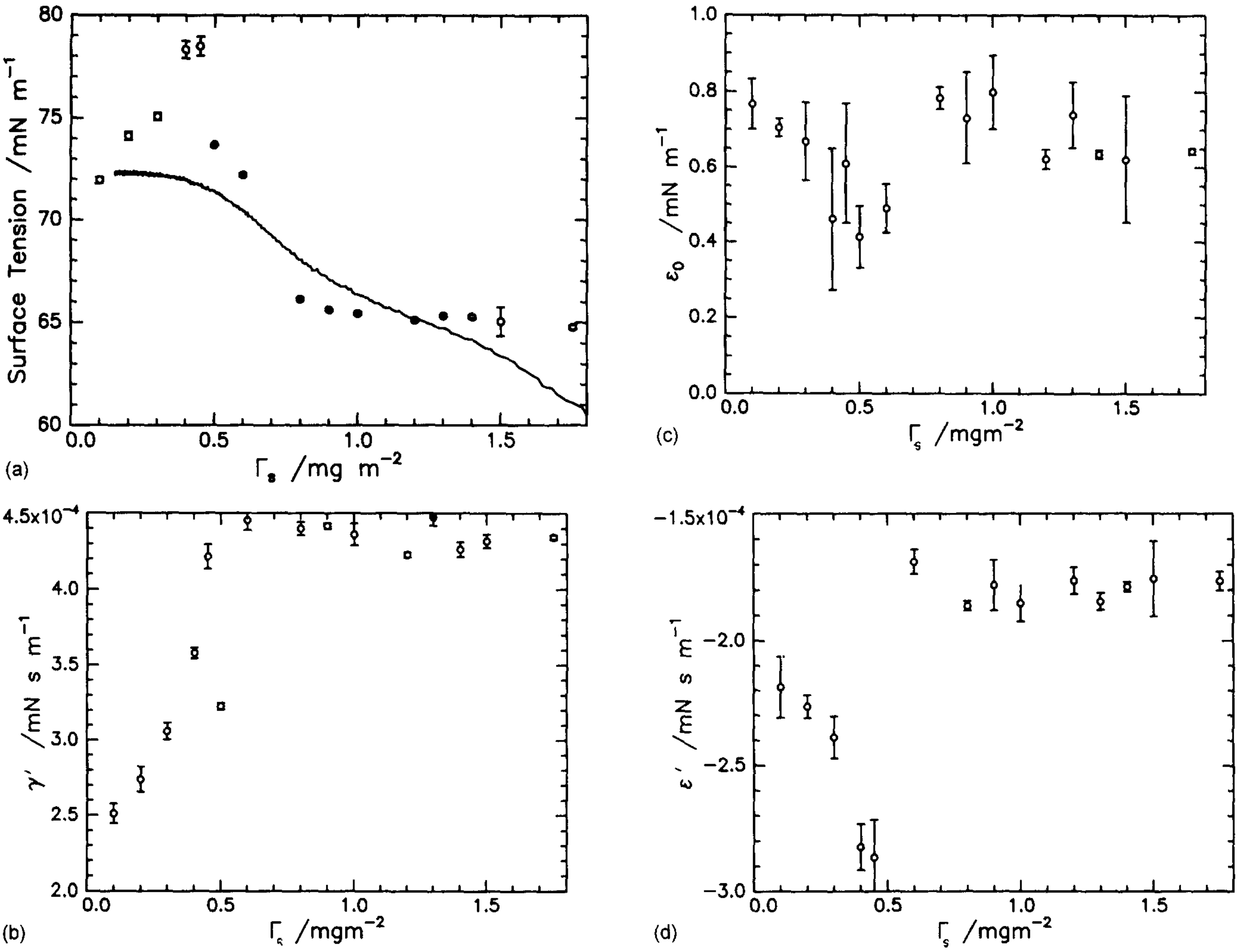


Figure 3 Dependence of surface visco-elastic parameters on surface concentration of graft copolymer: (a) surface tension, (b) transverse shear viscosity, (c) dilational modulus, (d) dilational viscosity. The line in (a) is the surface tension obtained from the surface pressure isotherm

DISCUSSION

A basis for comparison in our discussion of the surface visco-elastic properties is obtained by using the values of surface tension from the surface pressure isotherm (π as a function of Γ_s) and the dilational modulus obtained from this isotherm ($\epsilon_0 = \Gamma_s d\pi/d\Gamma_s$), this latter being shown in *Figure 4*. These data correspond to $\omega_0 = 0$ conditions. Clearly, there is no correspondence between the two surface tensions obtained by SQELS and the static value from the surface pressure isotherm. The disagreement is more apparent when the dilational moduli from SQELS are compared with the values from the surface pressure isotherm (*Figures 3b* and *4*). The static values are at least an order of magnitude larger over the concentration range where they are obtainable. These observations are completely at variance with similar comparisons for spread films of polymethyl methacrylate and polyethylene oxide[15]. For PMMA, surface tension values obtained by SQELS and from the surface pressure isotherm were identical within experimental error. For PEO differences in the surface tension from the two methods could be accounted for by the frequency dependence of the SQELS values and were describable using a Maxwell fluid model of the spread PEO. For the PEO the dilational moduli obtained by both methods (SQELS and surface pressure isotherm) were in reasonable agreement in that the values were both of the same magnitude and the variation with concentration (in the main) was similar.

Turning now to the viscosity terms γ' and ϵ'. The transverse shear viscosity for other spread films, (monomeric[9] and polymeric[14,15,21]) all have the same features. As surface concentration increases there is a rapid increases in γ' to a maximum followed by a somewhat less rapid fall. The behaviour observed here is

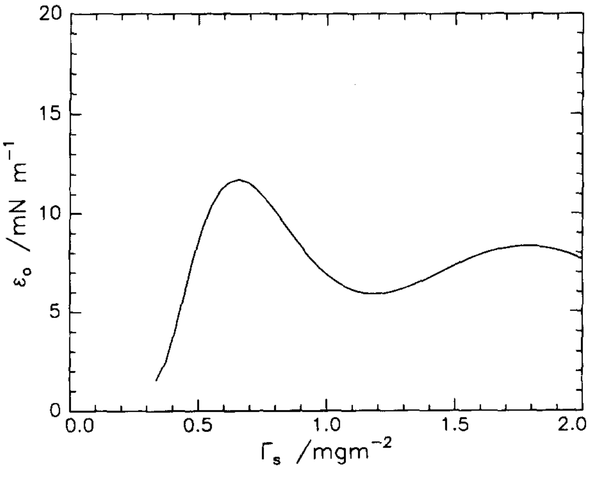


Figure 4 Dilational modulus obtained by compression of a spread film of the graft copolymer

quite distinct; there is a fairly rapid increase but after $\Gamma_s = 0.5\,\mathrm{mg\,m^{-2}}$ the transverse shear viscosity remains constant. We note here that the values of γ' obtained are an order of magnitude greater than those for spread films of low molecular weight materials but typical of spread polymer films. The dilational viscosity, ϵ', displays remarkable variations. Firstly the values are negative, secondly there appears to be a discontinuity in the variation with surface concentration. The negative values of ϵ' provide a clue as to what may be happening. Negative values of ϵ' are also obtained for spread films of polyethylene oxide, but only when the PEO penetrates the subphase[22] and this takes place at a reasonably well defined surface concentration of $0.6\,\mathrm{mg\,m^{-2}}$. At this juncture it is opportune to make some remarks regarding negative viscosities. Negative viscosities are a symptom of a destabilization of the waves from which they arise. This destabilization is due to energy being transferred into the waves from some other source. One way by which this can be obtained is by a mixing of the capillary and dilational modes[10,11]. On a phenomenological basis, mode mixing can be obtained by increasing the damping of the capillary waves (i.e. a large positive value for γ') and decreasing the damping of the dilational modes (i.e. a small or negative value for ϵ'). Furthermore, negative viscosity terms may arise due to the dispersion equation being incomplete in that terms descriptive of this additional energy source are absent. In this situation it has been suggested that negative viscosities should be viewed as *effective* parameters[11], i.e. they are a true viscosity convoluted by other parameters. An alternative view regarding the surface viscosity terms is that put forward by Goodrich[23] in his discussion of surface hydrodynamic moduli, i.e. they are *excess* quantities which can take both positive or negative values.

Whatever the true nature of ϵ', it is manifestly evident that we have negative values here, and consequently the possibility of mode mixing needs to be considered. Earnshaw and McLaughlin[10,11] have carried out a thorough discussion of mode mixing, its manifestations and diagnostic methods by which its presence can be deduced. To remove any uncertainties about the accuracy of the dispersion equation and hence the validity of the surface visco-elastic parameters, use is made of the surface wave frequency and damping. Although there are characteristic features in the variation of these parameters with ϵ_0 and γ' which clearly demonstrate mode mixing, it is only q which can be varied experimentally for a given system. A symptom of mode mixing is a down turn in the normalized damping at higher q values. Normalized damping is the experimentally observed damping divided by the theoretically calculated damping of capillary waves on the clean liquid surface. This last value depends only on the density and viscosity of the subphase and the q value of the scattered light. *Figure 5* shows the dependence of this normalized damping in the presence of mode mixing and in its absence.

Surface wave frequencies and dampings obtained from correlation functions for scattering at different q values have been normalized to the frequency and damping of clean water surface calculated using the theoretical relations. *Figure 6* shows the normalized damping as a function of q for surface concentrations of 0.2 and $1.25\,\mathrm{mg\,m^{-2}}$. Clear evidence of downward curvature is seen for both concentrations even with the limited frequency range currently accessible to us. The frequency dependence of the dilational viscosity (*Figure 7*) shows a correlation which provides an additional clue to a molecular explanation of the observed phenomena.

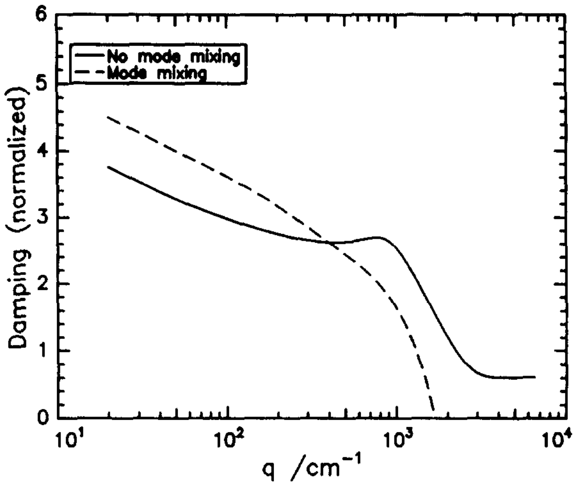


Figure 5 Normalized damping as a function of q in the presence of mode mixing (dashed line) and in its absence (solid line). For mixed modes the following parameters were used $\gamma_0 = 70\,\mathrm{mN\,m^{-1}}$, $\gamma' = 0$, $\epsilon_0 = 10\,\mathrm{mN\,m^{-1}}$, $\epsilon' = -2 \times 10^{-5}$. In the absence of mode mixing the values are identical except that $\epsilon_0 = 10\,\mathrm{mN\,m^{-1}}$. These data are identical to those first shown by Earnshaw and McLaughlin[11]

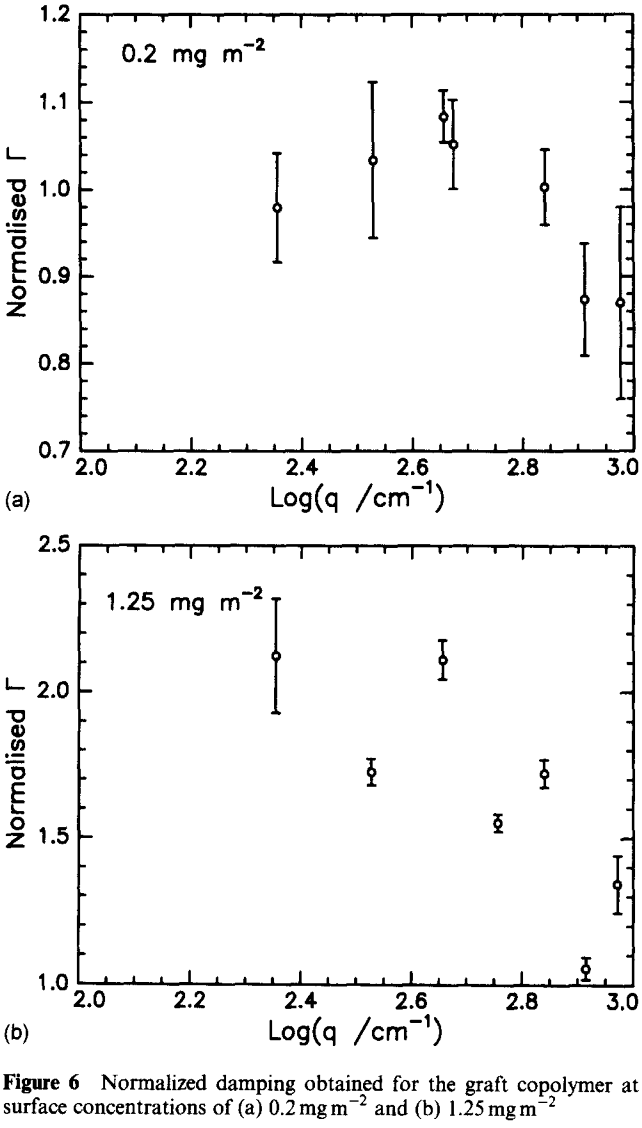


Figure 6 Normalized damping obtained for the graft copolymer at surface concentrations of (a) $0.2\,\mathrm{mg\,m^{-2}}$ and (b) $1.25\,\mathrm{mg\,m^{-2}}$

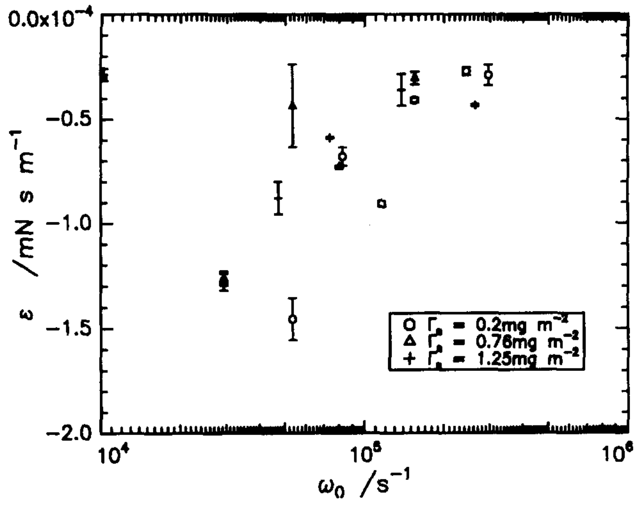


Figure 7 Frequency dependence of the dilational viscosity for the three surface concentrations investigated

This type of frequency dependence has been predicted for solutions of soluble surfactants where there is diffusive exchange between the surface excess layer and the bulk solution [24,25]. Negative terms can arise if there is a barrier to adsorption from the bulk and the frequency dependence obtained displays a curvilinear form of the type shown in *Figure 7*.

Before attempting to reconcile these observations with a possible molecular model, we summarize the SQELS data here.

1. At fixed q a maximum is observed in the surface wave frequency variation as a function of concentration. The damping rises to a plateau value at the same concentration as the maximum in ω_0.
2. The dynamic surface tension although of the same magnitude as the static value does not have the same dependence on concentration.
3. The dynamic dilational modulus values are small and approximately constant over the range of surface concentration. In no way do they correlate with the static values.
4. The transverse shear viscosity rises rapidly to a large, positive plateau value. This reflects the relationship between γ' and Γ.
5. The dilational viscosity values are negative and exhibit a discontinuity in concentration dependence at the same point that the maximum in surface wave frequency is observed.
6. For fixed surface concentrations the frequency dependence of the normalized damping coefficient indicated mode mixing at higher frequencies.
7. The frequency dependence of the dilational viscosity is reminiscent of that predicted in the presence of diffusive exchange between adsorbed and solvated species.

We remarked earlier that negative dilational viscosities were observed for spread polyethylene oxide monolayers when the polymer penetrated the subphase. Together with point 7 above, these suggest that the subphase is penetrated at all surface concentrations of the graft copolymer but the extent and nature of this penetration depends on the surface concentration.

We have evidence which supports this view from neutron reflectometry on this same copolymer when spread at the air–water interface (Peace and Richards, unpublished results). At this stage we only have neutron reflectometry data for two surface concentrations; 0.65 and 1.5 mg m^{-2}. At the lower surface concentration the surface consists of two layers, the upper (air adjacent layer) is 8 Å thick and composed of water, polymethyl methacrylate and polyethylene oxide with volume fractions of 0.46, 0.35 and 0.19, respectively. The lower layer is 21 Å thick and contains water and polyethylene oxide only at volume fractions of 0.98 and 0.02, respectively. When the surface concentration is increased to 1.5 mg m^{-2}, a three layer structure at the surface is obtained. The upper layer, which contains air and polymethyl methacrylate only, has a thickness of 9 Å the volume fraction of polymer being 0.79. All three components are contained in the 8 Å thick mid layer, the volume fractions being 0.17, 0.73 and 0.08 of water, polymethyl methacrylate and polyethylene oxide, respectively. A thickness of 30 Å was obtained for the lower layer which had a polyethylene oxide volume fraction of 0.06 with water as the only other component. There are indications that the polyethylene oxide stretches deeper into the subphase but the dilution is such that it contributes a negligible amount to the neutron reflectometry signal. These data are consistent with the idea that the polyethylene oxide grafts form a brush-like layer at the air–water interface. As the surface concentration of the copolymer increases, the areal density of the graft increases and they stretch into the subphase. Stretching of the grafted chains will take place when the grafted chains per unit area approaches the number of available grafted sites. If we take the Alexander–de Gennes[26,27] model using a lattice as a model for the solution and using a typical value for a statistical segment length as the dimensions of the lattice cells, then in combination with the known number of grafts per molecule we calculate that the grafting density (σ) exceeds the critical value for stretching of brushes (the grafts) at a surface concentration of circa 0.25 mg m^{-2}. In this calculation we have assumed that *all* grafted chains penetrate the subphase and this is certainly *not* true for the lower surface concentrations. Notwithstanding the artificiality of the model, the description of the grafts forming a brush-like layer is substantiated by the neutron reflectometry data. This model can then account for the frequency dependence of ϵ', albeit qualitatively, and also provides a source of stronger coupling between capillary and dilational modes.

Firstly, the brush chains will be subjected to osmotic fluctuations along their length. These osmotic fluctuations will have the same characteristics (albeit on a faster time scale) as the diffusional exchange postulated for surfactants. Furthermore, since the polyethylene oxide grafts are attached to the methacrylate backbone, capillary waves will impart motion to the grafts in the plane normal to the surface which will make further contributions to concentration fluctuations in this plane. Secondly, using the Alexander–de Gennes model and perturbing this about the equilibrium surface height, McLeish (personal communication) has shown that the free energy of the brush now has an additional term where longitudinal concentration fluctuations (dilational waves) are coupled to capillary waves. What has yet to be attempted is the incorporation of this free energy term in to the hydrodynamic equations so that a dispersion equation can be obtained which can then be compared with SQELS data.

There remains one aspect we have not discussed, that is the discontinuity in the surface concentration of ϵ'. Alexander–de Gennes scaling theory predicts overlap of grafted molecules at a grafting density (σ) of greater than $N^{-6/5}$, where N is the degree of polymerization of the grafted chain. For our polyethylene oxide grafts this critical σ value corresponds to a graft copolymer surface concentration slightly larger than $0.2\,\mathrm{mg\,m^{-2}}$. However, the transition from unstretched to stretched molecules is not as sharp as the simple equation implies; there will be a smooth cross over from unstretched to stretched state. Consequently, the properties pertaining to the stretched condition may not prevail until a higher concentration is exceeded. Such a transition may be the source of the discontinuity in ***Figure 3d*** but the abruptness of the change seems at odds with expectations. At this stage there is no complete theoretical model available and consequently we are unable to discuss the data further. Evidently what is needed are developments in theory which can be compared with experiments.

CONCLUSIONS

Analysis of surface quasi-electric light scattering by thermally driven surface waves of a spread film of an amphiphilic graft copolymer spread on water has produced surface visco-elastic parameters which have totally different characteristics to those for the simple homopolymer constituents. The observation of negative dilational viscosities and their variation with surface concentration indicates that penetration of the subphase by the hydrophilic grafts is the source of this behaviour. The combination of a high transverse shear viscosity, leading to damping of the capillary waves, and a negative dilational viscosity, leading to destabilization of the dilational waves, suggests that mode mixing of the two fluctuation modes is present. From the frequency dependence of the normalized damping of the surface waves the occurrence of mode mixing appears to be confirmed. Furthermore, the systematic dependence of the dilational viscosity on wave frequency points to concentration fluctuations in the graft normal to the surface being a source of the negative values. These concentration fluctuations are magnified by capillary wave perturbations leading to a stronger coupling between capillary modes and dilational modes which is obtainable using Alexander–de Gennes scaling model for brushes. Support for the notion of subphase penetration by the polyethylene oxide grafts and the subsequent use of the scaling model has been provided by the surface organization deduced from neutron reflectometry data. Quantitative evaluation is prevented by the current absence of appropriate theory and therefore of a more suitable dispersion equation.

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