

Dynamic surface elasticity of aqueous solutions of polyethylene glycol

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Measurements of the concentration dependence of the characteristics of surface waves in solutions of polyethylene glycol allow us to determine the dynamic surface elasticity and to show that the relaxation of the surface tension arises as a result of the redistribution of monomers between different regions of the surface layer.

Although the first studies of the surface properties of aqueous solutions of polyethylene glycols (PEG) and polyethylene oxides (PEO) were published more than half a century ago,^{1,2} the method of neutron reflectometry has only recently offered the possibility of obtaining reliable data on the structure of the surface layer in these systems.^{3–5} The non-equilibrium surface properties of solutions of PEG and PEO have been studied so far only by means of measurements of the surface tension.^{2,6,7} The results obtained allowed the role of diffusion in the bulk phase in the process of approaching equilibrium to be evaluated. However, the dynamics of polymer chains in the surface layer has not been considered.

The mechanism of relaxation processes in the surface layer of PEG solutions has been studied in this work by the methods of transverse⁸ and longitudinal^{9,10} surface waves in a broad concentration range. The method of transverse surface waves has been applied until now mainly to spread surface films of PEG and PEO.^{4,11,12} The only results of measurements of the damping coefficient of transverse capillary waves for PEG solutions were published in ref. 13, and only for one PEG concentration. Longitudinal waves have not been used for these purposes at all.

The experimental set-ups for measurements of the characteristics of transverse and longitudinal surface waves were described in detail elsewhere.^{8,10} Note only that we applied a capacity wave probe in the course of the investigation of transverse waves. The probe was based on the principle of a dynamic condenser.⁸ In order to measure the characteristics of low-frequency longitudinal waves we used transverse waves with a higher frequency which propagated in the perpendicular direction. This led to a low-frequency modulation of the high-frequency electrical signal which was proportional to the amplitude of the transverse waves. Application of the phase difference gauge allowed us to separate the electrical signal proportional to the amplitude of the longitudinal waves.¹⁰ The surface tension σ was measured by the Wilhelmy plate method.

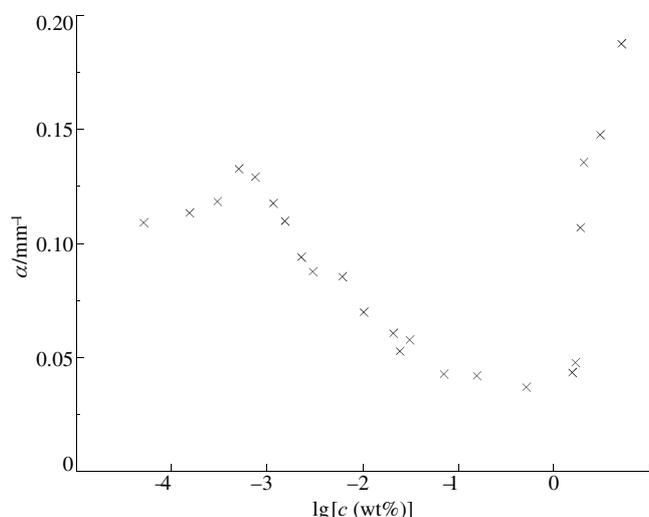


Figure 1 Dependence of the damping coefficient of transverse capillary waves on the concentration of PEG at a frequency 200 Hz.

PEG with molecular weight 4000 (Merck) was used as received. All the solutions were prepared immediately before the measurements using twice-distilled water.

Although the dependence of the damping coefficient α of transverse capillary waves on the PEG concentration c at a frequency of 200 Hz (Figure 1) is similar to the corresponding curves for conventional surfactants,⁸ more careful inspection allows us to determine some peculiarities. First, the damping coefficient for PEG solutions changes significantly more slowly with concentration. For most conventional surfactants all the changes of α in the region below the critical micellisation concentration take place in a concentration range of about one order of magnitude. In contrast, the concentration range for PEG solutions in Figure 1 spans over five decimal orders of the value. Second, the α values in the region of the local minimum (Figure 1) turn out to be about two times lower than for conventional surfactants.

The characteristics of both modes of the surface waves (longitudinal and transverse) can be connected with the surface properties by the dispersion equation. We have used the following form¹⁰ of this equation to calculate the dilational dynamic surface elasticity ε

$$\varepsilon = \varepsilon_r + \varepsilon_i = \frac{\rho\omega^2[\rho\omega^2 - (\sigma k^3 + \rho g k)\tanh(kh)] + 4i\rho\mu\omega^3 k^2 + 4\mu^2\omega^2 k^3 [m \tanh(kh) - k]}{mk^2[\rho\omega^2 - (\sigma k^3 + \rho g k)\tanh(kh)] + k^3(\sigma k^3 + \rho g k)} \quad (1)$$

where $k = 2/\lambda + i\alpha$ is the complex wave number; λ is the wavelength; ω is the angular frequency; $m^2 = k^2 - i\omega\rho/\mu$; $\text{Re}[m] > 0$; ρ is the density of the solution; μ is the viscosity; g is the gravitational acceleration and h is the depth of the liquid (in our set-up $h = 15$ mm).

Note that only the characteristics of longitudinal waves are sensitive enough to the surface elasticity in order to

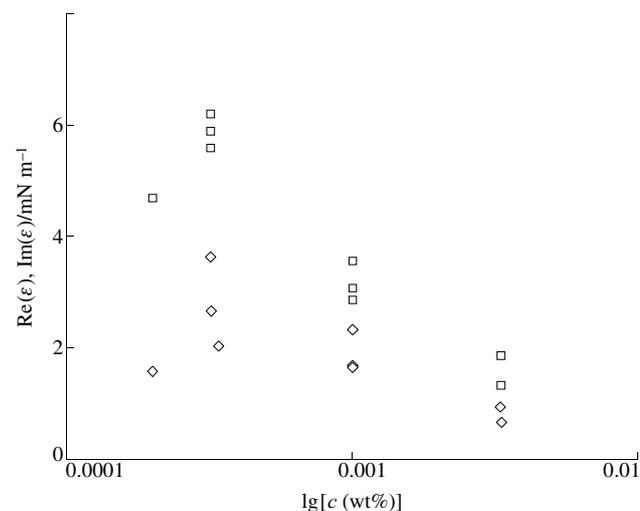


Figure 2 Dependence of the real (\square) and the imaginary (\diamond) parts of the dynamic surface elasticity determined from the characteristics of longitudinal surface waves at 2 Hz according to equation (1) on the concentration of PEG.

guarantee a reasonable accuracy of the calculations. The dynamic surface elasticity essentially influences the damping coefficient of transverse waves only when $|\epsilon| \leq 10 \text{ mN m}^{-1}$.⁸

Nevertheless, comparison of the experimental data on the damping coefficient of transverse waves with the results of calculations for a model system in the region of the local maximum allows us to estimate both components of the surface elasticity. The α value in this region proves to be close to the maximum value of the damping coefficient for a pure elastic film (0.122 mm^{-1} at $\sigma = 64 \text{ mN m}^{-1}$) when the real part of the surface elasticity is approximately 0.15σ and the imaginary part is zero.⁸ Therefore, for the region of the local maximum we have $\text{Re}(\epsilon) \approx 10 \text{ mN m}^{-1}$ and $\text{Im}(\epsilon) \approx 0$. The sensitivity of the wave characteristics to the surface rheological properties is higher in the region of the local minimum and the dispersion relation for capillary waves allows us to calculate directly the dynamic surface elasticity according to equation (1). In this case we have $\text{Re}(\epsilon) \approx 3 \text{ mN m}^{-1}$ and $\text{Im}(\epsilon) \approx 1 \text{ mN m}^{-1}$. Therefore, at a frequency of 200 Hz $|\epsilon|$ decreases while the concentration increases up to 0.3 wt% and the pure elastic film is converted gradually into a viscoelastic one. The abrupt increase of the α values for higher concentrated solutions can be explained only partly by the increase of the viscosity of the bulk phase and, consequently, this suggests an increase in the surface elasticity while approaching the range of semi-dilute solutions.

Unlike the case of transverse capillary waves, the dynamic surface elasticity can be calculated easily from the experimental results on the characteristics of longitudinal surface waves independent of the elasticity modulus.¹⁰ Figure 2 shows the corresponding concentration dependences of the real and imaginary components of the dynamic surface elasticity at a frequency 2 Hz. Both components of the elasticity go through a maximum at $c \approx 0.0003 \text{ wt\%}$. In the ranges $c \leq 0.0001 \text{ wt\%}$ and $c \geq 0.005 \text{ wt\%}$ longitudinal waves cannot be excited and, consequently, $|\epsilon| \approx 0$. Note that the concentration range, which corresponds to the non-zero values of $|\epsilon|$ (Figure 2), coincides approximately with the region of the local maximum of damping of transverse capillary waves (Figure 1). However, the adsorption film turns out to be viscoelastic in this region at a frequency 2 Hz [$\text{Im}(\epsilon) \neq 0$]. These results allow us to obtain a rough estimate of the mean relaxation time τ of the surface tension. In the region of local maximum of damping of transverse waves this quantity is comparable with the period of the applied longitudinal waves and significantly exceeds the period of transverse waves and, consequently, $\tau \sim 0.1 \text{ s}$. In the region of local minimum τ is comparable with the period of transverse waves and we have $\tau \sim 0.001 \text{ s}$. Therefore, the mean relaxation time decreases with the concentration of PEG.

The diffusional exchange of surfactant molecules between the surface layer and the bulk phase is the main relaxation process for solutions of conventional surfactants which determines the character of the dependence of α as a function of concentration.⁸ However, the characteristic diffusion time of PEG molecules to the surface τ_D exceeds the determined relaxation times for the solutions under consideration by several orders of magnitude ($\tau_D \sim 100 \text{ s}$).⁷ Therefore, it seems more probable that the small relaxation times determined correspond to the processes proceeding within the surface layer. According to recent studies the adsorption films of PEO and PEG at low bulk concentrations are similar to the spread surface films and the polymer chains lie on the surface without penetration into the depth of the bulk phase.⁷ The situation changes when the concentration is

increased and one can imagine that the surface layer consists of two regions: a narrow concentrated region just beneath the gas phase and a more extended region of 'loops and tails', where the concentration of monomers decreases with the distance from the surface.⁵ The processes of squeezing 'loops and tails' out of this concentrated region or of drawing in this region, which have been studied theoretically elsewhere,¹⁴ can be responsible for the relaxation of surface stresses, which arise due to surface wave propagation. In fact, the number of 'loops and tails' has to increase and the mean relaxation time has to decrease with increasing concentration, which agrees with the present findings. The equations of the theory,¹⁴ describing the dynamics of polymer chains at the interface, contain two groups of parameters: the intrinsic properties of the chains and the parameters characterising the packing of the polymer chains in the surface layer. Determination of the parameters of the latter group is the most difficult problem. However, studies of the dependence of the relaxation times on the length of the polymer chain, which are in progress now, can probably give the required information.

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