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ORIGINAL CONTRIBUTION

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Surface forces in foam films from ABA block copolymer: a dynamic method study

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Abstract The thinning of foam films from aqueous solutions of an ABA triblock copolymer of polyethylene oxide and polypropylene oxide (average molecular weight 14,000 g/mol) is studied experimentally. The dependence of the surface forces on film thickness is obtained by the dynamic method of Scheludko and Exerowa.

The total surface force measured in foam films (radius ≈ 60–70 μm) from 10^{-5} M (0.014 wt%) polymer solution with 0.1 M NaCl is positive at thicknesses from about 800 Å down to 460 Å. The electrostatic repulsion is negligible while the contribution of van der Waals attraction is small (within 15%). Therefore a positive surface force component predominates. Most probably it arises from steric interactions between the hydrophilic polyethylene oxide tails of the polymer. The dynamic method appears to be a suitable technique for exploring the stabilization of foam films from ABA copolymers.

Key words ABA block copolymers – free liquid films – dynamic method for surface force measurement – steric stabilization

Introduction

Free liquid (foam) films are the simplest yet powerful model for studying liquid interfaces, interacting surfaces as well as colloidal stability. They played a major role in the testing of the DLVO theory and its acceptance (see for instance [1–4] and references therein). Among others free liquid film studies have been carried out with various ionic [5] and nonionic [6] surfactants including phospholipids [7, 8]. This studies extended our knowledge on surface forces and revealed the importance of interactions not included into the classical DLVO theory. Nonetheless there is still much to learn about polymeric stabilization and the steric interactions between adsorbed polymer molecules [9]. With few exceptions [10, 11] free liquid films from polymers were seldom investigated so far.

Recently Exerowa et al. [12] carried out a detailed study of foam films from an ABA triblock copolymer with the equilibrium film technique. They have found that the van der Waals attraction is always present while depending on the polymer and salt concentration either the electrostatic repulsion or the steric one, or both may be operative.

The dynamic method for interaction forces measurement [13, 14] is an alternative of the equilibrium technique. It has been successfully applied to measure van der Waals attraction and retardation effects in foam films [1, 15]. Very recently the dynamic method has been employed to study surface forces of oscillating nature in foam films from an anionic surfactant [16].

In this paper the dynamic method is applied to foam films from an ABA triblock copolymer known to create significant steric interactions. Based on the findings of Exerowa et al. [12] conditions of predominant steric interactions were selected and a slightly modified version of the dynamic method was used to measure surface forces. Our objective was to initiate investigations of the interactions in foam films from polymers with the dynamic method which gives information about weaker interactions (in thicker films) otherwise inaccessible.

Materials and methods

The ABA triblock copolymer employed in this study is a commercial nonionic surfactant of the Synperonic PE Series referred to as F108. The polymer has been obtained from Imperial Chemical Industries PCL, Plant Protection Division (Courtesy of Dr. Th.F. Tadros) and used without further purification. It consists of a central polypropylene oxide (PPO) chain – the hydrophobic moiety, and two hydrophilic polyethylene oxide (PEO) tails as follows:

$$(EO)_{122}(PO)_{56}(EO)_{122}$$

It contains about 80 wt% ethylene oxide and its declared average molecular mass is 14,000 g/mol.

All experiments have been carried out at 23 °C with a fresh aqueous solution of the polymer F108 (10^{-5} M, i.e. 0.140 g/l, a concentration close to but below CMC) prepared by weighting. A 0.1 M electrolyte concentration has been created by dilution of 1 M NaCl stock solution. "Analar" NaCl from Merck roasted at 550 °C for several hours was used.

The film drainage has been carried out in a Scheludko–Exerowa cell [1, 17]. In this cell the film is formed in the middle of a biconcave drop hanging in a short vertical glass tube (diameter ca. 4 mm). When the liquid is sucked out of the drop the two liquid/gas interfaces approach each other and ultimately a thin liquid film is created. The drop environment is saturated with the solution vapors.

The evolution of the film thickness with time was monitored in monochromatic light (from an incandescent lamp equipped with a filter having a transmittance maximum at 546 Å) by the microinterferometric method [1]. The reflected light is captured with a photomultiplier. The resulting current is amplified and directed to a recorder. The photocurrent thus obtained, $I(t)$, is a periodic function of time. The film thickness is calculated from the reduced photocurrent $\Delta(t) = [I(t) - I_{\mathrm{MIN}}]/(I_{\mathrm{MAX}} - I_{\mathrm{MIN}})$, where I_{MAX} and I_{MIN} are the intensities of the last two interference maximum and minimum, in the manner described by Scheludko [1]. Thus a film thickness referred to as "equivalent film thickness" is obtained (the thickness the film would have if it was homogeneous and had a refraction index equal to that of the bulk solution). Details about the setup have been previously published (see for instance [5]).

The dynamic method for measuring interaction forces links film thinning behavior to the disjoining pressure $\Pi(h)$ at a given thickness h [13, 14, 18]. The film thinning rate is described by the equation:

$$[h^{-2}(t)]' = a_{\mathrm{Re}} P_0 \tag{1}$$

Essentially Eq. (1) is the so called Reynolds equation [19] that strictly holds if two solid cylindrical disks of radius r are coming closer in a fluid of viscosity μ under the action of a pressure P_0. Then h is the distance between the disks, i.e. the film thickness and $a_{\mathrm{RE}} = 4/3\mu r^2$. Reynolds equation (1) may be applied to foam films as well provided that the two liquid surfaces are rigid and immobile, the film viscosity is equal to that of the bulk liquid and evaporation is unimportant. In the case of a biconcave drop $P_0 = P_{\mathrm{C}}$, where $P_{\mathrm{C}} = const$ is the capillary pressure inside the drop. If the liquid film is thin enough for surface forces to be significant then $P_0 = P_{\mathrm{C}} - \Pi(h)$, and Eq. (1) reads

$$[h^{-2}(t)]' = a_{\mathrm{Re}}[P_{\mathrm{C}} - \Pi(h)] \tag{2}$$

The dynamic method is based on this expression which predicts a linear increase of h^{-2} with time when $\Pi = 0$ (in thick films). The determination of the disjoining pressure isotherm, $\Pi(h)$, from film thinning data is straightforward: the dependence $h(t)$ is experimentally found and transformed into $h^{-2}(t)$; then $\Pi(h)$ is obtained from the slope of $h^{-2}(t)$ through Eq. (2).

From a practical point of view the dynamic method is fast and relatively simple. However the hydrodynamic flow upon which Eq. (2) is based is a very first approximation. Such a simple model would hardly work in the general case [20]. Nevertheless in this short paper we confine ourselves to the use of this model and the resulting Eq. (2).

The capillary pressure, P_{C}, is measured in a separate experiment. A tube identical to that in which the biconcave drop is created, is vertically immersed into the solution. The liquid column height is measured with a cathetometer and P_{C} (it equals the hydrostatic pressure) is calculated [17]. The capillary pressure is a monotonically decreasing function of time and reaches saturation after several hours. Its value $P_{\mathrm{C}} = 400$ dyn/cm^2 (correct to within 10%) has no direct influence on the present results and is used for comparison only.

Results

After the biconcave drop has been created the two liquid surfaces were left for about an hour. Then the distance between the two drop surfaces was slowly reduced right to the point of appearance of the film and then the system has been left to reach equilibrium for another 30 min (this value has been empirically chosen; at shorter time the experimental $I(t)$-curves are considerably deformed).

A film was then created by sharply sucking off a very small portion of the liquid drop. Since films whose radii exceed about 100 μm are rarely planar [4] only films with radii $r = 60$–70 μm were considered in this study. The constancy of the radius was checked during the experiments and all runs with detectable radius variations have been discarded.

Visual inspection in reflected light revealed that film drainage was never perfect. In most cases a darker patch of irregular shape was observed, i.e. the films were not absolutely flat. Shortly after its formation the patch was ejected into the film periphery. The effect was more pronounced at higher order of interference, i.e. at larger film thicknesses but persisted even after the last maximum. Therefore only below about 1000 Å the films were uniform in thickness. The slower was the spot rejection from the film the more was the resulting $I(t)$-curve distorted. In order to minimize the influence of these effect numerous runs have been performed and only critically selected curves were processed.

In our experiments film thinning typically lasted about 20–30 min. However most interesting are the first several minutes since later the relative change in the photocurrent is less than 1%, i.e. practically $h = const$ and $\Pi = P_C$ (See Eq. (2)). From every run an average of about 50 points were chosen and the equivalent film thickness was calculated. The result is plotted in Fig. 1a. In some cases the final thickness has been additionally monitored for half an hour without any significant changes being detected. The average final thickness from 12 consecutive runs with the same drop is 456 ± 8 Å, in excellent agreement with the figure previously obtained in our laboratory by the equilibrium technique [12].

The run from Fig. 1a is recast into the scale of Reynolds equation (1), namely h^{-2} vs. t, and depicted in Fig. 1b. The solid line shows the linear part of the dependence at higher film thicknesses (shorter times) as detected by linear regression analysis. A linear regression has been consecutively drawn through the first 3,4,...,n points and the line with the highest F-test [21] has been chosen as a representative of the drainage regime with $P_0 = P_C$, i.e. $\Pi = 0$. The Reynolds law (1) is obeyed down to thicknesses of about 800 Å.

At thicknesses below 800 Å the experimental points clearly deviate from Reynolds equation (1). We have made use of the experimental value of the slope b, obtained from the solid line in Fig. 1b (Table 1) and calculated the dimensionless disjoining pressure, $\Pi^*(h)$, from the Scheludko–Exerowa equation (2) written in a slightly modified form:

$$\Pi^*(h) = \frac{\Pi(h)}{P_C} = 1 - \frac{[h^{-2}(t)]'}{a_{Re} P_C} = 1 - \frac{[h^{-2}(t)]'}{b} \qquad (3)$$

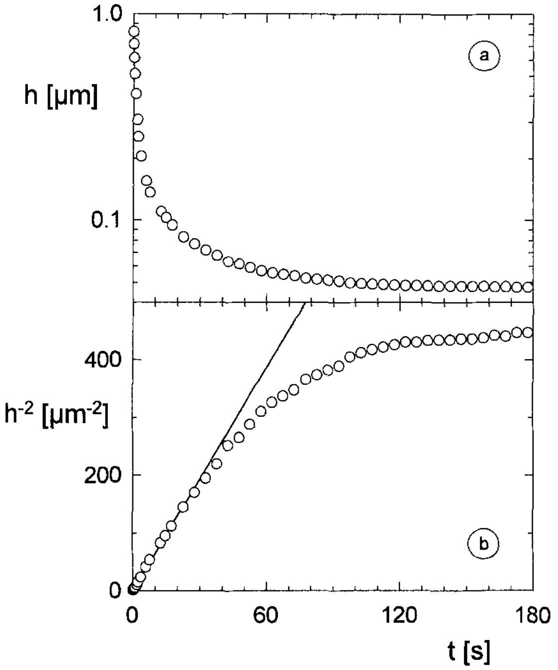

Fig. 1 **A** Time dependence of the equivalent film thickness (Run 1). Aqueous solution: 10^{-5} M F108 + 0.1 M NaCl, Film Radius $r = 68$ μm (23 °C); **B** Time dependence of the squared reciprocal equivalent film thickness (Run 1). Data from Fig. 1a

Table 1 Parameters extracted from the linear part of the $h^{-2}(t)$ dependence

Run	r [μm]	b [μm$^{-2}\cdot$s^{-1}]	a_{EXP}/a_{Re}	μ_{EFF} [cP]
1	68	6.45	0.521	1.8
2	62	6.87	0.462	2.0
3	70	6.77	0.580	1.6

The use of the slope b in Eq. (3) means that the prefactor in Reynolds equation (1) is postulated constant during the film thinning without any reference to its analytical form. This assumption was inspired from the experimental and theoretical evidence that the presumptions of Reynolds equation are never strictly fulfilled [4].

The derivative with respect to time $[h^{-2}(t)]'$ needed for the Π^* evaluation via Eq. (3) has been computed through a 3-point numerical differentiation. The isotherm thus obtained is shown in Fig. 2 (Run 1). The scatter is partly due to the experiment. Part of it arises from the numerical derivation procedure which is known to augment the raw data noise [22].

This result is compared in Fig. 3 to another run with the same drop (Run 2). A separate run with a fresh solution

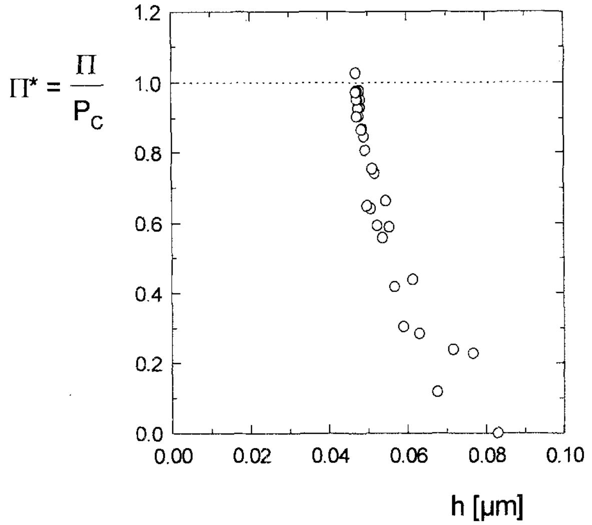

Fig. 2 Dimensionless disjoining pressure, $\Pi^* = \Pi/P_C$ (P_C = 400 dyn/cm^2 is the capillary pressure inside the drop), vs. equivalent film thickness, h (Run 1). Aqueous solution: 10^{-5} M F108 + 0.1 M NaCl, Film Radius r = 68 μm (23 °C)

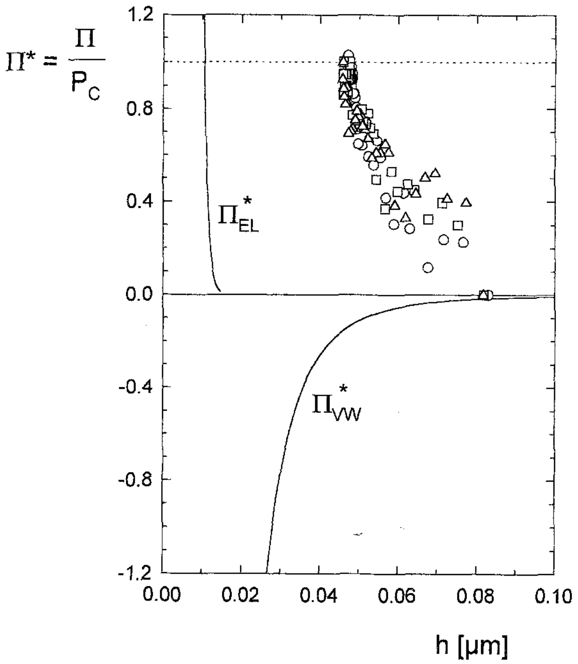

Fig. 3 Dimensionless disjoining pressure, Π^*, vs. equivalent film thickness, h (○-Run 1, r = 68 μm, □-Run 2, r = 62 μm, △-Run 3, r = 70 μm). Aqueous solution: 10^{-5} M F108 + 0.1 M NaCl, Film Radius r = 68 μm (23 °C). $\Pi^*_{EL} = \Pi_{EL}/P_C$ (P_C = 400 dyn/cm^2 is the capillary pressure inside the drop) – electrostatic double layer repulsion evaluated with the numerical procedure given in [23] for a surface potential φ_0 = 40 mV. $\Pi^*_{VW} = \Pi_{VW}/P_C$-van der Waals component of the disjoining pressure calculated with the formula given in [24] for a homogeneous water film

under the same conditions (Run 3) is also given. As can be seen in Fig. 3 the overall agreement between the three runs is rather good in spite of the inherent scatter. Since Run 3 was conducted with an open diaphragm one may conclude that the noise introduced by the meniscus reflectivity has little influence upon the main signal. This is hardly surprising since the films considered are rather thick and therefore the meniscus curvature (which is related to the meniscus reflectivity) is low.

Discussion

The experimental slope at thicknesses below about 800 Å is smaller than that predicted by Reynolds equation (1) – the solid line in Fig. 1b, and therefore the film thinning is decelerated, i.e. the disjoining pressure is positive. Figures 2 and 3 are essentially a refinement of this basic experimental fact. Thus our main result is that substantial repulsive forces stabilizing the foam film act at thicknesses from about 800 Å down to 460 Å.

It has been shown by Exerowa et al. [12] that forces of steric origin are responsible for the film stability observed under these conditions. Nevertheless we have checked how much of the present results may be attributed to the classical disjoining pressure components – Π_{EL} and Π_{VW}. To accomplish this we adopted at first the simplest film model – a homogeneous water film.

It is quite obvious that the double layer repulsion, Π_{EL}, should be very low since at 0.1 M NaCl the Debye length is only 10 Å. Nevertheless Π_{EL} is computed with the algorithm proposed in [23] as employed in [5] for a surface potential of 40 mV, and plotted in Fig. 3. By far and away Π_{EL} cannot account for the strong positive disjoining pressure found in the experiments. The value 40 mV is taken as an estimate from the results of Exerowa et al. [12]. Calculations with 20 and 60 mV gave practically the same result. As may be expected at that high electrolyte concentration the limiting cases of constant potential and constant charge are indistinguishable.

The van der Waals component, Π_{VW}, has been assessed in the manner proposed in [24] for the case of a homogeneous water film. The result is also shown in Fig. 3. Unlike Π_{EL}, Π_{VW} may have some influence (within 15%) on the total isotherm. Its values are strictly negative and therefore a larger positive component outweighs the van der Waals attraction.

The homogeneous water film model may be too crude when macromolecules are involved. Hence a three layer film model was considered. This model requires more parameters and though superior to the homogeneous film model it can hardly be viewed as more accurate.

The three layer model consists of an aqueous core (refractive index 1.33) and two adsorption layers of thickness 100 Å (as estimated from tensiometric measurements) and refractive index 1.42[11]. The equivalent water thickness measured is different from the thickness of such a three layer film because the optical density of the adsorption layers is higher than that of water. The difference between them was assessed by the method originated by Duyvis [25]. In comparison with the single layer model the three layer model predicts a Π_{EL} which is shifted to the right by some 250 Å (not shown in Fig. 3) but is still far from the experimental points. In order to calculate Π_{VW} one must adopt an appropriate value of the Hamaker constant for the adsorbed material. Many authors assume that the Hamaker constant for this type of polymers is very close or equal to that of water [10, 11, 26]. But even with drastically different values the model yields results that are very similar to those obtained with the homogeneous film model. Thus the calculations based on the three layer model corroborate the conclusion that the classical components – Π_{EL} and Π_{VW} – do not fit the present results.

It might be speculated that the strong repulsion found in these experiments is due to steric interactions between the hydrophilic tails of the polymer molecules. It has been experimentally found that amphiphilic block copolymers are very good steric stabilizers [9]. While the polypropylene oxide moiety of the F108 molecule should adsorb at the liquid/gas interface the two polyethylene oxide chains are water soluble and must protrude into the aqueous solution. Upon thinning of the liquid film the PEO chains extending from the two surfaces repel each other. The experimental isotherms shown in Fig. 3 decrease monotonically with thickness. It is to be noted that such behavior is characteristic of the interaction energy as a function of the distance between two mica surfaces bearing grafted polymer layers in good solvent (often referred to as "polymer brushes") as obtained with the surface forces apparatus (see for instance [27]). Such an analogy goes even further. The thickness at which surface forces come into play in our experiments is about 15 times the unperturbed radius of gyration of the polymer molecule. This figure is fully consistent with those reported for grafted polymer layers [27, 28].

The above treatment of the film thinning data only presumes that the prefactor in Reynolds equation (1) is constant during the film thinning. The evaluation of the dimensionless disjoining pressure via Eq. (3) depends solely on the experimental value of the slope b whose reproducibility is quite good (Table 1). This consistency between the initial thinning rate of different runs is encouraging. However the experimental values: $a_{\mathrm{EXP}} = b/P_{\mathrm{C}}$, differ significantly from the theoretical ones: $a_{\mathrm{Re}} = 4/3\mu r^2$ (Table 1). One may suppose that the film viscosity is higher than the that of the bulk solution. If this hypothesis is advanced the effective viscosity, μ_{EFF}, turns out to be almost twice as higher as the viscosity of water (Table 1). This seems rather unrealistic and the problem is currently investigated.

As already noted Reynolds equation (1) strictly holds only for immobilized surfaces. It has been found that for liquid films stabilized with soluble surfactants this condition is never rigorously fulfilled [4]. There are many articles on the subject (see for instance [20]) but the detailed analysis is beyond the scope of this short paper. For the sake of illustration we will shortly outline the two main routes that have been followed in incorporating the specific effects due to the presence of soluble surfactants into Reynolds equation (1).

The first was pursued by Radoev et al. [29]. They took into account the diffusion of surfactant molecules between the surface and the bulk as well as their surface diffusion. Their equation may be written in a form analogous to that of Eq. (1) with:

$$a = a_{\mathrm{Re}}\left(1 + T_1 + \frac{T_2}{h}\right) \geq a_{\mathrm{Re}} \tag{4}$$

The factor a is no longer constant but depends on the film thickness, h, the bulk and surface diffusion accounted for by the terms T_1 and T_2.

An alternative treatment has been proposed by Barber and Hartland [30]. They considered the effect of shear and dilatational surface viscosity on the drainage of a planar film. Their result may be given into the form:

$$a = \frac{4}{m^2} a_{\mathrm{Re}} \geq a_{\mathrm{Re}} \tag{5}$$

where $m \leq 2$ is the number of immobile surfaces. It is a function (analytically presented in [30]) of the film radius and the ratio of the surface and bulk viscosity.

It can be readily seen that both Eqs. (4) and (5) predict an accelerated rate of thinning with respect to Reynolds equation (1) while in our experiments a decelerated one is found (Fig. 1b and Table 1). Therefore the action of a repulsive surface force in our experiments does not arise from an improper hydrodynamic treatment.

The total surface force is positive at thicknesses between 800 Å and 460 Å. Under these experimental conditions electrostatic repulsion is negligible while the contribution of van der Waals attraction is small (within 15% estimated with the single water layer model). Therefore at any thickness a positive disjoining pressure component is predominant. Most probably this repulsion arises from the steric interactions between the long hydrophilic polyethylene oxide tails of the polymer molecules. The dynamic method appears to be a suitable technique for exploring the stabilization of a foam film from ABA copolymers. It is complementary to the equilibrium approach and gives unique information about interaction forces in a range otherwise inaccessible.

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