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Direct measurement of interaction forces in free thin liquid films stabilized with phosphatidylcholine

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Abstract. Microscopic foam films from suspensions of small unilamellar dimyristoylphosphatidylcholine (DMPC) vesicles have been obtained. The film formation is facilitated at temperatures above the gel-liquid crystalline transition of DMPC. A detailed study of the dependence of equilibrium thickness of DMPC foam films on electrolyte concentration at constant capillary pressure and a direct measurement of the disjoining pressure isotherm has been carried out. Formation of thick equilibrium horizontal microscopic films stabilized with DMPC at low external pressures and low electrolyte concentrations was found and interpreted as being due to the existence of long-range electrostatic interactions in these films. A diffuse electric layer potential of 36 mV has been calculated. The DMPC films have been compared to films obtained from non-ionic surfactant solutions where the long range electrostatic repulsion is explained as being due to specific adsorption of OH^- at the film interfaces. However, unlike the results obtained for surfactant films, in this study formation of common black films and thinning of the DMPC Newton film with pressure have been observed.

Key words: Thin liquid films – Unilamellar vesicles – Phosphatidylcholine – Interaction forces

Introduction

Free thin liquid films, known also as foam films or soap films, interfaced on both sides with a gas phase, have for many years been an object of thorough studies (e.g. Clunie et al. 1972; Exerowa 1978; Exerowa and Kashchiev 1986; Scheludko 1967). The direct measurement of important parameters of foam films (thickness, capillary pressure, etc.) offer a possibility for obtaining information about their thermodynamic and kinetic properties, interaction forces, and diffuse electric layer potential. Especially advantageous in this respect is the microscopic film model with a radius of about 0.01 cm which is readily formed even at very low surfactant concentrations and is geometrically well defined. Depending on the elctrolyte concentration of the solution two equilibrium states of the foam films have been found. Below the so-called critical electrolyte concentration formation of thick equilibrium (silver) and common black films is observed. It is generally accepted that these films consist of an aqueous core bound on both sides by adsorbed monolayers. Their thickness strongly depends on the electrolyte concentration (C_{el}) of the solution. Above the critical electrolyte concentration Newton black films (NBF) form, with thickness independent of C_{el}. The film formation and properties are strongly influenced by surfactant type (ionic or non-ionic) and concentration. It has been shown that in order to obtain NBF the surfactant concentration should correspond to adsorbed layer saturation, which is not a necessary condition for films of the common black type (Exerowa et al. 1981). It has been established also that the generally accepted theory of colloid stability of Derjaguin-Landau-Verwey-Overbeek (DLVO) is valid also for foam films (e.g. Clunie et al. 1972; Derjaguin et al. 1985; Mysels and Jones 1966; Scheludko 1967). It has been shown that for equilibrium silver and common black films the Van der Waals attraction and electric double layer repulsion forces balance the external pressure (hydrostatic for macroscopic and capillary for microscopic films) that tends to thin the film. Experiments with microscopic free foam films stabilized with ionic and non-ionic surfactants have led recently to elucidation of important aspects of the applicability of this theory. It has been shown that the experimental data for films stabilized with non-ionic surfactants are in good agreement with the theoretical predictions for film thicknesses higher than 20–30 nm (Kolarov et al. 1989), while for films stabilized with anionic surfactants deviations from the theory have been observed for film thicknesses below about 50 nm (Exerowa et al. 1987a). A review of the most important theoretical and experimental results for the common black to Newton film transition and the stability of the

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Newton films was given by Exerowa and Kashchiev (1986).

In recent years studies of the foam film model have been extended to the biological domain where they offer new opportunities for the investigation of interface phenomena. It is especially attractive for model studies of interaction forces between two approaching vesicles in a suspension where a thin liquid layer is formed between them with a configuration comparable to the structure of a foam film. Obtaining foam films stabilized with insoluble surface-active agents (such as the phospholipids) is an intriguing problem by itself, as there are only few studies dealing with formation of foam films stabilized with insoluble monolayers. Exerowa et al. (1987b) obtained Newton black films stabilized with the practically insoluble *n*-decanol monolayers by adsorption from the gas phase. Yamanaka et al. (1982) performed studies on macroscopic films (area about 1 cm^2) formed from sonicated suspensions of synthetic zwitterionic phospholipids and it was shown that NBF films were always formed, irrespective of the NaCl concentration. Richter et al. (1986) obtained foam films stabilized with dipalmitoyllecithin by producing a bubble under a planar insoluble monolayer spread at the air/water interface. Microscopic foam films stabilized with natural lung surfactant lipids, egg lecithin and other phospholipids were obtained by dissolving them in an aqueous 47 v.% alcohol solution (Exerowa et al. 1986; Exerowa and Lalchev 1986; Exerowa and Kashchiev (1986). Some of these results have been used for the development of new diagnostic methods in prenatal medicine.

Experimental investigation of interaction forces in free thin liquid films stabilized with amphiphiles can be carried out in different ways (e.g. Clunie et al. 1972; Exerowa et al. 1987a; Mysels and Jones 1966; Scheludko and Exerowa 1959, 1960). Most suitable for microscopic films are the methods allowing a precise measurement of the equilibrium film thickness at constant capillary pressure and a direct measurement of the disjoining pressure isotherm (Exerowa et al. 1979, 1987). In the present paper these methods are applied to films stabilized with a zwitterionic phospholipid dimyristoylphosphatidylcholine (DMPC). The aim of this work is to obtain microscopic films from a vesicle suspension of DMPC and to study the molecular interactions in them.

Materials and methods

Preparation of small unilamellar vesicles

1,2-dimyristoyl-sn-glycero-3-phosphorylcholine (DMPC) was purchased from Fluka AG and found to be over 99% pure by thin layer and gas chromatography. The lipid was dissolved in chloroform/methanol mixture (9 : 1, v/v) and the organic solvent removed by rotary evaporation under nitrogen. Solvent traces were removed by drying under vacuum for at least 4 h. As this lipid is practically insoluble in water, the experiments were carried out with suspensions of SUV. They were prepared in NaCl (Merck, p.a.) solutions in doubly distilled water (specific conductivity $10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, pH 5.5) by sonication in a bath type sonicator for 90 min under nitrogen. NaCl was roasted at 500 °C for 2 h in order to remove surface active impurities. The phospholipid suspension was kept at 10–20 °C above the transition temperature ($T_{\mathrm{tr}} = 23.5$ °C) of DMPC. The lipid concentration was 0.5 mg/ml in all experiments. The pH of the suspensions was about 5.5.

The vesicles were examined by electron microscopy after negative staining with 1% uranyl acetate solution as previously described (Tenchov et al. 1985). More than 95% of the vesicles were of diameters between 15 and 35 nm. Occasionally, vesicles of diameters up to 70–80 nm were encountered. From their substructure and also from their size range we conclude that the vesicles were unilamellar.

Formation of foam films from a DMPC suspension

The measurement of the equilibrium film thickness as a function of the electrolyte concentration of the solution was carried out by the interferometric method. Horizontal equilibrium foam films with a radius of about 0.01 cm were formed in the center of a doubly concave drop of the SUV suspension placed in the glass tube drop holder of the measuring cell as described in detail elsewhere (e.g. Exerowa et al. 1979, 1987a; Kolarov et al. 1989). The inner space of the measuring cell is closed so that the aqueous suspension is in equilibrium with its saturated vapour. As the interferometric measurement of the film thickness is based on photoregistration of the light, reflected from the film, the method requires regular film drainage. Our experiments showed that below the melting temperature of DMPC the film drainage was slow and irregular. For this reason it was necessary to work at temperatures above the melting temperature of DMPC where complications with the film drainage were not observed. The capillary pressure P_σ in these films is directly measured by the capillary-rise method using a tube which is identical with the tube in the cell where the film was obtained (Exerowa et al. 1979). The value of P_σ obtained was 24 N/m^2 and it did not appreciably depend on the electrolyte concentration. This result is in close agreement with the value that can be calculated from surface tension measurements for a similarly prepared DMPC suspension using the equation $P_\sigma = 2\sigma/R$ (σ-surface tension, R-radius of the drop-holder of the measuring cell; in our case $R = 0.2$ cm) (Yamanaka et al. 1982).

The direct measurement of the disjoining pressure isotherm was performed using the porous plate technique (e.g. Exerowa and Scheludko 1971; Exerowa et al. 1987a). In this case the film is formed in a hole with a diameter of 0.05 cm, drilled into a sintered glass plate welded to the capillary tube in the measuring cell. Thus, conditions are created for a significant increase of the pressure in the cell that balances the disjoining pressure in the film. A very convenient special arrangement allowed the pressure in the cell to be gradually and reversibly varied with an accuracy of 5 N/m^2 (Exerowa et al. 1987a).

All measurements were carried out at a constant temperature of 27 °C, which is above the melting transition of DMPC at 23.5 °C.

Determination of film thickness

As mentioned above, the film thickness was measured by the interferometric method of Scheludko and Exerowa (e.g. Exerowa et al. 1979; Scheludko and Exerowa 1959, 1960; Scheludko 1967). The processing of the interferometric data requires specification of a refractive model of the liquid film. In this paper we used the "equivalent water" model where the film is considered homogeneous with a refractive index n equal to the refractive index of the aqueous suspension from which the film is obtained (e.g. Exerowa et al. 1987a). Our measurements showed $n = 1.33$ and it did not depend on the electrolyte concentration of the DMPC SUV suspension.

Experimental results and discussion

The thicknesses h of equilibrium microscopic foam films stabilized with DMPC were measured in a range of C_{el} from 5.10^{-4} M to 0.5 M NaCl. The results are shown in Fig. 1. At the lowest electrolyte concentration comparatively thick (silver) films were formed. With increase of NaCl concentration film thickness decreases. At 0.015 M NaCl black spots begin to form and grow in size until the whole film becomes black. This is a common black film about 18 nm thick. After several minutes, however, thinner black spots of the Newton type start to appear in the common black film. They quickly expand until the whole film turns into a Newton black film (NBF). Formation of a common black film that subsequently turns into a Newton one is observed also at 0.02 M NaCl. At higher electrolyte concentrations Newton black films 8.1 ± 0.2 nm thick form directly in the whole range up to $C_{\mathrm{el}} = 0.5$ M NaCl.

Figure 2 shows the pressure-thickness isotherm of DMPC films at constant $C_{\mathrm{el}} = 0.001$ M NaCl. With increase of the external pressure that counterbalances the disjoining pressure, the equilibrium thickness decreases and a silver to Newton black film (NBF) transition occurs at 4.10^3 N/m^2. On further increase of the external pressure the NBF thickness remains constant and equal to 7.6 nm.

According to the classical DLVO theory the interactions in the film are characterized by the disjoining pressure Π, which is given by the expression:

$$\Pi = \Pi_{\mathrm{el}} + \Pi_{v\omega} \tag{1}$$

where Π_{el} is the electrostatic disjoining pressure, caused by electric double layer repulsion and $\Pi_{v\omega}$ is the van der Waals disjoining pressure determined by the van der Waals attraction. Π is defined as positive when it causes repulsion. At sufficiently low thicknesses an additional repulsive interaction is also observed (Derjaguin et al. 1985). For sufficiently thick horizontal microscopic foam films, at equilibrium, Π_{el} counterbalances P_σ and $\Pi_{v\omega}$:

$$\Pi_{\mathrm{el}} = P_\sigma + \Pi_{v\omega} . \tag{2}$$

The formation of equilibrium thick DMPC films is an indication of the existence of repulsion forces in them at

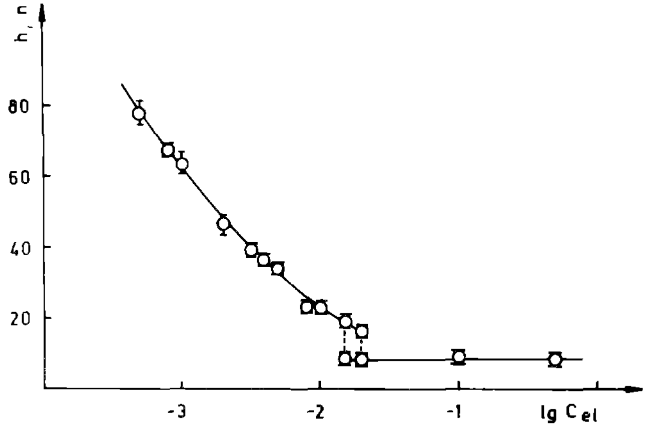

Fig. 1. Equilibrium microscopic foam film thickness as a function of NaCl concentration. T – 27 °C, film radius 0.02 cm

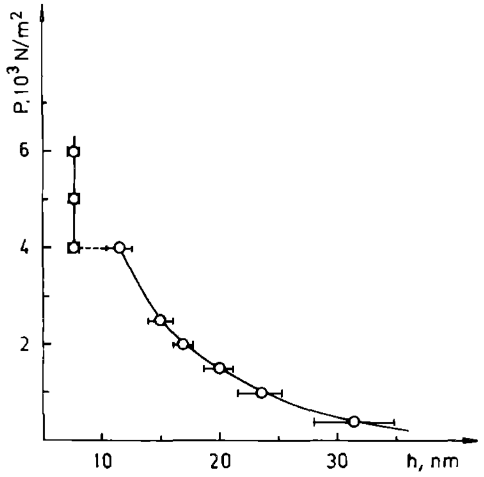

Fig. 2. Disjoining pressure – thickness isotherm of microscopic foam films obtained from a DMPC vesicle suspension. T – 27 °C

low electrolyte concentrations and at low pressures. Both the decrease of the equilibrium thickness with increase of electrolyte concentration (Fig. 1) and the course of the disjoining pressure isotherm with a clearly expressed barrier transition in it (Fig. 2) show the electrostatic origin of these forces. The electrostatic interactions in a film can be characterized by the potential of the diffuse electric layer at the solution/air interface. It can be calculated from the equations of the DLVO theory (Derjaguin et al. 1985) as has been done before (e.g. Exerowa 1969; Scheludko and Exerowa 1959, 1960):

$$\Pi_{\mathrm{el}} = 2\, C_{\mathrm{el}}\, RT (\cosh \gamma_{h/2} - 1) \tag{3}$$

$$\varkappa h = \sqrt{2} \int_{\gamma_{h/2}}^{\gamma_0} \frac{d\gamma}{\cosh \gamma - \cosh \gamma_{h/2}} \tag{4}$$

where $\varkappa = \sqrt{8 \pi z^2 F^2 C_{\mathrm{el}} / \varepsilon RT}$, $\gamma_{h/2} = z F \varphi_{h/2}/RT$, $\gamma = z F \varphi/RT$, $\gamma_0 = z F \varphi_0/RT$; C_{el} – electrolyte concentration, z – valency of the electrolyte, ε – permittivity of the solution, R – gas constant, T – absolute temperature, F – Faraday constant, h – film thickness, φ_0 – potential of the diffuse electric layer, $\varphi_{h/2}$ – potential in the middle of the film, φ – potential.

Π_{el} is determined from (2) and afterwards φ_0 is calculated by solving (3) and (4). P_σ is experimentally measured and Π_{vw} is estimated using a model for molecular interactions applicable to foam films. For the lack of a suitable model for a precise, and, at the same time, comparatively simple calculation of van der Waals interactions in foam films stabilized with phospholipids, Π_{vw} can be estimated using the empirical equation proposed by Donners et al. (1977) for foam films stabilized with amphiphilic surface active substances. This equation is a result of numerically solving the complete equations of the macroscopic theory of van der Waals attraction in films (Dzyaloshinskii et al. 1961) where the film structure is taken into consideration and the frequency dependence of the permittivity is estimated according to the method proposed by Ninham and Parsegian (1970). On the basis of the similarity between foam films stabilized with surface active agents and those, stabilized with DMPC, this method with some approximation can be applied also in the present study. Nevertheless, to decrease the error in such calculations it is better to use this method for comparatively thicker films where the van der Waals attraction is low and the film equilibrium is determined mainly by the electrostatic repulsion Π_{el}. Using this scheme we calculated φ_0 in the interval from 5.10^{-4} M NaCl to 10^{-3} M NaCl where the films are relatively thick and found $\varphi_0 = 36 \pm 3$ mV. This result can be compared with earlier data for foam films (Exerowa 1969; Exerowa et al. 1979). Here φ_0 is about 10 mV higher than the potential of a water/air interface estimated from experimental data for microscopic foam films obtained from an aqueous electrolyte solution without any surface active agent (Exerowa 1969). In this respect films stabilized with the zwitterionic lipid DMPC are very similar to those, stabilized with non-ionic surfactants (Exerowa 1969; Exerowa et al. 1976, 1979). The low φ_0 potential leads to a low barrier in the $\Pi(h)$ isotherm which can easily be overcome at relatively low electrolyte concentrations and low pressure values (Fig. 2). For this reason, similarly to films stabilized with non-ionic surfactants, the silver to Newton black film transition is observed at C_{el} and external pressures an order of magnitude lower than the respective values for films stabilized with ionic surfactants (Exerowa et al. 1987a; Kolarov et al. 1989). Here we should note the points where metastable common black films are formed, since such a phenomenon has not been observed for films stabilized with non-ionic surfactants. The reason for the appearance of common black films is not clear. This could be due to an eventual positive component of the disjoining pressure in the DMPC foam films which leads to increase in the barrier in the $\Pi(h)$ isotherm. Here we should note the experimental results of Gershfeld and Tajima (1979); Gershfeld et al. (1986), Tajima and Gershfeld (1985), showing a coexistence of DMPC monolayers and bilayers at the air-water interface in the temperature range 25–30 °C. Considering, however, the different mechanism of formation and the special conditions for stability of foam films it seems that here we detect common black films, and not multilamellar (stratified) films. The thinning of the films with the increase in C_{el} is in conformity with this conclusion. Nevertheless, the interesting possibility of surface bilayer formation in foam films deserves special attention when considering the structure and stability of common and Newton black films.

Studies of foam films obtained from aqueous electrolyte solutions and films stabilized with non-ionic surfactants at different pH values (Exerowa 1969) have shown that, with decrease of pH, a certain value, called pH isoelectric is reached, such that below it the formation of a silver film is not possible. The conclusion following from these results is that decrease of pH leads to a decrease of φ_0 and the electrostatic interactions, until they reach the zero point. These studies have led to the conclusion that most probably the electrostatic interactions in films stabilized with neutral molecules are caused by specific adsorption of hydroxyl ions at the two solution/air interfaces. The electrostatic character of the transition in the pH isotherm is revealed also by the common to Newton black film transition at constant C_{el} induced by decrease only of the solution pH (Exerowa 1978). Our studies of foam films, stabilized with DMPC at low ionic strength (from 0.0005 M to 0.001 M NaCl) at different pH of the suspensions also showed that a decrease of pH to about 3.8 leads to formation of NBF only (data not shown). This is an indication of the electrostatic origin of the repulsion forces, since a pH decrease here should also lead to disappearance of the diffuse electric layer potential and overcoming of the barrier in the $\Pi(h)$ isotherm. Therefore the long-range electrostatic interactions in DMPC films can be attributed to specific adsorption of hydroxyl ions to the film interfaces as well.

The results in Figs. 1, 2 show that Newton black films obtained during a direct measurement of the disjoining pressure isotherm are somewhat thinner than NBF obtained in the equilibrium thickness/electrolyte concentration dependence. Up to now investigations of NBF have shown (Exerowa and Kashchiev 1986; Exerowa et al. 1987a) that they are bilayer formations without any free water in the core. It is well known, however, that phosphatidylcholine molecules in aqueous media are strongly hydrated. The small difference, observed in NBF thicknesses, is almost within the limit of the experimental error and could be due to a partial dehydration of the phospholipid molecules at higher pressures.

The experimental results of Yamanaka et al. (1982) obtained by investigating macroscopic foam films, stabilized with DMPC in a wide range of electrolyte concentrations show formation of NBF only. This distinction between their and our results appears to be due to the larger surface area of the macroscopic films which results in: (i) higher probability of fluctuations overcoming the very low disjoining pressure barrier, and (ii) higher hydrostatic pressure in the vertical macroscopic films counterbalancing the long-range repulsion as compared to the capillary pressure in horizontal microscopic films.

The results of the present study show that the thickness of NBF is significantly smaller than the size of the vesicles in the stock suspension. On the other hand, investigations of NBF in connection with the state of the adsorbed layers at the solution/air interface have shown that they can be obtained only at close packing at the interface (Exerowa et al. 1981). Thus, the fact that we obtain NBF deserves special attention considering the very low concentration of monomers in the DMPC suspension and the small volume of the drop in the cell where the film is obtained. The mechanism of DMPC adsorption is not clear. Schindler (1979) has studied the formation of insoluble lipid monolayers from vesicles and the interaction of vesicles with phospholipid monolayers. He has proposed that vesicles concentrate below a monolayer and exchange of lipid occurs between the outer lipid layer of the vesicle bilayer and the monolayer. The experimental studies of Cordoba et al. (1990) conform with this mechanism. This process could be operative also in the case of foam films. Another possibility is that some kind of vesicle degradation takes place at the surface. Such a mechanism has been derived by kinetic studies of insoluble phospholipid monolayers (Ivanova et al. 1989). Taking into account the small portion of vesicles that needs to be disrupted to ensure close packing at the film interfaces, this mechanism cannot be ruled out. However, further studies of foam film formation from vesicle suspensions are necessary for a better understanding of the mechanism of formation of the adsorbed DMPC monolayers. It appears useful in this connection to perform a model calculation based on the experimental results. Assuming a three layer film structure (Frankel and Mysels 1966) that is valid for films, consisting of an aqueous core with thickness h_2 and refraction coefficient n_2, bound by two homogeneous monolayers with thickness h_1 and refraction coefficient n_1:

$$h_2 = h - 2h_1\,(n_1 - 1)/(n_2 - 1) \tag{5}$$

where h is the measured equivalent water thickness. This model has been derived for films stabilized with amphiphilic substances with a single hydrocarbon chain. It seems reasonable, however, to use the same model in the case of DMPC films where we can assume $n_2 = 1.33$ – the refraction coefficient of water, and $n_1 = 1.43$ – the refraction coefficient of tetradecane. On the basis of data obtained by X-ray diffraction, neutron scattering and NMR (Pearson et al. 1981) we obtain $h_1 \sim 16$ Å. In this way we obtain $h_2 = 3.8$ nm for $h = 8.2$ nm, and a total film thickness ($h_2 + 2\,h_1$) equal to 7.0 nm. The very small difference between the NBF thicknesses obtained in the common cell (Fig. 1) and the porous plate cell (Fig. 2) is an indication of the lack of a free aqueous core in the film. The calculated total film thickness is close to the result obtained by a completely different method for the thickness of two hydrated dipalmitoyl phosphatidylcholine monolayers – 6.8 nm (Marra 1986).

Conclusions

The formation of thick equilibrium horizontal microscopic films stabilized with DMPC at low external pressure and at low electrolyte concentration is evidence for long-range electrostatic interactions in these films. Thinking of neutral phospholipid vesicle suspensions where such interactions have not been observed, we should consider the different interface tension and different mechanism of eventual charge formation. Nevertheless, the possibility for using the microscopic foam film for model investigation of both long-range and short-range interactions between vesicles offer some advantages (easy formation, good experimental and theoretical background, etc.).

The films stabilized with DMPC seem to be very similar to the films obtained from solutions of non-ionic surfactants. However, unlike the results obtained for surfactant films, in this study of DMPC films we observed formation of common black films and a process of thinning of NBF under pressure. These phenomena seem to be closely related to the specifics of interaction forces in phospholipid films.

The comparison between the film, and especially the NBF, thickness, and the vesicle size shows that the film is stabilized by two DMPC monolayers that are possibly formed as a result of vesicle degradation. It seems likely that this process takes place at the interface. However, this mechanism still needs verification as another possibility for its formation, for instance, exchange of DMPC molecules between the film and the bulk cannot be ruled out at present. These problems will be considered in more detail in a further investigation.

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