

Effect of the Charged Lipid DMPG on the Thickness and Contact Angle of Foam Films

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The interactions in foam films stabilized by mixed monolayers of the zwitterionic lipid DMPC and the charged lipid DMPG were investigated. The film thickness and the contact angle between the film and the meniscus were measured. The free energy of interaction was determined from the contact angle. An increase in the film thickness with increasing content of DMPG in the lipid mixture at constant ionic strength and with decreasing concentration of sodium chloride at constant DMPC/DMPG ratio indicates an influence of the electrical double layer interaction in the system. The dependence of the film interaction energy on the content of DMPG or salt in the film forming lipid suspensions confirms this conclusion. The double layer potential φ of films made from mixture with constant DMPC/DMPG ratio was estimated. It results that φ in the case of the mixture increases with increasing concentration of NaCl. This confirms the results of Grigoriev et al. (*J. Phys. Chem. B* 1999, 103, 1013) about an increasing dissociation of DMPG in a surface monolayer on increasing concentration of sodium ions in the subphase. The measured film thicknesses are smaller than those estimated from a model which includes the electrical double layer interaction and the dispersion interaction. This indicates an additional unknown attractive contribution to the total disjoining pressure.

Introduction

Phospholipid bilayers constitute the main structural element of the biological membranes. They consist of mixtures of different charged and uncharged lipids.^{1–3} Roughness, hydration, and electrical potential of the interface between the lipid bilayer and the adjacent aqueous phase play important roles in the interaction between membranes across an aqueous phase, and ultimately for the fusion of two membranes. There is much research^{3–5} being done on models that resemble biological systems, mainly using vesicles^{6–9} or lipid monolayers on different aqueous subphases.^{10–12}

Foam films stabilized with phospholipids also may serve as a model for the investigation of the interaction between two lipid bilayers. Foam films consist of two adsorbed surfactant layers and an aqueous core between. Their properties are summarized in reviews and monographs.^{13–15} Such films play an important role in *in vivo* systems,¹⁵ for instance the terminal lung units are covered by a foam that consists of an agglomeration of small bubbles separated by thin foam films.¹⁶ However, there are only few investigations on foam films stabilized with phospholipids.^{15,17–20} In earlier papers^{21,22} we have reported on the stability and the interactions in foam films prepared from suspensions of dimyristoyl phosphatidyl choline (DMPC) as a function of the content of NaCl, CaCl₂, and ethanol in the aqueous phase. Here we present results from investigations of foam films stabilized by mixtures of DMPC and the charged lipid dimyristoyl phosphatidyl glycerol (DMPG). The content of the charged lipid in the mixture is varied to study the role of electrical double layer interaction in the film. Former investigations²³ of the effect of sodium ions on the dissociation of the phosphatidyl glycerol (PG) group at the air/water interface show

a higher dissociation of the PG group at the interface with increasing concentration of the sodium ion in the subphase. Foam films allow the investigation of this effect on the interaction between two approaching monolayers.

2. Experimental Section

1,2-Dimyristoyl-sn-glycero-3-phosphorylcholine (DMPC) and 1,2-dimyristoyl-sn-glycero-3-[phospho-rac-(1-glycerol)] (DMPG) were purchased from Fluka (P-41803) and Sigma (P-6412), respectively, and were used without further purification. Absolute ethanol (Merck, extra pure) was used in the preparation of some solutions. Sodium chloride (Riedel-de Haen), roasted at 600 °C for 5 h to remove surface-active contaminations, was used as electrolyte. Bidistilled water (pH 5.5, specific resistance 18 M Ω cm) purified by a Millipore desktop unit was utilized to prepare suspensions.

The lipids used in the experiments are not soluble in water. The films were formed from vesicle suspensions of the lipids. Using a water/ethanol mixture as solvent can accelerate the exchange of lipid molecules between the vesicles and the surface. Therefore, the films were formed from lipid suspensions in water/ethanol (52.5:47.5% v/v) mixtures in part of the experiments. The total concentration of the lipid in the suspensions was kept constant at 1.6×10^{-4} M in all experiments. The suspensions were prepared by adding the exact amount of lipid to water or a water/ethanol mixture containing different amounts of NaCl. The lipid suspensions prepared with water were kept overnight at room temperature. Those prepared with a water/ethanol mixture were kept in a refrigerator. The suspensions were used within 24 h. They were sonicated in a sonication bath (Sonorex RK52, BANDELIN Electronic, Berlin, Germany) for 30 min at 40 °C before starting the measurements. This procedure leads to the formation of small unilamellar vesicles with diameters below 100 nm²⁴ in the case of suspensions prepared with water/ethanol mixtures. Our light scattering investigations (Zetasizer 3000, MALVERN's Instru-

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ment, England) show that vesicles with diameters around 120 nm were obtained if the suspensions were prepared only with water. Suspensions prepared in such a way do not show any chemical changes during the time of investigation.²⁴

Horizontal microscopic foam films with a diameter of around 0.4 mm were formed in the middle of a biconcave drop in a glass ring of 4-mm diameter.²⁵ The atmosphere surrounding the film was saturated with the vapor of the solution. At these conditions the films were stable for at least 1 h.

The equivalent foam film thickness (h_w) was measured using the microinterferometric method^{15,25} assuming an optical homogeneous film. The foam film, however, consists of two adsorbed monolayers (thickness h_1 , refractive index n_1) and a water core (h_2 , n_2), including the region of the hydrated lipid headgroups. The water-core thickness (h_2) and the foam film thickness (h) can be calculated from the equivalent film thickness (h_w) and the monolayer thickness (h_1) by^{26,27}

$$h = 2h_1 + h_2 \quad h_2 = h_w = 2h_1 \frac{h_1^2 - 1}{n_2^2 - 1} \quad (1)$$

The monolayer thickness (h_1) can be obtained from ellipsometric²⁸ or X-ray diffraction²⁹ measurements.

The contact angle (θ) between the film and the surrounding meniscus was measured using the "expansion method".^{15,30,31} The free energy of film formation per unit of area (ΔF^f) is related to the contact angle, the surface tension (σ) of the suspension, and the foam film thickness (h)^{13,32}

$$\Delta F^f = 2\sigma(\cos\theta - 1) = -\int_{\infty}^{h_e} \Pi(h)dh + \Pi h_e \quad (2)$$

The surface tension of the suspensions was measured by a tensiometer (Lauda, KM5) equipped with a du Nouy ring, made from platinum-iridium, of 6 cm circumference. A constant equilibrium surface tension of 27 mN/m was reached after a few minutes for suspensions containing ethanol and after some hours for suspensions with only water. The value of the surface tension does not change by varying the ratio DMPC/DMPG in the lipid suspension and it is similar to that measured earlier.²¹ The surface tension of the lipid suspensions is lower than the value of 29 mN/m³³ for the water/ethanol mixture (52.5:47.5% v/v) at 26 °C by 2 mN/m.

All measurements of the film thickness and contact angle film/meniscus were carried out at 26 °C. This temperature is above the temperature of the main phase transition for the lipids used. It guarantees formation of stable and homogeneous films.^{15,18,21} At least 10 single measurements were performed for each experimental point.

Experimental Results and Discussion

DMPC foam films are basically stabilized by structural forces,^{21,22} even though a small effect of electrical double-layer interaction seems to be involved. The inclusion of DMPG ions should result in an increase in the double-layer potential and a stronger repulsion.³⁴ However, it was shown²³ that PG groups are hydrolyzed at the water/air interface and the dissociation of the resulting acid depends on the concentration of the electrolyte in the subphase.

The equivalent film thickness h_w and the contact angle θ of foam films prepared from suspensions with different DMPC/DMPG ratios at constant NaCl concentration (0.07 M) were measured. The foam films were obtained from suspensions prepared with water or a water/ethanol mixture. The experi-

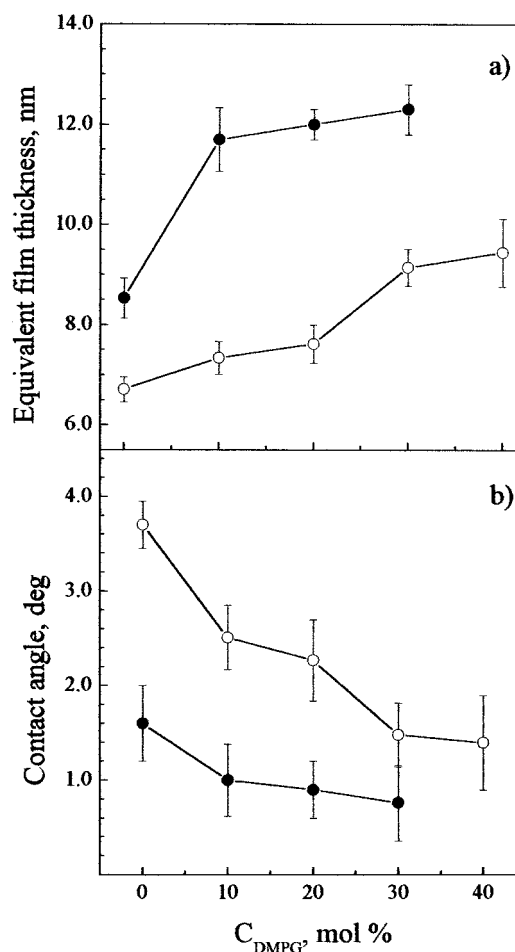


Figure 1. The equivalent foam film thickness h_w (a) and the contact angle θ (b) as a function of the concentration of the DMPG molecules in the film forming suspension (total lipid concentration 1.6×10^{-4} M, $C_{\text{NaCl}} = 0.07$ M). O — foam films made from water/ethanol suspensions; ● — foam films made from water suspensions.

mental cell was filled with the investigated lipid suspension and a biconcave drop was formed. The drop was left for some hours. This time is necessary to reach saturation of the adsorbed lipid monolayers of the film. The first foam film was made after that time. The equilibrium film thickness does not change with the time at those conditions. The films were homogeneous, which shows that the vesicles are depleted from it. However, because of the very small number density of the vesicles in the suspensions, there is no reason to expect any depletion attraction between film surfaces.

Experimentally obtained results are presented in Figure 1. Assuming the thickness of the adsorbed lipid monolayer $h_1 = 2$ nm,²² the values of the foam film thickness h and the aqueous core thickness h_2 were calculated. They are presented in Table 1 together with the free energy of film formation ΔF^f as a function of DMPG content. The film thickness increases with increasing content of DMPG in the film forming suspension. The dependence of the film interaction energy on the content of DMPG also shows that the repulsive component of the interaction increases if more DMPG is present in the suspension. The aqueous core thickness of films from suspensions in water is always larger than that from water/ethanol mixtures at the same DMPG/DMPC ratio.

Increasing the share of DMPG in the film forming suspension should lead to a increasing number of DMPG ions in the lipid monolayers at the film surfaces. This will result in an increase in the double layer potential and a stronger repulsion between

TABLE 1: Calculated Values Assuming the Thickness of the Adsorbed Lipid Monolayer $h_1 = 2 \text{ nm}^{22}$ of the Aqueous Core Thickness (h_2) and Foam Film Thickness (h) together with the Free Energy of Film Formation (ΔF^f) as a Function of the DMPG Content in Water and a Water/Ethanol (52.5:47.5%, v/v) Mixture

C_{DMPG} mol %	water			water/ethanol		
	h_2 nm	h nm	ΔF^f mJ/m ²	h_2 nm	h nm	ΔF^f mJ/m ²
0	3.56	7.56	-0.021	1.74	5.74	-0.111
10	6.73	10.73	-0.008	2.37	6.37	-0.051
20	7.03	11.03	-0.006	2.65	6.65	-0.042
30	7.33	11.33	-0.004	4.18	8.18	-0.018
40				4.48	8.48	-0.016

the film surfaces, while the Debye length remains constant. However, the ratio of the lipids in the monolayers may deviate from that in the vesicles of the suspension. Different solubilities and surface activities may cause this. The ratio of the two lipids in the monolayers may also depends on the content of ethanol in the solution. A hint of this is given in the results shown in Figure 1a. The exchange of 10% of DMPC by DMPG results in a larger increase of the film thickness in water than in the water/ethanol mixture. The fact that films containing ethanol are generally thinner than films with pure water is partially caused by dehydration of the lipid headgroups as discussed in ref 22. However, here the stronger surface activity of the charged lipid in pure water may additionally contribute to the effect.

The thickness h_w and the contact angle θ of foam films formed from solutions prepared from 9:1 DMPC/DMPG suspensions in water/ethanol mixture as a function of NaCl concentration are presented in Figure 2. The electrolyte concentration was varied from 0 to 0.15 M. The present results are compared with the same dependencies for foam films prepared from DMPC suspensions.²¹ At low electrolyte content, the films are thicker than those prepared from suspensions with higher electrolyte concentration as expected from the theory of the electrical double layer interaction. The decrease in the film thickness with the ionic strength is accompanied by a decrease of the free energy of film formation. A film with a smaller equilibrium thickness is in a more preferable thermodynamic state than a film with a large equilibrium thickness. Calculated values of the foam film thickness h and the aqueous core thickness h_2 , assuming $h_1 = 2 \text{ nm}^{22}$, and the free energy of film formation using eq 1 and eq 2 are presented in Table 2. These results allow, to a certain extent, a quantitative comparison with the DLVO theory.^{34,35} The dependence on salt concentration of the film aqueous core thickness h_2 at constant ratio of DMPC/DMPG was analyzed in comparison with that of the pure DMPC.

At equilibrium film thickness h , the disjoining pressure $\Pi(h)$ in the film equals the capillary pressure P_c in the surrounding meniscus

$$\Pi(h) = P_c = \frac{2\sigma}{R} \quad (3)$$

Here R is the radius of the capillary in which the film is formed. According to refs 13–15, 34, 35, the disjoining pressure has different contributions and it can be written as

$$\Pi(h) = \Pi_{\text{vw}}(h) + \Pi_{\text{dl}}(h) + \Pi_{\text{hyd}}(h) + \Pi_{\text{other}}(h) \quad (4)$$

where Π_{vw} is the van der Waals attraction, Π_{dl} is the double-layer repulsion, Π_{hyd} is the hydration repulsion, and Π_{other} refers to the other possible interactions. Supposing that only the van

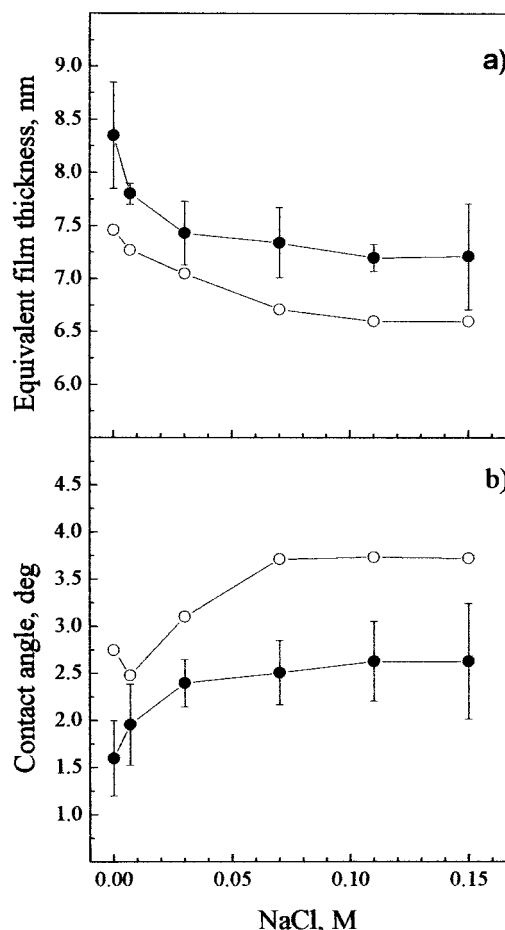


Figure 2. The equivalent foam film thickness h_w (a) and the contact angle θ (b) as a function of the NaCl concentration for foam films prepared from water/ethanol mixture. \circ – foam films with pure DMPC; \bullet – foam films with mixture 9:1 DMPC/DMPG.

TABLE 2: Calculated Values Assuming the Thickness of the Adsorbed Lipid Monolayer $h_1 = 2 \text{ nm}^{22}$ of the Aqueous Core Thickness (h_2) and Foam Film Thickness (h) Together with the Free Energy of Film Formation (ΔF^f) as a Function of the NaCl Concentration for Foam Films Stabilized from DMPC and 9:1 DMPC/DMPG Suspensions in a Water/Ethanol (52.5:47.5 vol %) Mixture

C_{NaCl} M	DMPC			9:1 DMPC/DMPG		
	h_2 nm	h nm	ΔF^f mJ/m ²	h_2 nm	h nm	ΔF^f mJ/m ²
0	2.49	6.49	-0.062	3.38	7.38	-0.021
0.007	2.30	6.30	-0.050	2.83	6.83	-0.031
0.03	2.08	6.08	-0.059	2.46	6.46	-0.071
0.07	1.74	5.74	-0.111	2.37	6.37	-0.051
0.11	1.63	5.63	-0.113	2.23	6.23	-0.056
0.15	1.63	5.63	-0.112	2.24	6.24	-0.056

der Waals attraction, the repulsive electrostatic double-layer, and the hydration repulsion influence the equilibrium thickness, and using the usual expressions of these disjoining pressure components^{34,35} we obtain

$$\Pi(h) = -\frac{A}{6\pi h^3} + 64kT\rho_{\infty}th^2(e\varphi/4kT)\exp(-\kappa h_i) + H_0 \exp(-h/\lambda) \quad (5)$$

where A is the Hamaker constant, k is the Boltzmann constant, T is the absolute temperature, ρ_{∞} is the bulk ionic concentration of ions at $h = \infty$, φ is the surface potential, $\kappa = (\rho_{\infty}z^2e^2/\epsilon\epsilon_0kT)^{1/2}$, e is the elementary electrical charge, z is the ionic valence, ϵ is

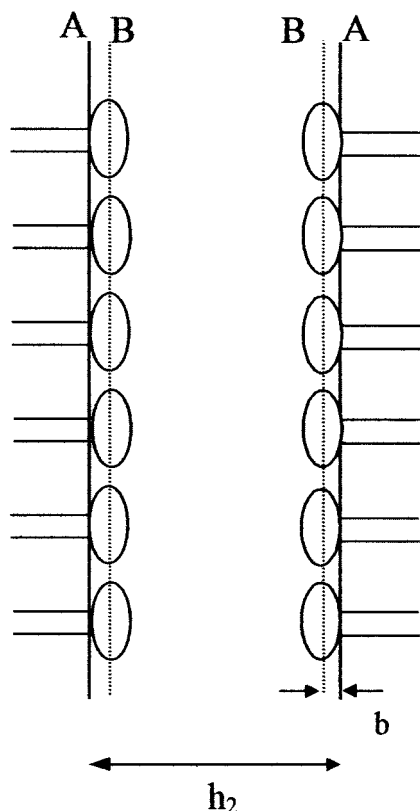


Figure 3. Model of the planes of interactions in the foam film (see the text).

the medium permittivity, and ϵ_0 is the permittivity of the free space. H_0 takes into account the hydration energy of a surface, and λ is the decay length of the hydration repulsion. The parameter h , is the distance between two surfaces, which in our case is equal to the aqueous core thickness h_2 .

The disjoining pressure of an equilibrium film stabilized by DMPC with a thickness h_i at a certain salt concentration and that of an equilibrium film stabilized by DMPC/DMPG mixture with a thickness h_j at the same salt concentration is equal to the capillary pressure. Because of the constant surface tension (27 mN/m) of all the used lipid suspensions and of the constant ring and film dimensions, the capillary pressure was equal.

$$\Pi(h_i) = \Pi(h_j) \quad (6)$$

For small arguments of x , as in our case, $th(x)$ can be approximated by $th(x) \approx x - x^3/3$. Then eq 6 can be solved for the double-layer potential φ_j of the DMPC/DMPG mixture since the surface potential of DMPC φ_i is known

$$\varphi_j^2 = C \left[-\frac{A}{6\pi} \left(\frac{1}{h_i^3} - \frac{1}{h_j^3} \right) + \frac{4e^2}{kT} \rho_\infty \varphi_j^2 \exp(-\kappa h_i) + H_0 \left(\exp\left(-\frac{h_i}{\lambda}\right) - \exp\left(-\frac{h_j}{\lambda}\right) \right) \right] \quad (7)$$

where C is defined as $C = kT \exp(\kappa h_j) / 4\rho_\infty e^2$.

The film thicknesses measured in the experiments are relatively small at all investigated conditions. The values of the surface potential φ_j , therefore, should be calculated taking into account the correct positions of the interacting planes. The results are sensitive to these positions. Figure 3 shows the model used for the calculations. The position of the charges of the DMPG headgroups is assumed to be away from the chain/headgroup interface by a quantity of about $b = 0.4$ nm, in

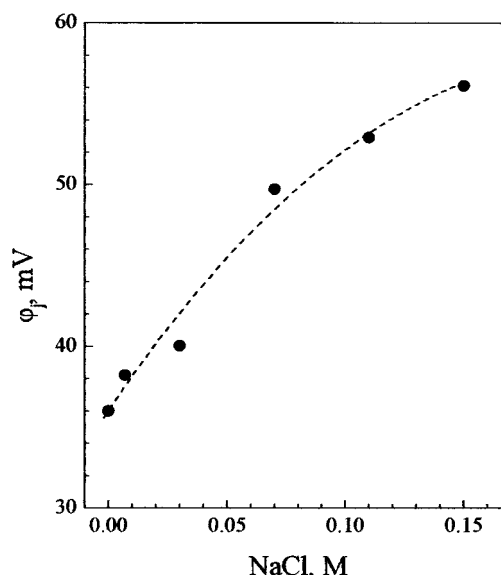


Figure 4. The surface potential φ_j (mixture 9:1 DMPC/DMPG) as a function of the NaCl concentration. The potential is calculated according to eq 7 accepting a value of $\varphi_i = 36$ mV for the surface potential of the pure DMPC suspension/air interface. The line is drawn only to guide the eye.

agreement with molecular dynamics simulations of the lipid/water interface.^{36,37} This is half of the full extension $a = 0.8$ nm of the DMPC headgroup layer. The electrical double layer interaction therefore acts between the planes B while the van der Waals interaction is considered as the interaction between the planes A, assuming a constant dielectric permittivity inside these planes.

The van der Waals contribution to the disjoining pressure was calculated using a Hamaker constant of $A = 6 \times 10^{-21}$ J. The value coincides with the experimentally obtained^{34,38} or theoretically estimated³⁹ values for similar systems. The hydration part of the disjoining pressure was calculated using the values for both constants $H_0 = 4 \times 10^{-7}$ Nm⁻² and $\lambda = 0.3$ nm.^{40,41}

We assume a value of $\varphi_i = 36$ mV for films of pure DMPC²⁰ as a reasonable estimate. This potential results from an excess of the hydroxyl ions of the water at the surface. Such a small negative surface potential was also found at the surface of pure water and in the case of foam films from water soluble nonionic surfactants.⁴² The double layer potential φ_j for the mixture DMPC/DMPG was calculated with eq 7 depending on the concentration of NaCl using the above-mentioned value of the potential φ_i . The obtained values are presented in Figure 4. It follows that φ_j rises when the salt concentration increases. This is in accordance with the observation that the dissociation of DMPG molecules at the air/aqueous salt solution interface increases with increasing NaCl concentration.^{23,43,44} It shows that the film thickness is sensitive to the electrical properties of the system and that the electrostatic contribution to the disjoining pressure does play an important role in the stabilization of lipid foam films prepared from mixed suspensions.

The shape of the dependence $h_w = h_w(C_{\text{NaCl}})$ for foam films stabilized from a 9:1 DMPC/DMPG mixture deserves more discussion. The reduction of h_w should be explained by the interplay of the terms $\gamma^2 = th^2(e\varphi_j/4kT)$ and $\exp(-\kappa h_j)$ in eq 5. The behavior of both terms as a function of NaCl concentration is shown in Figure 5. An increase in the concentration of NaCl leads to a higher surface potential (see Figure 4) and the term γ^2 rises, while the exponential term decreases. At low NaCl

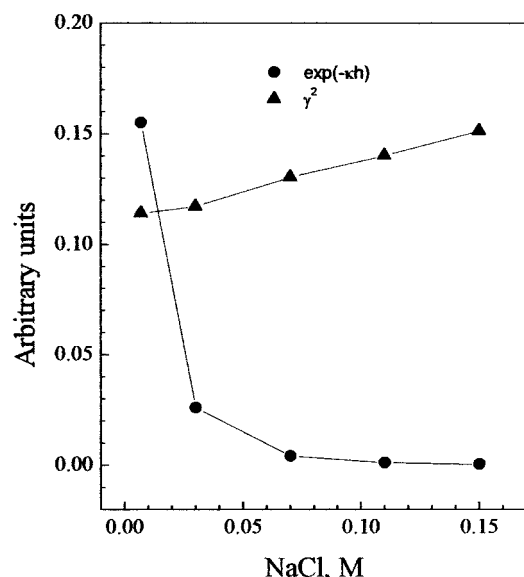


Figure 5. Comparison between the terms $\gamma^2 = th^2(eq_j/4kT)$ (▲) and $\exp(-\kappa h_j)$ (●) in eq 5 versus NaCl concentration. The contribution of the decrease in the Debye length dominates over the contribution of the increase in the surface potential.

concentrations the decrease in the exponential term is faster than the increase in the γ^2 . This leads to a reduction of the electrostatic repulsion and the free energy of film formation reaches more negative values (see Table 2). The plateau region of $h_w = h_w(C_{NaCl})$ at high NaCl concentrations would mean that γ^2 and $\exp(-\kappa h_j)$ balance each other.

The dependence of the film thickness on the increase of the content of the charged lipid or on the concentration of the electrolyte agrees qualitatively with predictions of the electrical double layer theory. However, the variation of the film core thickness h_2 with salt concentration is small. Therefore, the quantitative agreement seems to be questionable and needs a more detailed discussion.

The variation of the aqueous core thickness h_2 on the concentration of electrolyte at constant ratio of DMPC/DMPG (9:1) was compared with the theoretical values for h_2 calculated using the equation $P_c = \Pi_{vw} + \Pi_{dl}$ (Figure 6). The above-mentioned Hamaker constant was used for the calculation of the van der Waals contribution. The electrical double layer contribution was calculated using the surface potential φ_j given in Figure 4. A value of 30 Pa was taken for P_c . As can be seen from Figure 6, the experimental values of the thickness are essentially smaller than those estimated. In the calculation, the contributions of short-range interactions (like the hydration repulsion) were neglected. The inclusion of such contributions will not significantly change the final conclusion. Since these contributions are repulsive, the discrepancy with the experiment would become larger. The variation of the Hamaker constant used in the calculations in a reasonable range does not remove the discrepancy. The cause for the discrepancy remains an open question. It seems possible that there is a nonequilibrium of the osmotic pressure in the system as found in some cases.⁴⁵ However, the lipid concentration in our system is too small to give grounds for such speculations.

Conclusions

The investigation of foam films stabilized by mixtures of DMPC and DMPG enables to evaluate the role of electrical double layer interaction between biological membranes which are always composed from mixtures of neutral and charged

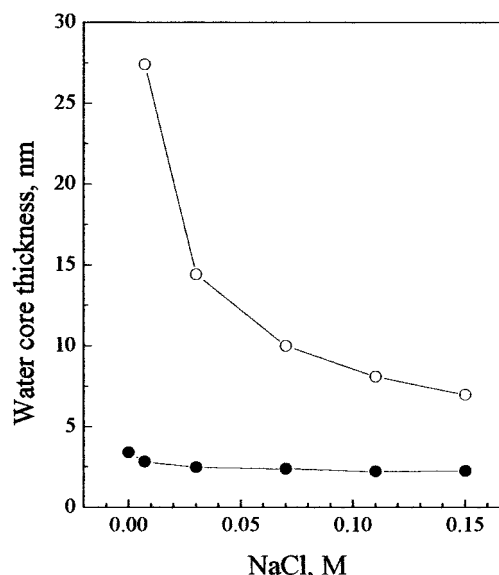


Figure 6. The aqueous core thickness h_2 (●) as a function of the electrolyte concentration at constant ratio of DMPC/DMPG (9:1) in water/ethanol mixture compared with the theoretical values (○) for h_2 calculated using the equation $P_c = \Pi_{vw} + \Pi_{dl}$ and the double layer potentials φ_j from Figure 4.

lipids. An increase in the film thickness and a decrease in the film interaction energy with increasing content of DMPG indicate an increasing contribution of the double layer repulsion to the interaction in the film. This is due to the adsorption of DMPG ions in the stabilizing monolayer. The composition of the stabilizing monolayers, however, may deviate from the ratio of the two lipids in the suspension caused by different solubility and surface activities, depending also on the presence of other components in the solution. The effect of salt is more complicated in the present case than in other systems with electrical double layer interaction. Increasing the salt concentration compresses the diffuse layer of counterions, but at the same time the degree of dissociation of DMPG in the monolayer increases with increasing concentration of sodium ions. The concurrence of both of the effects results in a relatively weak decrease of the film thickness with increasing salt concentration. The measured film thicknesses, however, are smaller than calculated from a model including double layer and dispersion interactions. The total disjoining pressure may include, therefore, an additional attractive component.

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