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SHORT COMMUNICATION

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Evolution of white spots in lipid foam black films of DMPC

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Abstract A new phenomenon in the kinetic behavior of thin liquid films is reported: thickening white spots (lenses) in black foam films of small unilamellar liposomes of dimyristoylphoshatidylcholine (DMPC). The time evolution of the lenses is registered and the shape changes are determined. Such structures form only at temperatures below the main phase transition temperature of the lipid bilayer (gel–liquid crystal first order phase transition).

Key words Thin liquid films – foam films – lenses in black films – lipid bilayer – gel/LC phase transition

Introduction

Here, we report a new observation of the time evolution of white spots (lenses) in black foam films of small unilamellar liposomes. This new phenomenon was observed only at temperatures below the main phase transition temperature of the lipid bilayer ($T < T_C$).

The "melting" of the hydrophobic tails in lipid aggregates (gel–liquid crystal first order phase transition at $T = T_C$) has various consequences of biological and pharmacological importance [1, 2]. In microscopic horizontal films it manifests itself in changes in the equilibrium thickness [3–5], in the probability of hole formation [4, 5], in the surface diffusion coefficient [6, 7], and in the overall kinetic behavior [3, 8, 9]. A change between "rigid" and "mobile" films with temperature was reported as early as 1959 for macroscopic vertical films, stabilized with synthetic surfactants [10].

In the initial stages of microscopic film thinning a dimple evolution has been recorded [11–13]: in all cases the dimple height diminishes with time; for wetting and emulsion films the dimple shape is almost symmetrical; for foam films the thinning of the dimple follows irregular pattern. The formation of symmetric lenses in emulsion films stabilized with lipids (BLM) has been reported [14], but has never been observed in lipid foam films. Moreover, in the present case the inverse trend is established: the thickness of the lense increases with time.

Experimental

The evolution with time of microscopic horizontal foam (free) films was studied with the microinterferometric method of Scheludko and Exerowa [15]. The kinetic behavior was registered by means of a TV camera and a videorecorder. The data were evaluated with a computerized image-processing system using the so-called topographical method [14, 16].

Films of radii in the range 0.1 to 0.6 mm were investigated. They were formed from solution of unilamellar DMPC (dimyristoylphoshatidylcholine) vesicles of concentration 1 mg/ml in the presence of 0.15 M NaCl (prepared by sonication [17]). The kinetic behavior was studied at temperatures above and below the phase

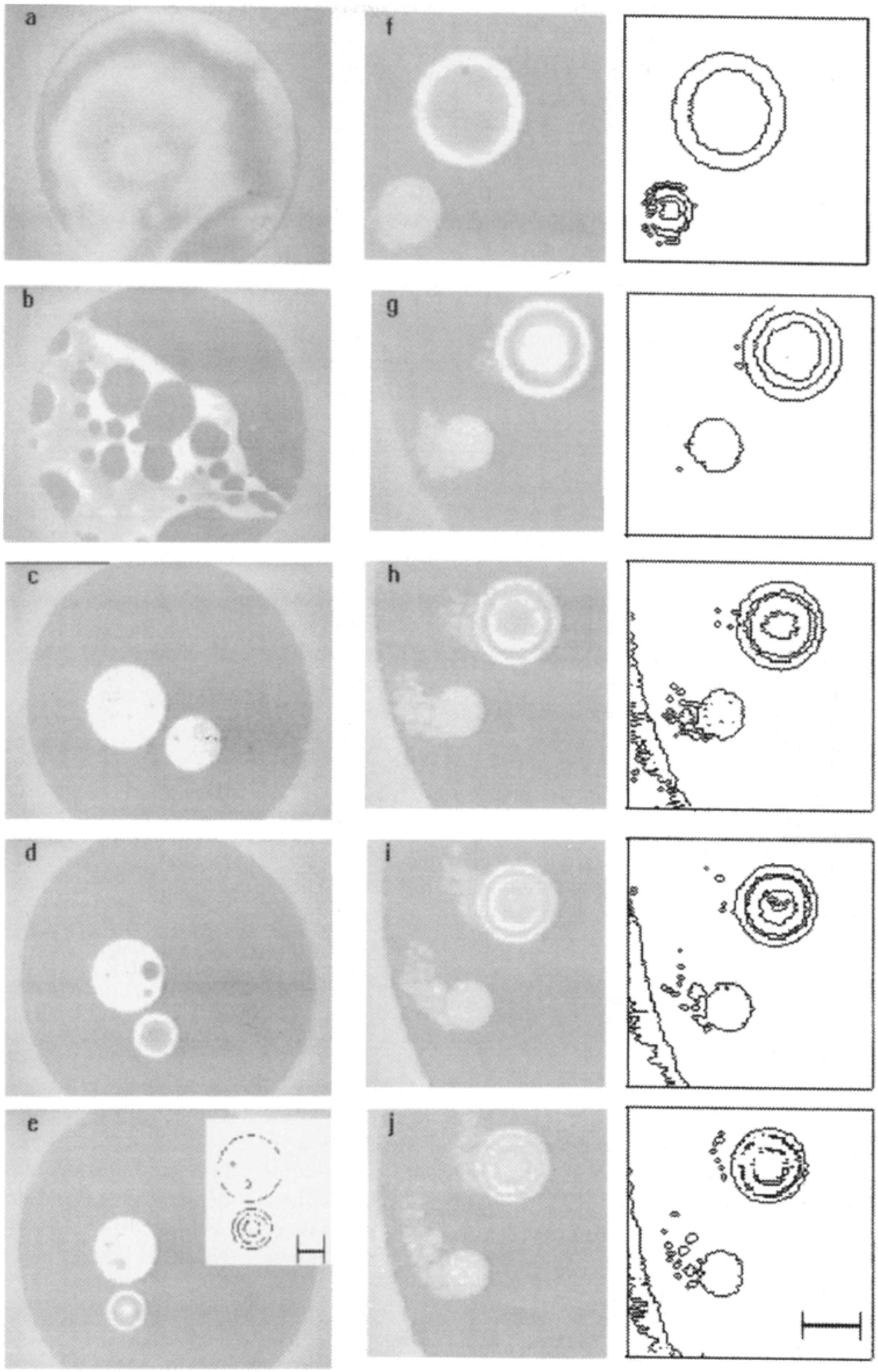

Fig. 1 Chronological sequence of the evolution of white spots in a black foam film of a DMPC unilamellar liposomal suspension at 19.2 °C (the time elapsed is measured from the instant of film formation): microscopic videoframes a) 30 s, b) 90 s, c) 150 s, d) 4 min, e) 5 min (inset – topographic cutout, length of the horizontal bar = 100 μm); cutouts at higher magnification and topographic equivalents f) 7 min, g) 9 min, h) 11 min, i) 13 min, j) 15 min (length of horizontal bar = 100 μm). Making use of the microinterferometric method of Scheludko and Exerowa [15] the kinetic behavior was registered by means of a TV camera and a videorecorder. The data were evaluated with a computerized image-processing system using the so-called topographical method [14, 16, 25]

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transition temperature (for DMPC $T_C = 23.8\,^{\circ}C$ [18]). Fine direct control of temperature ($\mp 0.1^{\circ}$) was realized by introducing a thermocouple into the measuring cell, in the vicinity of the film holder.

Results and discussion

Experiments at $T > T_C$ (24.7 °C) revealed the picture observed with foam films stabilized with a variety of soluble surfactants [19, 20]: initial irregular dimple formation and thinning, black spots formation in a "gray" film and, finally, the formation of a black film. Under the studied conditions it is a Newton black film with a (equivalent water) thickness [4, 5] of ca. 7 nm. Experiments at $T < T_C$ exhibited slower thinning in accordance with other observations [3, 8, 9].

The new finding at $T < T_C$ is illustrated in Fig. 1 for a film at 19.2 °C: the evolution of thickening "white" spots in a black foam film. The coalescing numerous black spots capture part of the thick film material to form a white spot. Instead of irregularly thinning, as a dimple in a foam film, or keeping a rapidly established constant regular shape, as a lense in BLM, these white spots slowly (within minutes) acquire a regular lense shape while thickening with time. The lens eventually starts releasing part of its content into the black film in the form of small white spots (of greater thickness than the black film). This process is shown in Fig. 1 as a chronological sequence. The time elapsed is counted from the first instant of film formation. The insets after 4.5 min show the topographic picture corresponding to the respective film images. The topographic lines, counted inwards from the spot periphery, correspond to thicknesses of 50, 150, 250, 350, and 450 nm, respectively (assuming a refractive index of pure water).

The small bright spots at later stages are probably due to the formation of surface mesophases [21].

Figure 2 shows schematically the evolution of the film profile in the same time interval. The shapes of the larger lens are estimated from the topographic pictures in Fig. 1.

The convex lens thus formed is apparently a non-equilibrium formation [22]. It gradually increases in thickness in its center, eventually reaching a maximum thickness of 500 nm, while the surrounding black film is of thickness not exceeding 7 nm. It is also of interest to follow the evolution of the lens volume, reflecting the amount of lipid material in it and of the contact angle θ, related to the excess energy of interaction [14, 16, 22]. Our estimates using the data from Figs. 1, 2 are given in Table 1.

In the volume estimate the lens shape is approximated by a doubled spherical segment of base radius a and height h ($h \ll a$). The actual maximal lens thickness equals $2h$. The lens volume V is, therefore, twice the volume of such

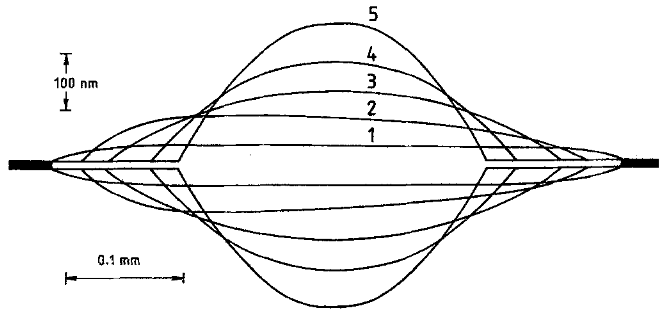

Fig. 2 Profile evolution of the larger white spot (same data as in Fig. 1; the refractive index is assumed to be that of pure water): (1) 4.5 min, (2) 6 min, (3) 8 min, (4) 10 min, (5) 15 min

Table 1 Lens volume, V, and contact angle, θ, evolution*)

t [S]	a [10^{-4} m]	h [10^{-7} m]	V [10^{-14} m^3]	θ [deg]
270	2.4	0.75	1.36	–
300	2.34	0.8	1.38	–
360	2.2	1.0	1.37	–
420	2.06	1.05	1.40	–
480	1.94	1.3	1.54	0.08
540	1.77	1.5	1.48	–
600	1.58	1.83	1.44	0.13
780	1.43	2.25	1.45	–
900	1.32	2.45	1.34	0.18
960	1.26	2.5	1.23	0.20

*) Lens shape is approximated by a (doubled) spherical segment of base radius a and height h ($h \ll a$); lens thickness equals $2h$ (cf. Fig. 2). Contact angle is estimated topographically through $\tan\theta$ at the lens perimeter.

a segment V_s:

$$V = 2V_s = 2[(\pi h/6)(3a^2 + h^2)] \approx \pi a^2 h \,.$$

The values of $\tan\theta$, and respectively θ, are estimated topographically from the slope of the lens profile at its perimeter (cf. Fig. 2).

The contact angle which the lens forms with the black film gradually increases, reaching a highest value of 0.2 degrees. It must be pointed out that this value is small, as compared to the contact angle formed between the Newton black foam film and the adjacent meniscus [23, 24] or that of a lense in BLM [14, 25].

The results in Table 1 show a well established trend of volume change: gradual increase (up to $t = 8$ min) and then a decrease during the next 8 min reaching about 20% of the greatest value for the volume. One can attribute the volume decrease to the release of lipid material from the white spot into the surrounding black film (the small bright spots, the onset of the formation of which coincides with the detected drop in volume).

The convex lens formation is, obviously, connected with free energy changes in a system with variable surface-to-volume ratio. The case of a convex lens in a plane-parallel film in contact with a concave meniscus is discussed in detail in ref. [22]. Most probably, the observed phenomena reflect also an increasing concentration of lipid material and/or rearrangement of lipid and water molecules in the white spot during the convex lens formation (e.g., ordered giant multilayer liposome-type or other, more planar, multilayer-type structuring). This should lead to an increase in both viscosity and refractive index in the white spot. The latter effect may account for some apparent volume increase.

In the much simpler situation of a foam film stabilized with a soluble surfactant the first stage of a similar experimental observation has found a plausible qualitative explanation following from a complex numerical computation of hydrodynamic, capillary and surface forces effects upon film shape evolution [26, 27].

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