

ORDERED STRUCTURES IN THINNING MICELLAR FOAM AND LATEX FILMS

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ABSTRACT

The stratification of thin liquid films formed from micellar solutions or latex suspensions can be explained as a layer-by-layer thinning of ordered structures of particles inside the film. These structures and the ordering in bulk latex suspensions have similar physical nature. The thickness of the metastable states of a stratifying film can be calculated by means of a new expression for the disjoining pressure of a film containing micelles. The calculated and the measured values of the film thickness are in good agreement. The driving force for the step-wise thinning of the film is attributed to the gradient of the chemical potential of the micelles at the film periphery. The appearance and expansion of spots in the film are thus controlled by the mechanism of micellar self diffusion rather than by normal instabilities. This explanation of the mechanism of stratification is supported by the data for expansion of spots. The phenomenon of stratification gives a method for investigating the ordering in microheterogeneous systems and their stability.

1. INTRODUCTION

Johnnott (1) and Perrin (2) long ago experimentally observed and described a phenomenon of step-wise thinning of liquid foam films. This phenomenon, called stratification, was later observed and investigated by many authors, both with foam films (3-6) and with emulsion films (7,8). Several researchers (5-8) explained the phenomenon by suggesting that a lamella liquid crystal structure is formed inside the stratifying film. Some recent experiments, however - experiments performed with both latexes and micellar surfactant solution (9,10) - revealed that the latex or micellar particles form a structure inside the film.

The stratification phenomenon can then be interpreted as a layer-by-layer thinning of this structure.

Hachisu, Kobayashi and Kose (11), for example, established experimentally that latex particles in an aqueous solution form an ordered structure (a solid-like arrangement of latex particles). This finding awoke considerable interest. When compared with the size of the particles, the interparticle distances in the latex-ordered structures are too large for the van der Waals forces to be important. The classical DLVO theory (12,13) thus cannot explain the ordering in such systems as a balance of van der Waals forces and electrostatic forces at the secondary minimum of the interaction energy.

Our aim here is to present some recent experimental results for stratifying films and to offer a theoretical explanation. These results show that the micellar structures inside a stratifying film resemble the latex-ordered structures observed by Hachisu et al. (11). Moreover, films formed from latex solutions also exhibit stratification. For this reason one can conclude that both phenomena (stratification of thin liquid films and ordering in latex solution) probably have the same physical origin. As is well known (14,16), this sort of ordering occurs because particles interacting via repulsive forces are forced into a restricted volume environment.

2. EXPERIMENTAL INVESTIGATION OF STRATIFYING FILMS

In one method for investigating stratifying films, a film is formed in a cylindrical capillary with hydrophilic inner walls (of radius $R = 1.5$ mm in our experiments). The films were created by sucking out the liquid from a biconcave drop inside the capillary through an orifice in the capillary wall. The resulting horizontal flat thin film is encircled by a biconcave liquid meniscus. This method is appropriate for investigating stratifying films formed both from micellar surfactant solutions and from latex suspensions (9,10).

Using films from micellar solutions, we observed the

following phenomenon: After the film is formed, it immediately starts to decrease in thickness. When it becomes less than about 104 nm (after the last interferential maximum due to the light reflected from the film), the film thickness changes in several steps. The film first rests for a few seconds in a metastable state with uniform thickness. Then one or several dark spots (with less thickness than the remaining part of the film) appear and gradually increase their area. Soon the spots cover all area of the film, and it rests for several seconds in a new metastable state. Then darker spots appear, and after their expansion a subsequent metastable state is reached. Finally the film reaches a stable state and no more step-wise transitions occur.

Films formed from latex solutions stratify in a similar fashion to those formed from micellar solutions. We observed only one difference: the spots of less thickness may be not only darker, but also brighter than the remaining part of the film (See Fig. 1). This difference is due to the large diameter of the particles (in our case 91 nm), a diameter that exceeds the thickness of the last interferential maximum. We thus observed both obstructive and constructive interference.

We used interferometric technique to record the thickness of the film during the step-wise thinning (9,10). In this technique the light reflected from a small portion of the film is conducted to a photomultiplier with the help of a fine optic probe. The photocurrent is then recorded as a function of time. A typical interferogram is presented in Fig. 2 (film formed from micellar solution of a nonionic surfactant). The minimum and maximum intensities of the reflected light correspond to the last interference minimum and maximum. The metastable states of the film appear in the interferogram as steps whose width is proportional to the lifetime of the respective state. The calculated height of the steps is also shown in Fig. 2. Its magnitude is approximately constant for all steps (about 10.6 nm). (For purposes of comparison, the diameter of a micelle is about

10 nm.) In other words, the thickness of a spot is one micellar diameter less than the thickness of the surrounding film. The same is true for the film formed from latex solution. As shown in Fig. 1, the average height of the step is 90 nm, and the diameter of a latex particle is 91 nm. One can then conclude (9,10) that the stratification is in fact a layer-by-layer thinning of an ordered micellar structure inside the film.

In the case of an anionic surfactant, say sodium dodecyl sulfate (NaDS)-Table I, the mean height of a step-wise film thickness transition, $\bar{\delta}$, is between 15.2 and 10.0 nm (depending on the surfactant concentration). The micellar diameter has a value of 4.8 nm (17), which is not dependent on the NaDS-concentration (in this concentration range). In this case, $\bar{\delta}$ should be compared with the Debye diameter of the electric double layer around a micelle rather than with the diameter of the micelle itself. Indeed, the values of $\bar{\delta}$ are very close to the mean distance, δ_{ρ} , between the micelles in the bulk solution (see Table I). Like the latexes, the ionic micellar solution can be considered as an effective "suspension" of particles with diameter δ_{ρ} , including the micelle and its Debye atmosphere. In other words, whether films are formed from solutions of latexes, or nonionic and anionic surfactants, the phenomenon of stratification can be explained in the same way: as the presence of an ordered structure of particles inside the film.

Another way to demonstrate the presence of ordered structure inside a stratifying film is to form a large film in a vertical frame (see Fig. 3). With films formed from latex solutions, one observes a series of stripes of uniform color at the upper part of the frame. The boundaries between the stripes are very sharp, a consequence of the step-wise profile of the film surface in this region. The region with gradually changing colors corresponds to the liquid meniscus below the film. We observed similar sharp stripes with films from 5.2×10^{-2} mol/l ethoxylated alcohol with 30 ethoxy groups (micellar diameter about 10 nm). All stripes,

however, are gray in color, though with different intensities, because the diameter of the micelles is small.

The amount of added salt strongly affects the phenomenon of stratification for films with micelles of ionic surfactants. Above a given (threshold) concentration, the added salt completely suppresses the stratification (there are no step-wise film thickness transitions). A stratification-nonstratification phase diagram is presented in Fig. 4. This diagram is similar to the order-disorder phase diagrams for bulk solutions of latexes (11,15), another demonstration of the close connection between ordering and stratification.

3. DISJOINING PRESSURE DUE TO THE MICELLAR STRUCTURE

As established in Ref. 19 the excess (disjoining) pressure Π in a stratifying film has the additional component Π^{ms} because of the micellar structure inside the film. By using the effective potential of the intermicellar repulsion $U^{eff} = (U_0/\delta) \exp(-\kappa\delta)$ (δ is the distance between two micelles, κ and U_0 are constants), as suggested by Beresford-Smith et al. (20), one can derive the following expression for Π^{ms} (19):

$$\Pi^{ms} = \frac{U_0}{\delta^2} \left[\left(\kappa + \frac{1}{\delta} \right) \frac{e^{-\kappa\delta}}{\delta} - \left(\kappa + \frac{1}{\delta_\ell} \right) \frac{e^{-\kappa\delta_\ell}}{\delta_\ell} \right]. \quad [3.1]$$

Here δ is the distance between two neighboring micelles along the normal to the film and δ_ℓ is the distance between two micelles in the bulk solution (the reference phase). During the process of thinning in general $\delta \neq \delta_\ell$ and then $\Pi^{ms} \neq 0$. The total disjoining pressure is (19)

$$\Pi_n = \Pi^{el} + \Pi^{vw} + \Pi^{ms}, \quad [3.2]$$

where

$$\Pi^{el} = \kappa C e^{-\kappa h} \quad \text{and} \quad \Pi^{vw} = - \frac{A}{6\pi h^3} \quad [3.3]$$

are the components of the disjoining pressure, due to the electrostatic repulsion and van der Waals attraction between film surfaces, h_n is the thickness of the film and n is the number of micellar layers inside the film. Π_n depends on n via

$$h = h_0 + n\delta$$

Here h_0 is the thickness of the final state of film without micelles. Figure 5 shows the disjoining pressure isotherms $\Pi_n(h)$ calculated from Eq. [3.2] for 0.03 mol/l concentration of NaDS (see Table I) and Hamaker constant $A = 4.5 \times 10^{-20}$ J. One sees that at given values of the capillary pressure P_c , there is a series of equilibrium thicknesses h_n ($n=0, 1, 2, \dots$) satisfying the equilibrium condition $\Pi_n(h_n) = P_c$. This condition, along with Eq. [3.2], permits one to calculate the values of h_n . As reported in (19) the calculated and the measured values of h_n are in good agreement (see Table II). Each h_n corresponds to a metastable state of the film, i.e. to a minimum of the excess energy ω_n per unit area of the film (19) (see Fig. 6). The greater the number of the micellar layers, n , inside the film, the larger the energy of the metastable state. For this reason, the metastable states with less values of n are energetically more favorable.

4. MECHANISM OF FORMATION AND EXPANSION OF DARK SPOTS.

The dimension of a stratifying film in the normal direction is much less than the dimension of the film in a lateral direction. For this reason, the equilibrium with respect to the forces acting normally to film surfaces is achieved faster, than the equilibrium between the film and the bulk solution in the meniscus. When the lateral equilibrium is reached, the process of step-wise thinning of the film stops. Depending on the experimental conditions (temperature, capillary pressure, film radius, concentration of added salt, etc.), the film in its final state can contain $n = 0, 1, 2$ or more micellar layers.

During the process of step-wise thinning, the presence of normal stability at the metastable states (the minimum in Fig. 6) is accompanied with lateral instability. The driving force of the thinning is the difference between the chemical potentials of the micelles inside the film and inside the meniscus. Under the action of the gradient of the chemical potential, the micelles leave the film and vacancies appear in their places. Because the micelles diffuse, the vacancies (initially created at the film periphery) move throughout the entire film area like molecules of a two-dimensional gas. As proven in (21), phase transitions occur at sufficiently large concentration of the vacancies, and dark spots are formed as a result of condensation of vacancies. After a dark spot has been formed, it gradually increases its area. The vacancies created at the film periphery "condense" at the dark spot, thus increasing its area.

Let us denote by J the total influx of vacancies in the film and let r be the radius of the spot. If J is constant during the spot expansion, one can derive

$$r^2 = \frac{\delta_{\ell}^2}{\pi} Jt + \text{const.} \quad [4.1]$$

(δ_{ℓ}^2 is the area of a vacancy); that is, r^2 should be a linear function of time. And we did in fact observe this experimentally. Line 1 in Fig. 7 represents experimental data for expansion of a single dark spot in film with an $n=1$ micellar layer inside. The process was recorded by a movie-camera at a velocity of 0.125s per frame. Line 2 in the same figure represents similar data but for two spots of approximately equal size in film with $n=2$ micellar layers inside.

5. CONCLUDING REMARKS

The experimental data for stratifying films formed from latex suspensions or from micellar solutions of anionic and nonionic

surfactants, and the theoretical analysis of these data, show that the phenomenon of stratification occurs when ordered structures of latex or micellar particles form inside the film. Like the ones observed in the latex suspensions, these structures depend on an ordering of particles, particles that interact via repulsive forces but are closed into a restricted volume. When the repulsion is due to electrostatic forces (latexes, micellar solutions of ionic surfactants), the stratification is very sensitive to the concentration of the added salt. When the repulsion is due to steric forces (micellar solutions of nonionic surfactants), the stratification is sensitive to temperature.

The phenomenon of stratification provides a method for investigating the interaction potentials and the ordering of particles in the microheterogeneous systems and provides the possibility for a new understanding of the stability of emulsions, suspensions and foams.

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TABLE 1. Data for micellar solutions of NaDS. The concentrations C_{Na^+} , C_{DS^-} and C_{mic} are taken from (18) and $\bar{\delta}$ and δ_l are the averaged height of a step-wise film thickness transition and the mean distance between the micelles in the solution, as reported in (9,10).

$C_{Na DS}$ (mol/l)	C_{Na^+} (mol/l)	C_{DS^-} (mol/l)	C_{mic} (mol/l)	$\bar{\delta}$ (nm)	δ_l (nm)
0.03	0.0123	0.0057	3.64×10^{-4}	15.2	16.6
0.06	0,0192	0.0041	8.34×10^{-4}	11.8	12.6
0.08	0.0238	0.0030	1.15×10^{-3}	10.8	11.3
0.10	0.0284	0.0019	1.46×10^{-3}	10.0	10.4

TABLE 2. Measured and calculated values of the film thickness (0.1 mol/l NaDS, temperature 25°C. $r_c = 0.03$ cm, $P_c = 50.5$ Pa).

n	h_n (nm) measured	h_n (nm) calculated
0	16.2	16.2*
1	26.1	26.1*
2	35.9	36.4
3	47.0	46.7
4	57.9	57.0
5	68.8	67.2

* These two values were used to calculate the parameters U_0 and C on Eq. [3.1] and [3.3].

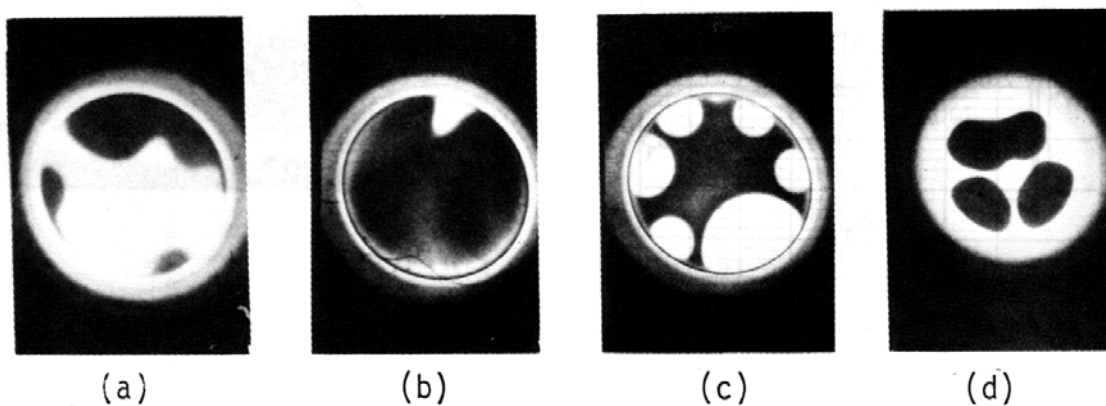


Figure 7

Fig. 1. Stratification of a foam film containing latex particles. The bright area in Fig. 1a corresponds to film thickness $h=281$ nm, the dark spots in 1a - to $h=190$ nm, the bright spots in 1c - to $h=99$ nm and the dark spots in 1d - to $h=8$ nm (film without latex particles inside).

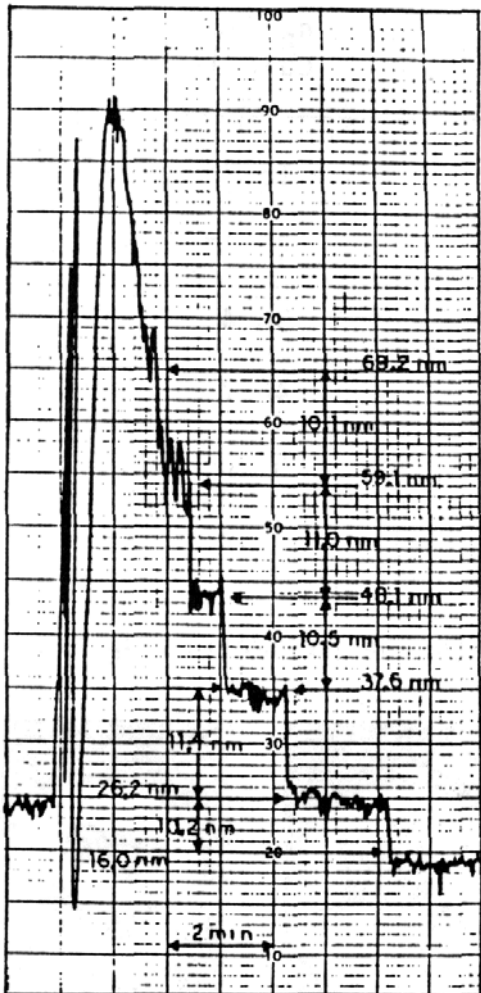


Fig. 2

Fig. 2. Photocurrent vs time interferogram for the non-ionic surfactant ENORDET AE 1215-30 at concentration 0.052 mol/l.

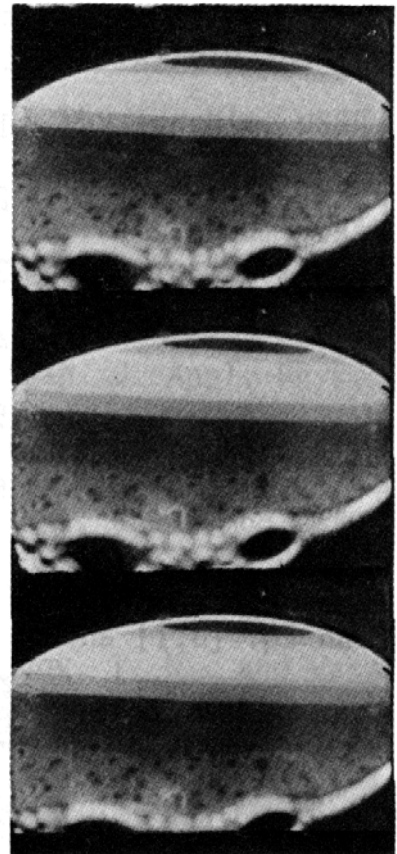


Fig. 3. Interference pattern in light reflected from a vertical thin film from 21 wt% latex suspension with particle diameter 0.38 μm .

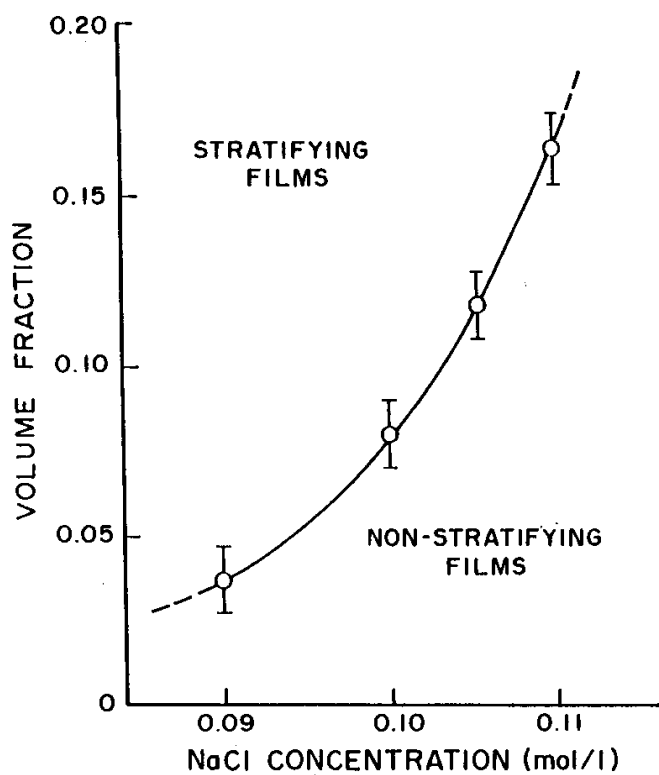


Fig. 4. The volume fraction of micelles vs concentration of added NaCl, phase diagram for stratifying films from micellar solutions of NaDS.

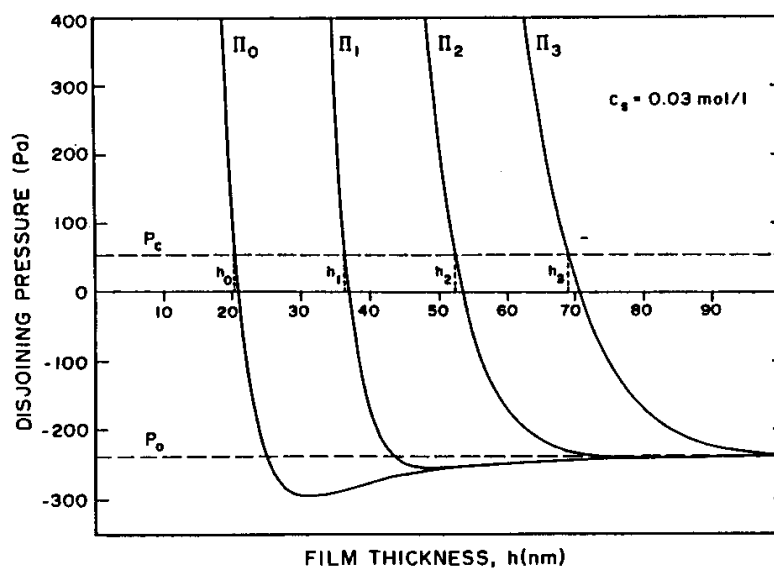


Fig. 5. Calculated disjoining pressure isotherms $\Pi_n(h)$ for thin films with n micellar layers inside (surfactant concentration 0.03 mol/l NaDS).

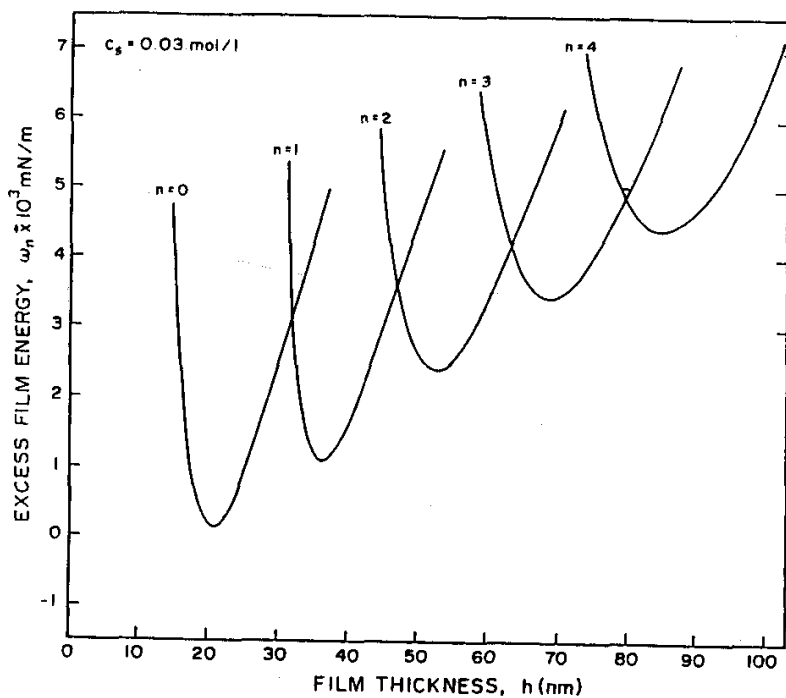


Fig. 6. Calculated isotherms of the excess energy per unit area of the film, $\omega_n(h)$, at 0.03 mol/l NaDS solution and different number, n , micellar layers inside the film.

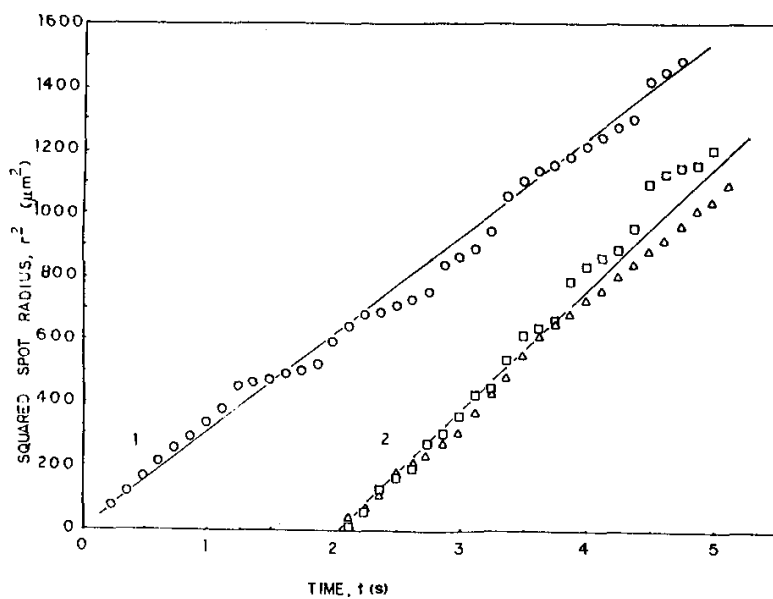


Fig. 7. Data for expansion of dark spots: (1) a single spot at $n=1$ and $r_c=0.017$ cm; (2) two spots of approximately equal size, $n=2$ and $r_c=0.018$ cm (NaDS-concentration 0.1 mol/l in both cases).