

Kinetics of Two-Dimensional Phase Transition of Langmuir Monolayers

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A theoretical model is introduced for the description of the two-dimensional condensation kinetics of Langmuir monolayers at the air/water interface. The dynamic jump of surface concentration of monomers and the dynamic jump of the surface pressure of compressible monolayers are theoretically described. For the dynamic jump of the surface pressure, the equation of state, introduced recently for Langmuir monolayers under equilibrium conditions, was used. The theoretical kinetic model accounts for different mechanisms of the monomer aggregation (dimerization, trimerisation, etc.) and different dependencies of the aggregation rate on t . The theoretical model is experimentally confirmed by the dynamic surface pressure–area curves of palmitoyl-D-allotheonin methylester monolayers recorded at different compression rates and temperatures. Good agreement between theory and experiment has been found with the consequence that the most preferred reaction at the aggregation is the attachment of molecules to large aggregates. The experimental results indicate that the rate constant depends quadratically on time. The activation enthalpies for the aggregation process in the palmitoyl-D-allotheonin methylester monolayers are calculated based on the dependence of the reduced rate constant k_0 on temperature.

Introduction

In recent years new methods have extended the knowledge of two-dimensional (2D) phase transition in Langmuir monolayers.^{1,2} The existence of a “plateau” region in the surface pressure–area (Π – A) isotherm refers to a two-phase coexistence for the main transition between a gaslike fluid phase of low density and a condensed phase. Condensed phase domains with an exiting variety in shape and size are formed in the two phase coexistence region in equilibrium.^{3,4} At rapid or jump-like compression of monolayers or a quick decrease in temperature, nonequilibrium domain textures are formed having fractal-like or dendritic shape. Such unstable branched textures of nonequilibrium systems can relax to the equilibrium domains.^{5,6}

Current interest is directed to the features of monolayers of amino acid derived amphiphiles because of their biological relevance.^{7,8} The chiral forms of these monolayers represent well-defined model systems that show pronounced chiral discrimination effects not only in the textural features,^{9–11} but also in the thermodynamic behavior.¹² Nonequilibrium effects occur also in the thermodynamic properties of amino acid derived amphiphiles so that a better understanding of the phase transition kinetics would be desirable.

However, theoretical studies of the phase transformation kinetics are nearly missing. Dynamic Π – A experiments can provide information on the kinetics of the 2D phase transition phase transition suitable for a comparison with theoretical results. In a previous work, we proposed a first theoretical model that allows the estimation of 2D aggregation rate constants from the data of dynamic Π – A experiments for Gibbs and Langmuir monolayers.¹³ On the basis of a quasichemical model for the formation of 2D aggregates by attachment of monomers to

aggregates, the 2D aggregation rate constants can be estimated from the data of the dynamic Π – A experiments.

The objective of the present paper is to develop a new theoretical model for the kinetics of the 2D condensation of Langmuir monolayers suitable to describe the dynamic Π – A experiments carried out with a special amino acid derived amphiphile. The dynamic Π – A experiments were performed with enantiomeric palmitoyl-D-allotheonin methylester monolayers.

Theory

Two-dimensional phase transition in insoluble monolayers at the air/water interface is usually treated as the transition from the fluid (gaseous) (G) to the condensed (C) state of a monolayer. The fluid state of a monolayer under the equilibrium conditions can be described satisfactory enough by the generalised Volmer’s equation,^{14,15} wherein the cohesion pressure Π_{coh} represents the existence of small aggregates in the monolayer and significant interaction between the molecules which constitute the monolayer

$$\Pi_g = \frac{kT/m}{A - \omega_1} - \Pi_{\text{coh}} = \frac{RT\Gamma}{m(1 - \theta)} - \Pi_{\text{coh}} \quad (1)$$

where Π_g is the surface pressure, k is the Boltzmann constant, R is the gas constant, T is the temperature, ω_1 is the partial molecular area for monomers, $A = 1/N\Gamma$, A is area per molecule, N is the Avogadro’s number, Γ is surface concentration (adsorption), $\theta = \omega_1/A = \Gamma N\omega_1$ is the monolayer coverage, and m is the aggregation number for small aggregates.

The two-dimensional main phase transition from the fluid to the condensed state for $A \leq A_c$ leads to the formation of condensed aggregates in the monolayer, characterized by the aggregation number $n \gg 1$, i.e., large aggregates in form of the condensed phase. This results in the decrease of the slope of

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the surface pressure dependence on A , as compared with that given by eq 1^{14,15}

$$\Pi_{\text{LC}} = \frac{(kT/m)(A/A_{\text{c}\Pi})^2}{A - \omega_1[1 + \epsilon((A/A_{\text{c}\Pi})^2 - 1)]} - \Pi_{\text{coh}} \quad (2)$$

where

$$A_{\text{c}\Pi} = A_{\text{c}} \exp\left(\frac{(\Pi_{\text{LC}} - \Pi_{\text{c}})\epsilon\omega_1}{RT}\right) \quad (3)$$

$\epsilon = 1 - \omega_n/n\omega_1$, $\omega_n/n = \omega_{(n)}$ is the area per monomer in a cluster, $A_{\text{c}} = 1/N\Gamma_{\text{c}}$ is the molecular area which corresponds to the point of the commencement of the phase transition, i.e., at $\Pi = \Pi_{\text{c}}$. Equation 2 is valid for the region $A \leq A_{\text{c}}$. For $A = A_{\text{c}}$, eq 2 becomes the Volmer's equation (eq 1) for small aggregates or monomers ($m = 1$).

Nucleation and growth of two-dimensional aggregates at water/air interface is different from the two-dimensional condensation from the gas phase at solid crystal surface,¹⁶ from three-dimensional condensation in the gas phase,¹⁷ and from the formation of three-dimensional nuclei from two-dimensional monolayers.^{18–21} In the present case and in contrast to the condensation at solid crystal surface, the effect of the substrate is almost negligible because the condensation is due mainly to the van der Waals interaction of the molecules in the monolayer. For ordinary three-dimensional condensation, the thermodynamically stable nucleus of a new phase with minimum size is formed, and therefore, the energy barrier of the nucleation is determined mostly by the formation of new interface. At the two-dimensional condensation at water/air interface, any new surface is not formed because of the reduced dimensionality so that the activation energy does not involve any contribution from the formation of new interface. Only a contribution of linear tension along the cluster perimeter into the energy barrier of the nucleation may be considered and was possibly overestimated.²²

The compression of a gaseous monolayer results in its oversaturation with monomers, which in turn leads to the formation of dimers, trimers, and other small aggregates from the monomers and also to the linkage of monomers or small aggregates to large aggregates in form of condensed phase nuclei. These processes lead to the decrease of the free energy of the system calculated per attached molecule. This conclusion is supported by the quantum chemical calculations of the thermodynamic characteristics for the formation of dimers of normal alcohols ($\text{C}_8\text{--C}_{16}$) at water/air interface²³ and by the calculations performed for larger aggregates (trimers to heptamers).²⁴ It has been shown²⁵ that in the monolayers of dodecanol, tetradecanol and hexadecanol, which undergo a two-dimension condensation in the monolayer at water/air interface, the aggregation of monomers to dimers, trimers, etc., always leads to the decrease of the free energy ΔG° of monomers of 7–17 kJ/mol. It follows from these calculations that the regularity exists in the variation of the free energy of the aggregate formation for even and odd aggregation numbers (for odd aggregation numbers the decrease is larger than for even aggregation numbers) and that at the aggregation the free energy increment per one methylene group is approximately -3.0 kJ/mol. The activation energy for the growth of two-dimensional nuclei at air/water interface should possibly involve the energy related to the rearrangement of the transition complex with arbitrary (nonoptimal) structure into the optimum aggregate structure, i.e., the structure which is characterized by the

minimum free energy of formation. For example, from all the possible structures of the 1-dodecanol pentamer, only that which is starlike in the plane (with one central molecule and another four located in the angles of a quadrilateral) corresponds to the minimum ΔG° value, while other structures lead to either positive or small negative ΔG° values. Therefore, the attempts made previously to describe the kinetics of the two-dimensional aggregation in the monolayer using models developed in the nucleation theory (e.g., the approach which involves the linear tension along the perimeter of the liquid-condensed cluster and the critical size of the thermodynamically stable cluster calculated from it²²) cannot be supported by the quantum chemical calculations of aggregation.

To incorporate rigorously the quantum chemical results calculated for the thermodynamic characteristics of the aggregate formation at the air/water interface, in the monolayer thermodynamics, one should account for the contribution of the aggregation to the variation of the mixing entropy. Here two states of the monolayer have to be compared: the state existing before the formation of n -mers and the state after this formation. Using an equation derived in ref 26, the entropy variation during the aggregation is obtained by

$$\Delta S_{\text{mix}} = R\left(1 - \frac{1}{n}\right) \ln\left(\frac{\omega_1}{A}\right) \quad (4)$$

As $\omega_1/A < 1$, the entropy variation due to the aggregation is always negative, which is obvious enough, because the number of possible states becomes lower. For large A/ω_1 , the mixing entropy decreases most significantly in the fluid state of the monolayer. This can explain the fact that for the medium-chain homologues of alcohols ($\text{C}_{12}\text{--C}_{14}$) formation of large aggregates has not been observed in fluid monolayers.²⁵ However, for negative ΔG° , the value of A close enough to ω_1 always exists, for which the contribution from the decrease of the system entropy is always lower than the decrease of free energy due to the clusterisation; i.e., the clusterisation becomes possible.

At the two-dimensional condensation, the energetic barrier for the nucleation is probably absent so that the analysis of the aggregation kinetics in the monolayer becomes essentially simpler. We proposed a quasichemical model for the formation of two-dimensional aggregates due to the attachment of the monomer to the aggregate. It has been suggested that bimolecular reactions involving monomers



and reactions for the formation of large aggregates from small aggregates



for the phase transition in monolayers. Here, Γ_j is the dynamic adsorption (surface concentration) value, subscript 1 refers to the monomer, and the i value can vary from 1 to $n - 1$.

Assuming small deviations from the equilibrium and taking into account only the reactions of attachment/detachment of monomers to/from a large aggregate, the equation which describes the balance of monomers in monolayers can be derived¹³

$$\frac{d\Delta\Gamma_1}{dt} = \frac{dA}{Adt}\Gamma_1^\circ - k_1\Delta\Gamma_1 \quad (7)$$

which, being integrated for $\Delta\Gamma_1|_{t=0} = 0$ and $dA/dt = \text{const}$, leads to the equation for a jump of the adsorption (surface

concentration) of monomers $\Delta\Gamma_1$ in incompressible monolayers

$$\Delta\Gamma_1 = \frac{(dA/dt)\Gamma_1^\circ}{Ak_1}[1 - \exp(-k_1t)] \quad (8)$$

where dA/dt is the compression rate of the monolayer, k_1 is the net rate constant for the disappearance of monomers, as the resultant of the rates of direct and inverse reactions (eq 5), t is the time since onset of aggregation, and Γ_1° is the equilibrium adsorption (surface concentration) of monomers. Noting that

$$\Delta\Pi = \frac{\partial\Pi}{\partial\Gamma_1}\Delta\Gamma_1 \quad (9)$$

and using eqs 1 and 8, one obtains the equation for the dynamic jump of surface pressure in the monolayer during the compression in the two phase transition region¹³

$$\Delta\Pi = \frac{kTA^2 \frac{dA}{dt}}{(A - \omega_1)^2 A_c^2 k_1} [\exp(-k_1t) - 1] \quad (10)$$

In contrast to ref 13, it is assumed in eq 10 that for $A < A_c$ the decrease in the equilibrium adsorption of monomers Γ_1° is proportional to A/A_c .¹⁴ It is interesting to note that the dependence of ω_1 on A and k_1 on t , A or dA/dt can be used to analyze small deviations of the system from equilibrium. The error introduced in this case would be comparatively small.

Equations 8–10 do not take into account the formation of dimers, trimers, and other oligomers from monomers, as well as the formation of large aggregates by association of small aggregates. It has been shown in the approach developed earlier that oligomerization processes lead also to eq 8, where in this case the kinetic constant k_1 becomes a function of the equilibrium surface concentration (adsorption) of the monomers. Assuming the rate of the inverse reaction to be slow enough and taking into account the factor A/A_c for the equilibrium adsorption of monomers^{14,15} one obtains for dimerization

$$k_1 = 2k_2\Gamma_1^\circ \cong 2k_2A/A_c^2 \quad (11)$$

for trimerisation

$$k_1 = 3k_3(\Gamma_1^\circ)^2 \cong 3k_3A^2/A_c^4 \quad (12)$$

and, for example, for the formation of pentamers

$$k_1 = 5k_5(\Gamma_1^\circ)^4 \cong 5k_5A^4/A_c^8 \quad (13)$$

Therefore, assuming that various types of reactions which involve the monomers take place, to calculate the surface pressure jump from the adsorption jump, one has to employ the relation

$$\Delta\Pi = \sum_j \varphi_j \frac{\partial\Pi}{\partial\Gamma_1} \Delta\Gamma_1 \quad (14)$$

instead of eq 9, where the summation over j is performed to account for all possible reactions involving monomers and φ is the normalizing factor ($\sum_j \varphi_j = 1$) which is determined by the values of free energy of the corresponding reactions. It follows from quantum chemical calculations that the most preferable reactions involving monomers (apart from the attachment of the monomer to the aggregate) are those leading to the formation of oligomers consisting of odd number of monomers (trimers,

pentamers, etc.).²⁴ The surface concentration in the monolayer at the onset point for large aggregation is very high (monolayer coverage is usually ca. 0.5), i.e., the distance between the molecules in the monolayer is a fraction of 1 nm. Therefore, in contrast to the aggregation in diluted solutions, i.e., to the micelle formation,²⁷ the diffusion effects need not be accounted for at the aggregation in monolayers. Thus, the simultaneous collision of several molecules, which is rather improbable in the diluted solution, seems to be quite probable in condensing monolayers.

It should be noted that, irrespective of the type of the reaction involving monomers, the same eq 8 is valid for the description of the adsorption dynamic jump of monomers. Thus, from eqs 8 and 14, one again obtains eq 10 where the k_1 value is the weighted average across all reactions involving monomers

$$k_1 = \lambda k_\lambda (\Gamma_1^\circ)^{\lambda-1} \cong \lambda k_\lambda A^{\lambda-1} / (A_c^{\lambda-1})^2 \quad (15)$$

and λ is the mean oligomerization number. The λ value i.e., the preferential mechanism of the aggregation of monomers, can be estimated for using this model to analyze the experimental results. Introducing the ω_1 dependence on A ^{14,15} into eq 10 and taking into account possible dependence of the rate constant on t and the existence of an induction time τ ^{17,18} (that is, the time required for the nucleation and slow growth of the nuclei), eq 10 can be represented in the generalized form

$$\Delta\Pi = \frac{kT \frac{dA}{dt} K^{\lambda+1}}{m\{A - \omega_1[1 + \epsilon(K-1)]\}^2 k^* (t - \tau)^\delta} \left[1 - \exp\left(-\frac{k^*(t - \tau)^{1+\delta}}{K^{\lambda-1}}\right) \right] \quad (16)$$

where $K = A/A_c$ and $t = (A_c - A)/(dA/dt)$. Now eq 16 involves only one independent variable, namely, A . The value $dA/dt = \text{const}$ is determined by the experimental conditions. The parameters A_c , m , ω_1 , and ϵ can be determined from the equation of state (eq 2) for the equilibrium conditions. The kinetic characteristics of the aggregation process are k^* , δ , λ , and τ . It can be expected that the induction time is an irrelevant kinetic parameter and thus, $\tau = 0$, as obviously an energy barrier does not exist for the two-dimensional condensation at the air/water interface. For the kinetics of the two-dimensional nucleation and growth, a value $\delta = 2$ is expected because for three-dimensional nucleation and growth usually $\delta = 3$ is assumed.¹⁷ It is shown below that both of these assumptions are supported by experimental evidence. Moreover, the best agreement with the experiment is generally observed for $\lambda = 1$ as attachment of a monomer to an aggregate is the most preferable reaction. Therefore, k^* is the only parameter additional to the equilibrium parameters of eq 16 and can be found from the best fit between theory and experiment.

The theoretical value for the dynamic surface pressure of a compressible monolayer Π_d in the $A < A_c$ region is equal to the sum of the equilibrium surface pressure and the dynamic pressure jump expressed by eq 16

$$\Pi_d = \Pi_{\text{Cond}} + \Delta\Pi \quad (17)$$

where the value Π_{Cond} should be calculated from eq 2. For $k^* \rightarrow 0$, the $\Delta\Pi$ value is maximum, and therefore, the Π_d values calculated from eq 17 are approximately equal to the Π_g values calculated from Volmer's equation (eq 1) extended to the transcritical range of the areas A (monolayer extremely over-saturated by the monomers). In fact, for $k^* \rightarrow 0$ and $\epsilon = \tau = 0$, one obtains from eq 16

$$-\frac{d\Pi}{dA} \cong \frac{\Delta\Pi}{A - A_c} = \frac{kTK^2}{m(A - \omega_1)^2} \quad (18)$$

which is just the derivative $-(d\Pi/dA)$ calculated from Volmer's equation (eq 1) without factor \mathcal{R}^2 . On the contrary, for $k^* \rightarrow \infty$, one obtains $\Delta\Pi \rightarrow 0$, and therefore, the dynamic pressure of the compressible monolayer is equal to the equilibrium pressure.

Experimental

The amino acid derived amphiphile N-palmitoyl-D-allothreonine methylester used was synthesized by condensation of D-threonine methylester and palmitoyl chloride in chloroform and aqueous potassium carbonate according to ref 28. The reaction product was purified by repeated crystallization in methanol. The chemical and chiral purity (99%) was checked by elemental analysis and HPLC. The spreading solvent was a 9:1 heptane (for spectroscopy, Merck)–ethanol (p.a., Merck) mixture. The water used was made ultrapure by a Millipore desktop system.

The surface pressure was measured using a computer-interfaced film balance equipped with a Wilhelmy balance for surface pressure determination and a temperature control system. The dynamic Π – A experiments were performed for different compression rates of the monolayer (0.01, 0.025, 0.05, 0.1, 1, and 2 nm² molecule^{−1} min^{−1}) at 5 °C and for different temperatures (3.5, 5, 10, 15, and 20 °C) at constant compression or expansion rate (1 nm² molecule^{−1} min^{−1}).

Results and Discussion

Figure 1 shows the experimental Π – A relationship measured for the compression of palmitoyl-D-allothreonine methylester monolayers at different dA/dt values at 5 °C. The curve obtained for the expansion of the monolayer at this temperature and the initial compression rate $dA/dt = 0.017$ nm²/s is also presented. The curve describing the slow expansion of the monolayer corresponds to the equilibrium state. It is seen that all compression curves are located above the expansion curve, and the higher the monolayer compression rate, the larger the dynamic surface pressure jump is. At each Π versus A curve, two extrema are present.

The effect of the temperature on the shape of the Π – A curves for a constant compression rate $dA/dt = 0.017$ nm²/s is illustrated in Figure 2. The Π – A curves for the expansion of the monolayer at different temperatures are shown in Figure 3; here the theoretical isotherms calculated from eq 2 are also shown. The parameters of the equation of state for the palmitoyl-D-allothreonine methylester monolayer at various temperatures are summarized in Table 1.

To illustrate the proposed theoretical model, the compression and expansion Π – A curves for the constant compression and expansion rate of $dA/dt = 0.017$ nm²/s and 5 °C are used. In Figure 4, in addition to this pair of curves, the curves calculated from Volmer's equation (eq 1) for extremely oversaturated monolayers in the gaseous state and the equilibrium curves for the formation of dimers, trimers, pentamers, and decamers are shown. Note that to extend eq 1 to the transcritical range of areas per molecule, a correction of the ω_1 value was made by introducing the factor $[1 + \epsilon((A/A_{c\Pi})^2 - 1)]$, cf. eq 2. It is seen that the formation of oligomers results in the decrease of the excess surface pressure of the monolayer. Here, the existence of the first maximum can be qualitatively explained by the fact that the aggregation rate is relatively slow and that the increase of the number of the monomers in the aggregate takes place.

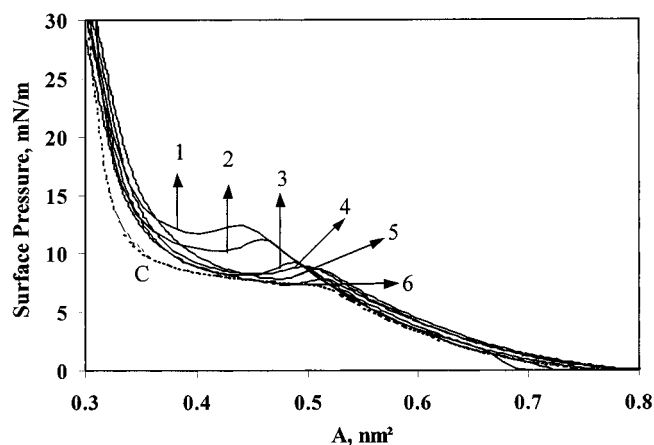


Figure 1. Dynamic surface tension for the compressed monolayers of palmitoyl-D-allothreonine methylester at 5 °C and $dA/dt = 0.033$ nm²/s (curve 1), 0.017 nm²/s (curve 2), 0.0017 nm²/s (curve 3), 0.000 83 nm²/s (curve 4), 0.000 42 nm²/s (curve 5), and 0.000 17 nm²/s (curve 6). The dashed line corresponds to the slow expansion of the condensed monolayer at the initial compression rate $dA/dt = 0.017$ nm²/s.

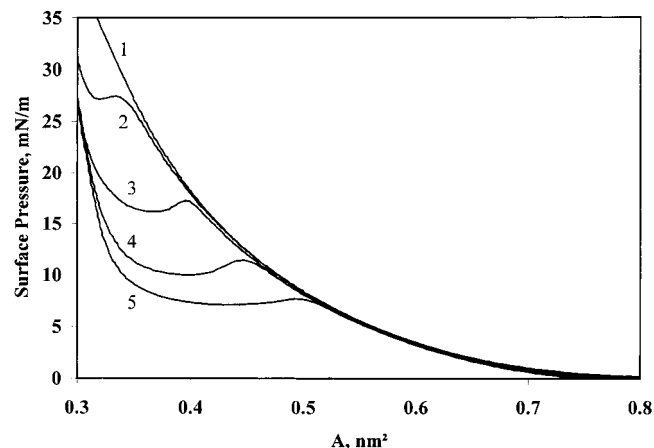


Figure 2. Dynamic surface tension for the compressed monolayers of palmitoyl-D-allothreonine methylester for $dA/dt = 0.017$ nm²/s at temperatures of 20 °C (curve 1), 15 °C (curve 2), 10 °C (curve 3), 5 °C (curve 4), and 3.5 °C (curve 5).

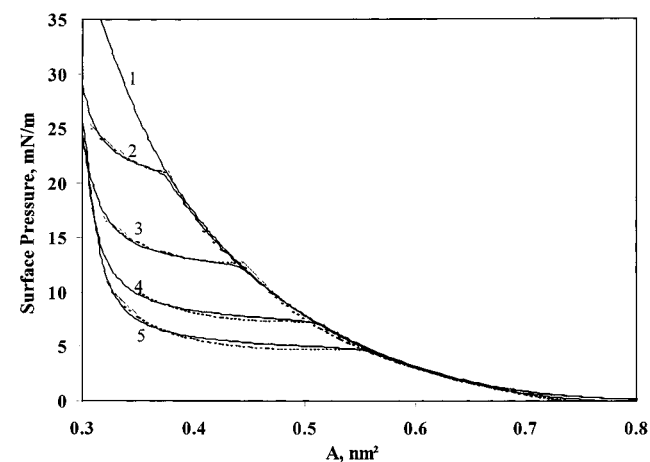
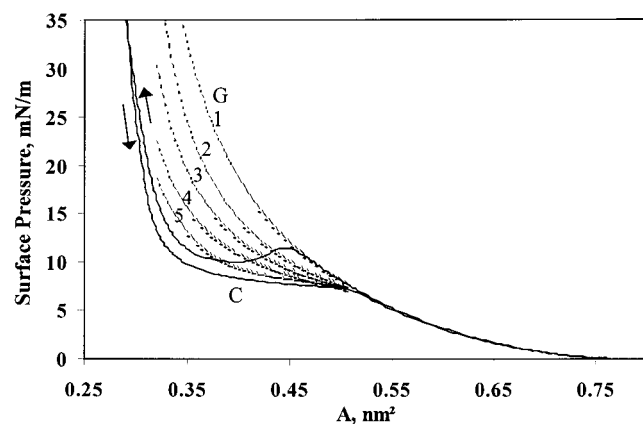
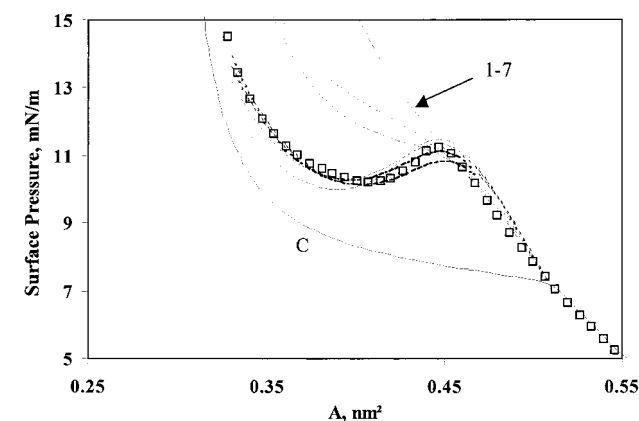


Figure 3. Experimental Π – A isotherms (solid lines) for expansion of palmitoyl-D-allothreonine methylester monolayers at 20 °C (curve 1), 15 °C (curve 2), 10 °C (curve 3), 5 °C (curve 4), and 3.5 °C (curve 5). The theoretical curves (dotted lines) are calculated from eq 2; the values of parameters are listed in Table 1.

The effect of the λ and δ parameters of eq 16 on the shape of the palmitoyl-D-allothreonine methylester monolayer theoretical compression isotherm at $dA/dt = 0.017$ nm²/s and 5 °C is

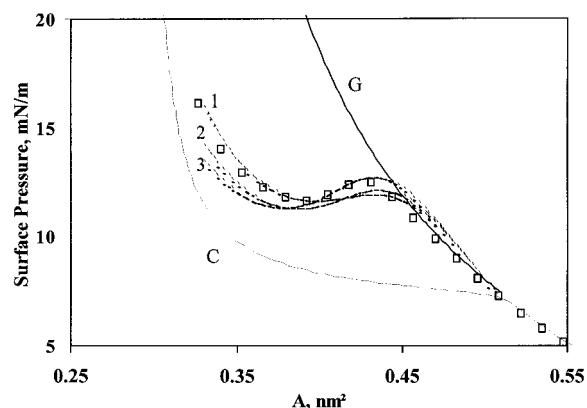
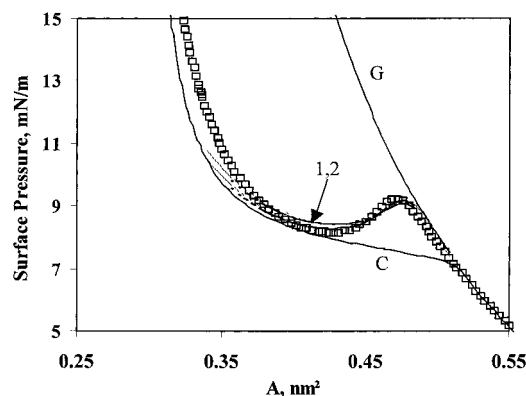
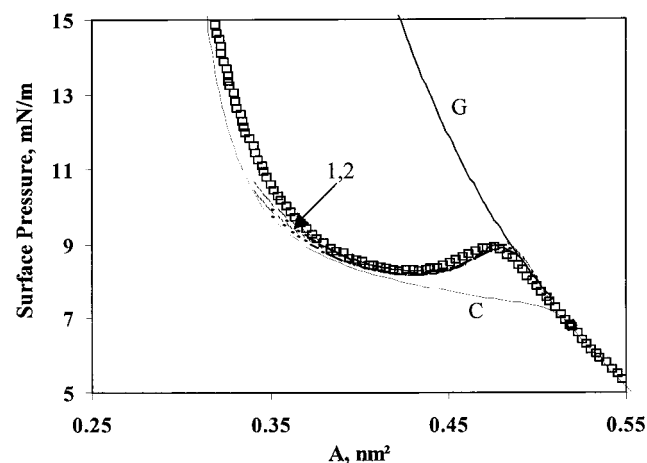
TABLE 1: Values of the Equilibrium Parameters of eq 2 for Palmitoyl-D-allotheonin Methylster Monolayers

temperature, °C	A_c , nm ²	ω , nm ²	Π_{coh} , mN/m	ϵ	m
3.5	0.554	0.29	6.74	0.11	1.25
5	0.51	0.29	7.1	0.14	1.21
10	0.445	0.29	6.29	0.17	1.34
15	0.376	0.28	1.0	0.18	1.90

**Figure 4.** Π - A curves of palmitoyl-D-allotheonin methylster monolayer compression and expansion (C) at 5 °C for $dA/dt = 0.017$ nm²/s (solid lines). The theoretical curves (dashed lines) were calculated from Volmer's equation for monomers (curve 1, G) and for the formation of dimers (curve 2), trimers (curve 3), pentamers (curve 4), and decamers (curve 5).**Figure 5.** Π - A curves for the compression (□) and expansion (C) palmitoyl-D-allotheonin methylster monolayers at 5 °C for $dA/dt = 0.017$ nm²/s. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 0$ (curve 1), $\lambda = 5$ and $\delta = 0$ (curve 2), $\lambda = 1$ and $\delta = 1$ (curve 3), $\lambda = 1$ and $\delta = 2$ (curve 4), $\lambda = 2$ and $\delta = 2$ (curve 5), $\lambda = 3$ and $\delta = 2$ (curve 6), and $\lambda = 5$ and $\delta = 2$ (curve 7).

illustrated in Figure 5. It is seen that for $\delta = 0$ (no dependence of the nucleation-growth rate on time) and for $\delta = 1$ (linear dependence of the nucleation-growth rate on time), the calculated curves do not agree with the experimental curve. Agreement is observed only for $\delta = 2$ at variation of the parameter λ (which accounts for the mechanism of monomer aggregation) in the range of 1 (attachment of monomers to clusters) to 5 (pentamer formation from monomers). It is obvious that λ has only a minor effect on the theoretical dependence of the surface pressure Π_d on A . However, Figure 5 shows clearly that the best agreement with the experiment is observed for $\lambda = 1$ or $\lambda = 2$.

The conclusion that the attachment of monomers to clusters ($\lambda = 0$) is the preferential process follows also from Figures 6–8, wherein the theoretical and experimental dependencies of

**Figure 6.** Π - A curves for the compression (□) and expansion (C) of palmitoyl-D-allotheonin methylster monolayers at 5 °C for $dA/dt = 0.033$ nm²/s. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 2$ (curve 1), $\lambda = 3$ and $\delta = 2$ (curve 2), and $\lambda = 5$ and $\delta = 2$ (curve 3). Curve G was calculated from Volmer's equation (eq 1) in the range $A < A_c$.**Figure 7.** Π - A curves for the compression (□) and expansion (C) of palmitoyl-D-allotheonin methylster monolayers at 5 °C for $dA/dt = 0.0017$ nm²/s. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 2$ (curve 1) and $\lambda = 5$ and $\delta = 2$ (curve 2).**Figure 8.** Π - A curves for the compression (□) and expansion (C) of palmitoyl-D-allotheonin methylster monolayers at 5 °C for $dA/dt = 0.00083$ nm²/s. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 2$ (curve 1) and $\lambda = 5$ and $\delta = 2$ (curve 2).

Π_d on A are shown for various dA/dt at 5 °C. The theoretical curves shown in Figures 6–8 are calculated for $\delta = 2$ and λ values of 1–5.

Perfect correspondence between theory and experiment for $\delta = 2$ and $\lambda = 1$ is also observed at other temperatures. This

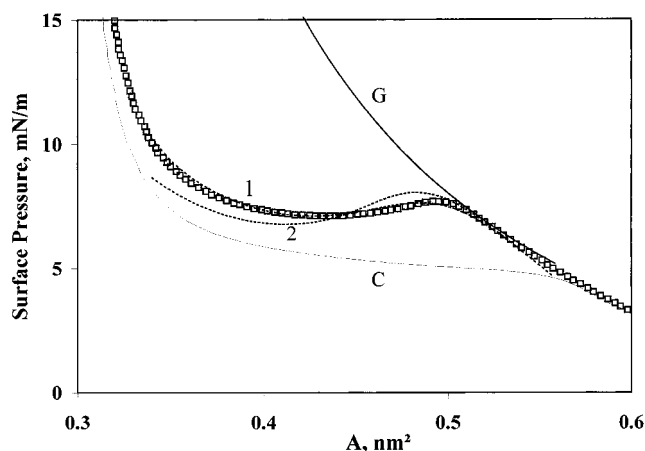


Figure 9. Π - A curves for the compression (\square) and expansion (C) of palmitoyl-D-allotheonin methylester monolayers at 3.5 °C for $dA/dt = 0.017 \text{ nm}^2/\text{s}$. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 2$ (curve 1) and $\lambda = 5$ and $\delta = 2$ (curve 2).

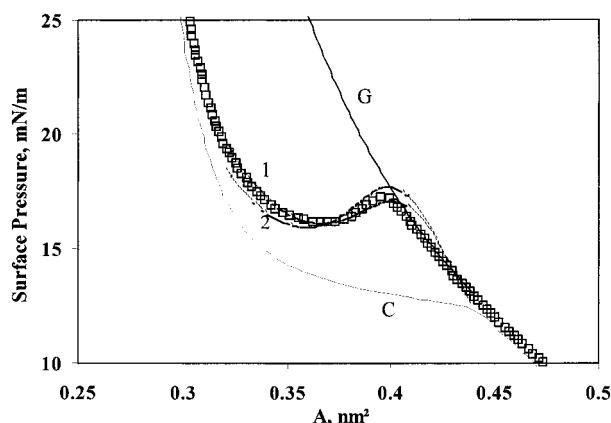


Figure 10. Π - A curves for the compression (\square) and expansion (C) of palmitoyl-D-allotheonin methylester monolayers at 10 °C for $dA/dt = 0.017 \text{ nm}^2/\text{s}$. The theoretical curves (dashed lines) are calculated from eqs 16 and 17 for $\lambda = 1$ and $\delta = 2$ (curve 1) and $\lambda = 5$ and $\delta = 2$ (curve 2).

can be seen in Figures 9 and 10, which show the dependency of Π_d on A for the compression rate $dA/dt = 0.017 \text{ nm}^2/\text{s}$ at 3.5 °C and 10 °C.

The values of the kinetic constant k^* obtained from the best fit of the curves by using eq 16 with $\delta = 2$ and $\lambda = 1$ for various compression rates and temperatures, were analyzed. It was found that the k^* value strongly depends on dA/dt : $k^* = 0.1 \text{ s}^{-3}$ for 5 °C and the maximum compression rate $dA/dt = 0.033 \text{ nm}^2/\text{s}$ available in our experiments, while for the minimum compression rate $dA/dt = 0.00017 \text{ nm}^2/\text{s}$, the optimum value was $k^* = 2 \times 10^{-6} \text{ s}^{-3}$. It is seen that the decrease of k^* is roughly quadratical in dA/dt . The influence of the $\frac{dA}{dt}$ on the kinetic constant can be eliminated, noting that $t = (A_c - A)/(dA/dt)$, see eq 16. Making this substitution, it follows that

$$k_1 = k^* t^2 = k^* \frac{(A_c - A)^2}{(dA/dt)^2} = k^0 (A_c - A)^2 \quad (19)$$

where $k^0 = k^*/(dA/dt)^2$. It is seen that, for the t^2 dependence of the nucleation-growth rate the constant k_1 could be expressed via the squared value of the area occupied by the large aggregates in the monolayer. Making this substitution for the kinetic constant in eq 16, and assuming $\lambda = 1$ and $\tau = 0$, one

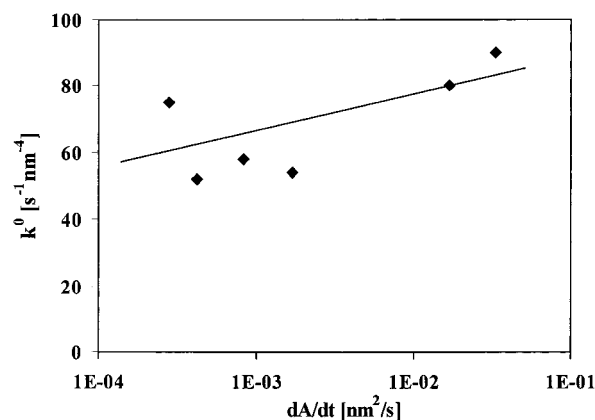


Figure 11. Dependence of the k^0 parameter of eq 20 on the compression rate of palmitoyl-D-allotheonin methylester monolayers at 5 °C.

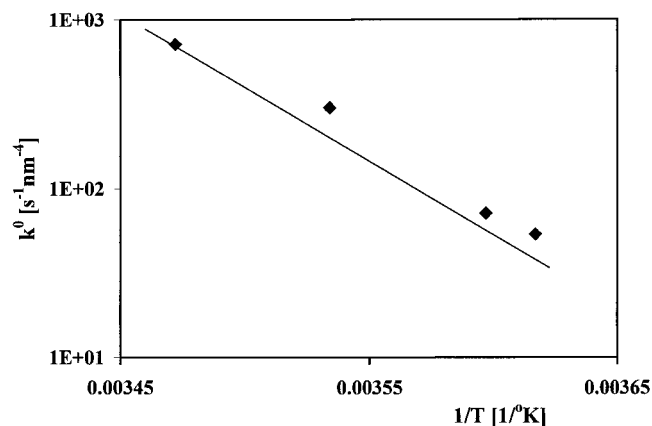


Figure 12. Dependence of the k^0 parameter (in eq 20) of palmitoyl-D-allotheonin methylester monolayers on $1/T$.

obtains

$$\Delta \Pi = \frac{kT \frac{dA}{dt} K^2}{m \{A - \omega_1 [1 + \epsilon(K - 1)]\}^2 k^0 (A_c - A)^2} \left[1 - \exp \left(- \frac{k^0 (A_c - A)^3}{\frac{dA}{dt}} \right) \right] \quad (20)$$

The dependence of k^0 on dA/dt at 5 °C is shown in Figure 11. In contrast to k^* , the k^0 parameter can be regarded as condensation rate constant of the Langmuir monolayer. It is interesting to note that the variation of this value does not exceed 30% throughout the dA/dt range extending over more than 2 decimal orders of magnitude, namely, from 0.00017 nm^2/s to 0.033 nm^2/s . It can be assumed that $k^0 = 70 \pm 20 \text{ s}^{-1} \text{ nm}^{-4}$ at 5 °C, independent of dA/dt .

The temperature increase from 3.5 °C to 15 °C results in an approximately 10 times increase of k^0 . According to the theory developed by Eyring,²⁹ the enthalpy of the formation of activated complex (in our case, the aggregate which possesses nonoptimal structure) can be estimated from this temperature dependence.

$$\frac{d \ln k^0}{d(1/T)} = - \frac{\Delta H^* + RT}{R} \quad (21)$$

Figure 12 illustrates the dependence of k^0 on T in the coordinates of eq 21, where the k^0 values were obtained for a compression

rate of 0.017 nm²/s and temperatures 3.5°, 5, 10, and 15 °C. The plot of $\ln k^0$ versus $1/T$ is represented by a straight line, in perfect agreement with eq 21. From the slope of the line the value $\Delta H^* = 160$ kJ/mol was calculated. This value is approximately equal to the energy required for the detachment of a hexadecanol monomer from an oligomer (aggregate).²⁴

Conclusions

A theoretical model is proposed for the kinetics of two-dimensional condensation of Langmuir monolayers at air/water interface. On the basis of the analysis of low deviations of the system from equilibrium, expressions were derived for the dynamic jump of surface concentration of monomers and for the dynamic jump of the surface pressure of compressible monolayers. In the last case, the equation of state obtained recently for Langmuir monolayers under equilibrium conditions was used. The theoretical kinetic model accounts for various mechanisms of the monomer aggregation (dimerization, trimerisation, etc.) and different dependencies of the nucleation-growth rate on t .

Experimental Π_d -A curves of palmitoyl-D-allotheonin methylester monolayers recorded at different compression rates and temperatures were used to verify the theoretical model. Good agreement between theory and experiment has been found; in particular, both the theoretical calculations and the experimental data show that two extrema exist for the Π_d versus A dependencies. It was shown in the experiments, quite expected for two-dimensional nucleation and growth, that the rate constant depends quadratically on time. Of all the reactions theoretically possible in monolayers, the most preferred reaction is the attachment of molecules to large aggregates. The fact that the reduced rate constant k^0 remains independent of the compression rate in a very wide range is also indicative of the consistency of the proposed model. The dependencies of k^0 on temperature were used to calculate the activation enthalpies of the aggregation process in the palmitoyl-D-allotheonin methylester monolayers.

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