

Equations of State for Langmuir Monolayers with Two-Dimensional Phase Transitions

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A generalized Volmer's equation is derived for a multicomponent Langmuir monolayer. This general equation is then used to derive the equations of state for the monolayer of a single amphiphile considering the two-dimensional (2D) main phase transition. A theory developed recently (*J. Phys. Chem.* **1996**, *100*, 15478) is extended to incorporate the important case that the area per one amphiphile molecule within the aggregate differs from that characteristic for the nonaggregated amphiphile. The general equation derived involves four parameters, two of which refer to the state of the gaseous monolayer whereas the other two parameters express the 2D aggregation constant and the difference between the area per one amphiphile molecule within the aggregate and the area per one nonaggregated molecule. The experimental Π - A isotherms for Langmuir monolayers of various amphiphiles, either measured by the authors or referred to elsewhere, agree well with the proposed model for physically reliable values of model parameters.

Introduction

Amphiphilic monolayers are representative of two-dimensional (2D) model systems. In recent years, most researchers have focused on phase transitions and ordering in two dimensions. General conclusions on the phase behavior of amphiphilic monolayers can be drawn by considering the surface pressure–area (Π - A) isotherms at different temperatures. The main feature of the Π - A isotherm is a nonhorizontal “plateau” region which is attributed to the main phase transition from a low-density fluid state to a condensed state.^{1–8} Consequently the main phase transition in Langmuir monolayers is indicated by a discontinuity in the Π - A isotherms at the main phase-transition point and behind it, a weak slope of the isotherm within the two-dimensional phase coexistence region. The main phase-transition point at which the phase transition region commences is shifted to higher surface pressures and lower area values with increasing temperature. The factors which cause the nonhorizontal behavior of Π - A isotherms within the 2D transition region have been discussed,^{9–18} and equations of state for Langmuir monolayers characterized by such a nonhorizontal shape have been proposed.^{12–17} In a recent paper,¹⁶ we proposed a model based on Volmer's equation of state¹⁹ valid for a 2D real gaseous phase and on a quasichemical approximation (mass action law) for describing the aggregation. With the introduction of the aggregation equilibrium constant as an extra parameter, Volmer's equation of state has been generalized and extended to the 2D phase-transition region. The equation of state thus derived agrees reasonably well with the experimental dependencies for actual values of the aggregation number (10^6 and higher).

However, the Volmer's equation generalization procedure used in ref 16, where all of the kinetic entities (monomers and aggregates) were taken into account, cannot be regarded as

sufficiently rigorous and complete. In the present study, two main objectives are pursued, namely, the rigorous thermodynamic derivation of the equation of state valid for Langmuir monolayers formed by amphiphile molecules subject to 2D aggregation and the compliance with the important case in which the molar area of molecules within the aggregate can differ from that characteristic for free monomers. This new theoretical model will be confronted with our experimental studies and the results reported in other papers.

Theory

The dependence of the chemical potential of components within a surface layer μ_i^s on the composition of the surface layer and its surface tension γ is given by the well-known Buttlar's equation²⁰

$$\mu_i^s = \mu_i^{0s} + RT \ln f_i^s x_i^s - \gamma \omega_i \quad (1)$$

where $\mu_i^{0s} = \mu_i^{0s}(T, P)$ is the standard chemical potential dependent on temperature T and pressure P , R the gas-law constant, f_i the activity coefficient, ω_i the partial molar area, and x_i the molar fraction. Here the superscript s refers to the surface (interface). Equation 1 can either be used to describe the surface layer which possesses finite thickness or be applied to the excessive quantities, i.e., the values characteristic for Gibbs' dividing surface.

Consider the surface layer which comprises, in addition to the solvent (denoted by subscript $i = 0$), other components or various states of a component ($i \geq 1$). The adsorption Gibbs' equation for this system is

$$d\Pi = \sum_{i=1}^n \Gamma_i d\mu_i \quad (2)$$

where Γ_i is the adsorption amount for the component or the state, $\Pi = \gamma_0 - \gamma$ is the surface pressure, and γ_0 and γ are the surface tensions of solvent and solution, respectively. The

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superscript at μ is omitted in eq 2 because this value for the case of soluble components can refer both to the bulk and to the surface layer (because equilibrium exists) and for the case of insoluble components to the surface layer only. It is seen from eq 2 that Gibbs' dividing surface is used here for which $\Gamma_{i=0} = 0$.

For the case of a single insoluble surfactant present within the monolayer, it follows from Buttler's equation (1) that

$$d\mu^s = RT d(\ln f^s + \ln x^s) - \omega d\gamma \quad (3)$$

Introducing this expression into Gibbs' equation (2) and taking into account the dependence of f^s on $x^s = \Gamma\omega$ given by the expression²¹⁻²³

$$\ln f^s = a(1 - \Gamma\omega)^2 \quad (4)$$

where a is the intermolecular interaction constant, one obtains

$$\frac{d\Pi}{d\Gamma} = \frac{RT}{1 - \Gamma\omega} - 2aRT\Gamma\omega \quad (5)$$

The approximate integration of eq 5 (with the expression $1/(1 - \Gamma\omega)$ being taken out of the integral sign) yields van der Waals' equation of state for a 2D nonideal gas

$$\Pi = \frac{RT}{A - \omega} - \frac{aRT\omega}{A^2} \quad (6)$$

where $A = 1/\Gamma$ is the area per mole in the monolayer. Note that the rigorous integration of eq 5 leads to Frumkin's equation of state²⁴

$$\Pi = -\frac{RT}{\omega} [\ln(1 - \Gamma\omega) + a(\Gamma\omega)^2] \quad (7)$$

Assuming $f^s = \text{const}$, one can obtain from eqs 2 and 3 Volmer's equation¹⁹

$$\Pi = -\frac{RT}{A - \omega} - B \quad (8)$$

where $B = \text{const} = \Pi^*$ and Π^* is the cohesion pressure. For a monolayer formed by i different insoluble components, provided that $f_i^s = \text{const}$, it follows from Gibbs' and Buttler's equations, eqs 2 and 1, respectively, that

$$d\Pi = RT \frac{d\sum_i \Gamma_i}{1 - \sum_i \Gamma_i \omega_i} \quad (9)$$

The approximate solution of eq 9 leads to the generalized Volmer's equation

$$\Pi = RT \frac{\sum_i \Gamma_i}{1 - \sum_i \Gamma_i \omega_i} - B_\Sigma \quad (10)$$

where $B_\Sigma = \text{const}$. The equation of state in eq 10 can next be transformed to the form capable of describing Langmuir monolayers of aggregating surfactant molecules. Two-dimensional aggregation in such monolayers results in the formation of aggregates which possess extremely high aggregation numbers ($n \geq 10^6$). In these cases, the two-phase coexistence region

is represented by a nonhorizontal line which describes the Π dependence on A ; see refs 1-8. For the case of one insoluble amphiphilic substance capable of 2D aggregation with formation of monodispersed n -mers, one can apply the relation

$$\Gamma_n = \Gamma_1 (\Gamma_1 / \Gamma_c)^{n-1} \quad (11)$$

which was obtained recently^{16,25} from the analysis of the equilibrium between the monomer and aggregate ($\mu_n^s = n\mu_1^s$).²⁶ Here Γ_1 and Γ_n are the values of the adsorption for monomers and aggregates, respectively, and Γ_c is the critical adsorption value for the two-dimensional aggregation. Assuming $\omega_n = n\omega_1$, one can transform eq 10 into

$$\Pi = RT \frac{\Gamma_1 [1 + (\Gamma_1 / \Gamma_c)^{n-1}]}{1 - \Gamma_1 \omega_1 [1 + n(\Gamma_1 / \Gamma_c)^{n-1}]} - B_\Sigma \quad (12)$$

The unknown value of the adsorption of monomers in eq 12 should be expressed via the observable value of area per 1 mol (or molecule) in the insoluble monolayer. The total adsorption expressed in terms of kinetic entities is $\Gamma_\Sigma = \Gamma_1 + \Gamma_n$. On the other hand, the measured value of the adsorption, i.e., the total adsorption recalculated in terms of monomers, is $\Gamma_\Sigma^* = \Gamma_1 + n\Gamma_n$. Therefore, using eq 11 one can represent the values of the total adsorption as

$$\Gamma_\Sigma = \Gamma_1 + \Gamma_n = \Gamma_1 + \Gamma_1 (\Gamma_1 / \Gamma_c)^{n-1} \quad (13)$$

$$\Gamma_\Sigma^* = \Gamma_1 + n\Gamma_n = \Gamma_1 + n\Gamma_1 (\Gamma_1 / \Gamma_c)^{n-1} \quad (14)$$

The introduction next of the physically observable value of the total area occupied by 1 mol of monomers in the surface layer gives

$$A = 1/\Gamma_\Sigma^* = 1/(\Gamma_1 + n\Gamma_n) \quad (15)$$

Equation 12 can be transformed into the form

$$\Pi = RTA \frac{\Gamma_1 [1 + (\Gamma_1 / \Gamma_c)^{n-1}]}{A - \omega_1} - B_\Sigma \quad (16)$$

After this, the introduction of the corresponding values of area per 1 mol of amphiphilic molecules in the monolayer, $A_1 = 1/\Gamma_1$ and $A_c = 1/\Gamma_c$, means that eq 16 can be transformed into the form

$$\Pi = RT \frac{(A/A_1) [1 + (A_c/A_1)^{n-1}]}{A - \omega_1} - B_\Sigma \quad (17)$$

Through the recognition of the equilibrium between monomers and aggregates at large values of the aggregation number, which is characteristic for insoluble monolayers of amphiphilic molecules ($n > 10^3$), one obtains from eq 11 simple relations which express the adsorption of monomers and the surface area per 1 mol of amphiphilic molecules within the monolayer¹⁶

$$\Gamma_1 \cong \Gamma_c \quad \text{or} \quad A_1 \cong A_c \quad (18)$$

$$1 + (\Gamma_1 / \Gamma_c)^{n-1} \cong 1 \quad \text{or} \quad 1 + (A_c / A_1)^{n-1} \cong 1 \quad (19)$$

Then, the equation of state in eq 17 is simplified to

$$\Pi = \frac{RT(A/A_c)}{A - \omega_1} - B_\Sigma \quad (20)$$

which coincides with that derived in ref 16. In eq 20, the value $A = 1/(\Gamma_1 + n\Gamma_n)$ is just the molar area of the amphiphilic molecules within the monolayer defined from the Π - A experiment. This equation describes the fluidlike state of the monolayer at $A > A_c$ where small 2D aggregates can also occur. In the case of the ideal gaseous state, one has to set the A_c/A ratio entering this equation to unity. Strictly speaking, eq 11 and the limiting relations in eqs 18 and 19 which follow from this equation are valid for the dilute monolayer when the surface concentration of the aggregates is relatively low ($\Gamma_1 \gg n\Gamma_n$).

For the concentrated monolayer, the requirement that the surface concentration (adsorption) of monomers should be constant, eq 18, has to be modified to account for the portion of the surface occupied by the aggregates at $A < A_c$. This means that the value of the adsorption of monomers at the monolayer surface free from the aggregates is to be equal to Γ_c . Through the use of the expressions for Γ_1 and $n\Gamma_n$ presented above, one can represent the ratio β of the area free from aggregates to the total area of the monolayer for $A < A_c$ as

$$\beta = 1 + \omega_1/A_c - \omega_1/A \quad (21)$$

It follows from eq 21 that $\beta \cong 1$ when either $A \cong A_c$ or both A and A_c are considerably larger than ω_1 . In these cases, the equation of state in eq 20 does not need to be corrected. For the values A_c within the range of $(1.0-2.0)\omega_1$, the most common for the 2D transition region, one can approximately express the β value in eq 21 as $\beta \cong A_c/A$. Therefore, for concentrated monolayers, the conditions in eq 18 become

$$\Gamma_1 \cong \Gamma_c \beta \cong \Gamma_c (A/A_c) \quad \text{or} \quad A_1 \cong A_c \beta \cong A_c (A_c/A) \quad (22)$$

It is seen that the adsorption of monomers decreases with the decrease in the monolayer area. This correction of the Γ_c value does not affect the limiting relations in eq 19. Through the use of eqs 19, 21, and 22, one obtains from eq 17

$$\Pi = \frac{RT(A/A_c)(1 + \omega_1/A_c - \omega_1/A)}{A - \omega_1} - B_\Sigma \cong \frac{RT(A/A_c)^2}{A - \omega_1} B_\Sigma \quad (23)$$

Consider next the possibility that the molecular area of the monomer within the aggregate can differ from ω_1 , that is

$$\omega_n = n\omega_1(1 - \epsilon) \quad (24)$$

where ϵ is the (positive or negative) value which is much less than unity. For this case, one obtains instead of eq 23 the relation

$$\Pi = \frac{RT(A/A_c)\beta}{A - \omega_1\{1 + \epsilon[(A/A_c)\beta - 1]\}} - B_\Sigma \quad (25)$$

where

$$\beta = 1 + \frac{\omega_1(1 - \epsilon)}{A_c} - \frac{\omega_1(1 - \epsilon)}{A} \quad (26)$$

As $A/A_c < 1$, then for $\epsilon > 0$ (tight packing of the monomers within the aggregate), the Π dependence on A is somewhat less sloping than that for the case $\epsilon = 0$. On the contrary, this dependence becomes more steep for loose aggregates, for which $\epsilon < 0$. For eq 26, similarly to eq 21, when A_c lies within the range of $(1.0-2.0)\omega_1$, the approximation $\beta \cong A_c/A$ is valid. Therefore one obtains the approximate relation

$$\Pi = \frac{RT(A/A_c)^2}{A - \omega_1[1 + \epsilon((A/A_c)^2 - 1)]} - B_\Sigma \quad (27)$$

This effect, which is the difference between the value of molar area per one monomer within the aggregates and that outside the aggregates, is in fact more complicated than it appears from eq 25 or 27. This effect influences the shape of the Π - A isotherm. From the Buttler's equation of eq 1 written for monomers and aggregates and the condition of the aggregation equilibrium $n\mu_1^s = \mu_n^s$, an important relation follows

$$\Gamma_n/\Gamma_1^n = K_n \exp(\Pi n \epsilon \omega_1/RT) \quad (28)$$

where $K_n = \exp\{[(n\mu_1^0 - \eta_n^0) - \gamma_{0n}\epsilon\omega_1]/RT\}$ is the constant of the aggregation equilibrium. This equation (28) is just the known adsorption relation proposed by Joos^{27,28} generalized onto the case of the aggregation within the insoluble monolayer. It follows from eq 28 that for $\epsilon \neq 0$ the variation of the monolayer pressure affects the distribution of the aggregates and monomers within the monolayer. Comparing eqs 11 and 28, one obtains

$$A_c^{n-1} = K_n \exp(\Pi n \epsilon \omega_1/RT) \quad (29)$$

Consequently the critical value of molar area which corresponds to the commencement of 2D aggregation, $A_c = 1/\Gamma_c$, is the constant (when recalculated in terms of the area free from aggregates) for the case $\epsilon = 0$ only. For more tight packing of monomers within the aggregates ($\epsilon > 0$), an increase of the surface pressure leads to an increase in both the portion of aggregates within the monolayer and the A_c value. On the contrary, for loose aggregates ($\epsilon < 0$), the increase in the surface pressure leads to the decrease of both values. For $n \gg 1$ and nonzero ϵ values, one can derive from eq 29 the approximate equation which gives the correction to the A_c value via the surface pressure

$$A_c(\Pi) = A_c \exp[(\Pi - \Pi_c)\epsilon\omega_1/RT] \quad (30)$$

where A_c is the value of surface area which corresponds to the commencement of phase transition, i.e., at $\Pi = \Pi_c$. It is seen that for $\Pi > \Pi_c$ and $\epsilon > 0$ an increase of $A_c(\Pi)$ takes place, which, according to eqs 25 and 26, results in a decrease of the surface pressure. Through the substitution of $A_c(\Pi)$ from eq 30 for A_c in eqs 25 and 26, one can derive a rigorous (while cumbersome) equation of state. Alternatively, from the approximate relation $\beta \cong A_c/A$ and eq 30, one obtains a more simple equation of state for the monolayer:

$$\Pi = \frac{RT(A/A_c)^2 \exp(-2\Delta\Pi\epsilon\omega_1/RT)}{A - \omega_1\{1 + \epsilon[(A/A_c)^2 \exp(-2\Delta\Pi\epsilon\omega_1/RT) - 1]\}} - B_\Sigma \quad (31)$$

where $\Delta\Pi = \Pi - \Pi_c$. For the values of A_c within the range of $(1.0 \div 2.0)\omega_1$, the error introduced by the approximate relation $\beta \cong A_c/A$ is on the order of a few percent only in comparison to the rigorous expression in eq 26. The dependence of Π on A from eq 31 for $\epsilon \neq 0$ can be calculated numerically, by successive approximations, starting from $\Delta\Pi = 0$. For the case $\epsilon = 0$, eq 31 simplifies into eq 23.

Results and Discussion

The general equation of state (25) and eqs 26, 30, and 31 depend on four parameters (B_Σ , A_c , ω_1 , and ϵ) and describe the

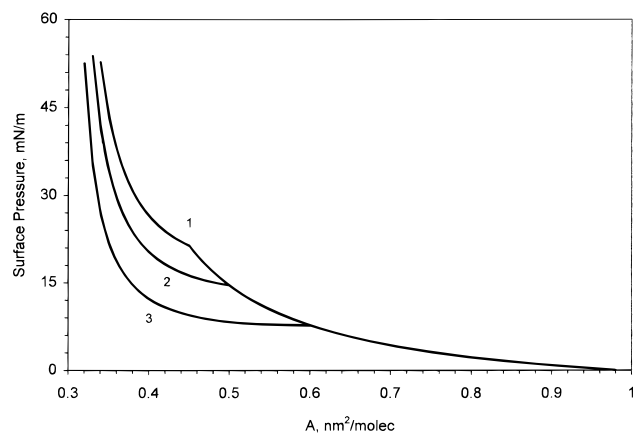


Figure 1. Theoretical Π -A isotherms calculated from eq 31 for $B_{\Sigma} = 6$ mN/m, $\omega_1 = 0.3$ nm², $\epsilon = 0$, and $A_c = 0.45$ nm² (curve 1), $A_c = 0.5$ nm² (curve 2), and $A_c = 0.6$ nm² (curve 3).

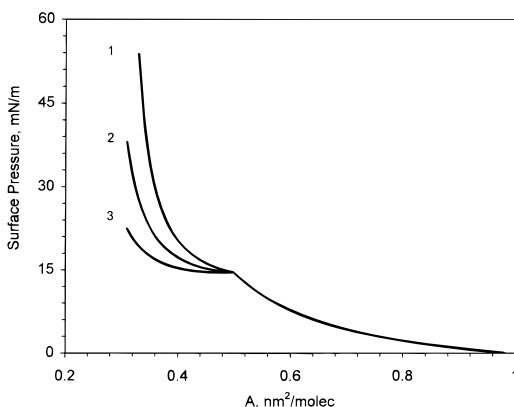


Figure 2. Theoretical Π -A isotherms calculated from eq 31 for $B_{\Sigma} = 6$ mN/m, $\omega_1 = 0.3$ nm², $A_c = 0.45$ nm², and $\epsilon = 0$ (curve 1), $\epsilon = 0.08$ (curve 2), and $\epsilon = 0.16$ (curve 3).

entire surface-pressure range from the gaseous monolayer to the condensed solid state. To describe the gaseous state of the monolayer, one has to set $A/A_c = 1$ and $\epsilon = 0$ in these equations. This results in the reduction of eqs 25 and 31 to Volmer's equation (8). It follows, therefore, that two of the four parameters, namely, B_{Σ} and ω_1 , refer to the gaseous monolayer. The A_c value is the coordinate of the inflection point of the Π -A isotherm where the phase transition commences. Thus, only the parameter ϵ refers explicitly to the 2D transition region and has an additional effect on the isotherm shape at $A < A_c$.

The Π -A isotherms calculated from the equation of state in eq 31 for various values of A_c and fixed values of ω_1 , B_{Σ} , and $\epsilon = 0$ are presented in Figure 1. It is seen that an increase of A_c results in a decrease of the isotherm slope in the 2D transition region. Figure 2 illustrates the effect of the difference between the molar area of aggregates and that of the free molecules for $\epsilon > 0$. The calculations show that the formation of tightly packed aggregates leads to a lower slope of the surface-pressure curve in the 2D phase-transition region, as compared with the case when the values of the molar areas outside and inside the aggregates are equal to each other.

The equation of state proposed above will be next compared with experimental data. The experimental Π -A isotherms of *rac*-1-(2-tetradecylhexadecanoyl)-2-hexadecylglycerophosphoethanolamine (THHGPEA) monolayers measured at various temperatures are shown in Figure 3 and Table 1. It is seen that the Π -A isotherms of this phospholipid having three long alkyl chains have a well-developed two-phase coexistence region in the low-density fluidlike phase and the condensed phase. The

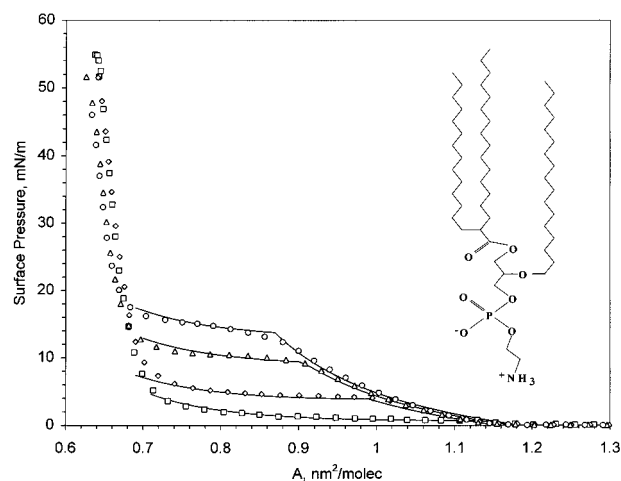


Figure 3. Π -A isotherms for *rac*-1-(2-tetradecyl hexadecanoyl)-2-hexadecylglycerophosphoethanolamine (THHGPEA) monolayers at 16 (squares), 20 (rhombus), 26 (triangles), and 30 °C (circles). The theoretical curves corresponding to various temperature values were calculated for the parameters of eq 31 shown in Table 1.

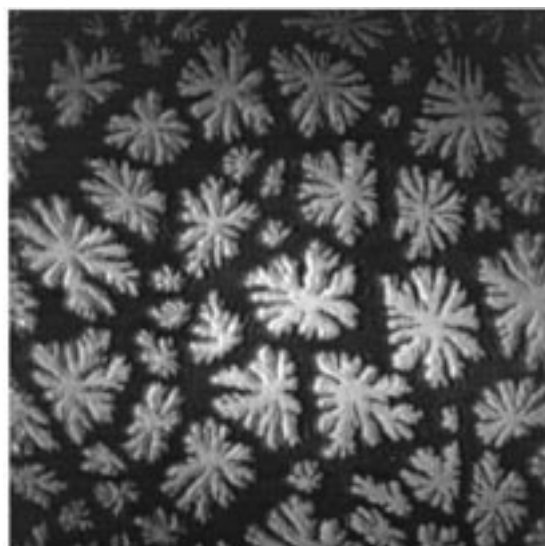


Figure 4. BAM micrographs of the condensed phase domains of THHGPEA monolayers obtained in the two-phase coexistence region of the Π -A isotherm at $T = 22$ °C.

TABLE 1

temperature, °C	ω_1 , nm ²	B_{Σ} , mN/m	A_c , nm ²	ϵ
16	0.65	7.6	1.13	0.12
20	0.65	8.0	0.99	0.15
26	0.67	8.2	0.91	0.17
30	0.68	8.3	0.88	0.18

corresponding Brewster angle microscopy image taken with BAM 2 (NFT, Göttingen, Germany) corroborates the two-phase coexistence between the dendritic condensed-phase domains and the surrounding low-density phase (Figure 4). The experimental setup and procedures were analogous to those used in our recent papers, and details are given elsewhere.² THHGPEA was prepared by Dr. F. Bringezu.²⁹

The theoretical isotherms calculated from eq 31 are in excellent agreement with the experimental data in both the region of the gaseous monolayer and the region where the monolayer undergoes the 2D phase transition. The parameters of the isotherms were calculated using a special fitting program which seeks the best correspondence between the theoretical and experimental curves. In the region of $A > A_c$, the

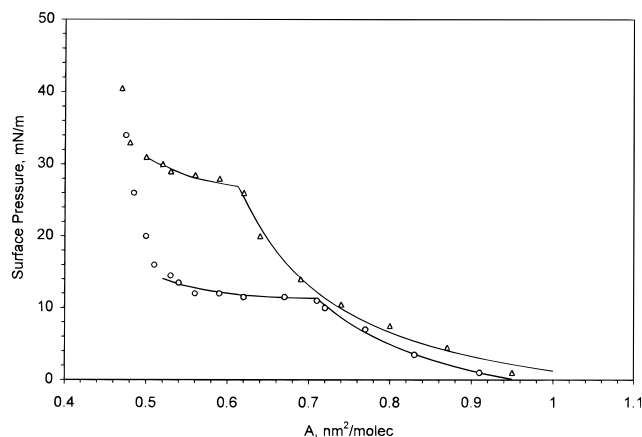


Figure 5. Π – A isotherm for 1,2-dipalmitoylphosphatidylcholine (data from ref 27) at 26 (circle) and 34 °C (triangle). The theoretical curves corresponding to various temperature values were calculated for the following parameters of eq 31 shown in Table 2.

TABLE 2

temperature, °C	ω_1 , nm ²	B_Σ , mN/m	A_c , nm ²	ϵ
26	0.51	9.3	0.715	0.22
34	0.50	7.1	0.615	0.21

optimization was performed with respect to the values of B_Σ and ω_1 , while the optimum value of ϵ was sought over the range of $A < A_c$. It is seen that in the region of the gaseous monolayer the increase of the temperature affects the isotherm parameters only slightly, resulting in a minor increase of the area per 1 mol (or molecule) of the nonaggregated THHGPEA, ω_1 , and a small decrease of the cohesion pressure, B_Σ . The critical aggregation area value decreases from 1.13 nm²/THHGPEA molecule at 16 °C to 0.87 nm²/THHGPEA molecule at 30 °C. According to eq 29, this means that the equilibrium constant characteristic of the aggregation process also decreases with increasing temperature. The theoretical model predicts that the aggregation of THHGPEA leads to the formation of tightly packed aggregates. The results obtained using the fitting program show that the area per one THHGPEA molecule within the aggregate is 12–18% (i.e., 0.08–0.12 nm²) lower than that within the gaseous monolayer. Both ϵ and ω_1 slightly increase with temperature. The calculations performed according to eq 24 have shown that the area per one THHGPEA molecule within the aggregate does not depend on the temperature and is equal to 0.58 nm², the value of which is only 0.04 nm² less than the area per one THHGPEA molecule in the point where the monolayer collapses; see Figure 3. This fact can be regarded as evidence supporting the reliability of the values obtained for model parameters from the fitting program and, therefore, adequate to the theoretical model developed.

The Π – A isotherms of 1,2-dipalmitoylphosphatidylcholine (DPPC) for two temperature values plotted using the data reported in ref 30 are shown in Figure 5 and Table 2. The theoretical curves are in good agreement with the experimental data. It is seen that the temperature dependencies of all parameters except A_c are weak. The Π – A isotherms of other phospholipids, presented in ref 29, can also be reproduced well by the equation of state in eq 31.

In our recent study,¹⁶ the approximate equation of state in eq 20 was used to obtain a rather satisfactory description of experimental Π – A isotherms for insoluble 1-monostearoyl-*rac*-glycerol (MSRG) and 1-monopalmitoyl-*rac*-glycerol (MPRG) in the 2D phase-transition region. This approximate equation involves neither the portion of the surface occupied by the

aggregates (parameter β) nor the difference of the molar areas (parameter ϵ); therefore, the value ω_1 in this equation served as the fitting parameter. This has resulted in the fact that for these amphiphiles the ω_1 values used for the calculations were essentially lower than the actual ones. In addition, these values sharply decrease with increasing temperature.¹⁶ The equation of state proposed in eq 31 satisfactorily describes the experimental Π – A isotherms of MSRG and MPRG throughout the entire temperature range studied ($12\text{ °C} \leq T \leq 45\text{ °C}$) for an almost constant value of $\omega_1 = 0.23\text{--}0.25\text{ nm}^2$ and small enough values of $\epsilon = 0.01\text{--}0.08$ with increasing values within these intervals corresponding to the increase in the temperature. The area per one monoglycerid molecule (0.23 nm²) calculated from eq 24, being virtually constant, coincides perfectly well with the area per one molecule at the collapse point for MSRG and MPRG monolayers.¹⁶ Therefore, all parameters in eq 31 seem also to be adequate for these monoglycerid monolayers.

Conclusions

A new equation of state valid for Langmuir monolayers has been derived by rigorous thermodynamic treatment. This new theoretical model considers the 2D aggregation of monolayer material and the compliance with the important case that the molar area of molecules within an aggregate can differ from that characteristic for free monomers. Buttlar's and Gibbs' equations were used to derive a generalized Volmer's equation of state for multicomponent insoluble monolayers. The particularization of the generalized Volmer's equation makes possible the derivation of the equation of state for the monolayers of a single surfactant capable of describing 2D phase transition. The general equation of state, which considers that the area per one surfactant molecule within the aggregate differs from that corresponding to the nonaggregated substance, involves four parameters, two of them referring to the state of the gaseous monolayer and the other two relating to the aggregation constant and the difference between the said areas per one molecule. The experimental Π – A isotherms, either measured by the authors or reported in other studies, exhibit good agreement with the proposed model for reliable values of the parameters.

Obviously, the theoretical approach based on the generalized Volmer's equation is not confined solely to the case of the single amphiphile considered here. This approach has the potential to be successfully used for deriving the equations of state for more complicated systems which are important from a practical point of view, for example, a mixture of insoluble (either aggregating or nonaggregating) surfactants or a mixture of soluble and insoluble surfactants (e.g., 2D aggregating phospholipids and proteins), etc. These problems will be dealt with in future work.

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