Equation of State for Monolayers under Consideration of the Two-dimensional Compressibility in the Condensed State

V. B. Fainerman[†] and D. Vollhardt*,[‡]

Medical Physicochemical Centre, Donetsk Medical University, 16 Ilych Avenue, Donetsk 83003, Ukraine, and Max-Planck-Institut für Kolloid und Grenzflächenforschung, Am Mühlenberg 1, 14424 Potsdam, Germany.

The equation of state for Langmuir monolayers proposed earlier (Fainerman, V. B.; Vollhardt, D. *J. Phys. Chem. B* **1999**, *103*, 145.) is generalized for the case that one, two or more phase transitions in the monolayer take place, provided that the two-dimensional compressibility undergoes a jump at the phase transition, whereas within any condensed phase of the monolayer this compressibility is proportional to the surface pressure. *N*-Tetradecyl-*β*-hydroxy-propionic acid amide (THPAA) monolayers undergo two phase transitions during the compression, demonstrated experimentally both by the cusps of the surface pressure−area (Π−A) isotherm and the results of grazing incidence X-ray diffraction (GIXD). The theoretical Π−A isotherm agrees satisfactorily with the experimental data if the THPAA molecular characteristics obtained from independent GIXD experiments are taken as model parameters.

Introduction

Under appropriate conditions, the surface pressure (Π) vs area per molecule (A) isotherms of Langmuir monolayers show a sharp inflection at the first-order phase transition point A_c from a fluid phase [gaseous (G) or liquid-expanded (LE)] to a condensed phase [liquid-condensed (LC)]. The slope of the isotherm in the following two-phase coexistence region ($A < A_c$) is much lower as that compared to the fluid state and it becomes more horizontal with the decrease of temperature and surface pressure. The A_c values corresponding to the onset of this main phase transition become lower with the increase of temperature. The theoretical models which describe the two-dimensional phase transition in the monolayer have been reviewed in ref 1. Simple models based on the generalized Volmer equation and the mass action law were found to agree satisfactorily with the experimental data.[2−5]

For some amphiphilic compounds, the existence of a second phase transition between the condensed phases can be concluded from another critical point in the Π−A isotherms. This phase transition between two condensed phases is accompanied by an abrupt change of the 2D-lattice parameters obtained by grazing incidence X-ray diffraction (GIXD).[6]

In the present work a first attempt is made to generalize the model proposed in ref 3 onto phase transitions for which the area per molecule in the condensed state exhibit either a linear decrease with increasing surface pressure or a sharp jump. It is shown that this model agrees satisfactorily with the experimental Π−A isotherms possessing two critical points. Moreover, the model parameters which characterize the lattice in the condensed state (the projected area of the amphiphilic molecule onto the horizontal plane and the compressibility coefficient) are found to coincide with those obtained from GIXD experiments.

Theory

Figure 1 illustrates the Π−A isotherm of the *N*-tetradecyl-*β*-hydroxy-propionic acid amide (THPAA) at 10°C, obtained
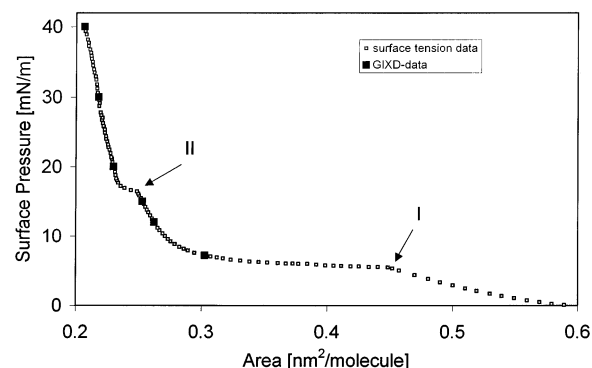
* Corresponding author.
† Medical Physicochemical Centre.
‡ Max-Planck-Institut für Kolloid und Grenzflächenforschung.

Figure 1. Experimental Π−A isotherm of the THPAA monolayer at $T = 10$ °C.[6] Dark points correspond to the values of pressure and area per molecule for which the GIXD experiments were performed.

in ref 6. The positions of two phase transitions on the isotherm are shown by arrows. The dark points correspond to the values of the surface pressure and area per molecule, for which the GIXD experiments were performed in ref 6. The values of the projected area of the THPAA molecule on the horizontal plane in the condensed state A_{xy} dependent on the surface pressure are shown in Figure 2. It is seen that in the surface pressure range between the two phase transitions shown in Figure 1 (5.5−16 mN/m), the area per molecule in the condensed state A_{xy} decreases linearly with the increase in the surface pressure. Above the second phase transition (16 mN/m and higher), the molecular area A_{xy} of the THPAA monolayer decreases also in the higher surface pressure range, but here the slope is approximately 4 times lower than that in the region of the first condensed phase. However, at the surface pressure value of 16 mN/m, which corresponds to the second inflection point of the Π−A isotherm in Figure 1, the area per THPAA molecule in the condensed state changes drastically. The arrow in Figure 2 shows the variation in the THPAA molecular area in second phase transition point. Therefore, the second phase transition in the monolayer is characterized by an abrupt change in the packing structure, such as the lattice parameters (intermolecular distances and angles).[6] As shown in ref 6 for the THPAA and

Letters

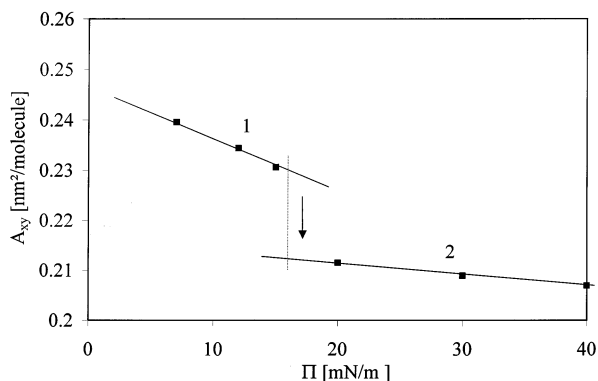*J. Phys. Chem. B, Vol. 107, No. 14, 2003* **3099**

Figure 2. Dependence of the THPAA molecule area in the condensed monolayer state on the surface pressure obtained from the GIXD data.[6] See detailed discussion in the text.

in refs 7−11 for a number of other amphiphiles, the polar tilt angle of the molecules varies monotonically within the range, where a definite condensed phase exists. This behavior is correlated with a two-dimensional compression of the monolayer.

The equation of state for monolayers in the fluid (G or LE) state is represented by Volmer's equation generalized either for dissociation ($m < 1$) or the formation of small aggregates ($m > 1$):[3,4]

$$\Pi = \frac{1}{m}\frac{kT}{A - \omega} - \Pi_{coh} \tag{1}$$

In the phase coexistence region ($A < A_c$) the generalized Volmer's equation leads to (see refs 3 an 4):

$$\Pi = \frac{1}{m}\frac{kT\alpha\beta}{A - \omega[1 + (\alpha\beta - 1)]} - \Pi_{coh} + \Delta\Pi_c, \tag{2}$$

In these equations, Π is the surface pressure, k is the Boltzmann constant, T is temperature, ω is the partial molecular area for monomers (or the limiting area of a molecule in the gaseous state), A is the area per molecule, A_c the molecular area which corresponds to the onset of the phase transition (i.e., at $\Pi = \Pi_c$), Π_{coh} is the cohesion pressure, which accounts for the intermolecular interaction, m is the aggregation number for small aggregates, α is a parameter expressing the dependence of the aggregation constant on the surface pressure, and β is the fraction of the monolayer free from aggregates. For the most simple model, which takes into account the fraction of the monolayer free from aggregates, it was shown in ref 3 that $\alpha = \beta$, and

$$\alpha = \frac{A}{A_c}\exp\left[-\epsilon\frac{\Pi}{kT}\omega\right] \tag{3}$$

where $\epsilon = 1 - \omega_{cl}/\omega$, and ω_{cl} is the area per one monomer in a cluster (or the projected area of the amphiphilic molecule onto the horizontal plane A_{xy}). Equation 3, which takes into account the dependence of the aggregation constant (or the critical concentration of monomers at the interface) on the surface pressure, was derived in ref 3 from Buttler's equation. For the sake of simplicity and to exclude the corrective parameter $\Delta\Pi_c$, the expression:

$$\alpha = \frac{A}{A_c}\exp\left[-\epsilon\frac{\Pi - \Pi_c}{kT}\omega\right] \tag{4}$$

TABLE 1: The Characteristics of the THPAA Monolayer

curve	1	2
ω, nm^2	0.247	0.247
A_c, nm^2	0.45	0.37
η, m/mN	0.004	0.001
ϵ_0	0.06	0.2
m	1.4	1.4
Π_{coh}	8.06	8.06

was used instead of eq 3. Determining α from the approximate eq 4 one obtains $\Delta\Pi_c = 0$, because in this case eqs 1 and 2 are identical to each other at $A = A_c$ for any parameter values. Alternatively, if eq 3 is used with $\epsilon \neq 0$, then the $\Delta\Pi_c$ value is nonzero, and can be determined from the condition that the surface pressure value calculated from eq 1 at $A = A_c$ should be equal to that calculated from eq 2 at the same point, i.e.,

$$\Delta\Pi_c = \frac{1}{mA_c - \omega}kT - \frac{1}{mA_c - \omega[1 + (\alpha_c\beta_c - 1)]}kT\alpha_c\beta_c \tag{5}$$

Note that the approximation $\alpha = \beta$ is acceptable only if $A_c \leq 2\omega$, otherwise the β parameter is defined as (see ref 3):

$$\beta = 1 + \omega(1 - \epsilon)(\alpha - 1)/A \tag{6}$$

The theoretical model used in ref 3 assumes that the area per molecule in the condensed state can be different from that in the gaseous state; this fact is accounted for by the parameter ϵ. It was suggested in ref 12 that the area of the molecule in the gaseous state ω is approximately equal to the area in the condensed state (in the cluster), extrapolated to the zero surface pressure, i.e., $\omega = \omega_{(cl,\Pi=0)}$. Therefore, the area per molecule at any Π value in the condensed monolayer can be expressed as

$$\omega_{cl} = \omega(1 - \epsilon) \tag{7}$$

This expression which determines the ratio between the molecular area in the condensed phase and that in the gaseous phase in eqs 3 and 4 is assumed to be valid for $\epsilon = $ constant. However, to reproduce the behavior shown in Figure 2, the ϵ value which describes the area variation, should consist of two terms:

$$\epsilon = \epsilon_0 + \eta\Pi \tag{8}$$

where ϵ_0 is the relative jump of the area per molecule and η is a relative two-dimensional compressibility. Thus, the model parameter ϵ involves the characteristics which could be determined from independent GIXD experiments.

Results and Discussion

It follows from the data obtained for the THPAA monolayer, see Figure 2, that $\omega = 0.247$ nm^2 (the intersection point of the straight line 1 with the ordinate axis), $\eta_1 = 0.004$ m/mN, $\eta_2 = 0.001$ m/mN (the slopes of the straight lines 1 and 2, respectively), and the variation of ϵ_0 at the pressure value of 16 mN/m (the jump between the lines 1 and 2) is $\Delta\epsilon_0 = 0.14$. The values of m and Π_{coh} which enter eqs 1 and 2 were calculated from the fitting of the isotherm branch at $A > A_c$ shown in Figure 1. The parameter values that describe the isotherm both in the gaseous monolayer region and in the phase coexistence region below the first inflection point are listed in the second column of Table 1, whereas the corresponding theoretical curve 1 is shown in Figure 3. To obtain the best fit between the theory and the experimental data, only one extra parameter was found to be relevant $\epsilon_0 = 0.06$, whereas the
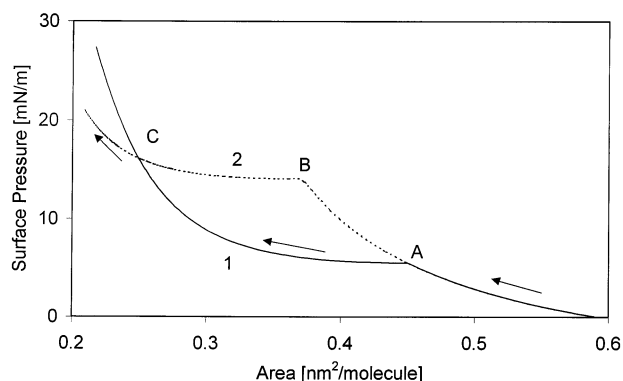
Figure 3. Theoretical $\Pi-A$ isotherms 1 and 2 for the THPAA monolayer, calculated from eqs 1–3 with the parameters listed in the table. See detailed discussion in the text.

Figure 4. Comparison between the experimental (points) and theoretical (line) $\Pi-A$ isotherms of the THPAA monolayer using the new theoretical model. I : first phase transition point. II: second phase transition point.

expected value of ϵ_0 is zero. This fact possibly reflects the approximate character of the theoretical model (especially, far from the inflection point), and the approximate choice of the ω value for the gaseous monolayer (taken to be equal to the area per molecule in the condensed state extrapolated to zero pressure). It should be noted, however, that the value $\epsilon_0 = 0.06$ corresponds to a quite low variation of the area per molecule (0.015 nm^2). Here also the experimental errors could be involved. Assuming $\omega = 0.23$ nm^2, one obtains $\epsilon_0 = 0$. For this case the theoretical curve cannot be distinguished from curve 1 shown in Figure 3.

To describe the second phase transition (see Figure 1), a value $\eta_2 = 0.001$ m/mN was assumed; the overall ϵ_0 value ($\epsilon_0 = 0.2$) was taken to be the sum of the ϵ_0 values corresponding to the first phase transition ($\epsilon_0 = 0.06$) and from the GIXD data for the second transition ($\Delta\epsilon_0 = 0.14$). The values of the model parameters which describe the second phase transition are listed in the third column of Table 1. The corresponding curve 2 is shown in Figure 3.

Next, the theoretical curves shown in Figure 3 should be analyzed. The behavior of any thermodynamic system is determined by the stability condition. The relevant criterion for spread or adsorbed monolayers is dΠ/d$A \leq 0$,[13] i.e., not only the surface pressure should decrease with area per molecule but also this dependence should possess a minimum slope to be thermodynamically stable. The thermodynamically stable course of the THPAA isotherm is shown by arrows in Figure 3. The arrow shown along the isotherm to the right of the A point corresponds to the fluid (LE) state of the monolayer. Of the two routes possible in point A, the system follows that along curve 1 across the phase coexistence region, i.e., the route characterized by lower slope of the isotherm. If the motion takes place in direction to point B, the system conserves an invariable number of components in the monolayer N, whereas at the motion in direction to point C the chemical potential of components in the monolayer μ is invariable. According to the theory [13] dΠ/d$A_N \leq$ dΠ/dA_μ, and consequently the system follows the lowest branch. Note that if the compression undergone by the monolayer is very rapid in comparison with the rates of nucleation and growth of a new two-dimensional phase, then thermodynamically unstable states can arise. In such cases the system, when reaching the A point, continues to proceed along curve 2 (the state of the monolayer oversaturated with monomers up to point B which arises due to the finite nucleation rate and growth of the nuclei). Then the system returns to curve 1. Examples of such dependencies for the palmitoyl-D-allo-threonin methylester monolayers were reported in ref 14. At point C, the system also begins to proceed along
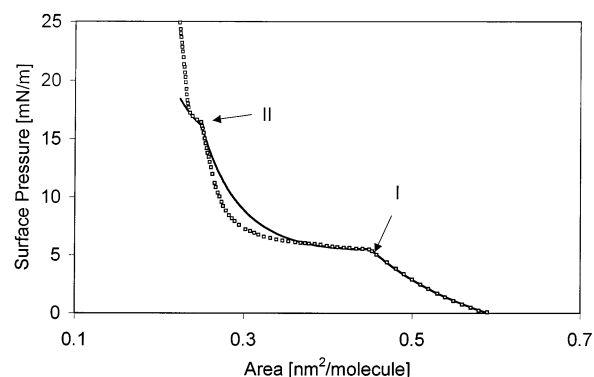
the branch corresponding to the condensed state of larger density ($\epsilon_0 = 0.2$), which possesses a lower slope. However, the route along the more steep line 1 can be also realized by instable monolayers during very rapid compression (monolayers oversaturated with the low-density condensed phase).

In Figure 4 the experimental THPAA isotherm shown in Figure 1 is compared with the theoretical isotherm corresponding to the thermodynamically stable curve discussed in Figure 3. The agreement between the theory and the experiment is seen to be quite satisfactory. It should be emphasized here that the theoretical model does not involve any arbitrary parameters (owing to the choice of $\epsilon_0 = 0.06$, as was noted above). All necessary model parameters are either calculated from the gaseous monolayer branch of the isotherm, or evaluated from the independent GIXD experiment.

To summarize, the model proposed in this publication, used in combination with the general stability principles, is capable to provide a satisfactory description of the $\Pi-A$ isotherms with two or more phase transitions in Langmuir monolayers.

References and Notes

(1) Vollhardt, D.; Fainerman, V. B. *Colloids Surf. A* **2001**, *176*, 117.
(2) Fainerman, V. B.; Vollhardt, D.; Melzer, V. *J. Chem. Phys.* **1997**, *107*, 243
(3) Fainerman, V. B.; Vollhardt, D. *J. Phys. Chem. B* **1999**, *103*, 145.
(4) Vollhardt, D.; Fainerman, V. B.; Siegel, S. *J. Phys. Chem. B* **2000**, *104*, 4115.
(5) Vollhardt, D.; Fainerman, V. B.; Emrich, G. *J. Phys. Chem. B* **2000**, *104*, 8536.
(6) Melzer, V.; Weidemann, G.; Vollhardt, D.; Brezesinski, G.; Wagner, R.; Struth, B.; Möhwald, H. *Supramol. Sci.* **1997**, *4*, 391.
(7) Gehlert, U.; Vollhardt, D.; Brezesinski, G.; Möhwald, H. *Langmuir* **1996**, *12*, 4892.
(8) Gehlert, U.; Weidemann, G.; Vollhardt, D.; Brezesinski, G.; Wagner, R.; Möhwald, H. *Langmuir* **1998**, *14*, 2112.
(9) Weidemann, G.; Brezesinski, G.; Vollhardt, D.; DeWolf, C.; Möhwald, H. *Langmuir* **1999**, *15*, 2901.
(10) Krasteva, N.; Vollhardt, D.; Brezesinski, G.; Möhwald, H. *Langmuir* **2001**, *17*, 1209.
(11) Gehlert, U.; Vollhardt, D. *Langmuir* **2002**, *18*, 688.
(12) Lyklema, J. *Fundamentals of Interface and Colloid Science, Volume 3: Liquid-Fluid Interfaces*; Academic Press: New York, 2000.
(13) Rusanov, A. I. *Fazovye Ravnovesija i Poverchnostnye Javlenija*; Khimija: Leningrad, 1967.
(14) Vollhardt, D.; Fainerman, V. B. *J. Phys. Chem. B* **2002**, *106*, 345.