

# Temperature Dependence of the Phase Transition in Branched Chain Phospholipid Monolayers at the Air/Water Interface

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A comparative analysis of theoretical models, which describes the displacement of the two-dimensional phase equilibrium in monolayers at the air/water interface, is performed. The thermodynamic characteristics for the first-order phase transition are calculated on the basis of various theoretical models. The calculations are performed for the experimental surface pressure–area ( $\Pi$ – $a$ ) isotherms of three branched chain phospholipids ( $n$ –16PEs) with different side chain length ( $n$ ) measured at different temperatures ( $T$ ). The phase transition pressure ( $\Pi_c$ ) depends linearly on the temperature. The models that account for the presence of the solvent lead to lower absolute enthalpy values for the two-dimensional phase transition at a given  $d\Pi_c/dT$  value. It seems impossible to prefer definitely either of the models, mainly because direct experimental values for the yield of aggregation heat in Langmuir monolayers are currently not available. Taking into account the monolayer compressibility, the effect of the molar area of the amphiphile ( $a_0$ ) in the condensed phase is studied. The variation of the  $a_0$  value for the surface pressures between monolayer collapse ( $0.53 \text{ nm}^2$ ) and zero pressure ( $0.62 \text{ nm}^2$ ) affects only slightly the theoretical predictions of the behavior of the isotherms and the estimated values of the thermodynamic characteristics for the phase transition. However, the low  $a_0$  value provides a slightly better description of the experimental data. The comparison of the effect of the side chain length ( $n$ ) in the  $n$ –16PE monolayers reveals that for  $n = 2$  the  $d\Pi_c/dT$  values and the absolute values of the phase transition enthalpies are roughly two times higher than those characteristic for  $n = 1$  and  $n = 14$ . Introduction and elongation of a side chain in the  $n$ –16PE causes up to medium side chain lengths an increasing disturbance of the lateral packing, but at long side chain length, the ordering is again improved as the conditions of a triple chain are approximated.

## Introduction

The temperature dependence of the surface pressure of the two-dimensional (2D) phase transition in the monolayers of amphiphilic molecules at the air/water interface can be employed to estimate entropy and enthalpy of the phase transition in Langmuir monolayers. This is usually done using the 2D Clapeyron equation, discussed in a number of textbooks (see, for example, refs 1–3). At the same time, the one-component monolayer approximation, on which the Clapeyron equation is essentially based, seems to be inappropriate in a number of cases. It is known that the properties of a monolayer (molecular area and surface pressure for the onset of the main phase transition, the structure of the 2D condensed phase) depend significantly on the properties of the substrate (pH, presence of electrolytes),<sup>3,4</sup> so the Clapeyron equation should be regarded as an approximate relation. Other approaches also exist for the analysis of the temperature dependence of the phase transition pressure, which treats the monolayer as a 2D solution.<sup>2,5</sup> In the present paper, we attempt (i) to analyze various theoretical approaches to the problem and (ii) to compare the thermodynamic characteristics of the 2D phase transition in branched chain phospholipid monolayers, calculated from various theoretical models.

## Theory

The displacement of the 2D phase equilibrium was analyzed by Rusanov on a thermodynamic basis.<sup>2</sup> The general differential equation, which describes the displacement of the equilibrium in the 2D phases  $\omega$  and  $\epsilon$  (phase transition  $\omega \rightarrow \epsilon$ ), is

$$S_{\omega\epsilon} dT - v_{\omega\epsilon} dP + a_{\omega\epsilon} d\gamma + \sum_{i,k=1}^{n-1} (x_i^{(\epsilon)} - x_i^{(\omega)}) g_{ik}^{(\omega)} dx_k^{(\omega)} = 0 \quad (1)$$

where  $T$  is temperature;  $P$  is the pressure;  $\gamma$  is surface tension;  $x_i$  is the molar fraction of the  $i$ th component in the 2D phases  $\omega$  and  $\epsilon$  (denoted by superscripts);  $g_{ik} = \partial^2 g / \partial x_i \partial x_k$ ;  $g = (\sum_i \mu_i m_i) / m$  is the molar Gibbs' potential;  $\mu$  is the chemical potential;  $m$  is the number of moles; and  $S_{\omega\epsilon}$ ,  $v_{\omega\epsilon}$ , and  $a_{\omega\epsilon}$  are the entropy, volumetric, and surface differential molar effects of the 2D phase transition  $\omega \rightarrow \epsilon$ , respectively. Assuming that the external pressure  $P$  is constant, one can transform eq 1 for the two-component system into the form

$$a_{\omega\epsilon} d\Pi = S_{\omega\epsilon} dT + (x_1^{(\epsilon)} - x_1^{(\omega)}) \times [(RT \ln x_1^{(\omega)}) / (1 - x_1^{(\omega)})] \quad (2)$$

where  $\Pi$  is the surface pressure and the surface and entropy

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effects are

$$a_{\omega\epsilon} = a^{(\epsilon)} - a^{(\omega)} - (x_1^{(\epsilon)} - x_1^{(\omega)})(\partial a / \partial x_1)^{(\omega)} \quad (3)$$

$$S_{\omega\epsilon} = S^{(\epsilon)} - S^{(\omega)} - (x_1^{(\epsilon)} - x_1^{(\omega)})(\partial S / \partial x_1)^{(\omega)} \quad (4)$$

respectively. It is easily seen that for a one-component system ( $x_1 = 1$ ) eq 2 becomes the 2D Clapeyron equation:<sup>1-3</sup>

$$\frac{d\Pi}{dT} = \frac{\Delta S}{\Delta a} = \frac{\Delta H}{T\Delta a} \quad (5)$$

where  $\Delta S = S^{(\epsilon)} - S^{(\omega)}$ ,  $\Delta a = a^{(\epsilon)} - a^{(\omega)}$ , and  $\Delta H$  is the differential molar enthalpy of the phase transition  $\omega \rightarrow \epsilon$ . The 2D Clapeyron equation (eq 5) is often used to estimate the enthalpy of the phase transition in Langmuir monolayers.<sup>4,6,7</sup>

Neglecting the last terms in the right-hand side of eqs 3 and 4 and noting that  $x_1^{(\epsilon)} = 1$  (the condensed phase comprises only the amphiphilic component 1), one obtains from eq 2 the approximate expression for the differential molar enthalpy  $\Delta H$  of the phase transition in the two-component monolayer (amphiphilic substance 1 and solvent):

$$\Delta H = T\Delta a \times (d\Pi/dT) - RT^2 \times (d\ln x_1^{(\omega)}/dT) \quad (6)$$

In this equation,  $d\Pi/dT > 0$ ,  $\Delta a < 0$ , and  $d\ln x_1^{(\omega)}/dT < 0$ ; therefore, the first term in the right-hand side is always negative (negative enthalpy of the phase transition), and the second term is always positive. Thus, the  $\Delta H$  value, calculated from the Clapeyron equation (eq 5 or the first term in the right-hand side of eq 6) by its absolute value is higher than the value calculated from eq 6.

With  $x_1^{(\omega)}$  kept fixed, it follows from eq 6 (and also from eq 2) that

$$\Delta H = T\Delta a (\partial \Pi / \partial T)_{x_1^{(\omega)}} \quad (7)$$

The form of this equation is the same as that of the Clapeyron equation (eq 5). Obviously, the  $\Delta H$  values determined from these equations can be different, because the partial derivative value  $(\partial \Pi / \partial T)_{x_1^{(\omega)}}$  can be different from that of the total derivative  $d\Pi/dT$ .

The equilibrium between the 2D phases can also be described from the analysis of the chemical potentials of the components present in the coexisting 2D phases. Making the assumption similar to that used to derive eq 6, namely, that in the condensed phase the relation  $x_1^{(\epsilon)} = 1$  is valid, one can express the chemical potentials of the coexisting phases (in the ideal approximation) as

$$\mu^{(\epsilon)} = \mu^{0(\epsilon)}(P, T, \Pi); \mu^{(\omega)} = \mu^{0(\omega)}(P, T, \Pi) + RT \ln x_1^{(\omega)} \quad (8)$$

It is seen that the standard potentials depend not only on the external pressure and temperature but also on the surface pressure. Equating the chemical potentials in the phases  $\omega$  and  $\epsilon$  to each other, one obtains<sup>5</sup>

$$\Delta G^\circ = RT \ln x_1^{(\omega)} \quad (9)$$

where  $\Delta G^\circ = \mu^{0(\epsilon)} - \mu^{0(\omega)}$  is the variation of the standard (Gibbs') free energy of the 2D phase transition  $\omega \rightarrow \epsilon$  at fixed temperature, external pressure, and surface pressure.

The derivative  $d\Pi/dT$  at a fixed external pressure can be expressed as

$$\frac{d\Pi}{dT} = \left( \frac{\partial \Pi}{\partial T} \right)_{x_1^{(\omega)}} + \left( \frac{\partial \Pi}{\partial x_1^{(\omega)}} \right) \times \frac{dx_1^{(\omega)}}{dT} \quad (10)$$

From eq 9, the derivative  $dx_1^{(\omega)}/dT$  can be calculated

$$\frac{dx_1^{(\omega)}}{dT} = x_1^{(\omega)} \frac{d(\Delta G^\circ / RT)}{dT} \quad (11)$$

To determine the derivative  $(\partial \Pi / \partial x_1^{(\omega)})_T$ , one can use the equation of state for the fluid (or gaseous) insoluble monolayer (Volmer's equation of state):<sup>8</sup>

$$\Pi = \frac{RT}{a - a_0} - \Pi_{\text{coh}} = \frac{RTx_1^{(\omega)}}{a_0(1 - x_1^{(\omega)})} - \Pi_{\text{coh}} \quad (12)$$

where  $\Pi_{\text{coh}}$  is the cohesion pressure, which arises from the nonideality of the system,  $a = a_0/x_1^{(\omega)}$ , and  $a_0$  is the molar area of the component 1 in the condensed phase  $\epsilon$ . Clearly, eq 12 cannot be valid throughout the entire range of the 2D phase equilibrium (other equations of state were proposed for this region, see below) but only at the limiting values of pressure and molar area (the critical  $\Pi_c$  and  $a_c$  values) for the transition of the fluid (gaseous) state of the monolayer to the condensed phase. It follows from eq 12 that

$$\left( \frac{\partial \Pi}{\partial x_1^{(\omega)}} \right)_T = \frac{RT}{a_0(1 - x_1^{(\omega)})^2} \quad (13)$$

The partial derivative  $(\partial \Pi / \partial T)_{x_1^{(\omega)}}$  corresponding to the critical value  $\Pi_c$  can also be calculated from the equation of state (eq 12). With  $x_1^{(\omega)}$  kept fixed, the differentiation of eq 12 yields

$$\left( \frac{\partial \Pi_c}{\partial T} \right)_{x_1^{(\omega)}} = \frac{R}{a - a_0} = \frac{Rx_1^{(\omega)}}{a_0(1 - x_1^{(\omega)})} \quad (14)$$

The value of the derivative  $(\partial \Pi_c / \partial T)_{x_1^{(\omega)}}$  calculated from eq 14 amounts only to a few percent of the experimental value of the derivative  $d\Pi_c/dT$ . Therefore, the first term in the right-hand side of eq 10 can be neglected.

Introducing eqs 11 and 13 into eq 10 and using the Gibbs–Helmholtz equation

$$(\partial / \partial T)(\Delta G / RT) = -(\Delta H / RT^2) \quad (15)$$

one obtains the equation for the temperature displacement of surface pressure in the critical point for the phase transition in the monolayer  $d\Pi_c/dT$

$$\frac{d\Pi_c}{dT} = - \frac{\Delta H^\circ x_{1c}^{(\omega)}}{Ta_0(1 - x_{1c}^{(\omega)})^2} = \frac{\Delta H^\circ}{T\Delta a_c(1 - x_{1c}^{(\omega)})} \quad (16)$$

where  $\Delta H^\circ$  is the standard enthalpy of 2D phase transition. It is seen that eq 16 differs only by the factor  $1/(1 - x_{1c}^{(\omega)})$  in the right-hand side from the Clapeyron equation (eq 5) for the molar enthalpy of the 2D phase transition, which was derived disregarding the presence of the solvent in the monolayer. Thus, for any given value of the derivative  $d\Pi_c/dT$ , eq 16 (similar to eq 6) yields the value for the 2D phase transition enthalpy, which is lower by an absolute value than that calculated from the

Clapeyron eq 5. For expanded monolayers ( $x_{lc}^{(w)} \rightarrow 0$ ), these equations are identical to each other. It should also be noted that a difference exists under the conditions for which the  $\Delta H$  value is defined by eqs 1, 2, 5, and 6 and the conditions for which the  $\Delta H^\circ$  value in eq 16 is defined. In the former case, the enthalpy is determined for the condensation of an infinitesimal amount of matter of the noncondensed phase (in other words, one mole of the condensed phase is formed from an infinite amount of noncondensed phase), while in the latter case all of the matter comprising the noncondensed phase is assumed to be condensed. This also can lead to differences between the  $\Delta H$  and the  $\Delta H^\circ$  values.

The generalized Volmer equation (eq 12)<sup>5,9</sup> involves a factor  $1/n$  in the first term of its right-hand side, where  $n$  is the average aggregation number in the  $a > a_c$  range ( $n > 1$ ) or the dissociation degree of the monolayer molecules in this range ( $n < 1$ ). Including this factor, one can rearrange eq 16 to

$$\frac{d\Pi_c}{dT} = \frac{\Delta H^\circ}{nT\Delta a_c(1 - x_{lc}^{(w)})} \quad (17)$$

The 2D main phase transition for  $a \leq a_c$  leads to the formation of condensed phase (LC) clusters in the monolayer characterized by an aggregation number  $m \gg 1$  ( $m \rightarrow \infty$ ). This results in a decrease of the slope of the surface pressure dependence on  $a$ , as compared with that given by eq 12<sup>10</sup>

$$\Pi_{LC} = \frac{(RT/n)(a/a_{c\Pi})^2}{a - a_0[1 + \epsilon((a/a_{c\Pi})^2 - 1)]} - \Pi_{coh}, \quad (18)$$

where

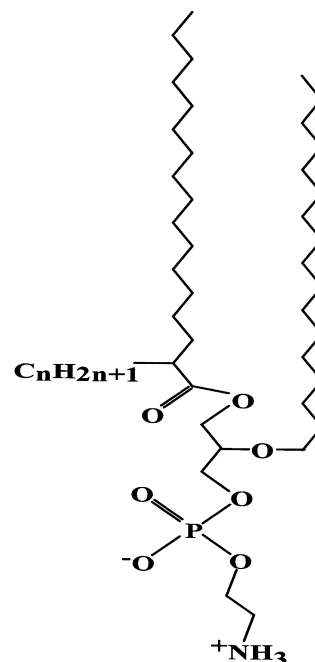
$$a_{c\Pi} = a_c \exp\left(\frac{(\Pi_{LC} - \Pi_c)\epsilon a_0}{RT}\right) \quad (19)$$

$\epsilon = 1 - a_m/ma_0$ ,  $a_m/m = a_{(m)}$  is the area per one monomer in a cluster. Equation 18 is valid for the region  $a \leq a_c$ . For  $a = a_c$ , eq 18 becomes the Volmer equation (eq 12) for small aggregates ( $n > 1$ ) or monomers ( $n = 1$ ). We compare below the values of the phase transition enthalpy calculated from the experimental data using the models summarized above.

## Experimental Section

The surface pressure–area ( $\Pi$ – $a$ ) isotherms were measured at different temperatures using a computer-interfaced film balance. The surface pressures measured with the Wilhelmy method using a roughened glass plate were reproducible to  $\pm 0.1$  mN m<sup>-1</sup> and the areas per molecule to  $\pm 0.005$  nm<sup>2</sup>. The film balance was sheltered in a cabinet to avoid excessive disturbances by convection and contamination by impurities. After the spreading solvent evaporated, the molecules remaining at the air/water interface were compressed at a constant compression rate  $r = (1/A) dA/dt$  instead of a constant barrier velocity with compression rates between  $1 \times 10^{-4}$  and  $5 \times 10^{-3}$  s<sup>-1</sup>. The equilibrium  $\Pi$ – $a$  isotherms are independent of the compression rate.

The monolayers of three chemically modified branched chain glycerophospho ethanolamines (PEs) have been studied. These PEs were a gift from Dr. F. Bringezu and synthesized by him. The synthesis of the PEs is described elsewhere.<sup>11,12</sup> The purity of the substances characterized by elemental analysis, MS, and high-performance liquid chromatography (HPLC) was  $\geq 99.8\%$ . The general structural formula of the studied alkyl chain



**Figure 1.** Chemical structure of the branched chain glycerophosphoethanolamines ( $n$ –16PE).

branched PEs is shown in Figure 1: *rac*-1-(2-methylhexadecanoyl)-2-*O*-hexadecyl-glycero-phosphoethanolamine (1–16PE), *rac*-1-(2-ethylhexadecanoyl)-2-*O*-hexadecyl-glycero-phosphoethanolamine (2–16PE), and *rac*-1-(2-tetradecylhexadecanoyl)-2-*O*-hexadecyl-glycero-phosphoethanolamine (14–16PE). In the following, we use only the abbreviations of the substances ( $n$ –16PE).

As spreading solvent, chloroform (p.a. grade) purchased from Baker, Deventer, Holland, was used to prepare  $10^{-3}$  M spreading solutions. The subphase water was Millipore-filtered.

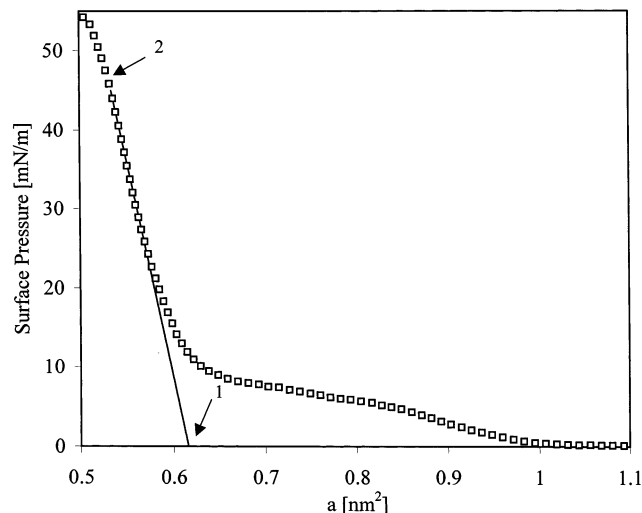
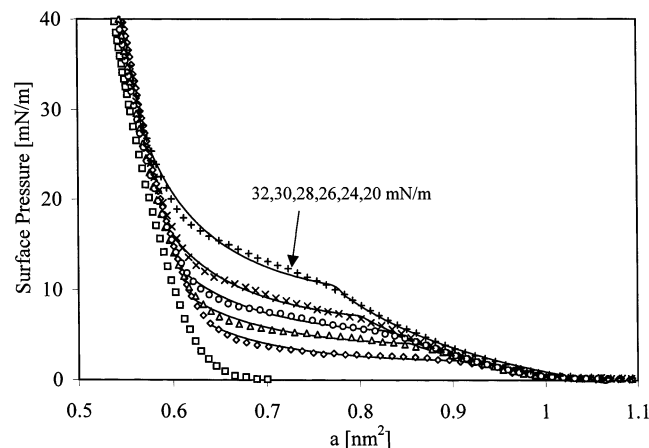
## Results and Discussion

The  $\Pi$ – $a$  isotherms of the three investigated branched chain phospholipids 1–16PE, 2–16PE, and 14–16PE show well-developed “plateau” regions indicating a main phase transition of first order. However, the temperature dependence of the main phase transition pressure  $\Pi_c$  is strongly affected by the side chain of the PEs. The existence of the plateau region at  $a < a_0$  for short side chain lengths (1–16PE and 2–16PE) as well as for long side chain lengths (14–16PE) indicates the transition to a more ordered condensed phase.

Equations 5, 6, and 17, which express the dependence of  $\Delta H$  ( $\Delta H^\circ$ ) on  $d\Pi_c/dT$ , and the equations of state (eqs 2 and 18) involve the  $a_0$  value, which is equal to the molar area of component 1 in the condensed phase  $\epsilon$ . Figure 2 illustrates the  $\Pi$ – $a$  dependence (here and below,  $a$  and  $a_0$  are the areas per one molecule) for 1–16PE at 28 °C. It is recommended to determine the  $a_0$  value from the intersection point of the tangent line to the  $\Pi$ – $a$  isotherm in the liquid-condensed state (shown by the dotted line in Figure 2) with the abscissa axis.<sup>3</sup> This value  $a_0 = 0.62$  nm<sup>2</sup> per one 1–16PE molecule is shown by the arrow 1 in Figure 2. Properly speaking, the phase transition at a given temperature takes place at certain (nonzero)  $\Pi$  value (the higher is the temperature, the higher is the transition pressure). Therefore, taking into account the compressibility of the monolayer in the condensed state (the slope of the dotted line in Figure 2), one can conclude that the  $a_0$  value should decrease with increase of surface pressure. The extremely low value  $a_0 = 0.53$  nm<sup>2</sup> per one molecule roughly corresponds to

TABLE 1: Characteristics of the 1–16PE Monolayer (Version 1)

temp (°C)	24	26	28	30	32
$a_0$ (nm <sup>2</sup> )	0.53	0.53	0.53	0.53	0.53
$a_c$ (nm <sup>2</sup> )	0.91	0.86	0.83	0.80	0.78
$\Pi_c$ (mN/m)	2.5	4.0	5.4	7.0	8.8
$\epsilon$	0.02	0.05	0.05	0.04	0.04
$N$	1.25	1.04	1.01	1.00	1.00
$\Pi_{\text{coh}}$	6.31	7.83	8.27	8.3	7.7
$\Delta G^\circ$ (kJ/mol)	−1.33	−1.20	−1.12	−1.04	−0.98
$\Delta H^\circ$ (kJ/mol)		−19.4	−12.0	−12.1	−9.1
$\Delta H$ (kJ/mol)		−32.3/−19.9	−26.5/−14.1	−26.2/−13.5	−26.4/−10.9
$(d\Pi_c/dT)_{\text{ex}}$ (mN/m·K)		0.75	0.7	0.8	0.9
$(d\Pi_c/dT)_{\text{th}}$ (mN/m·K)		0.84	0.62	0.77	0.91

Figure 2. Experimental  $\Pi$ - $a$  isotherm for 1–16PE monolayer at  $T = 28$  °C. See detailed discussion in the text.Figure 3. Experimental (solid curve) and theoretical (dashed curve)  $\Pi$ - $a$  isotherms for 1–16PE monolayers at different temperatures. The theoretical calculations were performed for the parameter values listed in Table 1.

the monolayer collapse pressure (arrow 2 in Figure 2). The estimates of the  $\Delta H$  ( $\Delta H^\circ$ ) values for 1–16PE and the theoretical calculations of the isotherms applying eq 18 were made using the two limiting  $a_0$  values above: the maximum value at  $\Pi = 0$  and the minimum value at the collapse pressure.

Figures 3 and 4 show the same set of the experimental  $\Pi$ - $a$  isotherms for 1–16PE at different temperatures, whereas the theoretical isotherms are plotted as calculated from eq 18 for the two versions (two different  $a_0$  values), respectively. The experimental results and values of model parameters with which the calculations were performed for the two versions are shown

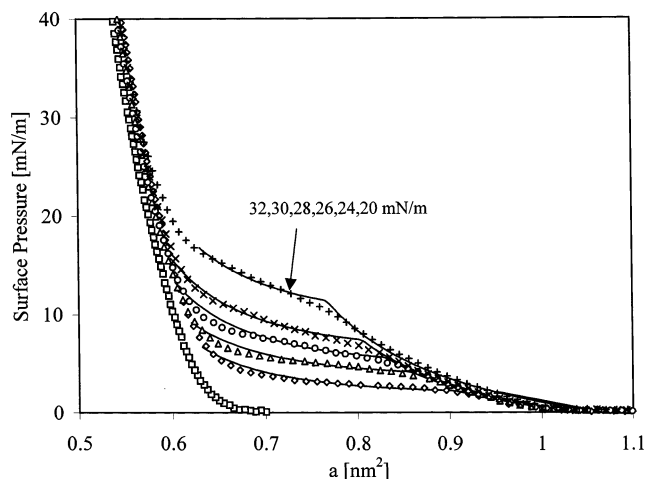


Figure 4. Same as in Figure 3. The theoretical calculations were performed for the parameter values listed in Table 2.

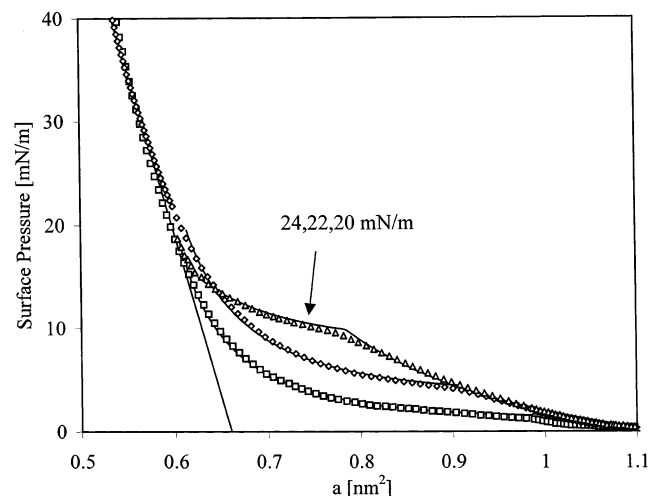
in Tables 1 and 2, respectively. The first row in each table shows the  $a_0$  value used in the calculations; in the next two rows, the experimental values of the area per molecule and surface pressure at the phase transition point are listed, as determined from the isotherms of Figures 3 or 4. The values of the parameters  $\epsilon$ ,  $n$ , and  $\Pi_{\text{coh}}$  were calculated from the best fit between the experimental and the theoretical isotherms. The  $\Delta G^\circ$  and  $\Delta H^\circ$  values were calculated from eqs 9 and 15, respectively. In the  $\Delta H$  entry, the value in the numerator corresponds to the value calculated from the Clapeyron equation (eq 5), and the value shown as the denominator was calculated from eq 6 with  $x_1^{(w)} = a_0/a$ . In the calculations, the experimental  $d\Pi_c/dT$  values were used, shown in the next-to-last rows of Tables 1 and 2. Finally, the last rows show the theoretical  $d\Pi_c/dT$  values, calculated from eq 17.

From the comparison between Figures 3 and 4 and between Tables 1 and 2, one can draw the following conclusions. The variations of the  $a_0$  value in a quite wide range (0.53–0.62 nm<sup>2</sup>) affect only slightly the theoretical predictions of the isotherms behavior and the estimated values of the thermodynamic characteristics for the phase transition. The value  $a_0 = 0.53$  nm<sup>2</sup> may be probably preferred, because in this case the theoretical model (eq 18) provides a somewhat better description of the experimental data, resulting in standard deviations between the experimental and the theoretical isotherms approximately two times lower than those in the alternative case. On the other hand, the use of the value  $a_0 = 0.62$  nm<sup>2</sup> with  $\epsilon = 0.15$ –0.17 (cf. Table 2) results in a minimum value for the area/molecule in the cluster  $a_{(m)} = a_0(1 - \epsilon) = 0.52$  nm<sup>2</sup>, which exactly corresponds with the area/molecule at the collapse pressure of 1–16PE monolayers. The  $\Delta H^\circ$  values calculated from eq 15



TABLE 2: Characteristics of the 1–16PE Monolayer (Version 2)

temp (°C)	24	26	28	30	32
$a_0$ (nm <sup>2</sup> )	0.62	0.62	0.62	0.62	0.62
$a_c$ (nm <sup>2</sup> )	0.91	0.86	0.83	0.80	0.78
$\Pi_c$ (mN/m)	2.5	4.0	5.4	7.0	8.8
$\epsilon$	0.15	0.17	0.16	0.16	0.15
$N$	2.1	1.78	1.74	1.72	1.55
$\Pi_{\text{coh}}$	4.61	5.64	5.76	5.8	5.94
$\Delta G^\circ$ (kJ/mol)	−0.93	−0.805	−0.702	−0.64	−0.57
$\Delta H^\circ$ (kJ/mol)		−18.6	−15.5	−9.1	−10.6
$\Delta H$ (kJ/mol)		32.3/−19.9	−26.5/−14.1	−26.2/−13.5	−26.4/−10.9
$(d\Pi_c/dT)_{\text{ex}}$ (mN/m·K)		0.75	0.7	0.8	0.9
$(d\Pi_c/dT)_{\text{th}}$ (mN/m·K)		0.94	0.93	0.72	1.19

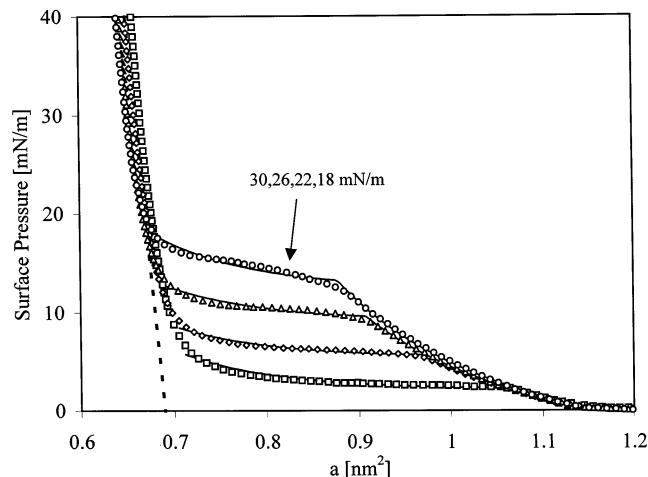


**Figure 5.** Experimental (solid curve) and theoretical (dashed curve)  $\Pi$ – $a$  isotherms for 2–16PE monolayers at various temperatures. The theoretical calculations were performed for the parameter values listed in Table 3.

are seen to be close to the  $\Delta H$  values calculated from eq 6, whereas the absolute  $\Delta H$  values calculated from eq 5 are 2–3 times higher than either of the two former values. The theoretical  $d\Pi_c/dT$  values calculated from eq 17 are practically equal to the experimental values. It is interesting to note that the value of partial derivative  $(\partial\Pi/\partial T)_{x_1^{(\omega)}}$ , e.g., at  $a = 0.78$  nm<sup>2</sup>/molecule (the maximum value of  $a$ , at which the derivative could be calculated in the whole temperature range studied) is lower than the  $d\Pi_c/dT$  derivative by approximately 10%.

The theoretical and experimental isotherms for 2–16PE and 14–16PE monolayers are shown in Figures 5 and 6, respectively, whereas the corresponding values of the experimental and model parameters are listed in Tables 3 and 4. Similar to what was observed for 1–16PE, also in this case, the choice of  $a_0$  affects only slightly the results; so, we present in Tables 3 and 4 the values calculated for the minimum  $a_0$ , which is close to the area corresponding to the collapse pressure. Here, similar to the 1–16PE monolayers, again good agreement exists between the experimental and the theoretical  $\Pi$ – $a$  isotherms. The discrepancy between the aggregation enthalpy values ( $\Delta H^\circ$  and  $\Delta H$ ) calculated from different models still exists. However, in contrast to the 1–16PE monolayers, the values calculated from eq 6 disagree with those calculated from eq 17.

The results obtained for  $n$ –16PE monolayers of various length of the additional hydrocarbon chain were analyzed. It was found that for the  $n$ –16PE with one methylene group in the additional chain (1–16PE) the values of the  $d\Pi_c/dT$  and the enthalpy of the 2D phase transition are approximately the same as those for the monolayer comprising the  $n$ –16PE



**Figure 6.** Experimental (solid curve) and theoretical (dashed curve)  $\Pi$ – $a$  isotherms for 14–16PE monolayers at different temperatures. The theoretical calculations were performed for the parameter values listed in Table 4.

TABLE 3: Characteristics of the 2–16PE Monolayer

temp (°C)	20	22	24	26
$a_0$ (nm <sup>2</sup> )	0.52	0.53	0.53	0.53
$a_c$ (nm <sup>2</sup> )	1.00	0.90	0.79	0.740
$\Pi_c$ (mN/m)	1.3	4.4	9.4	12.9
$\epsilon$	0.0	0.0	0.05	0.02
$N$	1.00	1.00	1.00	1.00
$\Pi_{\text{coh}}$	6.96	8.05	7.2	7.0
$\Delta G^\circ$ (kJ/mol)	−1.58	−1.3	−0.99	−0.83
$\Delta H^\circ$ (kJ/mol)		−41.2	−45.9	−23.8
$\Delta H$ (kJ/mol)		−118.0/−82.4	−115.8/−79.6	−65.9/−29.3
$(d\Pi_c/dT)_{\text{ex}}$ (mN/m·K)		1.55	2.5	1.75
$(d\Pi_c/dT)_{\text{th}}$ (mN/m·K)		1.30	2.9	2.25

molecules with 14 methylene groups in the additional chain (14–16PE). At the same time, the  $d\Pi_c/dT$  value for the  $n$ –16PE monolayer with the ethyl group in the additional chain (2–16PE) is approximately two times higher, which results in a more than 2-fold increase in the enthalpy for the 2D phase transition. This phenomenon may be possibly ascribed to the variation in the structure of the 2D aggregates. It can be expected that the introduction and elongation of a side chain at the second carbon atom of the *sn*-1 chain causes initially an increasing disturbance of the lateral packing, but finally at long side chain lengths, the ordering is improved as the conditions of a triple chain are approximated. This is in agreement with results obtained for 5–12PE monolayers with medium chain branching by the pentyl group.<sup>12</sup> In this case, the  $\Pi$ – $a$  isotherm shows neither a plateau region nor a dependence on temperature. The alkyl chain packing is disturbed so strongly that an ordered

**TABLE 4: Characteristics of the 14–16PE Monolayer**

temp (°C)	18	22	26	30
$a_0$ (nm <sup>2</sup> )	0.64	0.65	0.64	0.64
$a_c$ (nm <sup>2</sup> )	1.06	0.975	0.908	0.88
$\Pi_c$ (mN/m)	2.5	5.7	9.3	12.6
$\epsilon$	0.11	0.12	0.14	0.15
$N$	0.86	0.87	0.77	0.72
$\Pi_{coh}$	8.70	9.15	10.4	11.25
$\Delta G^\circ$ (kJ/mol)	−1.22	−1.00	−0.87	−0.79
$\Delta H^\circ$ (kJ/mol)		−16.1	−9.8	−6.0
$\Delta H$ (kJ/mol)		−46.0/−38.0	−38.5/−30.3	−32.8/−24.3
$(d\Pi_c/dT)_{ex}$		0.80	0.80	0.82
(mN/m·K)				
$(d\Pi_c/dT)_{th}$		0.96	0.87	0.68
(mN/m·K)				

condensed phase cannot be formed. According to the expected disturbance of the alkyl chain packing by the increasing length of the additional alkyl chain, its influence also leads to a significant increase in the compressibility of the 2–16PE monolayer in the condensed state (cf. the slope of the dotted line in Figure 5) as compared with the compressibility of the 1–16PE.

Analogous information on the effect of the side chain length has been obtained by studies of the 2D lattice structure of the different PEs.<sup>12</sup> The results of GIXD (grazing incidence X-ray diffraction) confirm that 5–16PE cannot form a crystal lattice, even at the highest surface pressures. In the case of short side chains, the alkyl chain packing needs to be increasingly distorted with the side chain length (2–16PE) to allow the adaptation of the alkyl chains to the headgroup. On the other hand, it is interesting to note that the compressibility of the 14–16PE monolayer (dotted lines in Figures 2 and 6, respectively) is approximately three times lower than that of the 2–16PE monolayer. This is also in agreement with the results of the GIXD studies,<sup>12</sup> which show that the alkyl chains are arranged in a hexagonal lattice with perpendicularly oriented chains and the lattice constants remain nearly constant at compression. Only at low surface pressures, the alkyl chains are slightly tilted in the 14–16PE monolayers. Obviously, the introduction and elongation of a side chain at the second carbon atom of the *sn*-1 chain causes initially an increasing disturbance of the lateral packing, but finally at long side chain lengths, the ordering is improved as the conditions of a triple chain are approximated.

## Conclusions

A comparative analysis of theoretical models, which describe the displacement of the 2D phase equilibrium in the monolayers at the water/air interface, is presented. The models that account for the presence of the solvent lead to lower absolute enthalpy values for the 2D phase transition at a given  $d\Pi_c/dT$  value. However, it seems impossible to prefer definitely either of the models, mainly because direct experimental values for the yield of aggregation heat in Langmuir monolayers are currently not available. Quantum chemical calculations of the thermodynamic

functions characteristic to the phase transitions in the monolayers<sup>13</sup> may possibly be one source of information, which would enable one to resolve this ambiguity. However, at this stage, these calculations are unable to provide for the correct account of the solvent. The description of the presence of the solvent in the framework of the conductor-like screening model (COSMO)<sup>14</sup> results in the additive decrease of the absolute enthalpy values. The related effect was found to be approximately 10 kJ/mol for *n*-alcohol monolayers.<sup>13</sup> It can be supposed that for the *n*-16PE monolayers the effect of the solvent on the enthalpy value may be higher. This result seems to be an argument in favor of the models that account for the presence of the solvent in the monolayer.

The comparison of the experimental  $d\Pi_c/dT$  values and aggregation enthalpies in the *n*-16PE monolayers shows that for *n* = 2 both the  $d\Pi_c/dT$  values and the absolute values of the phase transition enthalpy are roughly two times higher than those characteristic for *n* = 1 and *n* = 14. Introduction and elongation of a side chain at the second carbon atom of the *sn*-1 chain up to medium chain length cause an increasing disturbance of the lateral packing, but finally at long side chain lengths, the ordering is again improved as the conditions of a triple chain are approximated. Accordingly, the compressibility of the condensed 2–16PE monolayer is enhanced as compared to 1–16PE and 14–16PE monolayers.

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