

# Surface Equation of State for Insoluble Surfactant Monolayers at the Air/Water Interface

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A surface equation of state is derived and used to interpret the liquid-expanded (LE)–liquid-condensed (LC) phase transition. The monolayer is treated as a two-dimensional mixture consisting of LC domains, disordered molecules in the LE state, and free sites. The free sites are assumed to have two-dimensional size only and to be located at the internal surface between the headgroups and the tails of the surfactant. They are introduced to account for the translational freedom of the domains and of the disordered molecules on the surface. The model can explain the nonhorizontal LE/LC phase transition and its dependence on temperature. In addition, the equilibrium radius and equilibrium area fraction of the domains are calculated as a function of the average molecular surface area ( $A$ ). In the absence of domains, the surface equation of state reduces to a modified two-dimensional van der Waals equation. The dependence of the surface cohesion pressure on the molecular surface area  $A$  is calculated by including three contributions: the dipole–dipole interactions, the chain van der Waals interactions, and the chain conformation. The theoretical model is compared with the experimental  $\pi$ – $A$  isotherms for six phospholipid surfactants, and good agreement is obtained.

## Introduction

Most of the investigations regarding the  $\pi$ – $A$  isotherm for insoluble surfactant monolayers were focused on the phase transition from a liquid of a low surface density (liquid-expanded or LE monolayer) to one of a high surface density (liquid-condensed or LC monolayer). The phase transition is characterized by a nonhorizontal isotherm in the transition region and a smoothly continuous curve at its high-density end.<sup>1–7</sup> The slope of the isotherm in the transition region increases with increasing temperature. Regardless of the fact that almost all the experimental isotherms are nonhorizontal, they were considered artifacts produced by impurities<sup>8</sup> or some nonequilibrium effects such as the finite compression rate. The two-dimensional van der Waals equation as well as some other surface equations<sup>9–13</sup> of state predicted a horizontal line for the LE/LC phase transition.

To explain the nonhorizontal lines, Langmuir<sup>14</sup> and Smith<sup>15</sup> suggested that domains of the LC molecules are dispersed in a continuum of singly dispersed molecules. They proposed semiempirical surface equations of state which exhibited nonhorizontality. Ruckenstein and Bhakta<sup>16</sup> noted that during adsorption, even on a homogeneous surface, a size distribution of clusters can occur as a result of the competition between the entropy, which tends to disperse the molecules, and the interactions among the molecules, which tend to cause aggregation. They treated in this manner the adsorption of a gas on a homogeneous solid surface. Extending that approach to the LC domains and using the solution theory, theoretical treatments were developed for the transition from a gaseous to a condensed liquid monolayer<sup>17</sup> and from a LE to a LC monolayer.<sup>18</sup> In addition, a simple surface equation of state<sup>19</sup> was derived to account for the phase transition in phospholipid monolayers at an oil/water interface. On the basis of an analogy between the two-dimensional and three-dimensional aggregation, Israelachvili<sup>20</sup> proposed a simple surface equation of state which displays a nonhorizontal line in the transition region. Recently, Fainerman et al.<sup>21</sup> extended the two-dimensional equation of state

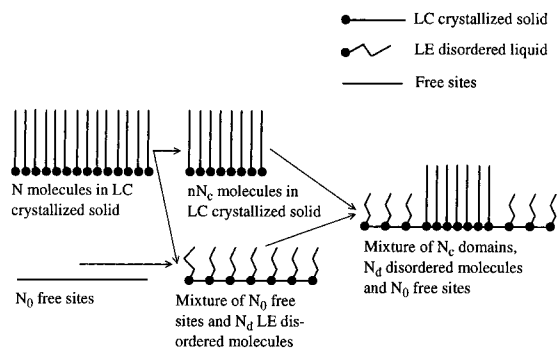
for a gaseous monolayer to a monolayer containing domains. The last two treatments were not concerned with any detail regarding the molecular structure.

Recent experiments<sup>22–26</sup> have identified the formation of LC domains distributed in a continuous phase of LE molecules. The domains have various shapes and are organized in a two-dimensional surface lattice. The size of these domains can range from a few micrometers to tens of micrometers corresponding to a number of molecules from  $10^6$  to  $10^8$ . The sizes and shapes of these domains are expected to affect the slope of the isotherm in the LE/LC transition region. McConnell et al.<sup>26–29</sup> considered that the long-range dipole–dipole interactions are responsible for the formation of the domains, since the repulsive free energy is decreased by the splitting of a bulk phase of LC molecules into domains. The size of the domains is determined by the competition between the dipole–dipole repulsive energy and the line tension energy. On this basis, McConnell et al.<sup>26–29</sup> derived an equation for the radius of the domains which is compatible with experiment. They were not, however, concerned with the LE/LC transition.

In the present paper, a theoretical model is proposed on the basis of which one can explain both the large sizes of the domains as well as the nonhorizontal nature of the LE/LC phase transition. The present calculations involve not only the long-range dipole–dipole interactions but also the van der Waals interactions among the hydrocarbon chains as well as the conformational free energy of the chains. In this manner, some of the molecular details are taken into account, and one can explain the dependence of the isotherms on the hydrocarbon chain length and the nature of the headgroup.

## Theory

**The Helmholtz Free Energy of the Insoluble Monolayer.** To describe the liquid-expanded (LE)–liquid-condensed (LC) phase transition, the insoluble monolayer containing  $N$  surfactant molecules at the air/water interface is treated as a two-dimensional mixture made up of  $N_d$  disordered molecules in



**Figure 1.** Schematic representation of the formation of an insoluble monolayer containing LC domains dispersed in a continuous phase of LE disordered molecules.

the LE state,  $N_c$  domains of equal size in the LC state, and  $N_0$  free sites, unoccupied by surfactant molecules. The free sites are introduced to take into account the translational freedom of the domains and of the disordered molecules at the surface. A two-dimensional lattice model is employed in the theoretical treatment. Each lattice site occupies a constant surface area  $A_0$  equal to the minimum surface area of a surfactant molecule (for phospholipid surfactants,<sup>9</sup>  $A_0 = 40 \text{ \AA}^2$ ). The free sites are considered to have two-dimensional size only and to be located at the interface (called for convenience internal surface) between the headgroup region and the tail region of the monolayer, each occupying one site. A domain is assumed to contain  $n$  surfactant molecules in the LC state, each having a constant surface area  $A_c$  and, consequently, occupying  $\gamma_c (=A_c/A_0)$  sites. Each surfactant molecule in the LE state is considered to occupy a surface area  $A_d$  in the cross section of the hydrocarbon chains, but an area  $A_0$  at the internal surface where there are free sites.  $A_d$  is allowed to vary with the surface pressure. The hydrocarbon chains in both the LC and LE state are considered to be compact because the LE/LC phase transition occurs at high surface densities and air is an extremely poor solvent for the hydrocarbon chains. They are, however, less extended in the LE state. Consequently, the insoluble monolayer behaves like a gas at the internal surface, because free sites are present, and like a liquid or solid in the region of the hydrocarbon chains, since the latter are compact. According to the model, one can write for the number of surfactant molecules  $N$  and the total surface area  $A_t$

$$N = N_d + nN_c \quad (1)$$

and

$$A_t = (N_0 + N_d)A_0 + nN_cA_c = N_dA_d + nN_cA_c = AN \quad (2)$$

where

$$A_d = \left(1 + \frac{N_0}{N_d}\right)A_0 \quad (3)$$

and  $A$  is the average surface area of a surfactant molecule. Equation 1 represents the number balance of the surfactant molecules and eq 2 their area balance. The quantities  $N_d$ ,  $N_c$ ,  $n$ , and  $N_0$  are predicted by the theory.

Figure 1 presents the physical picture regarding the formation of the two-dimensional mixture containing  $N$  surfactant molecules and  $N_0$  free sites. First,  $N_d$  surfactant molecules change their state from the LC crystallized solid to a disordered liquid by their mixing with  $N_0$  free sites. Thus, a LE monolayer is formed with an average cross sectional area  $A_d$  per molecule.

Then, the two-dimensional mixture is obtained by mixing the LE monolayer with  $N_c$  domains obtained by the splitting of a LC monolayer containing  $nN_c$  surfactant molecules. On the basis of this model, the total Helmholtz free energy ( $F$ ) of the two-dimensional mixture can be written as

$$F = N_0f_0^0 + Nf_c^0 + N_d\Delta f_{S/L}^0 + \Delta U_{\text{mix}} - T\Delta S_{\text{mix}} \quad (4)$$

where  $f_0^0$  is the Helmholtz free energy of a free site, which is equal to  $A_0\sigma_0$ , with  $\sigma_0$  denoting the pure water/air interfacial tension,  $f_c^0$  is the Helmholtz free energy of a surfactant molecule in the LC monolayer,  $\Delta f_{S/L}^0$  is the Helmholtz free energy change of a surfactant molecule from the LC crystallized solid state to the disordered LE liquid, and  $\Delta U_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  are the two-dimensional mixing energy and entropy of the two-dimensional mixture.

The quantity  $\Delta f_{S/L}^0$  does not involve the translational free energy change of a surfactant molecules since the latter is included in the mixing entropy contribution. The change from the LC crystallized solid to the disordered liquid is considered to occur in two steps; the first is from the LC crystallized solid (called below LC solid) to a liquid (called LC liquid), in which molecules become somewhat disordered but occupy the same surface area  $A_c$ , and the second step is from the LC liquid to the LE liquid, in which the molecular surface area varies from  $A_c$  to  $A_d$ . The former is a kind of melting process and has a melting free energy ( $\Delta f_m^0$ ), while the latter is an ordered-disordered change in the molecular state and has a free energy change denoted by  $\Delta f_{L/L}^0$ . Thus,

$$\Delta f_{S/L}^0 = \Delta f_m^0 + \Delta f_{L/L}^0 \quad (5)$$

To calculate the two-dimensional mixing entropy, the following generalized Flory equation, proposed by Donohue and Prausnitz,<sup>30</sup> is employed:

$$\Delta S_{\text{mix}} = -k \sum_i N_i \ln(y_i) \quad (6)$$

where  $N_i$  ( $i = 0, c, \text{ or } d$ ) is the number of molecules of species  $i$  and  $y_i$  is given by the following expression:

$$y_i = \frac{N_i \gamma_i^{p_i}}{\sum_j N_j \gamma_j^{p_j}} = \frac{x_i \gamma_i^{p_i}}{\sum_j x_j \gamma_j^{p_j}} = \frac{\Phi_i \gamma_i^{p_i-1}}{\sum_j \Phi_j \gamma_j^{p_j-1}} \quad (7)$$

In the above equation,  $\gamma_i$  is the number of sites occupied by species  $i$  at the internal surface,  $p_i$  is a parameter that has a value between zero and unity, and  $x_i$  and  $\Phi_i$  are the mole fraction and surface area fraction of species  $i$ , respectively, given by

$$x_i = \frac{N_i}{\sum_j N_j}, \quad \Phi_i = \frac{N_i \gamma_i}{\sum_j N_j \gamma_j} \quad (8)$$

The exponent  $p_i$  accounts for the effect of the size and shape of species  $i$ . When  $p_i = 0$ ,  $y_i = x_i$  and eq 6 reduces to the ideal mixing entropy, while when  $p_i = 1$ ,  $y_i = \Phi_i$  and eq 6 reduces to the Flory-Huggins equation. The former is suitable for mixtures of molecules of equal size and provides a lower limit of the mixing entropy, while the latter is suitable for mixtures of chainlike molecules of different sizes and provides an upper limit. The true mixing entropy lies between, and consequently  $p_i$  has a value between zero and unity.

Since a free site and a disordered surfactant molecule are assumed to occupy a single site each on the internal surface,  $\gamma_0 = \gamma_d = 1$  and eq 7 becomes

$$y_i = \frac{\Phi_i}{1 + \Phi_c(\gamma_c^{p-1} - 1)} \quad i = 0 \text{ or } d \quad (9)$$

and

$$y_c = \frac{\Phi_c \gamma_c^{p-1}}{1 + \Phi_c(\gamma_c^{p-1} - 1)} \quad (10)$$

In eqs 9 and 10,  $p = p_c$ ; that is, only one parameter is required in the present treatment for the entropy contribution. It will be shown latter that  $p$  can be considered constant for different surfactants and different temperatures.

The two-dimensional mixing energy is the energy required to divide the LC monolayer into domains and to disperse them in the LE monolayer and can be calculated using the equation derived by McConnell et al.<sup>26–29</sup> According to their treatment, the mixing energy involves two contributions; one is due to the dipole–dipole repulsion and another one arises from the line tension between the LC domains and the LE disordered molecules. The former tends to decrease and the latter to increase the size of the domain. Considering a hexagonal array of circular domains of the same radius ( $R$ ) dispersed in the LE phase, the mixing energy is given by<sup>29</sup>

$$\Delta U_{\text{mix}} = 2\pi R N_c \left[ \lambda - (\Delta\mu)^2 \ln\left(\frac{4R}{e^2\delta}\right) + (\Delta\mu)^2 \nu g \Phi_c^{3/2} \right] \quad (11)$$

where  $\lambda$  is the line tension,  $\Delta\mu$  is the difference in molecular dipole moment densities between the LC and the LE phases,  $\delta$  is the nearest neighbor intermolecular dipole–dipole distance,  $e = 2.718$ ,  $\nu = (3\pi/2)(\sqrt{3}/2\pi)^{3/2}$ , and  $g$  is given by

$$g = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} [2 - \delta(m_1, 0) - \delta(m_2, 0)] q(m)/m^3 \quad (12)$$

In eq 12,  $\delta(m_1, 0)$  and  $\delta(m_2, 0)$  are delta functions [ $\delta(m_i, 0) = 1$  for  $m_i = 0$  and  $= 0$  for  $m_i \neq 0$  ( $i = 1, 2$ )].

$$q(m) = 1 + 0.5168(\Phi_c/m^2) + 0.03117(\Phi_c/m^2)^2 + \dots \quad (13)$$

and

$$m = (m_1^2 + 3m_2^2 + 3m_1m_2)^{1/2} \quad (14)$$

accounts for the distance between the centers of two circular domains. The quantities  $m_1$  and  $m_2$  are integers and  $m_1 + m_2 > 0$ .

Neglecting the higher order terms in  $q(m)$  and inserting into eq 12, one obtains

$$g = g_0 + 0.5168g_1\Phi_c \quad (15)$$

where  $g_0$  and  $g_1$  are constants equal to 3.25 and 2.23, respectively (1092 terms were included in the summations).

Inserting eqs 6 and 11 into eq 4 yields

$$\frac{F}{kT} = \frac{N_0 f_0^0 + N_c f_c^0 + N_d \Delta f_{SL}^0}{kT} + \frac{2\pi R N_c (\Delta\mu)^2}{kT} \left[ \frac{\lambda}{(\Delta\mu)^2} - \ln\left(\frac{4R}{e^2\delta}\right) + \nu g \Phi_c^{3/2} \right] + \sum_i N_i \ln(y_i) \quad (16)$$

**The Equilibrium Radius and Equilibrium Area Fraction of Domains.** Using the Helmholtz free energy given by eq 16, the equilibrium radius of the domains and the equilibrium area fraction occupied by the domains can be calculated via its minimization with respect to  $R$  and  $\Phi_c$ , that is, using the equations  $(\partial F/\partial R)_{N, A_c, \Phi_c} = 0$  and  $(\partial F/\partial \Phi_c)_{N, A_c, R} = 0$ , respectively. For the equilibrium radius, one obtains

$$R = R_0 \exp[u(\Phi_c)] \exp\left\{ \frac{kT}{\pi R (\Delta\mu)^2} [\ln(y_c) + (1-p)(1-y_c)(1-\gamma_c^p)] \right\} \quad (17)$$

where

$$R_0 = \frac{e^3\delta}{4} \exp\left[ \frac{\lambda}{(\Delta\mu)^2} \right] \quad (18)$$

and

$$u(\Phi_c) = \nu g \Phi_c^{3/2} = \nu(g_0 + 0.5168g_1\Phi_c)\Phi_c^{3/2} \quad (19)$$

In eq 17,  $R_0$  is the equilibrium radius of a domain in the absence of other domains, the factor  $\exp[u(\Phi_c)]$  accounts for the effect of the dipole–dipole repulsion among the domains on the equilibrium radius  $R$  and indicates that the domain radius increases exponentially with the area fraction of the domains, and the last factor is due to the mixing entropy of the two-dimensional mixture. When the last factor is taken as unity, eq 17 reduces to that derived by McConnell et al.<sup>26–29</sup> Since the quantity  $kT/(\pi R (\Delta\mu)^2)$  is on the order of  $10^{-5}$  for a domain radius of  $5 \mu\text{m}$ , that factor is very close to unity, indicating a negligible effect of the two-dimensional mixing entropy on the equilibrium radius. Consequently, the last factor in eq 17 is taken to be unity in the present calculations.

For the equilibrium area fraction of the domains, the equation  $(\partial F/\partial \Phi_c)_{N, A_c, R} = 0$  leads to

$$y_c^{1/n} = y_d y_0^{(A_c/A_0-1)} \exp\left[ \frac{A_c y_c}{A_0 \Phi_c} (1 - y_c^{-p}) \right] K_m K \quad (20)$$

where  $K_m$  accounts for the effect of the melting free energy and  $K$  for the effects of the order–disorder free energy change from the LC liquid to the LE liquid and the dipole–dipole interactions among domains and between domains and disordered molecules. They are given by the expressions

$$K_m = \exp\left( \frac{\Delta f_m^0}{kT} \right) \quad (21)$$

and

$$K = \exp\left\{ P - (A_d - A_c)P' + \frac{2A_c(\Delta\mu)^2}{kTR} [1 - u'\Phi_c] + \frac{(A_c - A_0)\sigma_0}{kT} \right\} \quad (22)$$

In eq 22,

$$P = \Delta f_{\text{L/L}}^0/kT, \quad P' = \partial P/\partial A_d$$

and

$$u' = \frac{du(\Phi_c)}{d\Phi_c} = \nu \left( \frac{5}{2}g - g_0 \right) \Phi_c^{-1/2}$$

Since no molecular model is available to calculate  $\Delta f_m^0/kT$  (the dimensionless melting free energy),  $K_m$  is determined from the molecular surface area  $A_{\text{tr}}$  at the onset of the LE/LC phase transition as follows: First, it should be noted that the term  $(y_c)^{1/n}$  in eq 20 is always very near unity, because the number  $n$  of molecules in a domain is on the order of  $10^6$ – $10^8$ . Taking  $(y_c)^{1/n}$  equal to be unity and  $\Phi_c$  equal to zero and replacing  $A_d$  by  $A_{\text{tr}}$ , one obtains

$$K_m = \left( \frac{A_{\text{tr}}}{A_0} \right) \left( \frac{A_{\text{tr}}}{A_{\text{tr}} - A_0} \right)^{(A_c/A_0 - 1)} \exp \left[ \frac{A_c}{\gamma_{c,\text{tr}} A_0} (1 - \gamma_{c,\text{tr}}^p) \right] K_{\text{tr}}^{-1} \quad (23)$$

where  $K_{\text{tr}}$  and  $\gamma_{c,\text{tr}}$  are the values of  $K$  and  $\gamma_c$  for  $A_d = A_{\text{tr}} = A_{\text{tr}}/N$ .

**The Surface Equation of State.** Using eq 16 for the Helmholtz free energy and the thermodynamic definition of the surface tension  $\sigma$ ,

$$\sigma = \left( \frac{\partial F}{\partial A} \right)_{T,N} \quad (24)$$

one obtains

$$\frac{\pi A_0}{kT} = -\ln(y_0) - P'A_0 + \frac{2A_0(\Delta\mu)^2}{kTR} u' \Phi_c^2 + y_c(\gamma_c^{-p} - 1) + \frac{2u'\Phi_c \ln(y_c)}{\gamma_c} \left( \frac{\partial \Phi_c}{\partial A} A \right) \quad (25)$$

where  $\pi = \sigma_0 - \sigma$  is the surface pressure. Differentiating eq 20, one finally obtains

$$A \frac{\partial \Phi_c}{\partial A} = \frac{A_0}{A} \left( \frac{A_d}{A_c} - 1 \right) \left[ \frac{\Phi_d}{\Phi_0} + P'' A_0^2 \left( \frac{A_d}{A_0} \right) \right] / (S_A + U_A) \quad (26)$$

where

$$\begin{aligned} S_A &= \frac{2u'\Phi_d}{\gamma_c} \ln(y_c) - \left( \frac{A_0}{A_c} + \frac{\Phi_d}{\gamma_c \Phi_c} \right) + \\ &\quad y_d(\gamma_c^{p-1} - 1) \left[ \gamma_c^{-1} - 1 + \frac{y_c}{\Phi_c} (\gamma_c^{-p} - 1) \right] \\ U_A &= \frac{2y_d P u'}{\gamma_c} - (P'' A_0^2) \left( \frac{A_d}{A_c} - 1 \right)^2 + \\ &\quad \frac{2A_0(\Delta\mu)^2}{kTR} \Phi_d [(u')^2 \Phi_c - 2u' - u'' \Phi_c] \\ P'' &= \frac{\partial^2}{\partial A_d^2} \left( \frac{\Delta f_{\text{L/L}}^0}{kT} \right) \end{aligned} \quad (27)$$

$$u'' = \frac{d^2 u(\Phi_c)}{d\Phi_c^2} = \frac{3}{2} \nu \left( \frac{5}{2}g - 2g_0 \right) \Phi_c^{-3/2} \quad (28)$$

In eq 25, the first term accounts for the translational freedom of the domains and of the disordered molecules in the monolayer, the second accounts for the change in the state of the surfactant molecules from the LC liquid to the LE liquid, the third is due to the dipole–dipole repulsion among the domains, the fourth is due to the entropy, and the last one is due to the formation of the new domains.

Equation 25 reduces to a simple form in the absence of domains. Indeed, in this case, the two-dimensional mixture contains only two species: the free sites and the disordered molecules, each species occupying the same internal surface area  $A_0$ . Consequently,  $y_c = \Phi_c = 0$ ,  $A_d = A$ ,  $y_0 = 1 - A_0/A$ , and

$$\frac{\pi A_0}{kT} = -\ln \left( \frac{A - A_0}{A} \right) - P'A_0 \quad (29)$$

Using a low-density approximation for the first term of eq 29, one obtains

$$(\pi + kTP')(A - A_0) = kT \quad (30)$$

where  $kTP' = \partial(\Delta f_{\text{L/L}}^0)/\partial A$  represents the surface cohesion pressure, which will be calculated below. The above equation constitutes a two-dimensional equation of state for a gaseous monolayer.

**Helmholtz Free Energy Change ( $\Delta f_{\text{L/L}}^0$ ) from the LC Liquid to the LE Liquid.** The Helmholtz free energy difference  $\Delta f_{\text{L/L}}^0$  is considered to involve three contributions: a dipole–dipole interaction free energy change ( $\Delta f_{\text{dipole}}^0$ ), a chain conformational free energy change ( $\Delta f_{\text{con}}^0$ ), and a chain van der Waals interaction (volume-dependent) free energy change ( $\Delta f_{\text{vdw}}^0$ ); that is,

$$\Delta f_{\text{L/L}}^0 = \Delta f_{\text{dipole}}^0 + \Delta f_{\text{con}}^0 + \Delta f_{\text{vdw}}^0 \quad (31)$$

The three kinds of free energy changes are calculated below.

**The Dipole–Dipole Interaction Free Energy Change ( $\Delta f_{\text{dipole}}^0$ ).** Using an electrostatic capacitor as a model to represent the two-dimensional array of effective dipoles considered perpendicular to the air/water interface in a monolayer, the dipole–dipole interaction free energy can be approximated by the following equation:<sup>31</sup>

$$f_{\text{dipole}}^0 = \frac{e^2 d_e}{2\epsilon_0 \epsilon A} = \frac{e\mu}{2\epsilon_0 \epsilon} \quad (32)$$

where  $d_e$  is the effective charge separation of the dipole moment,  $e$  is the protonic charge ( $1.602 \times 10^{-19}$  C),  $\epsilon_0$  is the permittivity of vacuum ( $8.854 \times 10^{-12}$  C<sup>2</sup> J<sup>-1</sup> m<sup>-1</sup>), and  $\epsilon$  is the dielectric constant around the headgroup. The product  $d_e e$  stands for the effective dipole moment, and consequently, the quantity  $d_e e/A = \mu$  for the dipole moment density.

For a given surfactant, the effective dipole moment can be considered to be constant within the range of surface densities of concern here, but the dipole moment density ( $\mu$ ) varies with the two-dimensional molecular density. Indeed, for the 1,2-dilauroyl (DLPE) and 1,2-dimyristoylphosphatidylethanolamine (DMPE) monolayers in the LE state, the surface potential measurements indicated<sup>22</sup> that only the molecular density and not the dipole orientation was changed on compression of the monolayer, hence that the normal dipole moment remained constant. We assume that the same dipole moment can be used for the LC liquid, in which the molecules are more extended than in the disordered state. No equation is available for the

calculation of the effective dipole moment. In the present treatment, the unknown effective dipole moment and the dielectric constant are included into a single parameter, which was selected to fit the experimental  $\pi$ -A isotherms in the LE region. Thus, the dipole-dipole interaction free energy change is given by the expression

$$\frac{\Delta f_{\text{dipole}}^0}{kT} = \alpha_d \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A_d} - \frac{A_0}{A_c} \right) \quad (33)$$

where

$$\alpha_d = \frac{e^2 d_e}{2kT_0 \epsilon_0 \epsilon A_0} = \frac{e \mu_0}{2kT_0 \epsilon_0 \epsilon} \quad (34)$$

with  $T_0 = 298$  K as a reference temperature and  $\mu_0 = ed_e/A_0$  (the dipole moment density in the limiting case in which each molecule becomes completely ordered).

*The Conformational Free Energy Change* ( $\Delta f_{\text{con}}^0$ ). The hydrocarbon chains of the surfactant molecules are constrained to remain with the polar headgroups in contact with water and therefore have a conformational free energy relative to the unconstrained chains. The conformational free energy per chain ( $\Delta f_{\text{con}}^0$ ) can be calculated using the following expression:<sup>31,32</sup>

$$\frac{f_{\text{con}}^0}{kT} = \frac{\pi^2 N_c L^4}{8 A^2} \quad (35)$$

where  $N_c$  is the number of segments of a chain placed on a cubic lattice whose sites have a size  $L$  equal to the chain width (4.6 Å), and  $N_c = (n_c + 1)/3.6$  with  $n_c$  representing the number of carbon atoms of the chain. The above equation was derived for polymers; it can also be used for the short chains of concern here, since our evaluations have shown that it provides results near to those obtained for short chains when the lattice statistical mechanical approach of Cantor and Dill<sup>9</sup> is used.

Using eq 35, the conformational free energy per surfactant molecule (which has two identical chains) is given by

$$\frac{f_{\text{con}}^0}{kT} = \frac{\pi^2 N_c L^4}{A^2} \quad (36)$$

By increasing the molecular surface area from  $A_c$  to  $A_d$ , the packing constraint to a hydrocarbon chain is increasingly reduced, and this results in a conformational free energy decrease. Using the above equation, the conformational free energy change from the LC liquid to the LE liquid can be calculated from

$$\frac{\Delta f_{\text{con}}^0}{kT} = \alpha_c \left[ \left( \frac{A_0}{A_d} \right)^2 - \left( \frac{A_0}{A_c} \right)^2 \right] \quad (37)$$

where

$$\alpha_c = (\pi^2 N_c L^4)/(A_0^2) \quad (38)$$

*The chain van der Waals Interaction Free Energy Change* ( $\Delta f_{\text{vdW}}^0$ ). With the increase of the two-dimensional molecular density, the chains become increasingly aligned and the anisotropic short-range steric repulsive interactions are reduced due to the better packing of the chains. This leads to a dependence of the chain van der Waals interaction free energy on the two-dimensional molecular density or the surface area occupied by a molecule. For the calculation of the van der Waals interaction

free energy among the chains in a monolayer, the following equation was derived:<sup>9</sup>

$$F_v(X) = F_v^\infty - \frac{15 E_0}{2 \tilde{V}} (n_c + n_e)(1 - X) \quad (39)$$

where  $X$  accounts for the extent of the reduction of the repulsive component of the chain pair potential with increased chain alignment. For no alignment (completely disordered chains)  $X = 1$ , while for total alignment (highly ordered chains)  $X = X_r < 1$ . The quantity  $F_v^\infty$  represents the free energy per mole for the completely disordered chains,  $\tilde{V} = V/V^* = 1.23$  is the reduced volume of a completely disordered chain, with  $V$  and  $V^*$  the volume and the hard-core volume of the chain,  $E_0$  (=1.57 kcal/mol) is the energy at  $T = 0$  K,  $n_c$  is the number of carbon atoms in the chain, and  $n_e$  is a constant of order unity. Assuming that  $X$  is a linear function of the average order parameter ( $S^*$ ) and considering that  $S^*$  depends on the molecular surface area, the van der Waals interaction free energy can be expressed in terms of the molecular surface area.<sup>9</sup> In the present paper, we make the same assumption regarding  $X$ , but calculate differently the average order parameter  $S^*$ .

Generally, the average order parameter  $S^*$  is defined as

$$S^* = \frac{3}{2} P^* - \frac{1}{2} \quad (40)$$

where  $P^*$  is the average probability for a bond to be parallel to the normal to the interface. Denoting by  $n_0$  the number of vertical bonds in a chain containing  $N_c - 1$  bonds, one can write  $P^* = n_0/(N_c - 1)$ . Neglecting the bond's backtracks and considering that all the chains terminate at the same height (which are reasonable assumptions for short-chain compact monolayers), one can write  $n_0/(N_c - 1) = A_0/A$ . Consequently, the average order parameter  $S^*$  can be expressed in terms of the molecular surface area as

$$S^* = \frac{3}{2} \frac{A_0}{A} - \frac{1}{2} \quad (41)$$

The above equation provides reasonable extreme values. When  $A = A_0$ ,  $S^* = 1$ , and when  $A = 3A_0$  (=120 Å<sup>2</sup> for the phospholipid surfactants), which is a very large molecular surface area,  $S^* = 0$ , indicating complete disorder. In the LE monolayer and the LE/LC transition region,  $A$  is between  $A_0$  and  $3A_0$ , and consequently,  $S^*$  varies between 0 and 1.

Assuming a linear relationship between  $X$  and  $S^*$ , one can write

$$X = 1 + (X_r - 1) \left( \frac{3}{2} \frac{A_0}{A} - \frac{1}{2} \right) \quad (42)$$

where  $X_r$  is the value of  $X$  for the highly ordered solid phase with  $A = A_0$ . Cantor and Dill<sup>9</sup> calculated  $X_r$  as a linear combination of contributions from methylene and terminal methyl groups. In the present calculations, the value 0.9765 suggested by them for the methylene group is used, since the number of methylene groups is large and the values of  $X_r$  for methyl and methylene groups are near one another.

Substituting eq 42 into eq 39, one obtains the following expression for the van der Waals interaction free energy per chain:

$$\frac{f_{\text{volume}}^0}{kT} = \frac{F_v^\infty}{RT} + \alpha_v \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A} - \frac{1}{3} \right) \quad (43)$$

where

$$\alpha_v = -\frac{45E_0}{4\tilde{V}}(n_c + n_e)(1 - X_r) \quad (44)$$

Consequently, the van der Waals interaction free energy change from the LC liquid to the LE liquid (disordered state) can be calculated using the expression

$$\frac{\Delta f_{\text{volume}}^0}{kT} = \alpha_v \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A_d} - \frac{A_0}{A_c} \right) \quad (45)$$

Introducing the values of  $E_0$ ,  $\tilde{V}$ , and  $X_r$  and neglecting the small constant  $n_e$ , one obtains  $\alpha_v = -0.57n_c$  per hydrocarbon chain. For the phospholipid surfactants with two identical chains,  $\alpha_v$  is given by the expression  $\alpha_v = -1.14n_c$ .

**Parameters and Calculations.** For the calculation of the equilibrium radius and the equilibrium area fraction of domains and finally of the surface pressure as a function of the molecular surface area  $A$  by the eqs 17, 20, and 25, respectively, the following parameters are required:

$A_c$ :	the molecular area in the LC crystallized solid
$A_{tr}$ :	the molecular area at the onset of the LE/LC phase transition
$\alpha_d$ :	defined by eq 34 to account for the dipole–dipole interactions
$R_0$ :	the domain radius in the absence of other domains
$p$ :	the exponent in the expression of the mixing entropy (eqs 9 and 10)
$A_d = (1 + \Phi_0/\Phi_d)A_0$ :	the molecular area in the LE state, equal to $A$ in the LE monolayer and larger than $A$ in the transition region
$\alpha_c$ :	given by eq 38 for the chain conformational free energy
$\alpha_v$ :	given by eq 44 for the chain van der Waals interaction free energy
$\epsilon$ :	the dielectric constant taken equal to 14 in the present calculations
$\Delta\mu$ :	the dipole moment density difference between the LC and LE monolayers

$$P = \Delta f_{\text{LL}}^0/kT, \quad P' = \partial P/\partial A_d, \quad \text{and} \quad P'' = \partial^2 P/\partial A_d^2$$

$A_c$  was selected between 40 and 48 Å<sup>2</sup> in order to fit the experimental data.  $\alpha_d$  was obtained for each surfactant from a single point of one experimental isotherm in the LE region.  $A_{tr}$  is provided by the value of  $A$  at the onset of the phase transition. Since the effective dipole moment is assumed to be constant, the dipole moment density difference  $\Delta\mu$  between the LC and the LE phases is given by

$$\Delta\mu = \mu_0 \left( \frac{A_0}{A_c} - \frac{A_0}{A_d} \right) \quad (46)$$

where  $\mu_0$  represents the limiting dipole moment density given by (see eq 34)

$$\mu_0 = \frac{2kT_0\epsilon_0\epsilon\alpha_d}{e} \quad (47)$$

$P (= \Delta f_{\text{LL}}^0/kT)$  can be obtained by inserting eqs 33, 37, and 45 into eq 31.

$$P = (\alpha_d + \alpha_v) \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A_d} - \frac{A_0}{A_c} \right) + \alpha_c \left[ \left( \frac{A_0}{A_d} \right)^2 - \left( \frac{A_0}{A_c} \right)^2 \right] \quad (48)$$

$P'$  and  $P''$  can be calculated using eq 48, which leads to

$$A_0 P' = -(\alpha_d + \alpha_v) \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A_d} \right)^2 - 2\alpha_c \left( \frac{A_0}{A_d} \right)^3 \quad (49)$$

and

$$A_0^2 P'' = 2(\alpha_d + \alpha_v) \left( \frac{T_0}{T} \right) \left( \frac{A_0}{A_d} \right)^3 + 6\alpha_c \left( \frac{A_0}{A_d} \right)^4 \quad (50)$$

As noted before, for a pure LE monolayer ( $\Phi_c = 0$  and  $A_d = A$ )  $kTP'$  represents the cohesion pressure. According to eq 49, the cohesion pressure involves contributions due to the dipole–dipole interactions, the chain van der Waals interactions, and the chain conformation. Inserting eq 49 into eq 25 and replacing  $A_0/A$  by the molecular surface density  $\rho$ , one obtains for a pure LE monolayer

$$\frac{\pi A_0}{kT} = -\ln(1 - \rho) + (\alpha_d + \alpha_v) \left( \frac{T_0}{T} \right) \rho^2 + 2\alpha_c \rho^3 \quad (51)$$

Expanding the first term on the right-hand side of the above equation up to the third order in density, the following two-dimensional virial equation of state is obtained:

$$\frac{\pi A_0}{kT} = \rho + B_2 \rho^2 + B_3 \rho^3 \quad (52)$$

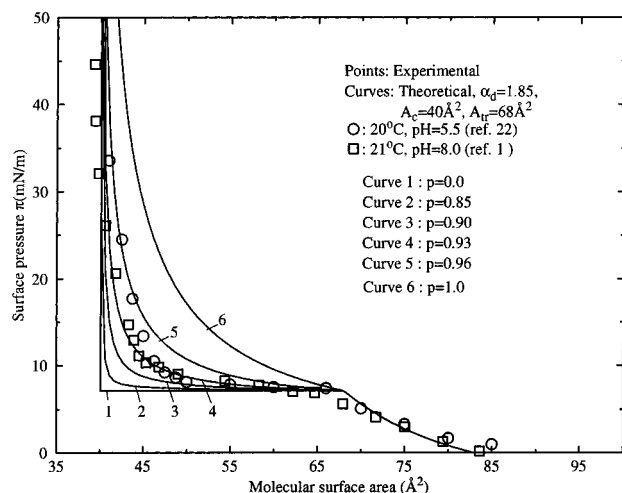
where  $B_2 = (\alpha_d + \alpha_v)(T_0/T) + 1/2$  and  $B_3 = 2\alpha_c + 1/3$  represent the second and the third virial coefficients, respectively. The dipole–dipole interactions and the chain van der Waals interactions affect the second virial coefficient, while the chain conformations affect the third virial coefficient. Since the parameter  $\alpha_d$  depends upon the nature of the headgroup and the parameters  $\alpha_v$  and  $\alpha_c$  upon the number of carbons in the hydrocarbon chain, the surface equations of state 25 and 52 account for both the nature of the headgroup and the length of the chain.

## Results and Discussions

In this section, the derived surface equation of state (eq 25) is compared with the experimental  $\pi$ – $A$  isotherms involving the LE/LC phase transition for the following six phospholipid surfactants: 1,2-dimyristoylphosphatidylcholine (DMPC), 1,2-dipalmitoylphosphatidylcholine (1,2-DPPC), 1,3-dipalmitoylphosphatidylcholine (1,3-DPPC), 1,2-dimyristoylphosphatidic acid (DMPA), 1,2-dilauroylcephalin (DLPE), 1,2-dimyristoylphosphatidylethanolamine (DMPE). The general formula of the phospholipid surfactants can be written as R–CO<sub>2</sub>–(h)–O<sub>2</sub>C–R, where R stands for the hydrocarbon chain, which has  $n_c$  carbon atoms, and h stands for the connecting chains and the headgroup.

### The Effect of the Parameter $p$ in the Entropy Model.

Figure 2 presents the effect of the two-dimensional mixing entropy on the theoretical  $\pi$ – $A$  isotherm of DMPE at 20 °C. Since the mixing entropy is characterized by the parameter  $p$  (eq 6), six isotherms for different values of  $p$  from zero to unity are presented in the figure. First, one can observe that with increasing value of  $p$ , the slope of the isotherm in the transition region increases. When  $p = 0$ , the mixing entropy is given by the ideal-solution expression and the isotherm in the transition

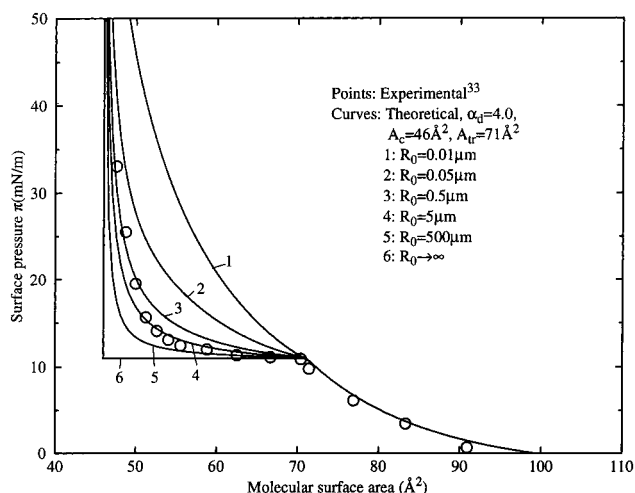


**Figure 2.** Effect of the parameter  $p$  of the mixing entropy model on the theoretical  $\pi$ - $A$  isotherm of DMPE at 20.5 °C.

region becomes horizontal (curve 1). Indeed, in this case, the domains provide a negligible contribution to the two-dimensional mixing entropy, and the molar composition of the mixture remains almost the same as at the onset of the phase transition. This arises because the mole fraction of the domains which are large is very small. With increasing values of  $p$  ( $p = 0.85$ , curve 2), the isotherm in the transition region starts to deviate from the horizontal line, and a smoothly rising continuous curve is obtained at the high surface density end of the phase transition. When  $p = 1$  (curve 6), the two-dimensional mixing entropy is given by the Flory-Huggins expression and the isotherm in the transition region exhibits the largest slope. For the DMPE surfactant, the theoretical  $\pi$ - $A$  isotherm is in good agreement with experiment when  $p = 0.93$ . It is worth noting that for all the systems and at different temperatures,  $p = 0.93$  results in good agreement with experiment. (In some cases, a somewhat better fitting can be reached by slightly changing the value of  $p$ ). Consequently, the parameter  $p$  is considered to be independent of both the system and temperature and is taken equal to 0.93 in all calculations.

The domains can have various shapes. The present model considers only circular domains for the calculation of the mixing energy, but no restriction regarding the domain shape is made in the calculation of the mixing entropy. As already noted, the parameter  $p$  in the entropy expression depends on the shape of the domain. In a three-dimensional solution, the molecular shape can be characterized by the ratio  $q/\gamma$ ,<sup>30</sup> where  $\gamma$  represents the number of lattice sites occupied by the molecule (or the number of the molecular segments) and  $qz$  ( $z$  is the lattice coordination number) provides the number of the nearest neighboring sites of the molecule. As  $\gamma$  becomes very large,  $q/\gamma \rightarrow 2/3$  for a linear chain and  $q/\gamma \rightarrow 0$  for a sphere. For a globular molecule,  $q/\gamma$  lies between zero and unity. Similarly, for the present two-dimensional solution, the shape of a domain can be characterized by the ratio  $L/nA_c$  between the perimeter ( $L$ ) and the surface area ( $nA_c$ ) of the domain. The analogy between the two-dimensional and the three-dimensional mixing entropy suggests that the parameter  $p$  should increase with increasing  $L/nA_c$ . Consequently, the large circular domains require a smaller value for  $p$  than the long striped domains with the same surface area. Thus, the large circular domains are expected to lead to a lower slope of the  $\pi$ - $A$  isotherm in the transition region than the long striped ones.

**The Effect of Domain Size.** According to eq 17, the equilibrium domain radius  $R$  is the product of two factors: one

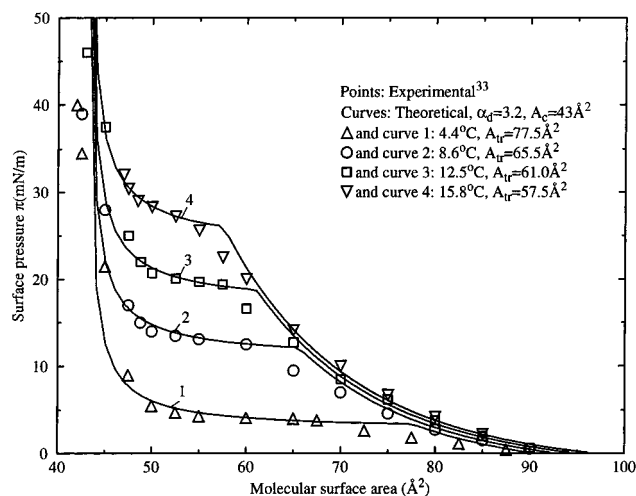


**Figure 3.** Effect of the domain size on the theoretical  $\pi$ - $A$  isotherm of 1,3-DPPC at 26 °C.

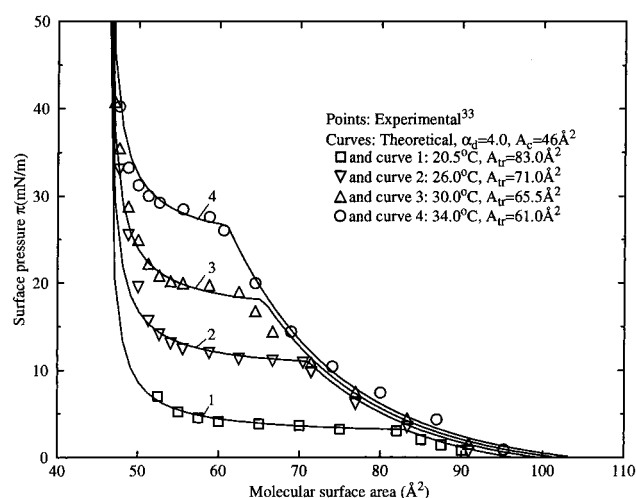
of them is the equilibrium radius  $R_0$  in the absence of other domains ( $\Phi_c = 0$ ), and the other one increases exponentially with the area fraction of the domains.  $R_0$  is determined by the line tension ( $\lambda$ ) and the difference  $\Delta\mu$  between the two-dimensional dipole moment densities of the LC domains and the LE molecules. Both  $\lambda$  and  $\Delta\mu$  depend on the molecular surface area difference ( $A_d - A_c$ ) between the LC and LE phases. Since  $A_c$  is assumed to be constant and  $A_d$  is considered to vary with the surface pressure,  $\lambda$  and  $\Delta\mu$  depend on the surface pressure (or on the area fraction of the domains). However, in the present treatment, the dependence (expected to be small) of  $R_0$  on the area fraction of the domains is neglected.

Figure 3 presents the effect of  $R_0$  on the theoretical  $\pi$ - $A$  isotherm of the 1,2-DPPC surfactant at 26 °C. As expected, a smaller domain size results in a larger slope in the LE/LC transition region, while a larger one, in a smaller slope. For the range in which the calculations have been carried out, the theoretical isotherm has the largest slope for  $R_0 = 0.01\mu\text{m}$ , which corresponds to a domain containing about 680 molecules. For  $R_0 \rightarrow \infty$ , the theoretical isotherm exhibits a horizontal line in the transition region. In the latter case, the two-dimensional mixture contains only a single LC domain, and the surface area of a disordered molecule  $A_d$  becomes independent of the surface pressure. The experimental  $\pi$ - $A$  data in the transition region lie between the theoretical isotherms for  $R_0 = 0.5\mu\text{m}$  and  $R_0 = 500\mu\text{m}$ . Using an intermediate value ( $5\mu\text{m}$ ) for  $R_0$ , good agreement between the theoretical and experimental results is obtained. In addition, one can see that increasing  $R_0$  by 2 orders of magnitude from  $5\mu\text{m}$  to  $500\mu\text{m}$ , the theoretical isotherm does not vary too much. For this reason, in the present calculation,  $R_0$  is taken to be equal to  $5\mu\text{m}$  for all surfactants and all temperatures (in some cases, a somewhat better agreement with experiment can be obtained by using a different value for  $R_0$ ). It is important to emphasize that the radius  $R$  given by eq 17 increases exponentially with  $\Phi_c$ . Taking  $R_0 = 5\mu\text{m}$ ,  $R$  increases to 13, 36, and  $105\mu\text{m}$  for  $\Phi_c = 0.5, 0.75$ , and  $0.95$ , respectively, values which are in the range found experimentally.

**Comparison with Experiments.** A comparison between the theoretical and experimental isotherms is presented in Figures 4–8. For all the surfactants, the exponent  $p$  in the mixing entropy model is taken to be equal to 0.93 and  $R_0$  to be  $5\mu\text{m}$ . The selected values of the parameters  $\alpha_d$ ,  $A_c$ , and  $A_d$  are listed in the figures. For all the systems, the theoretical and experimental isotherms exhibit a nonhorizontal line in the LE/



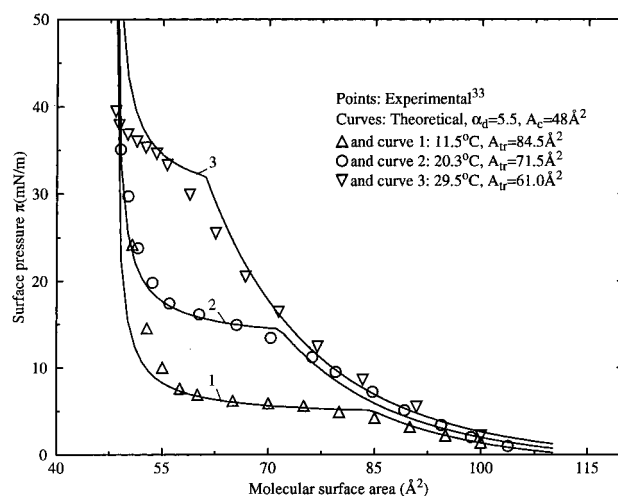
**Figure 4.**  $\pi$ - $A$  isotherms of 1,2-dimyristoylphosphatidylcholine at four temperatures.



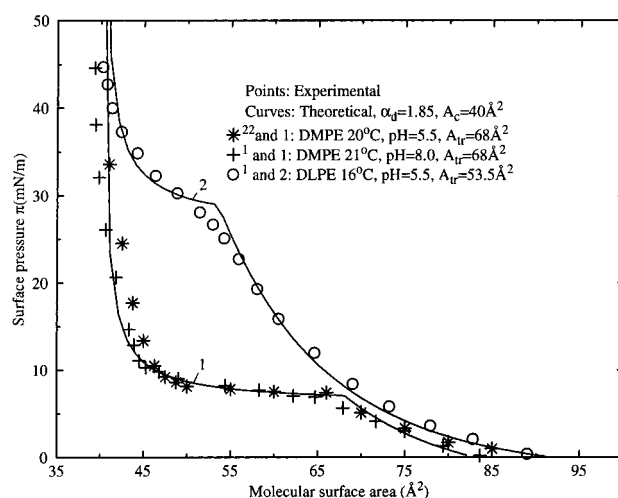
**Figure 5.**  $\pi$ - $A$  isotherms of 1,2-dipalmitoylphosphatidylcholine at four temperatures.

LC transition region and a smoothly rising continuous curve at the high surface density end of the transition. For most of the 19 isotherms, very good agreement between the theoretical and experimental isotherms is obtained over the entire range of molecular surface densities. For the 1,3-DPPC and DMPA surfactants at temperatures close to the critical point (curve 3 of Figure 6 and curve 6 of Figure 8), the theoretical isotherms exhibit a somewhat larger slope than the experimental one. This arises probably because the theoretical model overestimates the mixing entropy (by taking  $p = 0.93$ ) at the higher temperature. Good agreement can be, however, reached by using a somewhat smaller value for the parameter  $p$ .

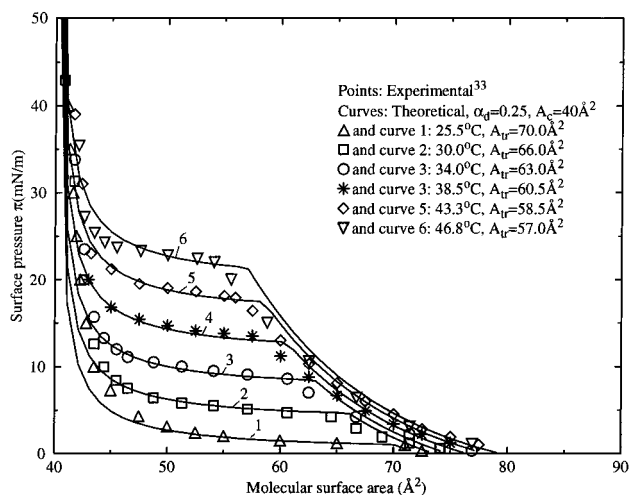
The value of  $\alpha_d$ , which accounts for the dipole-dipole interaction, was obtained by fitting the model to a single experimental point of the isotherm in the LE region. The determined value of  $\alpha_d$  allows one to estimate the effective dipole moment perpendicular to the air/water interface. Figures 4–6 and 8 show that using the values of  $\alpha_d$  determined from single points, the model can predict well the dependence of the isotherms on temperature in the LE region. For the surfactants with the same headgroup, the same value of  $\alpha_d$  is expected. Indeed, the value  $\alpha_d = 1.85$  can be used for both DMPE and DLPE surfactants (Figure 7). However, for the pair of surfactants DMPC and 1,2-DPPC, which have the same headgroup, two different values ( $\alpha_d = 3.2$  and  $4.0$ , respectively) were



**Figure 6.**  $\pi$ - $A$  isotherms of 1,3-dipalmitoylphosphatidylcholine at three temperatures.



**Figure 7.**  $\pi$ - $A$  isotherms of 1,2-dilauroylcephalin and 1,2-dimyristoylphosphatidylethanolamine.



**Figure 8.**  $\pi$ - $A$  isotherms of 1,2-dimyristoylphosphatidic acid at six temperatures.

required to fit the experimental data in the LE region. This probably occurs because the hydrocarbon chain of a surfactant molecule affects the dipole-dipole interactions. For the pair of surfactants, 1,2-DPPC and 1,3-DPPC, which possess the same headgroup and the same hydrocarbon chains but different connecting configurations between the hydrocarbon chains and



the headgroup, two very different values ( $\alpha_d = 4.0$  and  $5.5$ , respectively) were required to fit the experimental data in the LE region. Finally, the surfactant DMPA, which has a headgroup with a very small dipole moment, requires as expected a small value for  $\alpha_d$  ( $=0.25$ ).

In this model, the surface area of disordered molecules ( $A_d$ ) is considered to vary with the surface pressure. In the LE region,  $A_d$  is equal to the average molecular surface area  $A$ , while in the transition region,  $A_d$  is larger than  $A$  and tends to become constant with decreasing slope of the isotherm. The molecular surface area in the LC state ( $A_c$ ) is taken to be constant for a given surfactant, although experiment<sup>23</sup> shows that it varies in a small range. Among the factors that affect the value of  $A_c$ , the structure and size of the headgroup are expected to be the most important. Obviously, a large headgroup should result in a larger value of  $A_c$ . For the three surfactants, DMPC, 1,2-DPPC, and 1,3-DPPC (Figures 4–6), with a larger headgroup (–PC) larger values of  $A_c$  ( $=43 \text{ \AA}^2$  for DMPC,  $46 \text{ \AA}^2$  for 1,2-DPPC, and  $48 \text{ \AA}^2$  for 1,3-DPPC) while for the three surfactants, DMPE, DLPE and DMPA (Figures 7 and 8), with smaller headgroups (–PE or –PA) the smaller value of  $A_c$  ( $=40 \text{ \AA}^2$ ) was required to get agreement with the experimental isotherms.

## Conclusions

A surface equation of state is derived which leads to a  $\pi$ – $A$  isotherm that exhibits a nonhorizontal line in the phase transition region. The generalized Flory model suggested by Donohue and Prausnitz<sup>30</sup> is employed for the calculation of the two-dimensional mixing entropy and the equation derived by McConnell et al.<sup>26–29</sup> for the calculation of the mixing energy. By minimizing the Helmholtz free energy of the monolayer, the equilibrium radius and the equilibrium area fraction of the LC domains are obtained as a function of the average molecular surface area  $A$ . The mixing entropy provides a negligible effect on the domain size, but is very important in the calculation of the equilibrium area fraction of the domains. The  $\pi$ – $A$  isotherm in the phase transition region depends on the two-dimensional mixing entropy and on the size of the domains. The theoretical

$\pi$ – $A$  isotherms are in good agreement with the experimental ones for six phospholipid surfactants.

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