

# Influence of the Two-Dimensional Compressibility on the Surface Pressure Isotherm and Dilational Elasticity of Dodecyldimethylphosphine Oxide

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A model for the surface pressure isotherm and high frequency limit of dilational elasticity of a surfactant adsorption layers is proposed which assumes a two-dimensional compressibility of adsorbed molecules. While this compressibility has almost no significant effect on the isotherm, the elasticity is enormously affected. Experimental data for dodecyldimethylphosphine oxide (C<sub>12</sub>DMPO) show very good agreement with the model when a compressibility coefficient  $\epsilon$  of about 0.007 m/mN is introduced.

## Introduction

It is shown in a number of experimental studies that at high oscillation frequencies, when the exchange of matter with the solution can be ignored, and in the absence of other relaxation processes within the interfacial layer, the dilational elasticity of a surfactant solution levels off or even passes through a maximum with increasing surfactant concentration.<sup>1–6</sup> So far there was no satisfactory explanation given for this effect in the framework of existing concepts of surface elasticity. Only recently was a new interpretation published that explains this effect on the basis of a finite compressibility of the surfactant adsorbed molecules.<sup>7</sup> In the framework of the intrinsic compressibility of Langmuir type interfacial layers, experimental limiting (high frequency) elasticities of some surfactants have been satisfactorily described by a qualitative model. At the same time, the assumption of a two-dimensional compressibility does not significantly affect the shape of the surface tension isotherm.

This work aims at the generalization of the model presented in ref 7 to the case of the Frumkin isotherm and the comparison between experimental and theoretical values of the equilibrium surface tension (pressure) and limiting elasticity for solutions of the nonionic surfactant dodecyldimethylphosphine oxide.

## Theory

In our previous publication,<sup>7</sup> a large number of synchrotron X-ray diffraction (grazing incidence X-ray diffraction, GIXD) data for liquid-condensed monolayers were analyzed. It was shown that the molar area of a surfactant in the condensed state (i.e., the value inverse to saturation adsorption,  $\omega = 1/\Gamma_\infty$ ) can be approximately represented by a linear dependence on surface pressure  $\Pi$

$$\omega = \omega_0(1 - \epsilon\Pi) \quad (1)$$

where  $\omega_0$  is the molar area determined from zero monolayer pressure extrapolation and  $\epsilon$  is the two-dimensional relative

monolayer compressibility coefficient, which characterizes the intrinsic compressibility of the molecules in the monolayer.

It is commonly accepted to consider the saturation adsorption in Langmuir or Frumkin models,  $\Gamma_\infty$ , and the molar area of a surfactant,  $\omega = 1/\Gamma_\infty$ , as constants independent of surface pressure. This is obviously an idealization (corresponding to the “hard core” model), which can be used only when the monolayer is in a state not very close to saturation. Equation 1 represents the most simple, linear dependency of the molar area of a surfactant in a state close to saturation on surface pressure. For the saturation adsorption one obtains from eq 1  $\Gamma_\infty = \Gamma_{\infty(0)}(1 - \epsilon\Pi)^{-1}$  where  $\Gamma_{\infty(0)} = 1/\omega_0$ .

Here the “two-dimensional compressibility” is referred to, because a decrease in  $\omega$  can be accompanied by an increase in the thickness of the monolayer. Generally, the larger is the polar (alkyl chain) tilt angle with respect to the normal at low pressures, the higher is the  $\epsilon$  value.<sup>7</sup> During compression of the monolayer, the tilt angle becomes lower; therefore, the area per molecule becomes smaller and the monolayer becomes thicker.

Using eq 1 and the equations of state, the adsorption isotherm  $\Gamma(c)$  and the limiting elasticity  $E(c)$  derived in ref 7 a set of equations can be constructed, including the intermolecular interaction according to the Frumkin model

$$\frac{\Pi\omega_0(1 - \epsilon\Pi)}{RT} = -\ln(1 - \theta) - a\theta^2 \quad (2)$$

$$bc = \frac{\theta}{(1 - \theta)} \exp(-2a\theta) \quad (3)$$

$$E = \frac{d\Pi}{d(\ln \Gamma)} \quad (4)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $b$  is the adsorption constant,  $c$  is the surfactant bulk concentration,  $a$  is the (Frumkin) interaction constant, and  $\theta$  is the monolayer coverage, which is a function of surface pressure and the compressibility coefficient  $\epsilon$ :

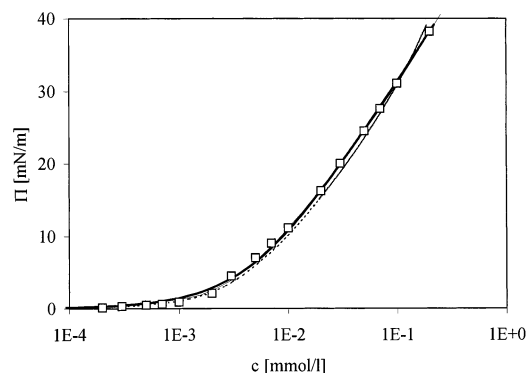
$$\theta = \Gamma\omega = \Gamma\omega_0[1 - \epsilon\Pi] \quad (5)$$

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**Figure 1.** Plots of experimental data from ref 8 ( $\square$ ) and theoretical dependencies calculated for case 1 (solid line) and cases 2–4 (thin dotted line) using the parameters of Table 1.

The limiting elasticity  $E(c)$ , eq 4, represents the high-frequency limit of the surface dilational elastic modulus, assuming that no exchange with the solution takes place, and in the absence of any other relaxation processes at the interface. This quantity is sometimes called Gibbs elasticity.<sup>5,6</sup>

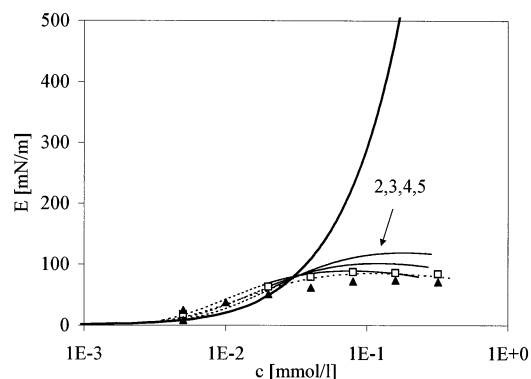
The set of eqs 2–5 cannot be solved analytically; therefore, an iterative numerical procedure was employed. The relative error for the calculation of surface pressure  $\Pi$  and limiting elasticity  $E$  did not exceed  $10^{-4}$ .

As it was shown by us previously,<sup>7</sup> two mechanisms determining the limiting elasticity  $E$  of a monolayer should be generally accounted for: the change of the surfactant adsorption  $\Gamma$  (change of the number of molecules on a unit surface area) and the intrinsic (two-dimensional) compressibility of the surface layer (change in the lateral sizes of molecules). At high surface pressures, the second mechanism determines the elasticity  $E$ : the two-dimensional compressibility  $\epsilon$  sets the upper limit for  $E$  (for the Langmuir model  $E = 1/\epsilon^7$ ). At relatively small surface pressures the elasticity  $E$  is determined mainly by changes of the surfactant adsorption  $\Gamma$  at practically constant values of  $\omega$  and  $\Gamma_\infty$ , and the two-dimensional compressibility can be ignored. This is illustrated by the results presented below.

## Results and Discussion

The experimental dependence of surface pressure of dodecylmethylphosphine oxide ( $C_{12}$ DMPO) solutions at 25 °C (as reported in ref 8) is shown in Figure 1. The experimental limiting surface dilational elasticities for  $C_{12}$ DMPO solutions as taken from ref 9 are shown in Figure 2. The experimental data refer to the limiting (high) oscillation frequencies above 100 Hz, i.e., the elasticities have reached the respective plateau values (when the exchange of matter between solution bulk and interface can be neglected) which is known to correspond with the Gibbs elasticity modulus as described by eq 4.<sup>5,6</sup> Note that the two experimental studies were performed by one group, and all the  $C_{12}$ DMPO samples are of the same origin.

The theoretical surface tension and limiting elasticity isotherms were calculated according to eqs 2–5 with  $\epsilon = 0$  (case 1, the model parameters taken from ref 8), and with the parameter  $\epsilon$  varied in the range 0.006–0.008 m/mN (cases 2–4). Note that with the variation of the compressibility coefficient, the Frumkin model parameters  $\omega_0$  and  $a$  were also varied in order to obtain the best fit of the theoretical surface pressure isotherm to the experimental values, both shown in Figure 1. The optimum parameters are listed in Table 1, while the corresponding theoretical curves are plotted in Figures 1 and 2. The theoretical  $\Pi(c)$  dependencies which correspond to cases



**Figure 2.** Experimental surface dilational elasticity of  $C_{12}$ DMPO solutions at limiting (high) oscillation frequencies obtained using the oscillation bubble method<sup>9</sup> (symbols, related to two separate experiments). Theoretical dependencies were calculated for case 1 (solid line) and cases 2–4 (thin dotted line) using the other three sets of parameters given in Table 1; curve 5 was calculated using eqs 6 and 7.

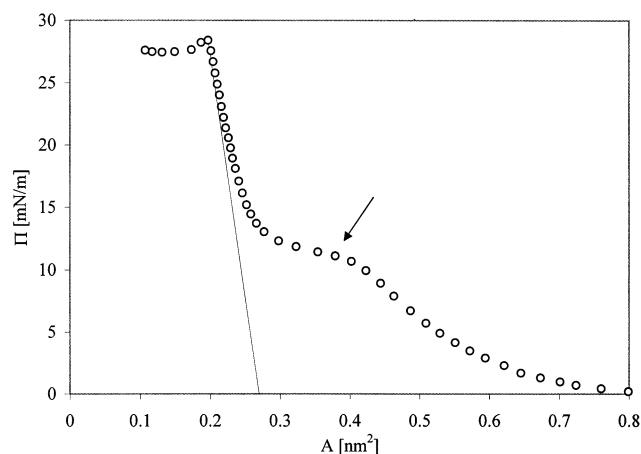
**TABLE 1: Parameters of the Theoretical Models of Eqs 2–5**

case	$\omega_0$ , $10^5$ m <sup>2</sup> /mol	$a$	$b$ , L/mmol	$\epsilon$ , m/mN
1	2.44	0.35	150	0.000
2	3.4	0.75	150	0.006
3	3.7	0.90	150	0.007
4	4.0	1.1	150	0.008

2–4 coincide with each other to within 0.2 mN/m. Thus, a single theoretical curve (that for case 3) is shown in Figure 1. This figure shows that the introduction of the parameter  $\epsilon$  into the theoretical model virtually does not affect the capability of the model to fit the experimental results. However, the higher is the  $\epsilon$  value, the higher (as compared to the case 1, with  $\epsilon = 0$ ) should be the values of the parameters  $\omega_0$  and  $a$ . It follows then, that there is an almost infinite number of compressibility coefficients which allow to describe the experimental  $\Pi(c)$  isotherm. In addition to the values indicated above, the  $\epsilon$  parameter was varied in the range between 0.001 and 0.01 m/mN. It is interesting to note that for the limiting surface pressures of the  $C_{12}$ DMPO solutions (e.g., 40 to 45 mN/m), the molar area values (with the compressibility taken into account) were found almost equal to  $\omega_0$  obtained for the case 1, where the compressibility was disregarded. In fact, introducing  $\omega_0$  and  $\epsilon$  from Table 1 into eq 1, one obtains  $\omega_0 = (2.5\text{--}2.7) \times 10^5$  m<sup>2</sup>/mol for cases 2–4 at  $\Pi = 40\text{--}45$  mN/m.

Figure 2 illustrates the dramatic influence of the compressibility coefficient on the limiting elasticity. If  $\epsilon = 0$  is assumed for  $C_{12}$ DMPO concentrations above 0.04 mmol/L, an almost exponential increase of the theoretical  $E$  values is observed (at a concentration of 0.3 mmol/L we obtain  $E = 1000$  mN/m), which is in contrast to the experimental data. For values of  $\epsilon$  between 0.007 and 0.008 m/mN, an almost quantitative agreement with the experiment is reached. In line with the experiments, also the theoretical dependencies exhibit a maximum in the  $E(c)$  dependence.

The optimum value of  $\epsilon = 0.007\text{--}0.008$  m/mN determined for  $C_{12}$ DMPO can be compared with independent experimental results. (Note that, unfortunately, up to now these experiments and estimates could be performed only for monolayers in the liquid-condensed state). Figure 3 illustrates the surface pressure dependence on the area per molecule for  $C_{20}$ DMPO monolayers.<sup>10</sup> It is seen that the monolayer of the insoluble  $C_{20}$ DMPO undergoes a two-dimensional phase transition from a liquid-



**Figure 3.** Dependencies of surface pressure as a function of the area per molecule in a  $C_{20}$ DMPO monolayer.<sup>10</sup> The line shows the molar area as a function of surface pressure for the liquid-condensed monolayer state.

expanded (gaseous) state to the liquid-condensed state (as shown by an arrow in Figure 3). It is recommended to determine the  $\omega_0/N$  value from the intersection point of the tangent line to the  $\Pi$ - $A$  isotherm in the liquid-condensed state (shown by the line in Figure 3) with the abscissa axis.<sup>11</sup> The straight line built in this way gives the dependence of the molecular area  $\omega/N$  for the  $C_{20}$ DMPO on the monolayer pressure (here  $N$  is the Avogadro number). Note that in refs 12–16 for various systems the GIXD technique was employed simultaneously for structural characteristics of the condensed phase, and studies of  $\Pi$ - $A$  isotherms. It can be seen from the analysis of these data that the  $\omega(\Pi)$  dependencies obtained from GIXD almost coincide with those calculated from the tangent to the  $\Pi$ - $A$  isotherm in the liquid-condensed state. The value of  $\epsilon = 0.0095$  m/mN for the  $C_{20}$ DMPO, which corresponds to the straight line in Figure 3, agrees well with the value of the two-dimensional compressibility coefficient for  $C_{12}$ DMPO calculated above from the best fit between experimental and theoretical dependencies of limiting elasticity on concentration.

Note that the form of the equation to describe the adsorption process can depend on the choice of the dividing surface. Equations 2 and 3 follow from a model of the two-dimensional solution theory (see eqs 13 and 14 in ref 17) using the dividing surface concept of Lucassen-Reynders. This concept is based on the assumption that the adsorption of the solvent is not zero and the molar area of solvent and solute are identical. In our theoretical model of a compressible interfacial layer both requirements are fulfilled by eq 1.

Let us compare the eqs 2 and 3 with the thermodynamic model of the Gibbs dividing surface (adsorption of the solvent is assumed to be zero). From the Gibbs adsorption equation and our eqs 2 and 3, we obtain

$$\Gamma = \frac{c}{RT} \frac{d\Pi}{dc} = \frac{c}{RT} \frac{d\Pi}{d\theta} \frac{d\theta}{dc} = \frac{\theta}{\omega_0(1 - 2\epsilon\Pi)} \quad (6)$$

Equations 5 and 6 differ from each other by a factor of 2. To agree with the model of Gibbs, eq 2 has to be modified:

$$\frac{\Pi\omega_0(1 - \epsilon\Pi/2)}{RT} = -\ln(1 - \theta) - a\theta^2 \quad (7)$$

The factor of  $1/2$  to  $\epsilon$  has no significant effect on the course of the surface pressure and elasticity isotherms. Moreover, a comparison with experimental data shows that the use of eq 7 instead of eq 2 yields about the same values for  $\epsilon$ . In Figures 1 and 2 the lines show the results of calculation using eqs 3–5 (curves 1–4) and eqs 6 and 7 for  $\epsilon = 0.008$  m/mN,  $a = 0.9$ ,  $b = 150$  L/mmol, and  $\omega_0 = 3.3 \times 10^5$  m<sup>2</sup>/mol (curve 5). We can see that the model is not very sensitive with respect to the choice of the dividing surface.

## Conclusions

To summarize, the consideration of a compressibility coefficient in the theoretical model of surfactant adsorption layers at the water/air interface yields good agreement between experimental and theoretical limiting elasticities. The obtained values of the compressibility coefficient are in very good agreement with independently determined data.<sup>12–16</sup> Note that this compressibility coefficient cannot be obtained from surface tension/pressure isotherms, as its influence on the shape of these dependencies is almost negligible. This coefficient can be determined only from dynamic experiments, such as harmonic perturbations at high frequencies. In turn, knowledge of the compressibility coefficient improves the quality of the description of the equilibrium properties of surfactant adsorption layers, such as the surface tension isotherm or the equation of state.

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