

Models of Two-Dimensional Solution Assuming the Internal Compressibility of Adsorbed Molecules: A Comparative Analysis

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The description of surface dilational rheology data by theoretical models has some general problems, essentially in the range of larger surface coverage. Typically, the dilational elasticity calculated from theoretical models increases with surfactant bulk concentration and reaches values so far not observed in any experiment. In contrast, the experimental elasticities in the high-frequency limit show an increase with concentration followed by a plateau or flat maximum. Various thermodynamic models for the state of interfacial layers are discussed with respect to the corresponding limiting dilational elasticity. With the reorientation model (Fainerman; et al. *J. Phys. Chem.* **1996**, *100*, 7669) and the additional assumption of an intrinsic compressibility of the assembled adsorption layer, the data for some oxyethylene surfactants and dodecyl dimethyl phosphine oxide are well described.

Introduction

In the absence of diffusional exchange of matter and other relaxation processes within the interface, the high-frequency limit of the surface dilational elasticity modulus (the limiting Gibbs elasticity) is given by $E_0 = d\Pi/d \ln \Gamma$, where Π is the surface pressure and Γ is the surfactant adsorption. Experimentally measured high-frequency elasticities at high surfactant concentrations are usually much smaller than those calculated according to the Langmuir or Frumkin isotherms.^{1–3} Recently, an explanation for this discrepancy on the basis of an intrinsic compressibility of interfacial layers was given.^{4–7} The proposed models describe experimental data on surface dilational elasticity, as well as on surface pressure at small and high surfactant concentration. It was shown that the two-dimensional compressibility coefficients obtained from these experiments were in a good agreement with data obtained from independent experiments.^{4,6}

In our previous work^{4,6,7} the compressibility was treated in the framework of approximate thermodynamic models. In the present manuscript, more rigorous equations are presented, based on the two-dimensional solution theory. The theoretical results are compared with experimental data obtained for dodecyl dimethyl phosphine oxide and oxyethylated alcohol solutions.

Theory

Thermodynamic models of adsorption layers that include solvent molecules are two-dimensional solution treatments. In

such models, expressions are derived for the thermodynamic surface potentials of solvent and solutes as a function of surface composition and surface tension. The expression proposed by Butler⁸ was generalized to be applicable to a properly localized Gibbs dividing surface, first for molecules of small surface area^{9,10} and subsequently for macromolecules.¹¹ In ref 12 more general relationships for the chemical potentials in the surface μ_i^s and in the solution bulk μ_i^α of each component i were presented, which follow from thermodynamic models for a two-dimensional solution:

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

which is the generalized Butler equation,^{13,14} and

$$\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln f_i^\alpha x_i^\alpha \quad (2)$$

Here R is the gas law constant, T is the temperature, γ is the surface tension, f_i are the activity coefficients (standardized at $f_i = 1$ for $x_i = 1$), ω_i are the partial molar areas, $x_i = N_i/\Sigma N_i$ are the molar fractions, and N_i are the numbers of moles of the i th component, whereas the superscript 0 denotes the standard state. Taking into account contributions to the activity coefficients caused by the nonideality of entropy (resulting from the difference between the molar areas of the solvent and surfactant) and the enthalpy of mixing (resulting from intermolecular interactions), and performing a rigorous reformulation of the problem in terms of surface coverage instead of surface molar fractions, one obtains the equation of state of the surface layer and the adsorption isotherm, respectively, for solutions of single surfactants adsorbed in a single state at the surface:¹²

$$\Pi = -\frac{RT}{\omega_0} [\ln(1 - \theta) + (1 - 1/n)\theta + a\theta^2] \quad (3)$$

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$$bc = \frac{\theta}{n(1 - \theta)^n} \exp[-2a\theta] \quad (4)$$

Here Π is the surface pressure, $\theta = \omega\Gamma$ is the surface coverage, Γ is the adsorption, ω is the molar area of the solute molecules, ω_0 is the molar area of a solvent molecules, $n = \omega/\omega_0$, c is the concentration of the surfactant in the solution bulk, a is the intermolecular interactions constant, and b is the adsorption equilibrium constant.

Model 1. Similarly to our previous work,^{4,6,7} it can be assumed that the molar area of the surfactant ω in eqs 3 and 4 depends linearly on the surface pressure:

$$\omega = \omega_0(1 - \epsilon\Pi) \quad (5)$$

where the proportionality factor ϵ is the relative two-dimensional compression ratio of the surfactant molecules in a packed surface layer. Note that using eq 5 under dynamical conditions of surface area oscillations at frequency f implies that the relaxation time of the molar area, determined mainly by the variation in the tilt angle of the surfactant hydrocarbon chain to the surface, is essentially lower than $1/f$.⁴ Using eq 5, one can express θ and n in eqs 3 and 4 as

$$\theta = \Gamma\omega = \Gamma\omega_0[1 - \epsilon\Pi] \quad (6)$$

$$n = 1 - \epsilon\Pi \quad (7)$$

Model 2. Neglecting the contribution of nonideality of entropy in eqs 3 and 4 results in $n = 1$. Therefore, these equations turn into the ordinary Frumkin model,

$$\Pi = -\frac{RT}{\omega_0}[\ln(1 - \theta) + a\theta^2] \quad (8)$$

$$bc = \frac{\theta}{(1 - \theta)} \exp[-2a\theta] \quad (9)$$

and the dependencies of ω and θ on Π obey eqs 5 and 6. This model was analyzed in ref 7.

In model 1, for $\Pi = 0$ the molar area of the surfactant is equal to that of the solvent, whereas at extremely high Π values (e.g., for $\Pi_{\max} = 40$ mN/m, which corresponds approximately to the CMC for ordinary surfactants) the value of ω becomes much less than ω_0 , because usually $\epsilon \cong 0.005\text{--}0.01$ m/mN.⁴

Model 3. Considering the actual geometry of the solvent and surfactant molecules, it is probably more appropriate to assume that the condition $\omega = \omega_0$ should hold for $\Pi_{\max} = \Pi_{\text{CMC}}$. In this case, for $\Pi = 0$ (and also for $\Pi < \Pi_{\max}$) the value of ω is larger than ω_0 . This corresponds to the model 3, which is described by eqs 3 and 4, and the additional relations

$$\omega = \omega_0(1 - \epsilon\Pi)/(1 - \epsilon\Pi_{\max}) \quad (10)$$

$$\theta = \Gamma\omega = \Gamma\omega_0[1 - \epsilon\Pi]/(1 - \epsilon\Pi_{\max}) \quad (11)$$

$$n = (1 - \epsilon\Pi)/(1 - \epsilon\Pi_{\max}) \quad (12)$$

instead of eqs 5–7.

Thus, models 1 and 3 differ in the choice of the solvent molar area. For the same value of the molar area of the surfactant (which in turn depends on Π), the value of ω_0 for model 3 is about 2 times lower than that for model 1; i.e. the dividing surface in model 3 is located about 0.1 nm deeper in the solution bulk as compared to model 1. This difference is, however, compensated by the factor n , which is higher for model 3.

Therefore, the values of adsorption, surface pressure, and limiting elasticity calculated for the two models are approximately the same. The fact that the results obtained from the two-dimensional solution model are quite insensitive to the choice of the ω_0 value is supported by the data reported in ref 17. It was shown there that a variation in ω_0 within the range of 1–4 times the actual molar area of water almost does not affect the results. Therefore, we present here only values calculated from model 1, which does not depend on the additional parameter Π_{\max} .

In addition to the models presented above, in which the ω_0 value is fixed (this is essential when the equation of state is derived from eqs 1 and 2; see ref 12), other models can be constructed, which assume that the molar surface area of the solvent ω_0^* depends also on Π in a manner similar to that determined by eq 5 for the ω dependence: $\omega_0^* = \omega_0(1 - \epsilon\Pi)$. This assumption corresponds to the ideal entropy of the surface layer ($n = 1$), again leading to the isotherm eq 9, and the equation of state (3) becomes⁴

$$\Pi = -\frac{RT}{\omega_0^*}[\ln(1 - \theta) + a\theta^2] = -\frac{RT}{\omega_0(1 - \epsilon\Pi)}[\ln(1 - \theta) + a\theta^2] \quad (13)$$

This model and also the semiempirical model based on the simultaneous solution of eqs 5 and 9 with the Gibbs equation

$$\Pi = -\frac{RT}{\omega_0(1 - \epsilon\Pi/2)}[\ln(1 - \theta) + a\theta^2] \quad (14)$$

were analyzed elsewhere.^{6,7} The last cannot be regarded as the two-dimensional solution model, because it assumes $\Gamma_0 = 0$. Note that this condition, in fact, corresponds to an infinitely large solvent molar area. In this case, however, the parameter ω_0 in eq 14 should be regarded as the molar area of the surfactant at $\Pi = 0$. The results that follow from the last two models are quite similar to those obtained from the approximate model 2 and will not be further discussed here.

Reorientation Model R. The relationships (5) or (10) in fact imply that the molar area of a surfactant is a variable quantity that becomes lower with increasing surface pressure or adsorption. This fact could be taken into account also in another way, assuming that there exist two (or more) orientations of the surfactant molecule adsorbed at the surface, with different molar areas ω_1 and ω_2 (for definiteness we assume $\omega_1 > \omega_2$). This reorientation model (R), for the case of ideal enthalpy and entropy of mixing of the surface layer, obeys the equation of state^{15,16}

$$\Pi = -\frac{RT}{\omega} \ln(1 - \theta) \quad (15)$$

and the adsorption isotherm equation

$$bc = \frac{\Gamma_2\omega}{(1 - \theta)^{\omega_2/\omega}} \quad (16)$$

where the total adsorption Γ and mean molar area ω are defined by

$$\Gamma = \Gamma_1 + \Gamma_2 \quad (17)$$

$$\omega\Gamma = \theta = \omega_1\Gamma_1 + \omega_2\Gamma_2 \quad (18)$$

TABLE 1: Characteristics of the Theoretical Models

model	characteristics of the interfacial layer
Fr	nonideal enthalpy ($a \neq 0$), no intrinsic compressibility ($\epsilon = 0$)
1	$a \neq 0$, $\epsilon \neq 0$, nonideal entropy, molar area of solvent (=const) and surfactant identical at $\Pi = 0$
2	$a \neq 0$, $\epsilon \neq 0$, ideal entropy, molar area of solvent = const
3	$a \neq 0$, $\epsilon \neq 0$, nonideal entropy, molar area of solvent (=const) and surfactant identical at $\Pi = \Pi_{\max}$
R	$a = 0$, $\epsilon = 0$, $\alpha \neq 0$, ideal entropy, two orientational states of the surfactant with different molar area and surface activity
RC	$a = 0$, $\alpha = 0$, ideal entropy, two orientational states of the surfactant with different molar area, $\epsilon \neq 0$ at minimum molar area

also involving the ratio of adsorption values in the two possible states of the molecule:

$$\frac{\Gamma_1}{\Gamma_2} = \exp\left(\frac{\omega_1 - \omega_2}{\omega}\right) \left(\frac{\omega_1}{\omega_2}\right)^\alpha \exp\left[-\frac{\Pi(\omega_1 - \omega_2)}{RT}\right] \quad (19)$$

where b_2 is the adsorption equilibrium constant in state 2 and α is a constant. The parameter α accounts for the fact that the adsorption equilibrium constant for the surfactant molecule in state 1 (with larger area) could exceed that in state 2, which results in an additional (in compare with $\alpha = 0$) increase of the fraction of the states of larger area. For $\alpha = 0$ the adsorption activity b_i of all states is the same. Other reorientation models (e.g., those which rigorously account for nonideal entropy of mixing) were discussed in ref 17. The reorientation model provides a perfect description of the adsorption behavior of oxyethylated surfactants,^{17,18} because the oxyethylene chain is capable of unfolding in the monolayer at low coverages, and for the desorption in a saturated surface layer. Note that the reorientation model differs essentially from models 1–3 with respect to the underlying principle employed to account for the variation of the molar area of the surfactant. In models 1–3 this is based on the phenomenological eq 5 or 10, which was verified experimentally for the condensed state of surfactant molecules in a monolayer.⁴ On the contrary, the reorientation model, eqs 15–19, is based solely on the Butler equation (1), which states that the chemical potential of adsorbed molecules is determined by their molar area. In this case, as the chemical potential depends on the surface pressure, the increase of the surface pressure leads to the increase in the fraction of states characterized by a minimum area, cf. eq 19, which results in a decrease of the mean molar area.

Combined Reorientation Model RC. As the mechanism responsible for the variation of the molar area in models 1–3 is different from that characteristic of the reorientation model, it seems possible to arrange a combined model (RC model), which assumes both the reorientation of molecules and the variation of the molar area in the state with lower area 2 caused by a two-dimensional compressibility according to eq 5, i.e., $\omega_2 = \omega_0(1 - \epsilon\Pi)$. For the sake of simplicity, we avoid the increase of the number of parameters in the RC model by assuming $\alpha = 0$. In Table 1 all proposed models with their peculiarities are summarized.

The limiting value of the Gibbs elasticity modulus $E_0 = d\Pi/d \ln \Gamma$ can be calculated by the differentiation of the equation of state taking into account the dependence of Γ on θ . For the Frumkin model (eqs 8 and 9 with $\omega = \omega_0 = \text{const}$) one obtains

$$E_0 = \frac{RT}{\omega} \left(\frac{\theta}{1 - \theta} - 2a\theta^2 \right) \quad (20)$$

The corresponding expression for model 2 was derived in ref 7. A summary of the expressions for E_0 for the various models given above, assuming the intrinsic compressibility of the surfactant molecules, is as follows:

Model 1

$$E_0 = \frac{\frac{\theta}{1 - \theta} + \frac{\epsilon\Pi\theta}{1 - \epsilon\Pi} - 2a\theta^2}{\frac{\omega_0}{RT} + \frac{\epsilon\theta^2}{1 - \epsilon\Pi} \left(\frac{1}{1 - \theta} - 2a \right)} \quad (21)$$

Model 2

$$E_0 = \frac{\frac{\theta}{1 - \theta} - 2a\theta^2}{\frac{\omega_0}{RT} + \frac{\epsilon\theta}{1 - \epsilon\Pi} \left(\frac{1}{1 - \theta} - 2a\theta \right)} \quad (22)$$

Model 3

$$E_0 = \frac{\frac{\theta}{1 - \theta} - \frac{\epsilon\theta[\Pi_{\max} - \Pi]}{1 - \epsilon\Pi} - 2a\theta^2}{\frac{\omega_0}{RT} + \frac{\epsilon\theta^2}{1 - \epsilon\Pi} \left(\frac{1}{1 - \theta} - 2a \right)} \quad (23)$$

It is interesting to compare the limiting Gibbs elasticity modulus for the Frumkin model (Fr) with those for models 1–3 at $\theta \rightarrow 1$. It follows from eq 20 for $\theta \rightarrow 1$ that $E_0 \rightarrow \infty$, in contradiction to all experimental results available. In contrast, each of models 1–3 yields the same finite value of E_0 at $\theta \rightarrow 1$:

$$E_0 = \frac{1 - \epsilon\Pi}{\epsilon} \quad (24)$$

In particular, for $\epsilon = 0.005$ – 0.01 m/mN, which is usual for common surfactants,⁷ and $\Pi = 40$ mN/m it follows from eq 24 that $E_0 = 160$ – 60 mN/m, in qualitative agreement with experimental data.

For the reorientation models (R and RC) described by eqs 15–19 the dependence of Γ on θ is rather involved, leading to quite complicated expression for E_0 . Therefore, this model was only analyzed numerically.

Results and Discussion

The experimental dependence of surface pressure of dodecyl-dimethylphosphine oxide (C₁₂DMPO) solutions at 25 °C, as reported in ref 18, is shown in Figure 1, and the experimentally determined surface dilational elasticities for C₁₂DMPO solutions are shown in Figure 2 (taken from refs 19 and 20). The experimental data refer to the limiting (high) oscillation frequencies; i.e., the elasticities have reached the respective plateau values where the exchange of matter between solution bulk and interface becomes negligible.

The theoretical surface tension and surface dilational elasticity isotherms were calculated according to models 1, 2, Fr, and R. For model RC the results are quite similar to those obtained for model R and therefore are not discussed here. The calculations were performed using a software described elsewhere in detail²¹ and modified to implement the formulation of the system

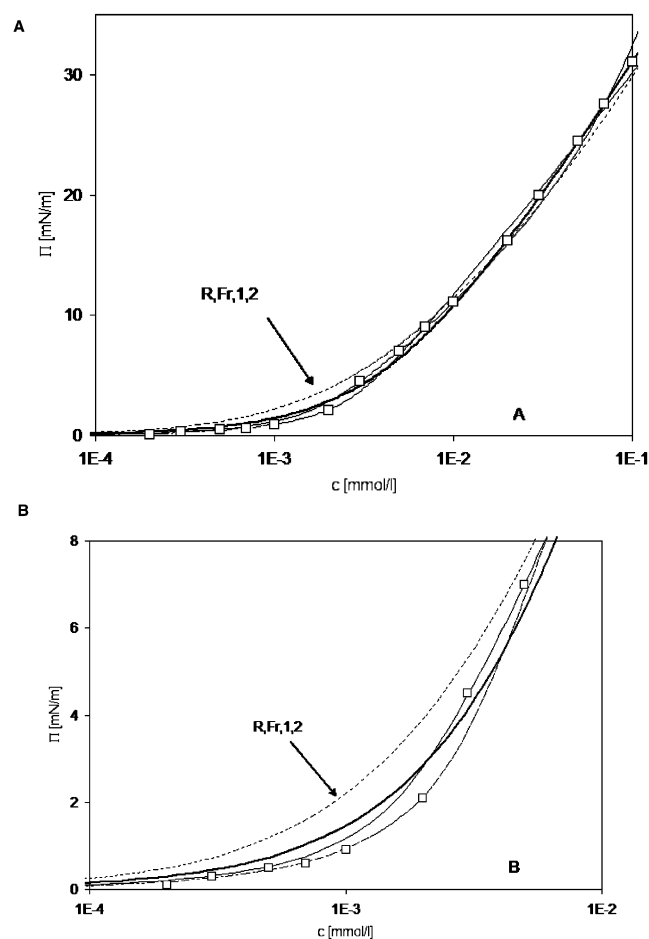


Figure 1. Experimental dependencies of surface pressure Π vs concentration for dodecyltrimethylphosphine oxide solutions from ref 18 (\square). The low-concentration range is shown in Figure B. Theoretical dependencies for the Frumkin model (bold line) and models 1, 2, and R (thin lines) were calculated with the parameters given in Table 2.

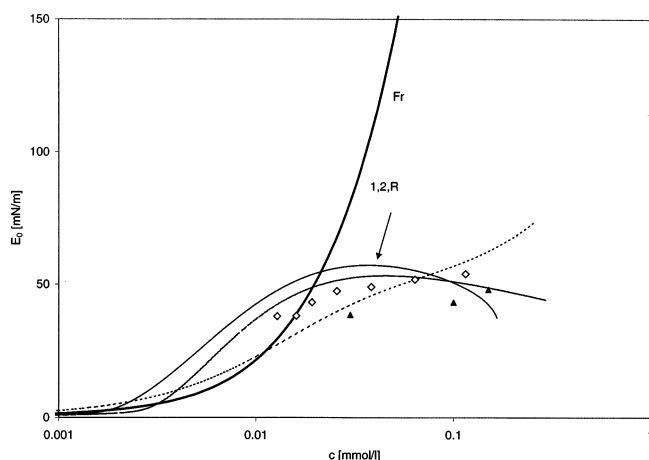


Figure 2. Experimental surface dilational elasticity of C_{12} DMPO solutions at limiting (high) oscillation frequencies obtained using the oscillating bubble method¹⁹ (\diamond) and ref 20 (\blacktriangle); notation of the theoretical curves as in Figure 1.

studied here. Model parameters were varied to obtain the best fit between the experimental and theoretical values, as shown in Figures 1 and 2. The optimum parameters are listed in Table 2, whereas those corresponding to theoretical curves are plotted in Figures 1 and 2. Models Fr, 1, and 2 lead to roughly equal errors when applied to describe the experimental Π vs c dependence, as shown in Figure 1, whereas for model R this

TABLE 2: Parameters of the Theoretical Models for C_{12} DMPO

model	ω_0 , 10^5 m ² /mol	a (or α)	b (or b_2), L/mmol	ϵ , m/mN
1	4.45	1.3	176	0.012
2	3.0	1.2	114	0.012
Fr	2.48	0.38	149	
R	4.0; 1.8 ^a	1.5	54	

^a ω_1 and ω_2 values, respectively.

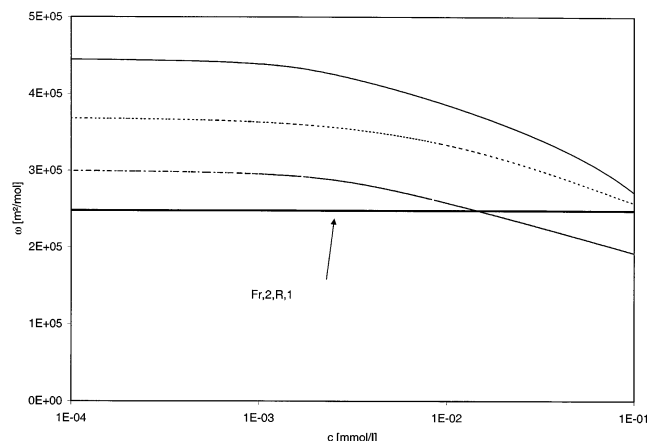


Figure 3. Dependence of the molar area of C_{12} DMPO on the concentration calculated from various models; notation of the theoretical curves as in Figure 1.

error is approximately 2 times higher. Figure 1b illustrates the initial portion of the Π vs c plot: also in this concentration range the models that account for the internal compressibility of the molecules provide better agreement with the experiments than Frumkin's model does.

The experimental dependence of E_0 on c (see Figure 2) is well described by models 1 and 2. The reorientation model provides quite satisfactory agreement of E_0 vs c data with the experimental dependence. At the same time, the Frumkin model (with $\omega = \text{const}$) predicts a sharp increase of E_0 with C_{12} DMPO concentration, in drastic contrast with the experimentally observed values.

The specific feature of the models that assume the internal compressibility and reorientation of surfactant molecules is the decrease of the molar area with increasing concentration. Therefore, in Figure 3 the dependence of ω on c is shown as calculated from models 1, 2, and R. All these models predict that the C_{12} DMPO molar area in the saturated monolayer is about 1.5 times lower than that in the dilute monolayer.

The oscillating bubble method provides another experimental characteristic that could be compared with the value predicted by the theory of Lucassen and van den Tempel.^{22,23} For a diffusion-controlled adsorption the derivative $d\Gamma/dc$ can be calculated from the phase angle φ of the complex elasticity modulus and the oscillation frequency f using the relation⁷

$$\frac{d\Gamma}{dc} = \frac{\cos \varphi - \sin \varphi}{\sin \varphi} \sqrt{\frac{D}{4\pi f}} \quad (25)$$

where D is the diffusion coefficient. The experimental dependence of $d\Gamma/dc$ on the concentration of C_{12} DMPO calculated from eq 27 with $D = 4.4 \times 10^{-10}$ m²/s is shown in Figure 4. This dependence is compared with theoretical curves calculated from models 1, 2, and R. The reorientation model and the models that assume an internal compressibility of the molecules provide a much better fit to the experimental dependence of $d\Gamma/dc$ than the Frumkin model does. It should be also noted

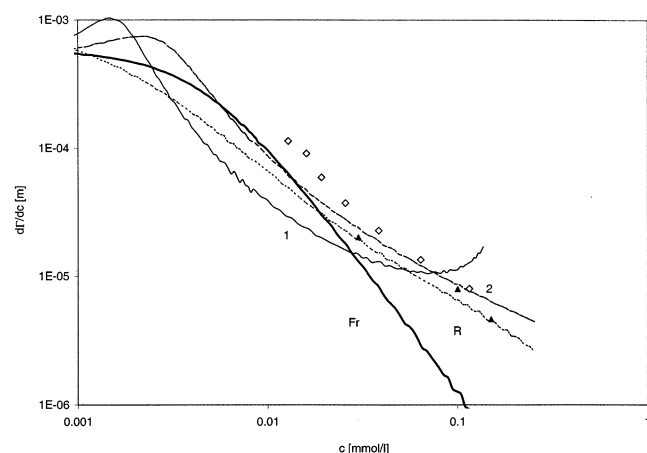


Figure 4. Average values $d\Gamma/dc$ vs concentration for $C_{12}DMPO$ solutions as obtained from the Lucassen/van den Tempel model from the data¹⁹ (\diamond) and ref 20 (\blacktriangle); notation of the theoretical curves as in Figure 1.

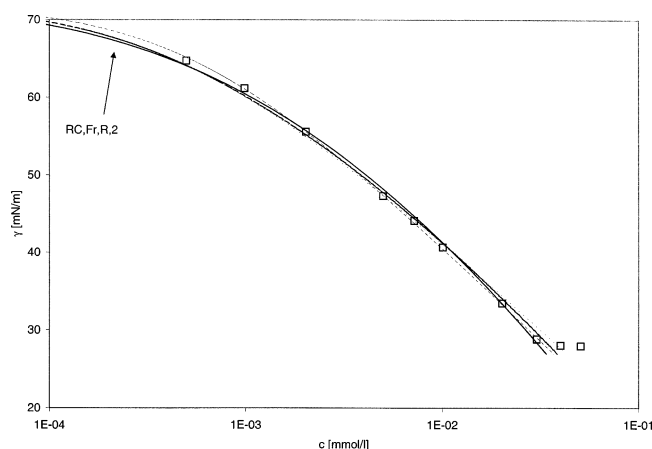


Figure 5. Experimental dependencies of surface pressure Π vs concentration for $C_{12}EO_3$ solutions from ref 24 (\square). Theoretical dependencies for the Frumkin model (solid line) and models 2, R, and RC (dotted lines) were calculated with the parameters given in Table 3.

that the experimental dependence of $d\Gamma/dc$ calculated for $D = 3 \times 10^{-10} \text{ m}^2/\text{s}$ is in perfect agreement with model 2. Note that the analytical expressions for $d\Gamma/dc$ corresponding to model 2 was derived in ref 7. The expressions for models 1 and 3 are quite cumbersome, and therefore not presented here.

Thus, only the account for the internal compressibility (or reorientation) of the $C_{12}DMPO$ molecules in the adsorbed layer leads to an agreement between the experimental and theoretical dependencies of the limiting dilational elasticity for $C_{12}DMPO$. The approximate model 2 (which disregards the nonideality of entropy) is capable of reproducing the experimental dependencies of E_0 and $d\Gamma/dc$ on concentration with an accuracy similar to that characteristic for the more rigorous models 1 (and 3), which both account for the two-dimensional entropy of mixing.

The data reported by Lucassen and Giles²⁴ for the oxyethylated dodecanol $C_{12}EO_3$ are illustrated in Figure 5 together with theoretical surface tension isotherms calculated from models 2, R and RC, and from the Frumkin model. The model parameters are listed in Table 3. Perfect agreement exists between all the models and the experimental data. Note, however, that the Frumkin model leads to large negative values of parameter a , which could not be ascribed to the van der Waals forces. This problem was discussed in more detail elsewhere^{17,18,25} with reference to oxyethylated alcohols of different

TABLE 3: Parameters of the Theoretical Models for $C_{12}EO_3$

model	$\omega_0, 10^5 \text{ m}^2/\text{mol}$	a (or α)	b (or b_2), L/mmol	ϵ , m/mN
2	2.32	0.0	1807	0.0075
Fr	1.5	-2.0	2354	
R	4.15; 1.95 ^a	1.1	789	
RC	4.3; 2.2 ^a		1210	0.0038

^a ω_1 and ω_2 values, respectively.

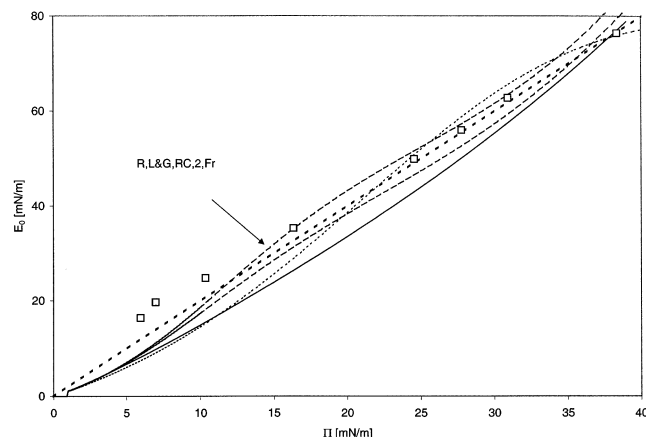


Figure 6. Dependence of the limiting Gibbs elasticity of $C_{12}EO_3$ solutions on surface pressure according to the data reported in ref 24 (\square); notation of the theoretical curves as in Figure 5. The bold dotted straight line represents the dependence $E_0 = 2\Pi$.

hydrocarbon chain lengths and different degree of oxyethylation. A negative value of the constant a corresponds to a repulsion between adsorbed molecules, which is characteristic to solutions of ionic surfactants.

Figure 6 illustrates the dependence of the limiting Gibbs elasticity of $C_{12}EO_3$ solutions on the surface pressure. The results obtained using all considered theoretical models agree well with the experimental data.²⁴ In Figure 6 the results for models Fr, R, RC and 2 are presented, and also the line of $E_0 = 2\Pi$, which was derived in ref 24 from eqs 8 and 20 for large negative a values, when the first term on the right-hand side of eq 8 becomes negligible. However, the a value is negative, and hence from a physical point of view the Frumkin model is inappropriate for a description of oxyethylated surfactants. Moreover, the fitting procedure with respect to parameters a and ϵ for the models Fr and 2 (and also for models 1 and 3) leads to very low values of the $C_{12}EO_3$ molar area at large concentrations. For example, at the CMC (which corresponds to $\Pi = 44 \text{ mN/m}$, cf. Figure 5) the ω values for the models Fr, 2, R, and RC are 1.5×10^5 , 1.55×10^5 , 2.18×10^5 , and $2.22 \times 10^5 \text{ m}^2/\text{mol}$, respectively, whereas the actual ω value for this surfactant at CMC (as obtained by the neutron reflection method²⁶) is $2.17 \times 10^5 \text{ m}^2/\text{mol}$, in good agreement with the values calculated from the reorientation models.

In ref 24 the oxyethylated alcohols $C_{12}EO_6$ and $C_{14}EO_6$ with long oxyethylene chain were also studied. The experimental surface tension isotherms for $C_{12}EO_6$ and theoretical isotherms calculated from the models 2, R and RC, and Fr are presented in Figure 7 (model parameters are listed in Table 4). Model 2 and Frumkin's model lead to very high negative a values. Note that also for models 1 and 3 the values obtained were $a = -(3-4)$, which is quite unjustified from physical considerations.

The data shown in Figure 8 for the dependence of the limiting Gibbs elasticity on surface pressure for $C_{12}EO_6$ ²⁴ agree well only with models 2 and RC. The RC model perfectly reproduces the experimental dependence indicating that the limiting value

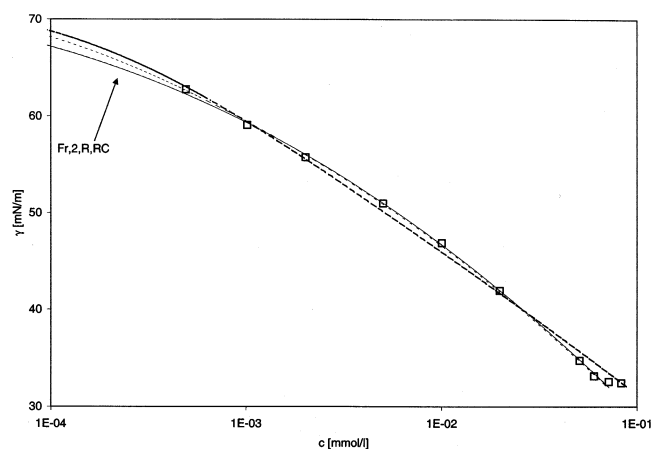


Figure 7. Experimental dependencies of surface pressure Π vs concentration for $C_{12}EO_6$ solutions from ref 24 (□). Theoretical dependencies for the Frumkin model (solid line) and models 2, R, and RC (dotted lines) were calculated with the parameters given in Table 4.

TABLE 4: Parameters of the Theoretical Models for $C_{12}EO_6$

model	ω_0 , 10^5 m ² /mol	a (or α)	b (or b_2), L/mmol	ϵ , m/mN
2	2.4	−3.5	15600	0.0052
Fr	2.1	−4.3	14965	
R	6.0; 2.7 ^a	2.5	990	
RC	6.0; 3.5 ^a		2775	0.009

^a ω_1 and ω_2 values, respectively.

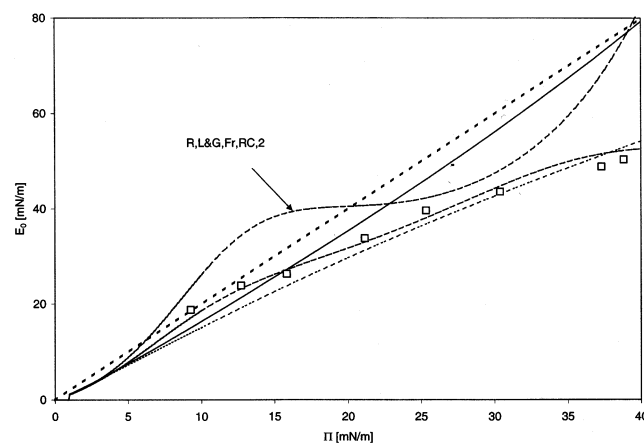


Figure 8. Dependence of the limiting Gibbs elasticity of $C_{12}EO_6$ solutions on surface pressure according to the data reported in ref 24 (□); notation of the theoretical curves as in Figure 7. The bold dotted line represents the dependence $E_0 = 2\Pi$.

of the elasticity modulus exists at high pressure (or concentration). In addition, only the RC model yields data that better agree with the molar area at CMC provided by the neutron reflection method: $\omega = 3.3 \times 10^5$ m²/mol as reported in ref 26 and 2.8×10^5 m²/mol from the RC model. At the same time, the corresponding values provided by models 2 and Fr are 1.9×10^5 and 2.1×10^5 m²/mol, respectively, which is much lower than the experimental data.

Conclusions

To summarize, the experimental data available for the adsorption and dilational rheological characteristics of the

monolayers of oxyethylated surfactants (especially those with high number of oxyethylene groups) at the solution/air interface are described in the best possible way by the combined reorientation model. This model assumes the ability of the oxyethylene groups to be adsorbed at the solution/air interface for low adsorption values, and to be partially desorbed with increasing surfactant adsorption,¹⁸ i.e., orientation of the EO groups, and also accounts for the internal compressibility of the molecule in the state with minimum molar area, i.e., the variation of the reorientation of the hydrocarbon chains. At the same time, the adsorption and rheological characteristics of surfactants that possess compact hydrophilic groups ($C_{12}DMPO$) are shown to agree well with the theoretical models that assume only the internal compressibility of the molecules, i.e., a reorientation of the hydrocarbon chains.

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