Note

Interpretation of surface-tension isotherms of *n*-alkanoic (fatty) acids by means of the van der Waals model

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Abstract

Here we apply the two-dimensional van der Waals model to interpret surface-tension isotherms of aqueous solutions of *n*-alkanoic (fatty) acids. We processed available experimental data for a homologous series of eight acids, from pentanoic to dodecanoic (lauric). Only three adjustable parameters have been varied to fit simultaneously all experimental curves. Excellent agreement between the theoretical model and the experiment has been obtained. The determined parameter values comply well with the molecular properties and allow one to calculate the surfactant adsorption, surface elasticity, and the surface pressure vs area isotherms. For the dodecanoic acid, the van der Waals model indicates the existence of a surface phase transition.
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1. Introduction

In a previous study [1] it was found that the van der Waals adsorption isotherm excellently fits the equilibrium surface tension of *n*-alkanols. The surface-tension isotherms for a homologous series of eight alkanols, from propanol to decanol (total 125 experimental points), have been fitted by variation of only 3 adjustable parameters. The agreement between the theoretical curves and the experimental points was very good, and the obtained parameter values were physically reasonable. In particular, the excluded area per molecule turned out to be equal to the geometrical cross section of the paraffin chain, and the adsorption energy per CH_2 group obeys the Traube rule. Having once determined the parameters of the van der Waals model, one can further predict the surface tension, adsorption, and the surface dilatational (Gibbs) elasticity for every given concentration of the amphiphilic substance (in this case for the alkanols).

It should be mentioned also that the van der Waals model has been successfully applied for interpreting the surface-tension isotherms of sodium dodecyl sulfate, SDS (at various salt concentrations) [2], of cationic surfactants—trimethyl ammonium bromides (C_nTAB, $n = 12, 14, 16$) [3], of sodium dodecylbenzene sulfonate [4] and cocoamidopropyl betaine [5]. In all cases, the excluded area per molecule (determined from the best fit) turned out to be equal to the geometrical cross section of the surfactant headgroup. The knowledge of the adsorption parameters for separate surfactants is very helpful when the van der Waals model is applied to surfactant mixtures, such as SDS + dodecanol [1], and SDS + cocoamidopropyl betaine [5].

Here our aim is to apply the van der Waals model to *n*-alkanoic acids (straight-chain fatty acids or *n*-alkyl carboxylic acids, $C_{n-1}H_{2n-1}COOH$); detailed review on their adsorption properties could be found in Ref. [6]. We processed available experimental data [6–8] for a homologous series of eight alkanoic acids, from pentanoic to dodecanoic (lauric). As in the case of alkanols [1], we varied only three adjustable parameters to fit simultaneously all experimental curves. The determined parameter values enable one to calculate the surfactant adsorption, surface (Gibbs) elasticity, and the surface pressure vs area isotherm (see below). The results would be useful for the interpretation of the surface tension of sodium alkanoate (soap) solutions which contain alkanoic acids due to hydrolysis of the alkanoates [9,10].

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2. Theoretical model

The van der Waals adsorption model can be derived by means of statistical mechanics, assuming nonlocalized adsorption [11–13]. The two-dimensional (surface) equation of state that relates the surface pressure, π_s, and adsorption, Γ, reads:

$$\pi_s = \frac{\Gamma kT}{1 - \alpha\Gamma} - \beta\Gamma^2. \tag{1}$$

Here k is the Boltzmann constant; T is the temperature; α is the excluded area per molecule; Γ has dimension of molecules per unit area, and β is a parameter, accounting for the interaction between the adsorbed molecules; $\pi_s = \sigma_0 - \sigma$ is the surface pressure, which equals the difference between the surface tension of the pure solvent, σ_0, and of the surfactant solution, σ. Substituting Eq. (1) into the Gibbs adsorption equation, $d\pi_s = -\Gamma kT\, d(\ln c)$, and integrating, we derive the adsorption isotherm that relates the surfactant concentration, c, with the adsorption, Γ [12–14]:

$$Kc = \frac{\alpha\Gamma}{1 - \alpha\Gamma} \exp\left(\frac{\alpha\Gamma}{1 - \alpha\Gamma} - \frac{2\beta\Gamma}{kT}\right). \tag{2}$$

Here K is an adsorption constant; see Eq. (5). Equations (1) and (2) give the theoretical dependence $\pi_s(c)$ (or $\sigma(c)$) in a parametric form: $c = c(\Gamma)$ and $\pi_s = \pi_s(\Gamma)$. The model contains three parameters, α, β, and K, which are to be determined from the fit of experimental data for $\sigma = \sigma(c)$. Having determined the latter parameters, one can calculate the surfactant adsorption, $\Gamma = \Gamma(c)$, from Eq. (2), and the surface (Gibbs) elasticity, $E_G = E_G(c)$, using the expression

$$E_G \equiv \frac{\partial\pi_s}{\partial\ln\Gamma} = \frac{\Gamma kT}{(1 - \alpha\Gamma)^2} - 2\beta\Gamma^2, \tag{3}$$

see e.g., [1,2]. To fit the data, we employed the least squares method. We numerically minimized the function

$$\Phi(\alpha, \beta, K) = \sum_{i=1}^{N} \big[\sigma_i(c_i) - \sigma_{th}(c_i; \alpha, \beta, K)\big]^2, \tag{4}$$

where N is the number of experimental points (c_i, σ_i), while σ_{th} is the theoretical value of the surface tension, calculated from Eqs. (1) and (2) for the same c_i.

3. Processing of isotherms for fatty acids

In Fig. 1, experimental surface tension isotherms for eight n-alkanoic acids from [6,7] are shown; see also [8]. To prevent dissociation of the alkanoic acid in water, the surface-tension measurements [6,7] have been performed in acid medium, in the presence of HCl at concentration $\geqslant 5$ mM (pH $\leqslant 2.3$).

Initially, we fitted separately the isotherm for each fatty acid using the model from Section 2. The calculated standard deviation, $\Delta\sigma \equiv [\Phi/(N-1)]^{1/2}$, was smaller than 0.3 mN/m for each isotherm (Φ and N are the same as in Eq. (4)). In all cases, the fitted areas per molecules were close to the value $\alpha = 23$ Å^2, which is about the area per headgroup in crystal structures of fatty acids [6]. The latter value is greater than the cross-sectional area of the paraffin chains, $\alpha = 20.7$ Å^2 for $n = 12$,

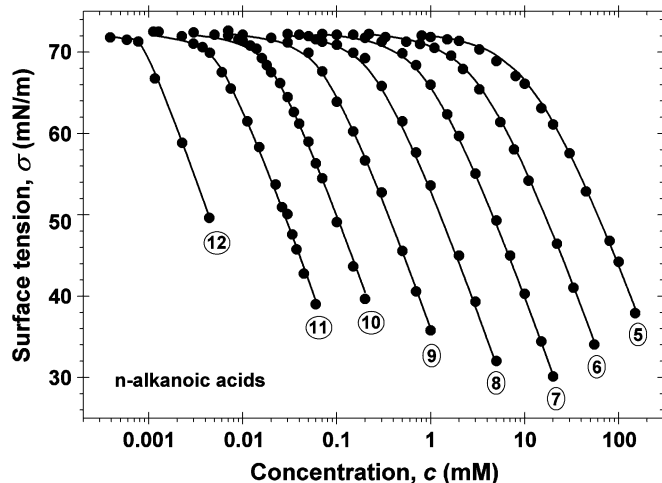Fig. 1. Equilibrium surface tension, σ, vs concentration, c, isotherms for aqueous solutions of n-alkanoic acids, $C_{n-1}H_{2n-1}COOH$, for $n = 5, \ldots, 12$, as denoted in the figure. The data for $n = 5, \ldots, 11$ are from Ref. [6] at $T = 22\,°C$, while the data for $n = 12$ are from Ref. [7] at $T = 20\,°C$. The solid lines represent the best fit by the van der Waals model; see Eq. (11).

estimated by means of the Tanford formula [15]; see also [1,16]. In other words, the excluded area for the n-alkanoic acids is determined by their headgroup, which is the same for all acids in Fig. 1. Consequently, we can try a model, in which α is *the same* for all fatty acids (see below). For this goal, we developed a new procedure for simultaneous processing of the surface-tension data for all acids, as follows.

The adsorption parameter, K, can be presented in the form [14,17]:

$$K = \alpha\delta\exp(E/kT), \tag{5}$$

where δ is the length of an adsorbed molecule (in direction normal to the interface) and E is the standard free energy of adsorption of a molecule from an ideal dilute solution in an ideal adsorption layer. In Eq. (5), α and δ scale the adsorption constant, K, with the characteristic molecular area and thickness of the adsorption layer, and thus define the characteristic adsorption energy per molecule; see Ref. [17]. After Tanford [15,16], we can estimate the molecular length as

$$\delta(n) = (0.154 + 0.1265n + 0.29) \text{ [nm]}. \tag{6}$$

Here n is the number of carbon atoms per molecule; the last additive, 0.29 nm, stands for the diameter of the terminal OH group of $C_{n-1}H_{2n-1}COOH$ [1,18], which is not dissociated at the experimental pH values. According to the Traube rule, we can express the adsorption energy in Eq. (5) in the form [1]:

$$E(n) = E_0 + 1.025nkT, \tag{7}$$

where $1.025kT$ ($= 604.5$ cal/mol) is the energy for transfer of one CH_2 group from the water into the air. It is convenient to introduce the dimensionless interaction parameter, $\hat{\beta}$:

$$\hat{\beta} \equiv \frac{2\beta}{\alpha kT}. \tag{8}$$

As in [1], we assume that the energy of interaction between two adsorbed surfactant molecules is proportional to their chain

lengths, i.e., to $0.154 + 0.1265n = 0.0275 + 0.1265(n + 1) \approx 0.1265(n + 1)$. Thus we could seek $\hat{\beta}$ in the form:

$$\hat{\beta} = (n + 1)\hat{\beta}_1, \qquad (9)$$

where $\hat{\beta}_1$ is the dimensionless energy of interaction per CH_2 group. Note that $\hat{\beta}$ depends not only on the chain length, but also on the minimal distance between the adsorbed molecules. As already mentioned, the area per molecule of n-alkanoic acids is larger that that of the n-alkanols, and therefore, $\hat{\beta}_1$ is expected to be somewhat smaller than the value 0.608 obtained for n-alkanols in [1]; see Eq. (11) below. Our preliminary fits of the separate isotherms showed that the expression $\hat{\beta} = (n + 1)\hat{\beta}_1$ is applicable for all fatty aids in Fig. 1, except that for $n = 12$.

The parameters α, $\hat{\beta}_1$, and E_0 are expected to be the same for all fatty acids in the range $5 \leqslant n \leqslant 11$. Therefore, we fitted simultaneously all data points belonging to these isotherms, total $N = 110$ points, and determined the values of the adjustable parameters corresponding to the best fit. The used merit function is analogous to that in Eq. (4) but expressed in terms of the parameters α, $\hat{\beta}_1$, and E_0:

$$\Phi(\alpha, \hat{\beta}_1, E_0) = \sum_{i=1}^{N} [\sigma_i(c_i) - \sigma_{th}(c_i; \alpha, \hat{\beta}_1, E_0)]^2. \qquad (10)$$

In the computations, K was expressed from Eqs. (5)–(7), and $\hat{\beta}$ from Eqs. (8) and (9). Further, we fixed the obtained values of α and E_0 (characterizing the headgroup) and fitted the isotherm for $n = 12$ by variation of a single parameter: $\hat{\beta}_1$. The solid lines in Fig. 1 represent the best fit.

4. Results and discussion

The best fit of the data for $5 \leqslant n \leqslant 11$ corresponds to the following parameter values:

$$\alpha = 22.61 \text{ Å}^2, \qquad \hat{\beta}_1 = 0.4751 \, (= 280.2 \text{ cal/mol}),$$
$$E_0 = 0.2381kT \, (= 140.4 \text{ cal/mol}). \qquad (11)$$

For the dodecanoic acid ($n = 12$), α and E_0 are the same, but $\hat{\beta} = 7.713$. Because the van der Waals model predicts phase transition at $\hat{\beta} > 6.75$, we may conclude that the two-dimensional (2D) van der Waals isotherm for the dodecanoic acid indicates the presence of a phase transition (from 2D gas to 2D liquid) in the adsorption monolayer. (Indications about such a phase transition for $n = 12$ have been found also in [6].) In contrast, the remaining fatty acids ($5 \leqslant n \leqslant 11$) have "supercritical" isotherms ($\hat{\beta} < 6.75$) at $T = 22\,°C$; see also Table 1.

For the procedure of data processing based on Eq. (10), the function $\Phi(\alpha, \hat{\beta}_1, E_0)$ has a sharp minimum, which allows an accurate determination of the values of α, $\hat{\beta}_1$, and E_0 from the simultaneous fit of the data for all acids (Fig. 1). This is not the case when the function $\Phi(\alpha, \beta, K)$ in Eq. (4) is minimized for a separate isotherm corresponding to a given acid—in the latter case the minimum is shallow and the determination of the three parameters, α, β, and K, is not so accurate. For that reason, from physical and statistical viewpoint, the simultaneous fit of all data for $5 \leqslant n \leqslant 11$ by minimization of $\Phi(\alpha, \hat{\beta}_1, E_0)$

Table 1
Results for the adsorption parameters of n-alkanoic acids, $C_{n-1}H_{2n-1}COOH$

n	$E(n)/kT$ Eq. (7)	$\hat{\beta}(n)$ Eq. (9)	St. dev. $\Delta\sigma$ (mN/m)
5	5.362	2.851	0.479
6	6.386	3.326	0.285
7	7.411	3.801	0.332
8	8.436	4.276	0.430
9	9.461	4.751	0.386
10	10.480	5.226	0.387
11	11.510	5.702	0.479
12	12.540	7.713	0.398
			Whole fit: 0.404

gives much more reliable results for the adsorption parameters. (We recall that for $n = 12$ a single parameter, $\hat{\beta}_1$, is varied.) The greater excluded area, α, for the n-alkanoic acids ($\alpha = 22.6 \text{ Å}^2$), in comparison with the alkanols ($\alpha = 20.7 \text{ Å}^2$) [1], can be due to the presence of a lateral $C=O$ group in the carboxylic headgroup.

A general thermodynamic approach to deriving an equation of state has been developed by Rusanov on the basis of the excluded volume [19–21] and excluded area [22] concepts. In this approach, the excluded area is a function of Γ, rather than a constant [22]. In contrast, in the conventional three- and two-dimensional van der Waals equations of state, the quantities characterizing the excluded volume and area represent constant parameters of the model [11,23]. As noted by Landau and Lifshitz [23], when the van der Waals equation of state is applied to process experimental data, the excluded volume (or area) is a constant that has to be determined from the best fit. (We follow the latter approach in the present article.) This constant must not be considered equal to four times the molecular volume [23] (or two times the molecular cross-sectional area), as it follows from the approach based on the second virial coefficient; for more details, see Section 2.3 in Ref. [1].

Summary of the results for the parameters of the best fits (the solid lines in Fig. 1) is given in Table 1. The values of the standard deviation, $\Delta\sigma$, characterize the quality of the fit for each separate alkanoic acid. The values of E and $\hat{\beta}$ in Table 1 enable one to calculate the adsorption, $\Gamma(c)$, and the surface (Gibbs) elasticity, $E_G(c)$, for each alkanoic acid ($n = 5, \ldots, 12$) with the help of Eqs. (2) and (3), along with Eqs. (5), (6), and (8). Calculated curves are shown in Figs. 2 and 3. For $n = 12$, the region of the phase transition is denoted with a dashed line. Because π_s is constant during the phase transition, the corresponding value of the surface elasticity is $E_G = 0$ (Fig. 3). The points in Fig. 3 represent values of E_G for $n = 7$ and 10, determined by Wantke et al. [24] directly from surface-tension isotherms with the help of the Gibbs adsorption equation, and without using a specific surface equation of state. The agreement between these points and our calculated curves is satisfactory. One of the possible reasons for the deviation of some points from the theoretical curves (Fig. 3) could be related to the calculation of the second derivative of the experimental surface-tension isotherm, which could introduce some inaccuracy; see Eq. (8) in Ref. [24].
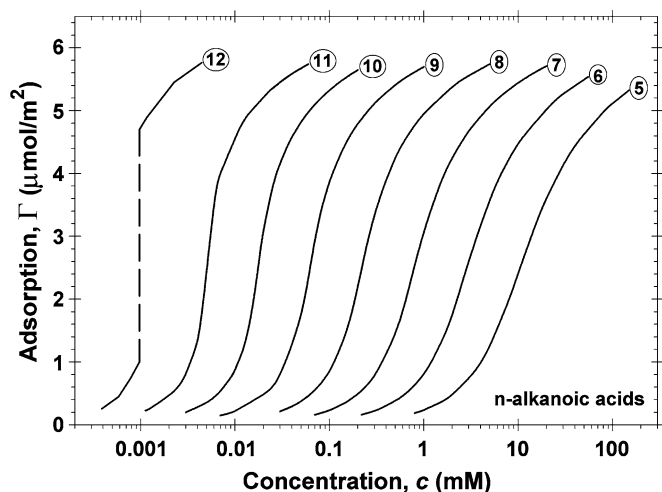
Fig. 2. Plot of adsorption, Γ, vs concentration, c, for n-alkanoic acids: theoretical curves calculated from Eq. (2), along with Eqs. (5)–(9), using the parameters of the best fit of the data in Fig. 1; see Eq. (11). The dashed line corresponds to the phase transition at $n = 12$.
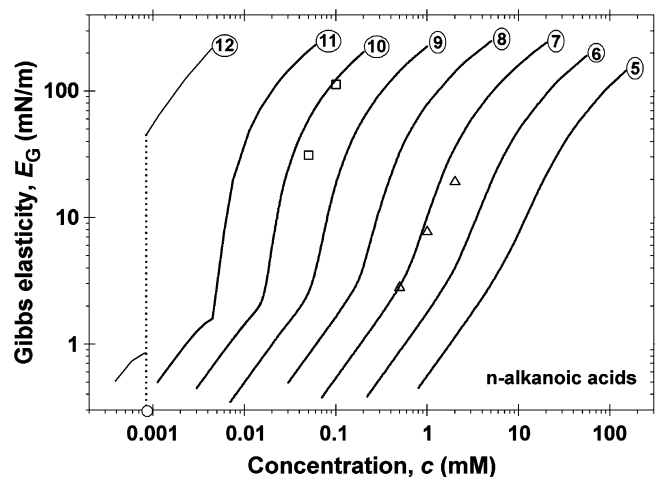

Fig. 3. Plot of the surface (Gibbs) elasticity, E_G, vs concentration, c, for n-alkanoic acids: theoretical curves calculated from Eq. (3) using the $\Gamma(c)$ dependencies in Fig. 2; see also Eqs. (8), (9), and (11). The vertical dotted line corresponds to the phase transition at $n = 12$. The points are values of E_G for $n = 7$ ($\triangle$) and 10 ($\square$) determined in Ref. [24] by differentiation of experimental surface-tension isotherms in accordance with the Gibbs adsorption equation.

Fig. 4. (a) Surface pressure, π_s, vs the dimensionless area per adsorbed molecule, $1/(\alpha\Gamma)$, for n-alkanoic acids. (b) Plot of the data in Fig. 4a as $\pi_s/(kT\Gamma)$ vs π_s. Theoretical curves calculated from Eq. (1) with α and β determined from Eqs. (8), (9), and (11). The dashed line corresponds to the phase transition at $n = 12$.

Fig. 4b is very close to the respective experimental points in Ref. [26].

The prediction of a phase transition (Fig. 4) by the van der Waals model for $n = 12$ calls for additional discussion. At present, there is no direct experimental proof, but there are indirect evidences that a G–LE (gaseous–liquid expanded) two-dimensional phase transition could exist for this acid [27]. As a rule, the G–LE transition occurs at very low surface pressure and low surface coverage [28], which makes difficult its detection by means of the Langmuir-trough method, especially for the lauric acid that exhibits solubility in the aqueous subphase. On the other hand, a gaseous–liquid phase transition has been unequivocally detected for surface monolayers of decanol (C_{10}) [29] and myristic acid (C_{14}) [30,31]. Because the lauric acid has an intermediate chain-length (C_{12}), one could expect that a G–LE transition should take place also for this acid. Indeed, Schofield and Rideal [32], and Petrov et al. [31] have noted that the properties of the monolayers of lauric acid are very similar to those of myristic acid in the liquid-expanded

The results for the surface pressure, π_s, are shown in Fig. 4. The data are cast in terms of two forms which are useful to assess the region of the phase transition for $n = 12$, as predicted by the van der Waals model. In particular, the dashed line at $\pi_s = 1.475$ mN/m in Fig. 4a, is drawn in accordance with the Maxwell rule for the equal areas of the two "humps." (In Fig. 4a the areas do not seem equal because of the used log scale along the abscissa.) The curves in Fig. 4b are to be compared with the known graph used in the textbooks [16,25], which are based on data published by Adam [26]. In the graph in Refs. [16,25], it seems that the curves for $n = 6$ and 8 touch each other or intersect, which is not the case in the original graph by Adam [26] and in our Fig. 4b. The latter figure contains also curves for $n = 7$, 9, and 11, which are missing in the respective figures in Refs. [16,25,26]. Our theoretical curve for $n = 12$ in
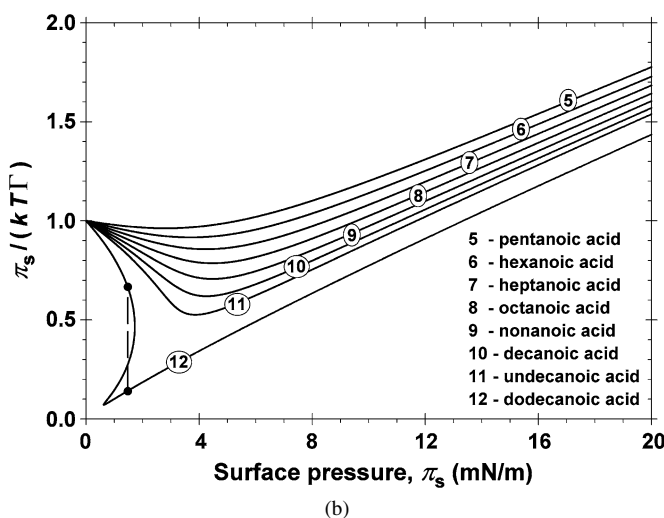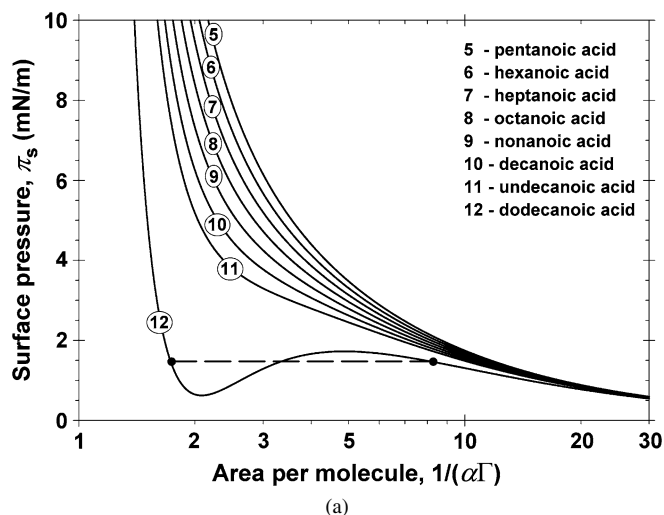
state (LE). If such is the case, then a transition G–LE should exist at lower surface densities and it could be detected by a sensitive method as ellipsometry, which indicated the existence of gaseous–liquid phase transitions in the monolayers of decanol [29] and myristic acid [31].

In summary, the van der Waals model provides an excellent fit of available [6,7] experimental surface-tension isotherms for n-alkanoic acids, $C_{n-1}H_{2n-1}COOH$, for $n = 5, \ldots, 12$ (Fig. 1). All data for $n = 5, \ldots, 11$ (total 110 experimental points) are simultaneously fitted by variation of only three parameters, see Eqs. (10) and (11). The excluded area per headgroup is the same, $\alpha = 22.61$ Å^2, for all investigated alkanoic acids. The latter value is close to the area per headgroup in crystal structures of these acids [6]. The surface-tension data for the n-dodecanoic (lauric) acid, $n = 12$, was fitted by variation of a single parameter—the intermolecular interaction parameter $\hat{\beta}_1$, the other two parameters (α and E_0) being the same as for $n < 12$. The value $\hat{\beta}_1 = 7.71$ obtained from the best fit indicates the presence of a surface phase transition for $n = 12$ (Fig. 4). Having determined the parameters of the model (Table 1), we calculated the adsorption (Fig. 2), surface (Gibbs) elasticity (Fig. 3), and the surface pressure vs area isotherms (Fig. 4) for all investigated alkanoic acids ($n = 5, \ldots, 12$).

Acknowledgments

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