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Molecular area dependences of monolayers at the air/water interface

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ARTICLE INFO

ABSTRACT

The quantum chemical approach and a thermodynamic model for amphiphilic monolayers are used to find the temperature dependence of the area per amphiphile molecule in a monolayer at the onset of liquid-expanded – liquid-condensed phase transition (A_c). Quantum chemical calculations within the semiempiric PM3 method for clusterization thermodynamics and structure of surfactant dimers and trimers are used, as well as for assessment of their molecular area in an aggregate. Calculations are done for seven amphiphile classes: saturated and ethoxylated alcohols, saturated and unsaturated carboxylic acids, α-hydroxylic acids, *N*-acyl-substituted alanine and dialkyl-substituted melamine that are well experimentally explored. Calculations reflect the experimental data and show that a temperature increase leads to decrease of A_c for an amphiphile with a given alkyl chain length, and vice versa with a chain length increase at a fixed temperature the A_c value grows. It was shown that as the temperature increases the increment of A_c per methylene unit of the hydrocarbon chain becomes less significant. The average values of the slope reflecting the change of A_c per 1 °C for saturated and ethoxylated alcohols, saturated, *cis*- and *trans*-unsaturated carboxylic acids, α-hydroxylic acids, *N*-acyl-substituted alanine and dialkyl-substituted melamine are 0.57, 1.32, 1.14, 1.26, 1.15, 0.66, 1.07 and 0.67 Å^2/°C, respectively. These data are quite similar to the experimental values of $-\frac{dA_c}{dT}$ for tetradecanoic acid, dipalmitoyl-phosphatidylcholine and dipalmitoyl phosphatididic acid. The proposed approach can be used as a predictive tool for amphiphiles lacking experimental data.

1. Introduction

Insoluble monolayers of surfactants can exist in various 2D states depending on the degree of their compression. Experimental investigation of the structure of surfactant monolayers has been carried out using a number of experimental methods, such as IR spectroscopy [1], Brewster microscopy [2,3], atomic force [4] and fluorescence microscopy [5], grazing incidence X-ray diffraction [6]. The classical method of surfactant monolayer investigation is obtaining the dependence of the monolayer surface pressure on the area per molecule using Langmuir trough experiments [7,8]. As a result of such experiments a so-called Π-A isotherm is obtained, which gives an opportunity to determine the relationship between the nature of the formed film and the structure of the studied surfactant, as well as the dependence of the monolayer structure on the temperature [9]. It is known that the formation of surfactant monolayers at interfaces is governed by intermolecular interactions between them. Such interactions differ in their nature and, as a consequence, in their strength (from hydrogen to van der Waals interactions).

Compression of the monolayer to the transition points between different 2D states allows one to evaluate the thermodynamics of interactions between surfactant molecules.

There are four main regions of the Π-A-isotherm, which are characterized by a different structure of the studied monolayer (see Fig. 1) [10]. Thus, at very low concentrations surfactant molecules orientate themselves at the interface at large distances from each other and form a so-called gaseous film (G). The behavior of molecules can be described by a 2D analogue of the equation of state for an ideal gas [11]. Such a monolayer is characterized by large areas per molecule and, accordingly, low surface pressure. Compression of the gaseous film leads to the formation of a liquid-expanded film (LE) described by the presence of weak intermolecular interactions, which are still insufficient for the formation of large aggregates. The phase transition of a gaseous film into a liquid-expanded is seen at Π-A isotherm in Fig. 1 as a horizontal section (G-LE plateau), which, however, merges with the abscissa axis in most experimental isotherms within the selected scale. A further decrease in the area per molecule of the monolayer leads to the appearance of a

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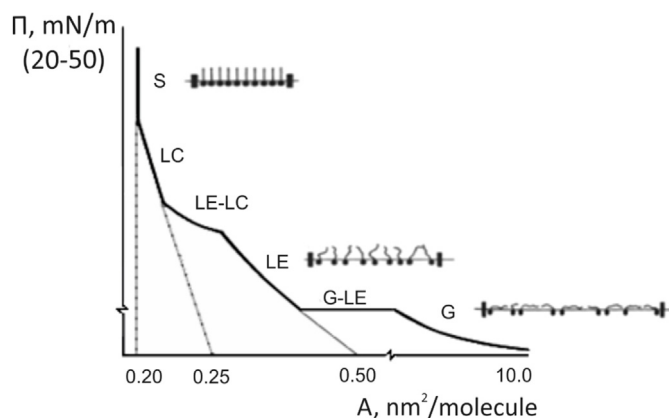 *E-mail address:* vollhardtd@mpip-mainz.mpg.de (D. Vollhardt).

Fig. 1. Surface pressure – area per surfactant molecule isotherm.

second inflection point and plateau (LE-LC) at the Π-A isotherm, which indicates the rearrangement of the molecules of the liquid-expanded phase (LE) and the formation of regular domains of the liquid-condensed phase (LC), which are characterized by translational order. The subsequent compression of such a liquid crystal film leads to the complete transition of the monolayer to the condensed state (S). The following compression of the monolayer to the values of Π = 40–70 mN/m caused destruction of the monolayer. As noted in Ref. [12] surfactant molecules in the solid-crystalline phase, unlike weakly ordered molecules of liquid-expanded films, are in a linear conformation and are oriented almost perpendicular to the interface.

There are many interpretations of the LE-LC phase transition. In earlier works, Gershfeld [13] concluded that the LC phase is metastable, which slowly passes into a solid-crystalline (S). Barret et al. [14] provided evidence that the LE-LC phase transition is a transition of the second order resulting in a change of the rotational symmetry of the liquid monolayer molecules. However, in most studies [15–18] the authors agree that this transition is a transition of the first order despite the fact that it may have some other features [19]. That is why it is possible to apply classical method based on the use of 2D variant of Clausius-Clapeyron equation to determine the thermodynamics of phase transitions in surfactant monomolecular films [20–23] and polymeric systems as well [24,25]. Here we mention just a few of such studies.

Clausius-Clapeyron equation for 2D systems is applied to calculate entropy changes during observed phase transitions in which changes of area per molecule in different monolayer phases can be directly measured via Langmuir trough technique and Π-A isotherm depicting. Such approach was successfully used in ref. [20] for calculation of the transition entropy between I (L_2) and I′($L_{2''}$) phases of behenic acid. The two-dimensional Maxwell relation with Clausius-Clapeyron equation was also used as method to evaluate the phase transition thermodynamics of DPPG monolayers in Ref. [21]. The entropy changes during the phase transition at constant temperature can be expressed as:

$$\frac{dS_{tr}}{d\Pi} = -\left(\frac{\partial A}{\partial T}\right)_\Pi \tag{1}$$

After integrating the eq. (1) ΔS_{tr} has the form:

$$\Delta S_{tr} = -\int_{\Pi_1}^{\Pi_2} \left(\frac{\partial A}{\partial T}\right)_\Pi d\Pi \tag{2}$$

In order to get an integral in eq. (2) one should follow the next procedure, described in detail elsewhere [21]. The set of experimental π-A isotherms recorded at different temperatures allow getting the dependencies $A = f(T)$ in a numerical form in a range of the surface pressure values from π_1 to π_2. These values are taken on the isotherm just after the onset of the phase transition and after the plateau region, respectively.

Then obtained dependencies $A = f(T)$ should be fitted by a polynomial in order to calculate the derivatives $\left(\frac{\partial A}{\partial T}\right)_\Pi$. Finally, the pressure dependence of this derivative is numerically integrated and the entropy change at LE-LC phase transition ΔS_{tr} is obtained. Then, substituting the ΔS_{tr} value into the Clausius-Clapeyron equation:

$$\frac{d\Pi_{tr}}{dT} = \frac{S_{LE} - S_{LC}}{A_{LE} - A_{LC}} \tag{3}$$

the value of A_{LC} can be corrected, which in turn allows more precise calculation of ΔS_{tr}. This method is suitable for homogeneous systems. In the eq. (3) S_{LE}, A_{LE}, S_{LC}, and A_{LC} are the molecular entropy and area per molecule in the liquid-expanded and liquid-condensed phases respectively. Initially the value of A_{LE} is estimated approximately in described approach.

In study of ref. [22] Clausius-Clapeyron equation was used for calculation of molar heat of S–S′ phase transition for cholesterol. Authors of the other study [23] applied this approach to the thermodynamics of dipalmitoylphosphatidylcholine monolayers. This approach was also used for polymer monolayers [24,25]. In case of application of the Clausius-Clapeyron equation to the plateau region of poly(isobuty1 cyanoacrylate) monolayers it yields small positive ΔH and ΔS values. It was interpreted as reflecting reorientation of the polar groups of the polymer under compression. The same ideology was used by authors of Ref. [26] investigating the thermodynamics of 7-hydroxycholesterol epimers.

It should be noted that many other mathematical models and theories have been developed to describe LE-LC phase transition [27]. The criterion for the adequacy of these theories is the agreement of experimentally obtained and calculated Π-A isotherms. For example, the liquid-crystal phase transition in monolayers according to the authors of Ref. [29] is not an analogue of the phase transition in the bulk. It is considered as a transition involving domains of the liquid crystal phase containing from 10 to 1000 molecules [28,29]. This explains the deviation of the plateau region (LE-LC) on the Π-A isotherm from the horizontal line. According to the authors of Ref. [29], the structure of the solid phase in the bulk is determined by the intermolecular interactions of all parts of the molecule and differs from that in the monolayer, since only the interaction of hydrocarbon chains at the interface contributes to the compaction and structuring of the monolayer. A number of theoretical models developed by Vollhardt, Miller and Fainerman are based on the application of the Butler [30] and Volmer [31] equations. The 2D aggregation process is considered as quasi-chemical [32] between surfactant monomers and small clusters – dimers and trimers. Drach et al. [33] used a 2D hard disk model and suggested considering the adsorption layer as a mixture of oblate aggregates of various dimensions. As a result, the application of the latter theory on the example of N-alkyl-dimethylphosphine oxides showed that the LE-LC transition is carried out on the basis of small surfactant aggregates. The same conclusion can be drawn from the works of Ruckenstein and Lee [34], who investigated the Π-A isotherms of a number of carboxylic acids C14–C16 using the Flory-Huggins theory. The authors showed that the nature of the Π-A isotherms depends on the parameter that takes into account the interactions between surfactant molecules and the maximum number of monomers in the cluster. The deviation of the LE-LC plateau region from linearity in the isotherm depends on the value of the latter parameter, from which it can be concluded that the considered phase transition is carried out on the basis of small clusters with i_{max} = 2–5.

A number of works should also be noted in which the authors carried out MD modeling of the behavior of various surfactants at vacuum/water [35], air/water and water/oil interfaces [36–38]. Thus, Olzynska and coworkers [39] present modeled Π-A isotherms for pure mono- and dialkyl derivatives of phosphocholine, as well as their mixtures obtained at 25 and 37 °C. These calculated data rather qualitatively reflect the shape of the experimental curves, although the LE-LC transition was not recorded at the calculated curves. The calculation reflects much better

the experimental data for the same classes of surfactants in the work of Javanainen et al. [40], as well as in study of Baoukina et al. at 25 and 27 °C [41]. The results of modeling the LE-LC transition in the DPPC monolayer by the Mohammad-Aghaie group [42] are also rather qualitative, although the dependence of the surface pressure with temperature as well as the reduction of the width of the plateau with increasing temperature is consistent with the experimental data.

Note, that the clusterization is very sensitive to temperature, pH, the presence of impurities in the subphase, etc. Previously, we developed a quantum chemical approach that allows us to calculate the temperature of the onset of surfactant spontaneous clusterization at the air/water interface [43]. In addition, in one of the recent works [44] a method was proposed for estimation of the A_c – area per surfactant monolayer molecule at the beginning of the LE-LC phase transition, based on a quantum chemical approach and a thermodynamic model of the behavior of amphiphilic monolayers with account of the non-ideality of the mixing entropy. Dependences of A_c on the temperature were experimentally revealed for a number of surfactant monolayers [45,46]. This logically implies the desire to apply the developed approach to the assessment of the temperature dependence of the A_c. This was the aim of this work: to propose an approach accounting for the dependence of $A_c = f(T)$ on the basis of thermodynamic parameters of surfactant clusterization calculated within the semiempiric quantum chemical method PM3 using the thermodynamic model of the diffusion kinetics of surfactant adsorption from solutions, which assumes the formation of small and large aggregates in the adsorbed monolayer [32,47].

2. Model and method

In the present paper a thermodynamic model developed by Fainerman and Vollhardt was used, which allows to describe the region of the LE-LC phase transition at the Π-A isotherm of insoluble surfactant monolayers. This theory is described in detail in Ref. [48] and based on the use of the Volmer-type equation. This equation contains a number of parameters: the partial molecular area for monomers ω, the area per molecule A, the cohesion pressure Π_{coh}, which accounts for the intermolecular interaction, the parameter m describing a bimodal distribution of monomers and monodisperse aggregates. Note, that the contribution of the non-ideality of the mixing entropy for monomers and clusters was taken into account. As a result the equation of state for a 2D film takes the form:

$$\Pi = \frac{1}{m} \cdot \frac{kT\alpha\beta}{A - \omega[1 + \varepsilon(\alpha\beta - 1)]} - \frac{kT}{A}(1 - \alpha\beta) - \Pi_{coh} \quad (4)$$

In addition to those listed above, there are three more adjustable parameters in this equation: parameter α expresses the dependence of the aggregation constant on the surface pressure, β is the fraction of the monolayer free from aggregates, parameter ε affects additionally the isotherm shape at $A > A_c$, $\varepsilon = 1 - \omega_{(Cl)}/\omega$, where $\omega_{(Cl)}$ is the area per monomer in a cluster. The ε parameter is Π-dependent and should consist of two terms, $\varepsilon = \varepsilon_0 + \eta\Pi$: ε_0 is the relative jump of the area per molecule during phase transition, and η is a relative 2D compressibility of the condensed monolayer.

Experimentally obtained Π-A isotherms for surfactant monolayers at different temperatures processed according to the thermodynamic model described above give the possibility to estimate the enthalpy, entropy and Gibbs energy of surfactant film formation. To do this, one should have ω_C and A_c parameters for each of the available temperatures. Based on the quasi-chemical model of 2D aggregation described in detail in Ref. [32] an equation can be obtained that allows to calculate with a certain degree of accuracy the Gibbs energy of surfactant clusterization per one monomer of the film:

$$\Delta G^{Cl} / m = RT\ln\left(\omega_{(Cl)} / A_c\right) \quad (5)$$

The temperature dependence $\Delta G^{Cl}/m$ subsequently enables to

calculate the enthalpy and entropy of clusterization using the Gibbs-Helmholtz equation.

As noted above, we have previously developed an approach for the assessment of the temperature dependence $\Delta G^{Cl}/m$ for a number of surfactant classes [43]. It is known that the equation for determining the clusterization Gibbs energy per one monomer molecule

$$\Delta G_T^{Cl} / m = \Delta H_T^{Cl} / m - T \cdot \Delta S_T^{Cl} / m \quad (6)$$

is valid for any temperature. At the same time, as it was shown in a series of our papers on the assessment of thermodynamic parameters of surfactant clusterization [49–55], the values $\Delta H_T^{Cl}/m$ and $\Delta S_T^{Cl}/m$ are linearly related to the number of intermolecular CH···HC interactions per monomer of infinite surfactant films:

$$\Delta A_T^{Cl} / m = V_i + U_i \cdot K_a / m \quad (7)$$

where $\Delta A_T^{Cl}/m$ is a thermodynamic parameter of interest. Here, the values of the coefficients V_i and U_i depend on the surfactant class, temperature and cluster structure; K_a/m is the number of intermolecular CH···HC interactions per monomer of the cluster, which depends on the length of the hydrocarbon chain of substituted alkanes (n) and the structural features of the clusters. Substituting the expressions for calculation of the clusterization enthalpy and entropy into equation (7), we obtain:

$$\Delta G_T^{Cl} / m = V_{\Delta H} + U_{\Delta H} \cdot K_a / m - V_{\Delta S} \cdot T - U_{\Delta S} \cdot T \cdot K_a / m \quad (8)$$

Since the values of the clusterization enthalpy and entropy and, consequently, the coefficients of the regression dependencies $U_{\Delta H}$, $V_{\Delta H}$, $U_{\Delta S}$ and $V_{\Delta S}$ necessary for their description depend on the temperature, then for description of the temperature dependence of the clusterization Gibbs energy several different possibilities for temperature accounting can be proposed. They differ from each other by the degree of their theoretical validity. The simplest of the schemes neglects the dependence of the values of the coefficients $U_{\Delta H}$, $V_{\Delta H}$, $U_{\Delta S}$ and $V_{\Delta S}$ on the temperature, and its accounting is carried out only by the corresponding multiplier in eq. (8). The values of the coefficients $U_{\Delta H}$, $V_{\Delta H}$, $U_{\Delta S}$ and $V_{\Delta S}$ used in this work were obtained for T = 298 K (see Table 1). In ref. [43] we showed that the application of the simplest scheme to the calculation of $\Delta G_T^{Cl}/m$ gives quite satisfactory results, since the values of the errors for estimation of the temperature corresponding to the onset of surfactant spontaneous clusterization is only 3–8%. Since experimental Π-A isotherms for surfactant monolayers, as usual, cover a narrow temperature range (no more than 20 °C), the use of the simplest scheme for calculation $\Delta G_T^{Cl}/m$ in this case is justified.

Thus, having the temperature dependence of the Gibbs clusterization energy per monomer of the surfactant film, it is possible to reveal the temperature dependence of the area per surfactant molecule at the beginning of the LE-LC phase transition:

$$A_c = \frac{\omega_{(Cl)}}{\exp\left(\frac{\Delta G_T^{Cl}/m}{RT}\right)} \quad (9)$$

3. Results and discussion

3.1. Structural and thermodynamic parameters of surfactant association

In the framework of the quantum chemical model for estimation of the thermodynamic parameters of surfactant film formation we considered eleven classes of amphiphilic compounds, among which a number of Π-A isotherms were experimentally obtained: for saturated and ethoxylated alcohols, saturated and *cis*-unsaturated carboxylic acids, α-hydroxylic acids, *N*-acyl-substituted alanine and dialkyl-substituted melamine at various temperatures. Grazing incidence X-ray diffraction studies of the condensed monolayers of these compounds have shown that, as a rule, a hexagonal or oblique unit cell is typical for condensed

Table 1

Values of coefficients for calculation of thermodynamic characteristics of clusterization of dimers and trimers of various classes of surfactants.

Surfactant class	Number of CH···HC-interactions, K_a	ΔH^{Cl}_{298}, kJ/mol		ΔS^{Cl}_{298}, J/(mol•K)		Area per monomer in a cluster $\omega_{(Cl)}$, Å^2	
		$V_{\Delta H}$	$U_{\Delta H}$	$V_{\Delta S}$	$U_{\Delta S}$	Calc.	Exptl.
Alcohols:						15.7	16.0 [55]
Dimer 1s	$\{n/2\}$[b]	−2.69	−10.19	−110.1	−17.9		
Trimer 1	$2\{\frac{n}{2}\} + \{\frac{n-1}{2}\}$	−18.41	−9.15	−212.3	−19.8		
Etoxylated alcohols C_nE_1: Trimer 2	$3\{\frac{n}{2}\}$	−53.43	−8.51	−295.8	−19.0	14.8	16.0[a]
Saturated carboxylic acids:						17.5	20.0 [64,65]
Dimer 1p	$\{\frac{n}{2}\}$	0.07	−10.39	−51.9	−22.7		
Trimer 1	$2\{\frac{n}{2}\} + \{\frac{n-1}{2}\}$	−12.86	−9.34	−283.8	18.4		
Cis-unsaturated carboxylic acids: Dimer 1s	$\{\frac{n-6}{2}\}$	−21.61	−9.20	−132.9	−18.4	23.2	23.3 [66]
Trans- monoenic carboxylic acids: Dimer 1p	$\{\frac{n-4}{2}\}$	−31.81	−9.20	−185.3	−18.4	20.4	22.5 [66]
α-Hydroxylic acids: Dimer 5 p	$\{\frac{n}{2}\}$	−5.93	−10.11	−107.1	−20.0	25.4	20.0 [51]
N-acylsubstituted alanine: Dimer 1p	$\{\frac{n-1}{2}\}$	−9.10	−10.24	−115.0	−22.4	30.6	31,2 [67]
Substituted melamine	$\{\frac{n-3}{2}\} + (n-1)$	−6.97	−10.50	−253.8	−18.7	51.2	36.0 [68]

[a] For ethoxylated alcohols, the experimental value of $\omega_{(Cl)}$ is missing and for subsequent calculations it was assumed to be the same as for n-alcohols.

[b] Denote the integer part of the number.

amphiphilic monolayers. Moreover, monolayers of surfactants with a minimum value of the hydrophilic part (alcohols, carboxylic acids) have a hexagonal structure, and monolayers of surfactants with a more voluminous head group have an oblique structure. It should be noted that it is possible to construct and to get on practice the oblique structure of monolayers of alcohols and carboxylic acids, which according to our calculated data on the clusterization thermodynamics are practically isoenergetic [50,56]. In this case, the structural units on the basis of which further aggregation of surfactants occurs are dimers and trimers. For surfactant monolayers with an oblique unit cell the content of dimers during the LE-LC transition is predominant, and for surfactant monolayers with a hexagonal unit cell the content of trimers is major. These data obtained on the basis of the quantum chemical approach are also consistent with the results of processing experimentally obtained Π-A isotherms within the framework of the thermodynamic theory of the diffusion kinetics of surfactant adsorption from solutions, which assumes the formation of small and large aggregates in the adsorbed monolayer, which gives the value of the aggregation number m = 1–3 [57]. It should be noted that this parameter depends on temperature and decreases with its increase, indicating predominant dimer content during phase transition. For example, for N-tetradecanoyl-L-alanine, the value of the aggregation number m varies from 1.9 to 2.2 in the temperature range of 20–32 °C [58]. For α-hydroxylic acids with alkyl chain lengths of 16 and 18 carbon atoms m = 1.38–1.625 and m = 1.52–2.0 in the temperature range of 30–40 °C and 36–44 °C, respectively [51]. For ethoxylated alcohols m = 3 [59], and for saturated n-alcohols, m is 2.8–4.0 at 25–45 °C for 1-tetradecanol and 1-hexadecanol [55]. Regarding carboxylic acids for them m = 2–3 [54]. Dialkyl-substituted melamines stand somewhat apart in terms of the aggregation number among the considered surfactants. According to the thermodynamic model of the diffusion kinetics of surfactant adsorption from solutions, m = 0.91–1.02 in the temperature range of 12–29 °C [60–62]. This can be explained by the fact that the dialkyl-substituted melamine monomer can be considered as a dimer in which intramolecular CH···HC interactions between methylene groups of hydrocarbon chains are realized. A slight deviation of the value m from unity to the smaller side may be caused by some isolation of the hydrocarbon chains of melamine substituents. As can be seen from the experimental data the value of the aggregation number varies depending on the class of surfactants, chain length and temperature. However, in our further calculations within the framework of the quantum chemical model we will take the value m constant: for saturated and ethoxylated

alcohols m = 2.75 and 3 respectively, for carboxylic acids m = 2.5, for other classes of surfactants (except substituted melamines) m = 2. Thus, to calculate the A_c value we will use mainly clusterization thermodynamic parameters of dimers and trimers of surfactants. Fractional values of m for saturated alcohols and carboxylic acids are achieved as a weighted average value under the assumption that during the phase transition dimers and trimers are present in a molar ratio of 1:3 and 1:1, respectively. In compliance with mentioned above, the thermodynamic parameters of the aggregation of these surfactants are further calculated as weighted averages of the corresponding parameters of dimers and trimers. Thus, the values of regression parameters of linear dependencies $\Delta H^{Cl}_T/m$ and $\Delta S^{Cl}_T/m$ are used to estimate the temperature dependence of the A_c (see Table 1).

The structural parameter required for calculation the A_c, is the area per monomer in a cluster. It can be calculated using the distances between the surfactant molecules in the unit cell of the monolayer according to the formula proposed in Ref. [63]:

$$\omega_{(Cl)} = \pi \left(\frac{1}{N} \sum_{i=1}^{N} \frac{R_i}{2} \right)^2 \qquad (10)$$

where R_i is the distance between neighboring molecules in the cluster: for an oblique cell these are the two sides of the parallelogram and its diagonal, for a hexagonal cell – the lengths of the sides of the triangle in the basic trimer (N = 3).

Among the surfactants listed in Table 1 attention should be paid to dialkyl-substituted melamine. Its regression parameters V_i and U_i are given for the case of formation of an infinite 2D film, but not small associates, since the value of the aggregation parameter m ∼ 1, which indicates the passing of the LE-LC transition via monomers. In addition, the value of $\omega_{(Cl)}$ for this surfactant class is one and a half times higher than that obtained on the basis of the thermodynamic model of the diffusion kinetics of surfactant adsorption from solutions. This is probably due to the fact that for the size of the area per monomer in the film is taken the doubled cross-sectional area of the hydrocarbon chain, which is about 20 Å^2 and considered the minimal area occupied by the surfactant monomer in the film (19–26 Å^2) [69]. But this does not take into account the length of intramolecular CH···HC bonds realized between the alkyl chains of substituted melamine. Taking into account these intramolecular bonds, the area per one molecule of dialkyl-substituted melamine should be

increased by another half of the cross-sectional area of the alkyl chain, which will be about 50 Å^2. A similar conclusion can be made if we consider the experimentally fixed geometric parameters of the unit cell: $a = 4.4$ Å and $b = 5.0$ Å, the angle between them $\theta = 116.4°$. Then the value of $\omega_{(Cl)}$ will be 20.6 Å^2 [68], which is possible if the monomer of dialkyl-substituted melamine is considered as a dimer, which in fact is not true. Therefore, the area per one monomer molecule in the film for this surfactant class is calculated on the basis of the dialkylmelamine tetramer optimized in the PM3 method.

It should also be noted that the PM3 method exaggerates the energy of intermolecular CH⋯HC interactions [70]. In study of ref. [71], the authors showed that the energy value of CH⋯HC interactions between methane and neopentane molecules in dimers differs depending on the calculation method. In particular, the PM3 method overestimates the binding energies of CH⋯HC bonds in the methane dimer by two times, and in the neopentane dimer by about four times compared to the value estimated by *ab initio* methods. In this regard the values $\Delta G_T^{Cl}/m$ estimated in the PM3 method are reduced fourfold for the surfactant classes under consideration when estimating the area per surfactant molecule at the beginning of the LE-LC phase transition. The exceptions are saturated and unsaturated carboxylic acids, for which the value $\Delta G_T^{Cl}/m$ is reduced by half, as well as dialkyl-substituted melamine, for which a reduction $\Delta G_T^{Cl}/m$ is required by a factor of twenty. We resorted to a similar action in one of the previous works devoted to the assessment of the surface pK_a of carboxylic acids, which led to a good agreement of the calculated and experimental values [72]. It should be noted that the PM3 method qualitatively allows us to estimate the threshold length of the surfactant chain, starting from which this class of compounds is able to form a monolayer. That means for surfactants with a shorter alkyl chain length the clusterization Gibbs energy is positive, and for surfactants with a longer chain length it is negative. Thus, this method perfectly copes with the qualitative assessment of the possibility of film formation of the considered surfactant classes, but in quantitative terms requires the use of adjustments in accordance with the available experimental data in cases where the absolute value of the thermodynamic parameter is of fundamental importance.

3.2. Temperature dependence of the A_c

The values of the area per surfactant molecule at the beginning of the LE-LC phase transition are calculated using eq. (9), the corresponding temperature dependences are shown in Fig. 2 on the example of aliphatic alcohols. For other amphiphilic compounds the dependences $A_c = f(T)$ are given in the Supporting materials (Figs. S1-6). As can be seen, the calculated values of the A_c are in quite good agreement with the available experimental data. The exponential nature of the temperature dependence of the A_c is also consistent with the data of LE-phase modeling by
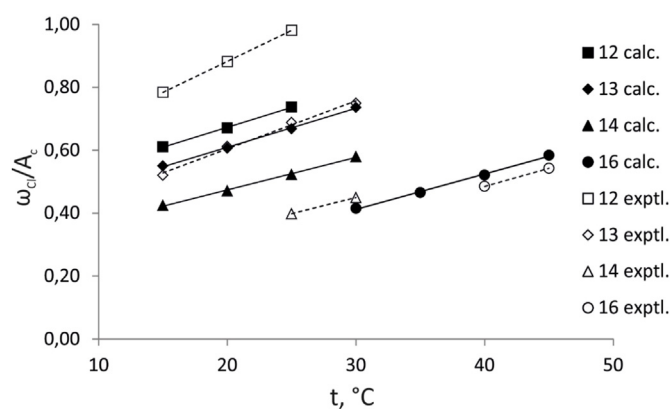
Fig. 3. Dependence of the ratio of the area per one monomer in a small cluster to the area per monomer molecule at the onset of the LE-LC phase transition on the temperature $\omega_{(Cl)}/A_c = f(T)$ for aliphatic alcohols. Experimental data are taken from Refs. [55,57,73,74] Lines are guides for the eyes.

Smith [45] and experimental studies of carboxylic acid esters behavior by Rettig and Kuschel [46]. Note, that the dependence of the ratio $\omega_{(Cl)}/A_c$ on the temperature in a narrow temperature range can be approximated by a line (see Fig. 3 and Figs. S7-12 of the Supporting materials) similarly to that is given in the literature regarding the temperature dependences of the surface pressure Π_c. It can be seen that the calculated and experimental dependences of $\omega_{(Cl)}/A_c = f(t)$ have the same slope to the temperature axis. Their possible discrepancy is due to the difference in the estimated values of $\omega_{(Cl)}$ using the PM3 method and according to the model of the diffusion kinetics of surfactant adsorption from solutions, which assumes the formation of small and large aggregates in the adsorbed monolayer, when processing the experimental Π-A isotherms.

The available calculated and few experimental dependences $A_c = f(T)$ with minimal error can be approximated by linear dependences of the form: $A_c = A_c^0 + k \cdot t$, where t is the clusterization temperature in degrees Celsius. The values of the slope k reflecting the change of the A_c value with an increase of temperature by 1 °C are given in Table 2. It can be seen that the values of the temperature coefficient k estimated for the calculated and experimental data are in good agreement with each other. In cells containing dashes we do not give the values of the coefficient k due to the presence of only two experimental points, on the basis of which it is difficult to talk about the reliability of the resulting estimates. Baret and coworkers in their study [14] list the values of the derivative $-\frac{dA_c}{dT}$ for tetradecanoic acid, dipalmitoyl-phosphatidylcholine and dipalmitoyl phosphatidic acid. For these compounds the values $-\frac{dA_c}{dT}$ are in the
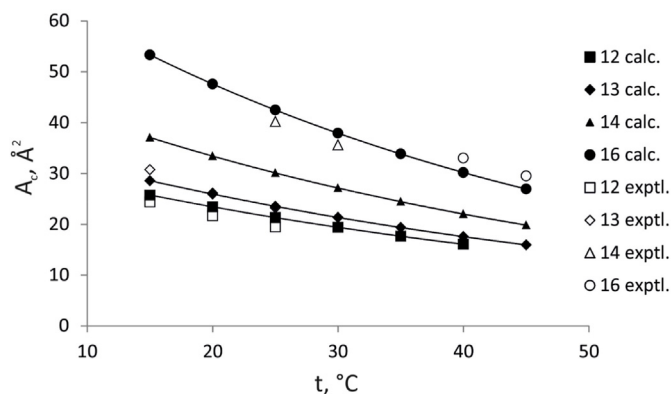
Fig. 2. Dependence of the area per monomer molecule at the onset of the LE-LC phase transition on the temperature for aliphatic alcohols. Experimental data are taken from Refs. [55,57,73,74] Lines are guides for the eyes.

Table 2
The value of the coefficient k, reflecting the change of the A_c value with an increase in temperature by 1 °C (correlation coefficient R = 0.95–0.99).

Number of carbon atoms in the surfactant chain, n	k, Å^2/°C		Number of carbon atoms in the surfactant chain, n	k, Å^2/°C	
	Calc.	Exptl.		Calc.	Exptl.
Alcohols			α-Hydroxylic acids		
C12	−0.44	−0.49	C16	−0.59	−0.84
C13	−0.48	−0.62	C18	−0.74	−0.78
C14	−0.66	–	*N*-acylsubstituted alanine		
C16	−0.69	–	C14	−1.07	−1.43
Saturated carboxylic acids			*Cis*-unsaturated carboxylic acids		
C14	−0.97	–	C22	−1.23	−1.23
C15	−1.38	−0.92	C24	−1.30	−1.38
C16	−1.06	−0.74	Ethoxylated alcohols C$_n$E$_1$		
Trans-monoenic carboxylic acids			C14	−1.39	−1.24
C18	−0.87	–	C16	−1.35	−1.33
C22	−1.44	−1.32	C18	−1.23	−1.58
Dialkylsubstituted melamines					
C11	−0.65	−0.52			
C12	−0.70	−0.56			

range of 0.37–1.60, 0.77–3.13 and 0.4–1.2 Å^2/°C, respectively. However, the authors also note that an insufficiently large array of experimental data makes it very inaccurate to estimate the necessary parameters. Nevertheless, the values of the temperature coefficients of A_c obtained by us for various classes of surfactants are quite consistent with each other and with the data of Baret et al., which indicates the same nature of the CH⋯HC interactions that make a decisive contribution to the Gibbs energy of the surfactant clusterization.

The thermodynamics of the LE-LC transition can be estimated on the basis of the temperature dependences of A_c. To do this it is necessary to construct a regression dependence $\ln \frac{\omega_{Cl}}{A_c}$ on the inverse temperature for the regarded surfactant with a given chain length. Then the slope of this regression is equal to $\frac{\Delta H_T^{Cl}}{R}$ and the free term is $\left(-\frac{\Delta S_T^{Cl}}{R}\right)$, from which it is easy to estimate the desired thermodynamic parameters. For all the considered amphiphiles the corresponding regression parameters of the dependence $\ln \frac{\omega_{Cl}}{A_c} = f\left(\frac{1}{T}\right)$ are given in Table 3. As seen from this table, the estimating error of the thermodynamic parameters of surfactant clusterization in the framework of the quantum chemical model increases with increasing chain length, and the maximum is about 20–35% for tridecanol, penta- and hexadecanoic acids and almost 50% for *trans*-9-octadecenoic acid. It should be noted, however, that experimental data are available for *trans*-15-octadecenoic [18] and *trans*-13-docosenoic acids [66] obtained by various author groups under different conditions. As it is known, the shape of the Π-A isotherms for monolayers is extremely sensitive to the experimental conditions [15], therefore, in this case it is very difficult to go by these experimental data when comparing them with the calculated ones obtained within the framework of the quantum chemical model. In other cases, the average error of assessment of the clusterization enthalpy and entropy variation does not exceed 7–10%. As noted above, the nature of this error may be due to a greater or lesser discrepancy of the experimental value $\omega_{(Cl)}$ with estimated one in PM3.

It would be interesting to estimate the growth of the area per surfactant molecule at the beginning of the LE-LC transition with an increase in the surfactant chain length by one methylene fragment. Fig. 4 shows graphs of the temperature dependences of the A_c on the alcohol chain length. They are exponential as it should be expected from the analysis of eqs. (8) and (9). Unfortunately, there is very few experimental data for
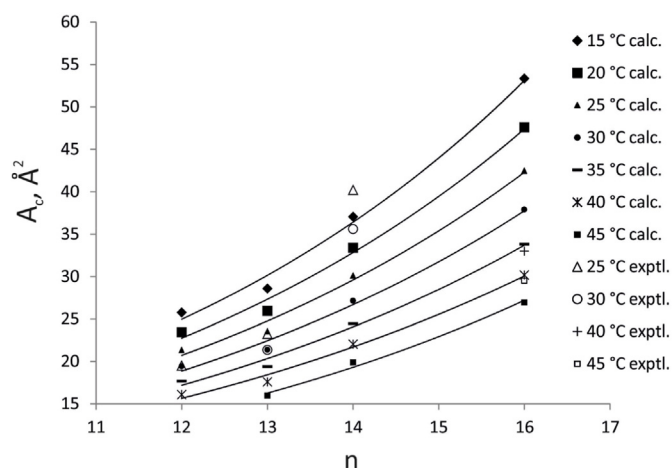

Fig. 4. Dependence of the area per monomer molecule at the onset of the LE-LC phase transition on alkyl chain length (*n*) of aliphatic alcohols. Lines are guides for the eyes.

constructing such dependencies, so it is not possible to estimate the experimental value $\left(\frac{dA_c}{dn}\right)_T$ for its comparison with the corresponding calculated one. For amphiphile homologues with chain lengths varying in a narrow range of about 3–4 carbon atoms, the dependence of A_c on the surfactant chain length can be approximated with a small error (about 2%) with a line similarly to how it was done in the work of Lunkenheimer et al. [69] only for soluble homologues of carboxylic acids with $n < 11$. In our case the value $\left(\frac{dA_c}{dn}\right)_T$ for insoluble alcohol monolayers is: 7.2; 6.3; 5.5; 4.8; 4.2; 3.7 and 3.6 Å^2 per carbon atom for temperatures from 15 to 45 °C. For ethoxylated alcohols [75] the values of $\left(\frac{dA_c}{dn}\right)_T$ using the calculated data are 9.8, 8.8 and 4.5 Å^2 per carbon atom, and using the experimental data – 10.0, 8.0 and 10.2 Å^2 per carbon atom at 15, 20 and 35 °C, respectively. Note, that the experimental data are extremely small to obtain a reliable estimate – only two surfactants for each of the temperatures. Therefore, we provide these data only for an approximate comparison. It can be seen that with temperature growth the increase in

Table 3

Regression parameters of correlation dependencies of the form $\ln \frac{\omega_{Cl}}{A_c} = a \cdot \frac{1}{T} + b$ (correlation coefficient $R = 0.94$–0.99 for experimental data).

C_n in the surfactant chain	$a \cdot 10^{-3}$	b	$\Delta H^{Cl}/m$, kJ/mol		Error, %	$\Delta S^{Cl}/m$, J/(mol·K)		Error, %
			Calc.	Exptl.		Calc.	Exptl.	
Alcohols								
C_{12}	−1.79	5.97	−14.85	−14.09	5.1	−49.65	−44.79	9.8
C_{13}	−1.69	5.47	−14.08	−17.62	25.2	−45.53	−55.90	22.8
C_{14}	−1.81	5.63	−15.08	−18.25	21.0	−46.85	−53.57	14.3
C_{16}	−2.08	6.20	−17.33	−18.56	7.1	−51.57	−53.27	3.3
Ethoxylated alcohols C_nE_1								
C_{14}	−2.23	6.97	−18.81	−19.34	2.7	−57.44	−57.97	0.9
C_{16}	−2.50	7.32	−20.78	−21.47	3.2	−60.88	−62.73	3.0
C_{18}	−2.95	8.35	−24.57	−23.60	4.1	−69.41	−67.49	2.8
Saturated carboxylic acids								
C_{14}	−2.81	4.11	−23.39	−11.01	3.6	−74.75	−23.39	0.3
C_{15}	−3.15	9.70	−26.23	−20.11	23.3	−80.65	−63.56	21.2
C_{16}	−3.25	9.89	−26.99	−17.67	34.5	−82.19	−52.64	35.9
Cis-monoenic carboxylic acids								
C_{22}	−3.22	11.23	−29.43	−103.25	7.2	−31.74	−111.63	7.5
C_{24}	−3.90	12.87	−32.40	−106.97	6.9	−34.80	−103.73	7.1
Trans-monoenic carboxylic acids								
C_{18}	−2.11	6.47	−17.53	−24.05	37.2	−53.79	−79.71	48.2
C_{22}	−3.44	10.55	−31.97	−28.65	11.6	−88.91	−102.4	15.1
α-Hydroxylic acids								
C_{16}	−1.85	5.95	−15.34	−14.92	2.8	−49.46	−44.25	10.5
C_{18}	−2.09	5.07	−16.70	−14.56	12.8	−42.13	−53.46	21.2
Dialkylsubstituted melamines								
C_{11}	−0.93	3.01	−7.23	−7.70	6.0	−21.51	−25.77	16.5
C_{12}	−0.99	3.21	−7.91	−8.22	3.8	−22.77	−26.70	14.7

the A_c value per methylene unit becomes less significant. This conclusion is consistent with the "temperature effect" of clusterization: the elongation of the alkyl chain of the amphiphiles by one methylene fragment corresponds to a decrease in the subphase temperature during clusterization by 5–10 °C, and with an increase in the alkyl chain length this temperature decrease becomes less significant [43].

The available experimental data gives the possibility to estimate the values of A_c derivatives by alkyl chain length also for carboxylic acids [14,15,45,76–79], disubstituted melamine [68], and α-hydroxylic acids [51]. For carboxylic acids the best agreement of experimental and calculated values $\left(\frac{dA_c}{dn}\right)_T$ is observed at 30 °C and amounted to 6.38 and 6.99 Å² per carbon atom, respectively. In the case of disubstituted melamines there are only two experimental points at different temperatures. Nevertheless, we estimated the change in A_c with the elongation of the chains of substituted melamine by one methylene fragment for n = 10–11 and 11–12. This increase is in the range of 5.2–6.8 and 5.4–5.9 Å² per carbon atom for experimental and calculated data, respectively at temperatures of 20–25 °C. A similar situation is for α-hydroxylic acids. For the available α-hydroxylic acids with a chain length of 16 and 18 carbon atoms the increase in A_c with chain elongation is 3.3 and 2.6 Å² per carbon atom for experimental data and 4.8 and 5.5 Å² per carbon atom for calculated data at 35 and 40 °C, respectively. Regarding unsaturated carboxylic acids there are no experimental data for a reliable estimate of $\left(\frac{dA_c}{dn}\right)_T$, but it is possible to obtain the value of this derivative using calculated data. The values of derivatives $\left(\frac{dA_c}{dn}\right)_T$ for *trans*-acids exceed those for *cis*-acids by almost a half (44%) and amount to 14.9 and 10.2 Å² per carbon atom respectively, which is probably due to a smaller number of intermolecular CH···HC interactions realized in associates of *cis*-acids.

4. Conclusion

In the present paper we consider an approach to estimate the temperature dependence of the area per surfactant molecule at the beginning of the LE-LC phase transition using two models. Thermodynamic and structural parameters of surfactant aggregation are assessed using the quantum chemical approach within the framework of the semi-empirical PM3 method and used in the model of the diffusion kinetics of surfactant adsorption from solutions, which assumes the formation of small and large aggregates in the adsorbed monolayer, which adequately describes the behavior of amphiphilic compounds and the shape of the experimentally obtained Π-A isotherms.

The performed calculations show that the structural parameters used in the assessment of the A_c (ω_{Cl} is the area per monomer in a cluster estimated within the framework of the PM3 method) are in good agreement with the available experimental data, whereas the thermodynamic parameters of the association of small surfactant clusters require adjustment due to their overestimated values. It is revealed that the obtained temperature dependences of A_c have an exponential character, which can be approximated by linear function in a narrow temperature range. The temperature coefficient indicating the change in the A_c value with an increase in the clusterization temperature by 1 °C for the considered surfactant classes is in the range of –(0.44–1.44) and –(0.49–1.58) Å²/°C for the calculated and experimental values, respectively. The calculated values of these increments are also in good agreement with the data of Baret et al. [14], who considered tetradecanoic acid, dipalmitoyl-phosphatidylcholine and dipalmitoyl phosphatididic acid. The A_c value increase with lengthening of the alkyl chain of the amphiphiles by one methylene fragment at a fixed temperature is also estimated. The calculation showed that with temperature growth the increase in the A_c value per methylene fragment becomes less significant that is consistent with the "temperature effect" of clusterization, which we considered earlier [43]. This confirms the applicability of the proposed approach to assessment the area per surfactant molecule at the onset of the LE-LC phase transition and indicates its predictive value in cases when the available experimental data on a particular class of

surfactants are insufficient.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jciso.2022.100057.

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