

# On Hexagonal Orientation of Fatty Alcohols in Monolayers at the Air/Water Interface: Quantum-Chemical Approach

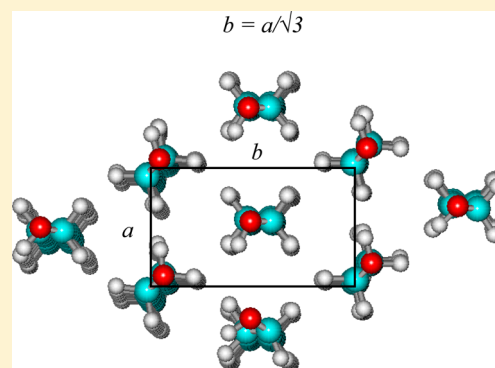
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**ABSTRACT:** In the framework of the quantum chemical PM3 method, the monolayers of the aliphatic alcohols  $C_nH_{2n+1}OH$  ( $n = 6-16$ ) of the hexagonal monolayer structure at the air/water interface are described. The calculated parameters of the monolayer unit cell are  $a = 4.3$  Å;  $b = 7.4$  Å, and  $t = 4^\circ$ , which are in good agreement with the results of grazing incidence X-ray diffraction (GIXD) experiments  $a = 5.0$  Å;  $b = 7.5$  Å, and  $t = 0-9^\circ$ . The optimized structures of small aggregates (dimers, trimers, tetramers, octamers, and nonamers) that comprised the hexagonal monolayer are obtained. The correlation dependencies of the clusterization enthalpy, entropy, and Gibbs' energy on the number of pair  $CH\cdots HC$  interactions and interactions between the functional groups realized in the cluster are obtained on the basis of calculated data. It is shown that spontaneous clusterization of aliphatic alcohols at the air/water interface under standard conditions is possible for molecules with an alkyl chain no shorter than 11 carbon atoms, which is in good agreement with the characteristics of the surface pressure–molecular area ( $\pi$ –A) isotherms. A way of hexagonal monolayer formation is proposed via preferential formation of trimers and their subsequent aggregation, which also agrees with existing experimental data processed using the thermodynamic model of equation of state for insoluble monolayers.



## INTRODUCTION

Langmuir monolayers have remarkable properties that enable their use for the construction of artificial membranes and multilayers with predefined qualities. Permanent interest to the monolayers of alcohols and their mixtures with other nonionic surfactants and polymers has been caused by their ability to prevent the water evaporation. A variety of recent studies in particular using molecular dynamic simulations should be noted.<sup>1–3</sup> These studies concern the dependence of structure and stability of the regarded monolayers on temperature, surface density, and concentration of the additives.

The development of the modern instrumental methods for investigations of Langmuir monolayers enables the detailed examination of the structure of their condensed phases as well. Generally, the structural peculiarities of amphiphilic monolayers depend on the conformational flexibility, length, and structure of the alkyl chain(s), type, and location of the functional group with respect to the alkyl chain.<sup>4</sup> The analysis of numerous experimental data<sup>5–10</sup> have shown that amphiphiles with less voluminous headgroup (alcohols, carboxylic acids, amines, thioalcohols, and amides of carboxylic acids) tend to form condensed phases with hexagonal unit cell, whereas amphiphiles with more bulky functional groups (hydroxycarboxylic acids, amino acids, acid amides) show phase diagrams with orthorhombic and oblique unit cells. The first studies using quantum chemical methods to characterize condensed phases

of Langmuir monolayers on the basis of clusterization processes started with aliphatic alcohols.<sup>11–13</sup> This type of compounds along with carboxylic acids has been frequently used as standard model for experimental studies of monolayer properties. Therefore aliphatic alcohols have been selected for quantum chemical simulations because of the considerable experimental data array for the comparison of the theoretical model-results with experimental data.

The existing experimental data show that condensed Langmuir monolayers of aliphatic alcohols with alkyl chains of 10–12 carbon atoms are formed at 4–25 °C.<sup>14–23</sup> The geometric parameters of their hexagonal unit cell are close to the relation  $b = a*\sqrt{3}$  and vary within the range of  $a = 4.75-5.0$  Å,  $b = 7.5-8.5$  Å,  $t = 0-9^\circ$ .<sup>20,24–31</sup> The molecules are arranged parallel to each other and are in linear conformation when all hydrogen atoms of methylene groups are in trans-configuration.<sup>32</sup> It should be noted that molecular dynamic simulations of alcohol monolayers provided interesting new information (see, for example, refs 24 and 33–35).

It is shown<sup>33</sup> that alcohols with alkyl chain lengths of 29–31 carbon atoms at temperatures below 0 °C tend to form hexagonal aggregates with the next geometrical parameters:  $a =$

Received: October 6, 2013

Revised: February 4, 2014

Published: February 4, 2014



5.1–5.3 Å,  $b = 7.7$ – $7.8$  Å. It is apparent that the temperature conditions accepted for simulations are far from standard.

In this connection it seems interesting to define how adequately it is possible to describe the structural parameters of hexagonal monolayers of nonionic amphiphiles in the framework of the quantum chemical model, which was successfully applied for the study of the thermodynamic clusterization parameters.<sup>11–13,36–45</sup> The aim of the present work is to investigate the structural parameters of hexagonal lattice structures of aliphatic alcohols with unbranched alkyl chain at the air/water interface using the quantum chemical semiempirical PM3 method. The calculations were done for molecules with the general formula  $C_nH_{2n+1}OH$ , where  $n$  is in the range from 6 to 16.

## MODEL AND METHOD

The model used in this paper for the calculation of the thermodynamic (enthalpy, entropy, and Gibbs' energy) and structural parameters of clusterization for the hexagonal lattice structure of alcohol monolayers was described in detail elsewhere.<sup>38</sup> So, here we remind only its main key points

1. The intermolecular  $CH\cdots HC$  interactions realized between two methylene groups of the alkyl chains of interacting amphiphile molecules arranged oppositely to each other provide the main contribution to Gibbs' energy of cluster formation (because of the decrease of interaction energy inversely proportional to  $r$ ,<sup>6</sup> that is, the  $CH\cdots HC$  interactions are additive in pairs).

2. The calculation of the thermodynamic parameters of the cluster formation of considered types of amphiphiles was carried out in the supermolecule approximation. This approximation acts on the premise that all the atoms in the cluster are treated equally despite they belong to several monomer molecules and the aggregate is considered as one big molecule.

3. The additive scheme was constructed on the basis of the results of direct calculations. This scheme defines the values of the thermodynamic parameters of clusterization as total contribution of the  $CH\cdots HC$  interactions and the interactions of hydrophilic parts of the amphiphile molecules realized in the cluster.

The influence of the interface was accounted indirectly through its orienting and stretching effect on the amphiphile molecules. As shown,<sup>46</sup> the water phase retracts the alcohol functional group and two–four methylene fragments of the alkyl chain adjoining to the functional group, whereas the hydrophobic part of amphiphilic molecule pushes off from the water surface and locates in the gaseous phase, and all the hydrogen atoms of the methylene fragments of the hydrocarbon chain of the amphiphile are in the trans-position.

The calculation of the thermodynamic and structural parameters of clusterization for the hexagonal lattice structure of alcohol monolayers is carried out using quantum chemical package MOPAC2000<sup>47</sup> in the framework of semiempirical method PM3 in compliance with the next procedure

1. Conformational analysis, which includes the construction of the potential energy surface of the monomer depending on the values of the torsion angles of the functional groups in the hydrophilic part of the amphiphile with respect to the hydrophobic alkyl chain, and calculation of the thermodynamic parameters of the formation for the found conformers.

2. Determination of the tilt angle of the alkyl chains of the amphiphiles in the monolayer with respect to the interface,

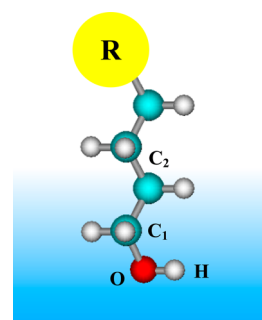
according to the scheme described in detail elsewhere,<sup>45,48,49</sup> and finding the geometric parameters of the unit cell of the 2D lattice.

3. Calculation in supermolecular approximation of the thermodynamic parameters of clusterization of small aggregates (dimers, tetramers, hexamers) constructed on the basis of the found conformers that orient with a tilt angle to the interface found previously.

4. Construction of the additive scheme on the basis of the results of direct calculations.

## RESULTS AND DISCUSSION

**Monomers.** Previously<sup>12</sup> the conformational analysis for aliphatic alcohol monomers was done. Two stable conformations were found as a result. They are the mirror reflections with the dihedral angles of the OH-group  $\angle\alpha = C_2-C_1-O-H$   $60^\circ$  and  $300^\circ$  ( $-60^\circ$ ), respectively (cf. Figure 1). An additional



**Figure 1.** Torsion angle of the functional group of alcohol (R, hydrophobic chain).

optimization confirmed the isoenergetic formation of these two structures. Thus, the alcohol monomer structure with the dihedral angle  $\angle\alpha = 60^\circ$  was used in all further calculations. The optimized structure of the alcohol monomer is shown in Figure 2 on the example of a molecule with 10 carbon atoms in the alkyl chain.

For the described monomer structures, the thermodynamic parameters (enthalpy, entropy, and Gibbs' energy) of the monomer formation were calculated previously.<sup>48</sup> So, here we list only the correlation dependencies of the thermodynamic formation parameters on the alcohol alkyl chain length ( $n$ ):

$$\Delta H_{298, \text{mon}}^0 = -(22.68 \pm 0.00)n - (30.84 \pm 0.01) \quad (1)$$

[SD = 0.02 kJ/mol;  $N = 15$ ]

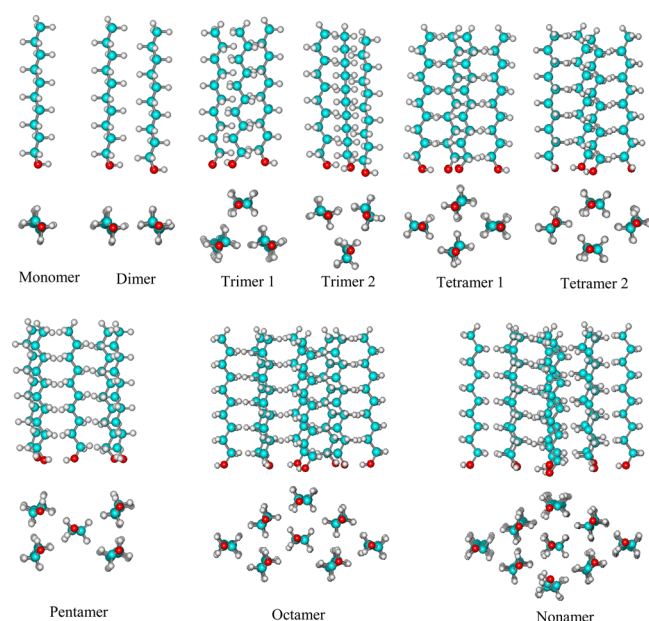
$$S_{298, \text{mon}}^0 = (32.22 \pm 0.04)n + (181.65 \pm 0.42) \quad (2)$$

[SD = 0.61 J/(mol·K);  $N = 15$ ]

$$\Delta G_{298, \text{mon}}^0 = (8.32 \pm 0.01)n - (46.08 \pm 0.13) \quad (3)$$

[SD = 0.19 kJ/mol;  $N = 15$ ]

Here and further, SD is the standard deviation and  $N$  is a sample size. The corresponding correlation coefficients exceed 0.9999. Note that calculated parameters of absolute entropy of formation for the alcohol monomers are smaller than the experimental values because PM3 method does not take into account the increment of the free rotation of the methylene groups in the alkyl chain to the entropy. Therefore, these increments were considered in the calculation of the absolute

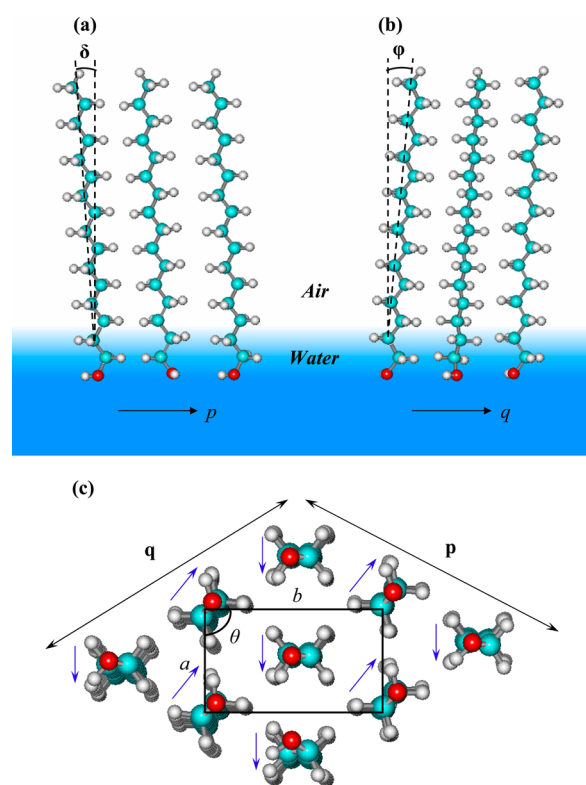


**Figure 2.** Optimized structures of small aggregates of fatty alcohols for the hexagonal monolayer phase.

entropy of formation using corresponding corrections. This correction is found on the basis of experimental data for the absolute entropy of formation and is  $(6.12 \pm 0.22)$  J/(mol·K) per one methylene group.<sup>48</sup>

**Structural Parameters.** Previously we considered the alcohol monolayers with an oblique unit cell.<sup>11–13,48</sup> In the present work, the monomer molecules described above are organized in such a way that the formed monolayer has a hexagonal lattice structure. The numbers of molecules in both directions of the spread monolayer are defined as  $p$  and  $q$  (see Figure 3c). Small one-edged arrows in Figure 3c define the direction from carbon atom to hydrogen atom of the methylene fragment. They show the herringbone arrangement of the molecules in the monolayer in agreement with the existing experimental data.<sup>5</sup> For the determination of the molecular tilt angle with respect to the normal to the interface we use the procedure, which became standard in the studies of the regarded issue and is described in detail elsewhere.<sup>45</sup> It should only be mentioned that in the dimers, which are the sides of the monolayer unit cell in both  $p$  and  $q$  directions, a parallel shift of one molecule with respect to another one is applied. In the obtained dependencies of the dimerization Gibbs energy on the  $\delta$  and  $\varphi$  angles the minima were found. These minima correspond to optimum  $\delta$  and  $\varphi$  values, which define the value of the general tilt angle  $t$  of the alkyl chain of the amphiphile with respect to the normal to the interface. Thereby the values of angles are found to be  $\delta = 3^\circ$  and  $\varphi = 3^\circ$ ,  $t = 4^\circ$ , agreeing well with the existing experimental data.<sup>20,25–28</sup>

In order to determine the geometric parameters of the unit cell, the nonamer is constructed. On the basis of its optimized structure the unit cell with the geometric parameters  $a = 4.3$  Å;  $b = 7.4$  Å,  $\theta = 87^\circ$  is singled out. The obtained values are in reasonable correspondence with GIXD results:  $a = 5.0$  Å;  $b = 7.5$  Å,  $\theta = 90^\circ$ .<sup>28</sup> Therefore, we consider only such aggregates, which form the monolayer of the structure regarded above, in further calculations of the thermodynamic parameters (enthalpy, entropy, and Gibbs' energy) of the alcohol clusterization.

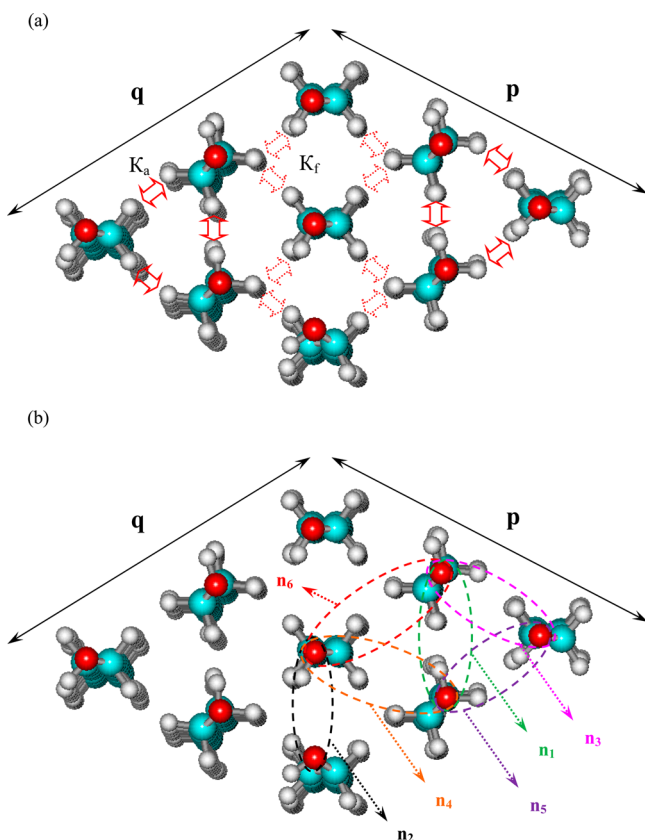


**Figure 3.** Structure of the unit cell of the hexagonal 2D cluster of alcohols: (a) view along the  $p$  axis; (b) view along the  $q$  axis; (c) view along the alkyl chain axis.

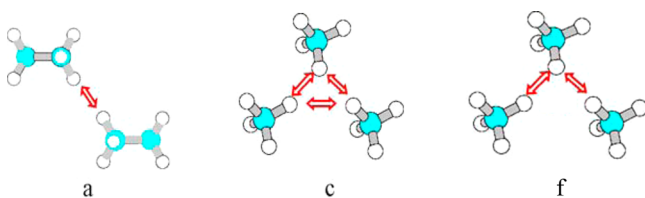
**Small Aggregates.** Figure 3 illustrates the fragment of the aliphatic alcohol monolayer (bottom view), in which two types of intermolecular  $\text{CH}\cdots\text{HC}$  interactions formed between hydrocarbon chains are marked. These types of interactions are designated as  $K_a$  and  $K_f$  (see Figure 4a) in analogy to previously.<sup>12,13</sup> It should be noted, that the  $K_f$  interactions structurally differ from the interactions found previously. In formation of one  $\text{CH}\cdots\text{HC}$  interaction of “a”-type between two alkyl chains only one hydrogen atom participates from every second methylene fragment of each interacting chain whereas for the  $\text{CH}\cdots\text{HC}$  interaction of “f”-type every second methylene fragment of one molecule form an interaction with analogous methylene fragments of two other molecules at the same time. The interactions of f-type resembles to some extent the structure of the interactions of “c”-type. The only difference is that the interactions of f-type involve only two molecules out of three, whereas the interactions of c-type involve all three molecules (see Figure 5). However, it will be further proved that the interactions of both a and f-types are virtually isoenergetic.

Six possible types of interactions between the hydroxylic groups of the alcohol molecules can be singled out. They are represented in Figure 3b. The increments from these interactions differ from each other because of the different mutual orientation of alcohol hydrophilic parts with respect to one another. In order to describe the 2D monolayer phase one should define the increment of each  $\text{CH}\cdots\text{HC}$  interaction and the interaction between the functional groups in the clusterization enthalpy and entropy. To accomplish this requirement the structures of small aggregates (dimers, trimers, tetramers, pentamers, octamers, and nonamers) are marked in the cluster (see Figure 4). These aggregates involve all the





**Figure 4.** Types of pair intermolecular (a) CH...HC interactions and (b) interactions between the hydroxylic groups.



**Figure 5.** Intermolecular CH...HC interactions of different types.

considered interactions in their structure. Figure 2 illustrates the optimized structures of alcohol small aggregates, which are used for the correlation analysis of the increments of the intermolecular interactions to the values of the thermodynamic clusterization parameters depending on the number of these interactions realized in the cluster.

Consider now the structure of regarded aggregates in detail. It is possible to single out six types of dimers by the number of interaction types between the hydroxylic groups of alcohols for the hexagonal 2D cluster given in Figure 4. However, it is possible to get the optimized structure without any edge effects<sup>42</sup> only for a dimer with  $n_1$  interaction of hydrophilic parts (see Figure 4b). The structure of this dimer is illustrated in Figure 2 on the example of the aggregate with the alkyl chain length of 10 carbon atoms. Note, that the CH...HC interactions between the alkyl chains of alcohols are not realized in the fragment possessing  $n_2$  interaction (see Figure 4a). Therefore, the regarded dimer is out of consideration while the optimization procedure. The considered fragment of the monolayer has also two types of trimers and tetramers. There are the next interactions between the monomers in these

trimers:  $n_1$ ,  $n_3$ , and  $n_5$  for trimer 1 and  $n_2$ ,  $n_4$ , and  $n_6$  for trimer 2. However, only trimer 2 has the hydrogen interaction  $n_4$ . It should be noted that there are only CH...HC interactions of a-type in the described structures of dimers and trimers whereas in tetramers the alcohol molecules orientate in such way that tetramer 1 has CH...HC interactions of a-type, and tetramer 2 has CH...HC interactions of f-type as well. But during the optimization of the tetramer 2 another "b" type of CH...HC interactions appears between the middle monomers, whereas these interactions are not realized in larger clusters and 2D monolayer phases. That is why it would be unreasonable to calculate the thermodynamic parameters of clusterization for such aggregates and include them in the further construction of the additive scheme. Larger clusters, such as, octamers and nonamers were built to obtain the energetic increments of the interactions  $n_2$ , because in dimers, trimers, and tetramers they are not realized or distorted by edge effects. The chosen clusters are presented in Figure 2 on the example of structures with 10 carbon atoms in the alkyl chains. Octamers and nonamers have one or two interactions  $n_2$  correspondingly. In addition, these clusters possess the considered two types of intermolecular CH...HC interactions. Note, that for nonamers only several structures are built with alkyl chains of 11–14 carbon atoms. It is given rise by the fact that the clusters with shorter alkyl chains has edge effects, and for clusters with longer chains it is impossible to calculate the thermodynamic properties of formation because of atom number restriction.

For all the small aggregates described above the thermodynamic parameters of their formation and clusterization are calculated. Enthalpy, entropy, and Gibbs' energy of clusterization are calculated as previously<sup>11–13,36–45</sup> according to the formulas:  $\Delta H_{T,m}^{\text{Cl}} = \Delta H_T^0 - m \cdot H_{T,\text{mon}}^0$ ;  $\Delta S_{T,m}^{\text{Cl}} = S_T^0 - m \cdot S_{T,\text{mon}}^0$ ;  $\Delta G_{T,m}^{\text{Cl}} = \Delta H_{T,m}^{\text{Cl}} - T \cdot \Delta S_{T,m}^{\text{Cl}}$ , where superscript "Cl" indicates the thermodynamic parameters of the clusterization process,  $\Delta H_T^0$  and  $S_T^0$  are enthalpy and entropy of the aggregates at a certain temperature  $T$ ,  $H_{T,\text{mon}}^0$  and  $S_{T,\text{mon}}^0$  are enthalpy and entropy of the corresponding monomers at the same temperature  $T$ , and  $m$  is the number of monomers in the cluster. The corresponding values of enthalpy, entropy, and Gibbs energy of clusterization are listed in Table 1. Here, we do not give the values of the thermodynamic clusterization parameters for tetramers 2 and nonamers (except the structures possessing 11–14 carbon atoms in the alkyl chains). These clusters have edge effects, so they are excluded from the further construction of the additive scheme for hexagonal monolayers of alcohols.

The correlation dependencies on the number of intermolecular CH...HC interactions and interactions between the functional groups are built on the basis of calculated thermodynamic clusterization parameters (see Table 1):

$$\Delta H_{298,m}^{\text{Cl}} = -(9.15 \pm 0.07)(K_a + K_f) - (18.42 \pm 1.22)n_1 + (11.11 \pm 1.53)n_4 \quad [R = 0.9998; \text{SD} = 7.00 \text{ kJ/mol}; N = 70] \quad (4)$$

$$\Delta S_{298,m}^{\text{Cl}} = -(19.79 \pm 0.19)(K_a + K_f + n_4) - (117.24 \pm 3.59)n_1 - (80.44 \pm 5.19)n_5 - (95.08 \pm 4.85)n_6 \\ [R = 0.9999; \text{SD} = 15.47 \text{ J/(mol} \cdot \text{K)}; N = 70] \quad (5)$$

where  $K_a$  and  $K_f$  are the number of CH...HC interactions of both a and f type realized in the regarded cluster. They can be obtained (see Figure 4) as follows

Table 1. Thermodynamic Parameters of Fatty Alcohol Aggregates

molecule	$\Delta H_{298,m}^{\text{Cl}}$ kJ/mol	$\Delta S_{298,m}^{\text{Cl}}$ J/(mol·K)	$\Delta G_{298,m}^{\text{Cl}}$ kJ/mol	$\Delta H_{298,m}^{\text{Cl}}$ kJ/mol	$\Delta S_{298,m}^{\text{Cl}}$ J/(mol·K)	$\Delta G_{298,m}^{\text{Cl}}$ kJ/mol
Dimer			Trimer 1			
C <sub>6</sub> H <sub>13</sub> OH	−29.93	−154.53	16.12	−84.79	−369.80	25.41
C <sub>7</sub> H <sub>15</sub> OH	−37.96	−165.11	11.24	−110.62	−420.52	14.69
C <sub>8</sub> H <sub>17</sub> OH	−40.44	−173.61	11.30	−114.33	−427.83	13.17
C <sub>9</sub> H <sub>19</sub> OH	−48.34	−173.42	3.34	−140.08	−476.41	1.89
C <sub>10</sub> H <sub>21</sub> OH	−50.86	−191.52	6.22	−143.85	−478.24	−1.33
C <sub>11</sub> H <sub>23</sub> OH	−58.73	−205.34	2.46	−169.58	−528.49	−12.09
C <sub>12</sub> H <sub>25</sub> OH	−61.25	−217.91	3.68	−173.35	−546.22	−10.57
C <sub>13</sub> H <sub>27</sub> OH	−69.12	−237.98	1.79	−199.09	−576.48	−27.30
C <sub>14</sub> H <sub>29</sub> OH	−71.66	−251.97	3.42	−202.87	−589.71	−27.13
C <sub>15</sub> H <sub>31</sub> OH	−79.53	−266.50	−0.12	−228.63	−635.49	−39.25
C <sub>16</sub> H <sub>33</sub> OH	−82.07	−264.68	−3.20	−232.40	−643.92	−40.51
Trimer 2			Tetramer 1			
C <sub>6</sub> H <sub>13</sub> OH	−86.88	−376.52	25.33	−129.86	−602.56	49.70
C <sub>7</sub> H <sub>15</sub> OH	−96.15	−395.00	21.56	−154.04	−659.61	42.52
C <sub>8</sub> H <sub>17</sub> OH	−116.42	−436.12	13.54	−173.93	−695.47	33.32
C <sub>9</sub> H <sub>19</sub> OH	−125.61	−451.46	8.92	−198.32	−752.55	25.94
C <sub>10</sub> H <sub>21</sub> OH	−146.00	−490.11	0.05	−218.24	−785.10	15.72
C <sub>11</sub> H <sub>23</sub> OH	−155.13	−506.60	−4.16	−242.66	−838.31	7.16
C <sub>12</sub> H <sub>25</sub> OH	−175.56	−562.19	−8.02	−262.62	−899.69	5.49
C <sub>13</sub> H <sub>27</sub> OH	−184.68	−559.75	−17.87	−287.07	−936.00	−8.14
C <sub>14</sub> H <sub>29</sub> OH	−205.13	−607.65	−24.05	−307.07	−982.68	−14.23
C <sub>15</sub> H <sub>31</sub> OH	−214.23	−619.08	−29.74	−331.45	−1031.30	−24.12
C <sub>16</sub> H <sub>33</sub> OH	−234.68	−664.81	−36.56	−351.44	−1069.99	−32.58
Pentamer			Octamer			
C <sub>6</sub> H <sub>13</sub> OH	−171.31	−757.85	54.53	−320.28	−1441.59	109.31
C <sub>7</sub> H <sub>15</sub> OH	−206.44	−830.10	40.93	−379.29	−1570.30	88.66
C <sub>8</sub> H <sub>17</sub> OH	−230.50	−875.97	30.54	−429.04	−1667.58	67.90
C <sub>9</sub> H <sub>19</sub> OH	−265.47	−943.27	15.62	−488.24	−1796.68	47.17
C <sub>10</sub> H <sub>21</sub> OH	−289.71	−987.74	4.63	−538.08	−1898.65	27.71
C <sub>11</sub> H <sub>23</sub> OH	−324.59	−1057.39	−9.49	−597.34	−2076.03	21.32
C <sub>12</sub> H <sub>25</sub> OH	−348.90	−1123.70	−14.04	−647.31	−2212.05	11.88
C <sub>13</sub> H <sub>27</sub> OH	−383.79	−1167.71	−35.82	−706.62	−2362.18	−2.69
C <sub>14</sub> H <sub>29</sub> OH	−408.13	−1218.81	−44.93	−756.68	−2410.92	−38.23
C <sub>15</sub> H <sub>31</sub> OH	−442.98	−1286.90	−59.48	−815.99	−2532.51	−61.30
C <sub>16</sub> H <sub>33</sub> OH	−467.27	−1332.86	−70.08	−866.06	−2628.24	−82.84
Nonamer						
C <sub>11</sub> H <sub>23</sub> OH	−695.15	−2377.45	13.33			
C <sub>12</sub> H <sub>25</sub> OH	−754.36	−2519.44	−3.56			
C <sub>13</sub> H <sub>27</sub> OH	−822.64	−2629.85	−38.94			
C <sub>14</sub> H <sub>29</sub> OH	−882.02	−2758.36	−60.03			

$$K_a = \left\{ \frac{n-1}{2} \right\} \text{for dimers with the interactions } n_1 \text{ and } K_a$$

$$= \left\{ \frac{n}{2} \right\} \text{for dimers with } n_3 \text{ and } n_5 \quad (6)$$

$$\text{and } K_f = \left\{ \frac{n+1}{2} \right\} \text{for the dimers with } n_4 \text{ and } n_6$$

$$, \text{ respectively} \quad (7)$$

where  $n$  is the number of methylene groups in the alkyl chain of the alcohols; the braces denote the integer part of the number;  $n_i$  are the descriptors of interactions of the monomer functional groups in the structures of the regarded clusters. In the case that interactions between the functional groups of the hydrophilic part exist in the aggregate structure then the value of the corresponding descriptor  $n_i$  is equal to the number of such interactions. If the considered interaction is absent, this descriptor is zero.

Using equation  $\Delta G_{298,m}^{\text{Cl}} = \Delta H_{298,m}^{\text{Cl}} - T \cdot \Delta S_{298,m}^{\text{Cl}}$  the correlation dependency for clusterization Gibbs' energy is obtained

$$\Delta G_{298,m}^{\text{Cl}} = -(3.26 \pm 0.13)(K_a + K_f) + (16.52 \pm 2.29)n_1$$

$$+ (17.01 \pm 1.59)n_4 + (23.97 \pm 1.55)n_5 + (28.34 \pm 1.44)n_6 \quad (8)$$

It is plain to see from the correlation dependencies 4, 5, and 8 that the energetic increments of the intermolecular CH $\cdots$ HC interactions of both types are identical. This allows one not to distinguish these interactions in further calculations according to the additive scheme for larger clusters up to 2D films and assuming them as one a type. It should be mentioned that the values of the standard deviations of clusterization enthalpy and entropy for small aggregates of alcohols forming a hexagonal monolayer are commensurable with those forming monolayers with an oblique unit cell.<sup>12</sup>

**Large and Infinite Clusters.** It is possible to use the values for the regression coefficients from the correlation eqs 4, 5 and 8 in order to build the additive scheme. This scheme allows one to calculate the values of the thermodynamic clusterization parameters for the aggregates of amphiphiles of any dimensions up to condensed monolayer phases as a sum of the corresponding increments of the intermolecular CH $\cdots$ HC interactions and the interactions between the hydrophilic parts of molecules.

Using the monolayer fragment shown in Figure 4 it is possible to calculate the number of the chosen six types of interactions between the hydrophilic parts of monomers as follows

$$n_1 = \left\{ \frac{(q-1)(p-1)}{2} \right\},$$

$$n_2 = (q-1)(p-1) - \left\{ \frac{(q-1)(p-1)}{2} \right\} \quad (9)$$

$$n_{3,6} = (p-1) \left\{ \frac{q}{2} \right\}, \quad n_{4,5} = (q-1) \left\{ \frac{p}{2} \right\} \quad (10)$$

while the dependence of general number of intermolecular CH $\cdots$ HC interactions on the alkyl chain length obeys the expression

$$K_a = n_1 \left\{ \frac{n-1}{2} \right\} + (n_3 + n_5) \left\{ \frac{n}{2} \right\} + (n_4 + n_6) \left\{ \frac{n+1}{2} \right\} \quad (11)$$

where  $n$  is the number of methylene groups in the alcohol alkyl chain and the braces denote the integer part of the number.

In order to calculate the number of interactions described above per one monomer molecule of the infinite 2D cluster, one has to divide eqs 9 and 10 by the number of monomers in the cluster ( $m = pq$ ) and to calculate the limits of the resulting expressions at an infinite number of molecules in the cluster. Therefore, for infinite 2D clusters of alcohols ( $p = \infty$ ,  $q = \infty$ ) eqs 9 and 10 become

$$\frac{n_{1-6,\infty}}{m} = 0.5 \quad (12)$$

The number of intermolecular CH $\cdots$ HC interactions per one monomer molecule of the 2D clusters can be calculated using the expression:

$$\frac{K_{a,\infty}}{m} = 0.5 \left\{ \frac{n-1}{2} \right\} + n \quad (13)$$

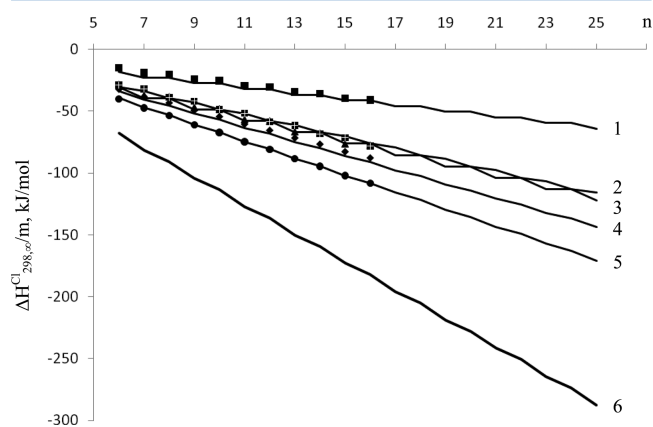
After introduction of eqs 12 and 13 into the correlation eqs 4, 5, and 8, respectively for enthalpy, entropy, and Gibbs' energy of clusterization, one obtains the expressions for the clusterization thermodynamic characteristics of alcohols per one monomer molecule

$$\frac{\Delta H_{298,\infty}^{\text{Cl}}}{m} = -9.15 \left( 0.5 \left\{ \frac{n-1}{2} \right\} + n \right) - 3.65, \text{ kJ/mol} \quad (14)$$

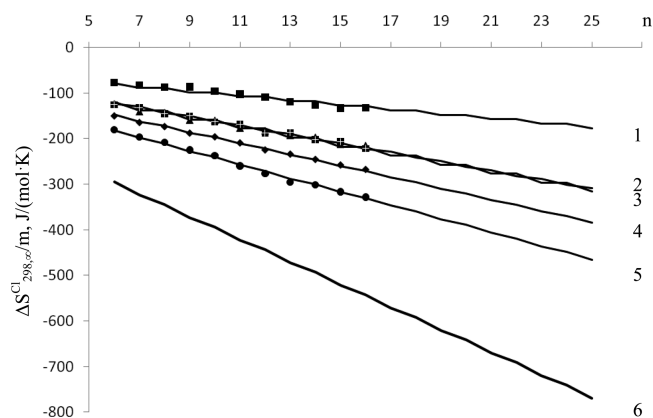
$$\frac{\Delta S_{298,\infty}^{\text{Cl}}}{m} = -19.79 \left( 0.5 \left\{ \frac{n-1}{2} \right\} + n \right) - 156.28, \quad \text{J/(mol}\cdot\text{K)} \quad (15)$$

$$\frac{\Delta G_{298,\infty}^{\text{Cl}}}{m} = -3.27 \left( 0.5 \left\{ \frac{n-1}{2} \right\} + n \right) + 42.92, \text{ kJ/mol} \quad (16)$$

The dependencies of the clusterization parameters per one monomer molecule on the alkyl chain length of alcohol at 298 K are shown in Figures 6–8. Here, the lines correspond to the



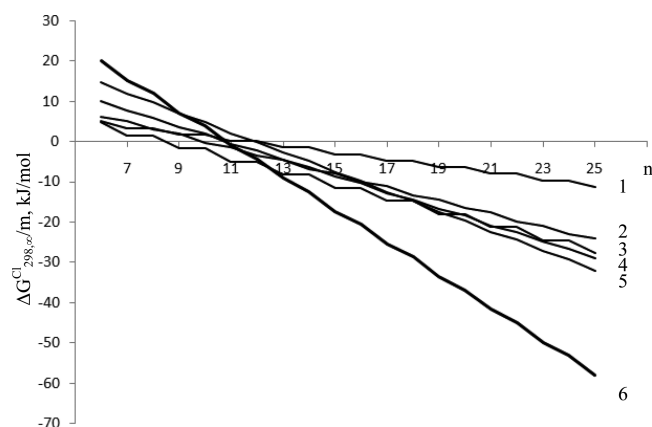
**Figure 6.** Dependence of the variation of the clusterization enthalpy of aliphatic alcohols on the alkyl chain length: 1, dimer; 2, trimer 2; 3, trimer 1; 4, tetramer 1; 5, octamer; 6, hexagonal monolayer phase.



**Figure 7.** Dependence of the variation of the clusterization entropy for hexagonal monolayer phase of aliphatic alcohols on the alkyl chain length (definitions 1–6 have the same meaning as in Figure 6).

dependencies calculated according to the additive scheme using eqs 14–16, whereas the points define the results of the direct calculations using the PM3 method. Note that the parameters for small aggregates calculated according to the correlation expressions 4, 5, and 8 are divided by the number of the monomers in the regarded cluster (by  $m = 2$  for dimers, by  $m = 3$  for trimers). This is necessary because the thermodynamic clusterization parameters of the 2D clusters are accounted per one monomer molecule. The presented graphs show that the results obtained in the framework of additive scheme agree well with the results of the direct calculation.

On the basis of obtained graphical dependencies, one can see that spontaneous clusterization of aliphatic alcohols in the



**Figure 8.** Dependence of the variation of the clusterization Gibbs' energy for hexagonal monolayer phase of aliphatic alcohols on the alkyl chain length (definitions 1–6 have the same meaning as in Figure 6).

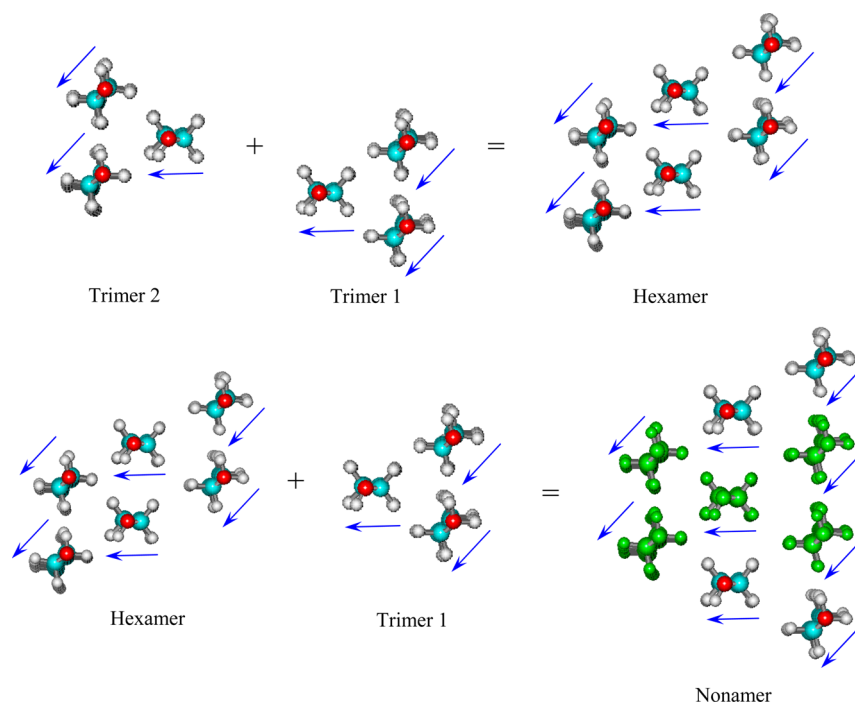
condensed monolayer phases of hexagonal structure is possible for molecules having no less than 11 carbon atoms in the alkyl chain. This conclusion agrees well with the existing experimental data, obtained for condensed monolayer phases of alcohols with alkyl chain length of 12 carbon atoms at 25 °C.<sup>14–19</sup> In addition, analysis of given dependencies of the clusterization Gibbs' energy allows assumptions about the possible way of the formation of the hexagonal lattice structure. Figure 8 indicates that the smallest values of clusterization Gibbs' energy belong to the structures of trimers 1 and 2 among all the aggregates of alcohols with alkyl chain lengths of 11–13. The formation of trimer 1 is slightly more favorable. This suggests that the alcohol hexagonal structures with alkyl chain lengths of 11–13 carbon atoms are formed from these two trimer structures. In what follows, the aggregation of mentioned trimers will go on via formation of hexamers and

larger clusters up to 2D condensed phases. The schematically proposed way of clusterization is illustrated in Figure 9. As in Figure 3c, the arrows define the direction from the carbon atom to one of the hydrogen atom in the  $\text{CH}_2$  fragment, and the unit cell is highlighted.

The foregoing assumption about the possible way of formation of alcohol hexagonal films conforms to the results of the simulation of the experimental  $\pi$ -A isotherms for alcohol homologues series with 12–14 and 16 carbon atoms in the alkyl chain.<sup>11–13</sup> The thermodynamic model exploited in these studies is capable of the theoretical description of adsorption monolayer behavior at the air/water interface, including the thermodynamic clusterization parameters and aggregation number  $m$  for small clusters, which are the basic structures during the clusterization process. These studies reveal that liquid expanded–liquid condensed (LE–LC) phase transition in alcohol monolayers takes place between aggregates with  $m = 2.3$  for dodecanol (at 15 °C);  $m = 2.75$  for tridecanol (at 25 °C); and  $m = 3.0$  for tetradecanol (at 25 °C).<sup>11–13,18</sup> Consequently, it is reasonable to conclude that the hexagonal phase of alcohol monolayers is formed on the basis of the trimer formation and their subsequent aggregation (see Figure 9).

## CONCLUSION

The structural parameters of the hexagonal phase of alcohol monolayers at the air/water interface are described in the framework of quantum chemical semiempiric PM3 method. The introduced approach is capable of reproducing available experimental data concerning the nonionic surfactant behavior at the air/water interface and predicting missing data without carrying out expensive and effortful experiment. The results conform to the main conclusions obtained using molecular dynamic simulations<sup>1</sup> and with it the exploited approach requires less time and less sophisticated equipment. It is shown that the calculated parameters of the alcohol unit cell  $a = 4.3$  Å,



**Figure 9.** Scheme of the formation of the hexagonal monolayer phase for aliphatic alcohols.



$b = 7.4 \text{ \AA}$  agree well with the corresponding experimental values  $a = 5.0 \text{ \AA}$ ;  $b = 7.5 \text{ \AA}$ .<sup>28</sup> The tilt angle of alcohol molecules with respect to the normal to the interface is  $t = 4^\circ$  whereas the corresponding experimental values were found in the range of  $0\text{--}9^\circ$ .<sup>20,25–28</sup>

The thermodynamic clusterization parameters are calculated for molecules with the general formula  $C_nH_{2n+1}OH$  ( $n = 6\text{--}16$ ). It is found that spontaneous clusterization process is possible for surfactants having no less than 11 carbon atoms in the alkyl chain, agreeing well with the results of numerous experimental studies.<sup>14–23</sup> The analysis of the calculated dependencies of the thermodynamic clusterization parameters per one monomer for small aggregates and 2D films suggests the possible way of the formation of the hexagonal monolayer phase via formation of alcohol trimers and their further aggregation up to the infinite monolayer structure. This assumption corresponds well with the small aggregation numbers  $m = 2.3\text{--}3.0$  for the LE phase obtained by thermodynamic analysis of experimental  $\pi$ -A isotherms of homologues  $C_{12}\text{--}C_{14}$  alcohols.<sup>11–13</sup>

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### Notes

The authors declare no competing financial interest.

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