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Quantum chemical analysis of thermodynamics of 2D cluster formation of alkanes at the water/vapor interface in the presence of aliphatic alcohols

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Abstract

Using the quantum chemical semi-empirical PM3 method it is shown that aliphatic alcohols favor the spontaneous clusterization of vaporous alkanes at the water surface due to the change of adsorption from the barrier to non-barrier mechanism. A theoretical model of the non-barrier mechanism for monolayer formation is developed. In the framework of this model alcohols (or any other surfactants) act as 'floats', which interact with alkane molecules of the vapor phase using their hydrophobic part, whereas the hydrophilic part is immersed into the water phase. This results in a significant increase of contact effectiveness of alkanes with the interface during the adsorption and film formation. The obtained results are in good agreement with the existing experimental data.

To test the model the thermodynamic and structural parameters of formation and clusterization are calculated for vaporous alkanes C_nH_{2n+2} (n_{CH_3} =6-16) at the water surface in presence of aliphatic alcohols $C_nH_{2n+1}OH$ (n_{OH}=8-16) at 298 K. It is shown that the values of clusterization enthalpy, entropy and Gibbs' energy per one monomer of the cluster depend on the chain lengths of corresponding alcohols and alkanes, the alcohol molar fraction in the monolayers formed, and the shift of the alkane molecules with respect to the alcohol molecules Δn.

Two possible competitive structures of mixed 2D films alkane-alcohol are considered: 2D films 1 with single alcohol molecules enclosed by alkane molecules (the alcohols do not form domains) and 2D films 2 that contain alcohol domains enclosed by alkane molecules. Formation of the alkane films of the first type is nearly independent of the surfactant type present at the interface, but depends on their molar fraction in the monolayer formed and the chain length of the compounds participating in the clusterization, whereas for formation of the films of the second type the interaction between the hydrophilic parts of surfactant is essential and different for various types of amphiphilic compounds.

The energetic preference of the film formation of both types depends significantly on the chain length of compounds. The surfactant concentration (in range of X=0-10%) exerts a slight influence on the process of film formation.

Introduction

Investigations of the monolayer formation by surfactants at different interfaces are of interest at present time despite the almost centennial history of the development of this issue. The systems at the air/water interface are most examined. [1,2] Whereas the surfactant behavior at the oil/water interface can still not be perfectly predicted due to the fact that such systems are multicomponent and multiphase.[3] Moreover, mechanism and factors influencing the monolayer formation by fully hydrophobic molecules are not completely clarified and the existing data are quite controversial.

The authors of ref. [4] found the possibility of film formation by heptane and octane at water surface at 25°C using neutron and X-ray reflectometry. This fact is proved also by authors of ref. [5, 6] dedicated to investigation of wetting layers of n-alkanes with $5 \leq n < 8$. Pfohl *et al* [7] using ellipsometric method declared that hexane and heptane form monomolecular films at the air/water interface saturated with alkane vapor. At the same time the ref. [8] states that alkanes with chain length more than 5 carbon atoms do not cover the water surface. In the study of ref. [9] the preference of adsorption of hexane vapor at mercury surface was shown as compared with water.

The authors of refs. [10-12] ascertained the possibility of formation of crystalline monolayers of completely hydrophobic compounds that do not contain any hydrophilic part, which could be an anchor and keep the molecules at the interface. For example, Π-A isotherms were obtained for perfluoro-n-eicosane. This indicates the possibility of formation of crystalline monolayers by this compound; the structural parameters of its unit cell were determined by the grazing incidence X-ray diffraction (GIXD). In the study of ref. [13] it is claimed that long-chained molecules form usual lamellar crystals with too weak interactions between the lamellas. That is why the authors of ref. [11] supposed that in some cases the interactions realized between hydrophobic molecules are capable of ordering and holding the molecules in such a way that their hydrophobic chains are vertically oriented, and Van-der-Waals' interactions between the monolayer and water molecules ensure the stability of the system as a Langmuir monolayer. The authors of ref. [14] believe that the stability origin of hydrophobic Langmuir monolayers is entropic, rather than energetic as in the stabilization of common amphiphilic monolayers, primarily driven by the interaction between the polar head and water.

As shown in the studies, [15, 16] the fluorinated surfactant molecules are typical of dispersion interactions realized between fluorocarbon fragments of the chains. The energy of CF···FC interactions is two times higher than that of the corresponding CH···HC ones [17], and they are more rigid. This results in the possibility of spontaneous clusterization for fluorinated surfactants with shorter fluorocarbon chain than for corresponding surfactants with hydrocarbon chain, [18] and leads to better structural ordering of crystalline monolayers of fluorocarbon surfactants. [19-21]

The authors of the ref. [10] investigated five alkanes C_nH_{2n+2} with n=23, 24, 28, 29, and 36 and showed their capability of spontaneous monolayer formation with crystalline structure at the air/water interface. The obtained films have some peculiarities. In the case of short-chained alkanes (n=23, 24) the films consist of 20 monolayers, the unit cells of the monolayer are oblique with alkane molecules inclined with respect to the normal to the interface. Lengthening of the alkane chain results in vertical orientation of the molecules with respect to the interface and changing of the unit cell structure from oblique to hexagonal. At the same time the monolayers become thinner. The thickness of the $C_{28}H_{58}$ and $C_{29}H_{60}$ films have a thickness of four monolayers, whereas that of the $C_{36}H_{74}$ film is one monolayer. It should be noted that addition of 5-10% alcohols leads to the formation of bilayers for more short-chained alkanes with 23 and 24 carbon atoms.

A number of papers are devoted to the investigation of the behavior of liquid alkanes (from hexane to hexadecane) at the pure water surface and with surfactant additives. As it was shown in refs. [3, 22], the short-chain alkanes (with chain length shorter than 11 carbon atoms) are capable of wetting the water surface with adsorbed surfactant whereas long-chain alkanes form lenses in equilibrium with the surfactant monolayer comprising adsorbed alkane. In addition, there are experimental data [23-30] indicating that monolayers of ionic (sodium dodecylsulphate) and non-ionic (aliphatic and perfluorinated alcohols, phospholipids) at the oil/water interfaces are less densely packed than the corresponding ones at the air/water and water/alkane vapor interfaces. This proves that the alkane molecules of the second liquid phase are incorporated into the surfactant monolayers.

Alkane vapor adsorption at the pure water surface and also in presence of ionic (SDS, $C_{12}TAB$) and non-ionic ($C_{10}EO_8$) surfactants is investigated in a number of papers. [31-38] These studies revealed that the presence of surfactants at the water surface even in small amounts (e.g. 10^{-5} mol/l) favors the process of alkane adsorption when the time for reaching the adsorption equilibrium is ~700 s. The higher the surfactant concentration (up till CMC), the faster the adsorption equilibrium is reached, whereas it requires significant time (up to ~8000 s) to reach the adsorption equilibrium without surfactant at the water surface. These experimental data suggest that it must be an energetic barrier for adsorption of the vaporous alkanes at the pure water surface when not each contact of the alkane molecules with the interface is effective. But addition of the surfactant significantly reduces this barrier. So, the adsorption of alkanes at the pure water surface can possess barrier mechanism, while their adsorption at the interface containing the surfactants may be regarded as non-barrier.

The theoretical model proposed in this paper allows adequate interpretation of the mentioned experimental data. In the framework of this model the amphiphilic compounds act as 'floats', their hydrophilic parts are immersed into the water phase and at the same time their hydrophobic parts interacts with alkane molecules of the vapor phase. This results in an essential increase of the effectiveness of alkane contact with the interface, which leads to the change from barrier to non-barrier mechanism of the alkane adsorption and a quicker reaching of the adsorption equilibrium. At the same time the type of the surfactant almost does not matter.

All said above requires the quantum chemical analysis of the clusterization of alkanes C_nH_{2n+2} ($n_{CH_3} = 6-16$) from the vapor phase at the water surface in presence of classical surfactant – aliphatic alcohols $C_nH_{2n+1}OH$ ($n_{OH} = 8-16$).

Methods

The quantum chemical program package Mopac2000 [39] in approximation of the semi-empirical PM3 method is used for optimization of the geometrical structure and calculation of the thermodynamic parameters of the formation of alkane and alcohol monomers and their aggregates. This choice is stipulated by the fact that the PM3 method is parametrized with respect to the formation heats. [40] In addition we have shown [41] that only this method describes adequately van-der-Waals' molecules, which comprise the intermolecular CH···HC interactions between the hydrocarbon chains of the monomers in the aggregates that have the determinative contribution to the process of the surfactant film formation. The reasonableness to apply this method for calculation of thermodynamic and structural parameters of surfactants clusterization was shown in a number of papers [41-48] for ten types of substituted alkanes (fatty alcohols, thioalkohols, saturated and unsaturated carboxylic acids, amines, amides of carboxylic acids, α-amino and α-hydroxycarboxilic acids, and substituted melamines). Therefore, this method is used in the present study for calculation of the thermodynamic parameters of clusterization of alkane monolayers C_nH_{2n+2} ($n_{CH_3} = 6-16$) in the presence of aliphatic alcohols $C_nH_{2n+1}OH$ (n_{OH}=8-16) with a molar fraction smaller than X=10% at the water/vapor interface.

Model

The model for calculation of the thermodynamic clusterization parameters of vaporous alkanes at the vapor/water interface is developed with consideration of the following basic prerequisites:

- As shown by using GIXD, [10] monolayers are formed by compounds with chain length of 36 carbon atoms, whereas molecules with shorter chains of 23-29 carbon atoms form multilayers with a thickness between 2 and 20 monolayers;

- The experimental data [49, 50] indicate that the monolayer thickness of surfactants is equal to the maximal chain length of the amphiphilic molecule (be subjected to the tilt angle of the molecule with respect to the interface), provided all hydrogen atoms of the methylene units in the chain are in *trans*-position. This is proved by the type of Π-A isotherm of $C_{36}H_{74}$, and it is also indicated that the area per one alkane molecule in the crystalline monolayer is 20 $Å^2$ approximately equal to the molecular cross-section; [10]
- In ref. [10] it is found that the addition of 5-10% alcohols structures more short-chained alkanes $C_{23}H_{48}$ and $C_{24}H_{50}$ so that they are capable of bilayer formation;
- investigations of the collective adsorption of vaporous alkanes and amphiphilic compounds (SDS, $C_{12}TAB$, $C_{10}EO_8$) at the water surface [31-38] show that the adsorption of alkanes without surfactants takes place too slow (~8000 s to reach the equilibrium), whereas the presence of ether ionic or non-ionic surfactants favors the alkane adsorption and leads to a significant decrease of the time required for reaching equilibrium (~700 s);
- according to ref. [51] the ionic surfactant molecule is immersed in the water phase with its hydrophilic part and 3-4 methylene units adjacent to it, whereas non-ionic surfactants locate right at the water surface.

With regard to said above the developed model uses the following assumptions:

1) Competitive film formation of two types is possible for alkanes in the presence of alcohols: 2D films 1 with single distributed alcohol molecules enclosed by alkane molecules without alcohol domains and 2D films 2 comprising alcohol domains enclosed by alkane molecules.
2) For the small clusters of alkanes and alcohols belonging to 2D film 1, only such mixed alkane-alcohol aggregates are considered, that do not comprise alcohol molecules located next to each other, because alcohol molecules act as single distributed ‘floats’ among the alkane molecules. Thus, the hydrophilic parts of alcohols situated in the water phase, keep the molecule at the interface and promote the aggregation of completely hydrophobic alkanes at the water/vapor interface through the formation of intermolecular CH···HC interactions between hydrophobic parts of the interacting molecules.
3) The influence of the interface is indirect and is realized by its orienting and stretching effect on the surfactant molecules. That means the water phase retracts the functional group of the alcohol. At the same time, the hydrophobic part of the alcohol molecule is pushed off from the water surface and sticks into the gaseous phase. All hydrogen atoms of the methylene groups of the surfactant and alkane chains are in *trans*-position.
4) As the alkane molecules are totally hydrophobic it is reasonable to assume that they do not penetrate into the water phase, rather they orient straight at the interface during their

clusterization in the presence of alcohols. However, the alkane molecules from the vapor phase can be located at the interface on several methylene units higher as compared with the functional alcohol group (see Δn in Fig. 1). This assumption does not contradict to the results obtained in ref. [10], where the crystalline structure of the alkane monolayers and the influence of alcohol additives on it, was studied. This work shows that the above mentioned difference Δn between alkyl chain of alcohols and alkanes amounts to four methylene groups. Note, that we consider two structurally and energetically different films of alkanes possible to be realized: one of them has the maximal number of intermolecular CH···HC interactions and another has the number of intermolecular CH···HC interactions by one less than for the maximal. The effect of the shift of the nearest alkane molecules with respect to the alcohol molecule on the thermodynamics of clusterzation for these two alkane monolayers are illustrated on examples of two possible values Δn=2 and 3 correspondingly, whereas the scheme used here allows the calculation of the structural and thermodynamic parameters of clusterization of alkane monolayers from the vapor phase in the presence of alcohols with any Δn value.

The calculations of the thermodynamic parameters (enthalpy, entropy, Gibbs' energy) of clusterization of alkane monolayers in the presence of alcohols are carried out according to the procedure described in detail elsewhere [52] and successfully tested for ten classes of amphiphiles investigated earlier. [41-48]

Results and discussion

Monomers. The conformational analysis of alcohol monomers was carried out in a previous study [41]. It resulted in the determination of two stable monomer conformations with the following values of the torsion angle for the hydroxylic group $\angle\alpha=C_2–C_1–O–H$ 60º and 300º (– 60º), respectively (see Fig. 2). In ref. [41] the values of the thermodynamic parameters of formation for these conformers were proved to be identical. So, the monomer structure with the torsion angle of the OH-group $\angle\alpha=C_2–C_1–O–H=60º$ is used in the following calculations. According to the findings of the experimental studies, [10, 49, 50] the monomers of alcohols and alkanes are in the maximum extended 'linear' conformation, when hydrogens of the methylene units are in *all-trans* conformation.

The optimized structures of alkane and alcohol monolayers are shown in Fig. 3 for the compounds with 10 carbon atoms in the chain taken as an example. The calculated values of enthalpy, absolute entropy and Gibbs' energy of formation for alkanes and alcohol are in good agreement with the corresponding experimental data. [53] They are listed in a preceding paper [54] investigating the vaporous alkane incorporation into surfactant monolayers.

The correlation dependences of thermodynamic parameters of formation on the chain length are built on the basis of the calculated values (Table 1). The obtained regression equations are linear with a corresponding correlation coefficient higher than 0.9999. The analysis of the listed data reveals that the values of the increments of the methylene units (the slope *a*) almost coincide for alkanes and alcohols. It should be mentioned that the presence of the free term *b* in the correlation dependence of absolute entropy for alkanes is caused by the structural difference between the methylene and methyl units in the molecular chain, whereas the enthalpy of formation of these units is almost the same. However, such a structural difference between CH_2 and CH_3 fragments is difficult to distinguish for the alcohol molecule, because the regression free term *b* contains both the increment of the alcohol hydrophilic part and the mentioned difference to the entropy of monomer formation.

Dimers. In this section we consider such clusters of alkanes and alcohols, in which alcohol molecules do not interact with each other and are quite far from each other, so that they are single distributed among alkane molecules (2D film 1). The results of the direct calculations for pure and mixed dimers of alkanes and alcohols reveal that alcohol dimerization is possible for compounds with 10 carbon atoms in the chain (ΔG^{dim}_{298}= –1.31 kJ/mol), whereas for alkanes the required chain length is 18 carbon atoms (ΔG^{dim}_{298}= –2.77 kJ/mol). Collective dimerization of alkanes and alcohols is possible for compounds with 14 and 10 carbon atoms in the chain, respectively (ΔG^{dim}_{298}= –0.61 kJ/mol). Thus, it is intermediate between dimerization of pure alcohols and alkanes. Hence, one can suppose that formation of mixed alkane-alcohol dimers will take place in case of low surface concentrations of alcohols.

So, the molecules of classical surfactants (alcohols) act like a ‘float’ promoting the aggregation of totally hydrophobic alkanes from the vapor phase at the water surface due to formation of intermolecular CH···HC interactions between the hydrophobic chains of the interacting molecules. Therefore, alcohol molecules can be considered as clusterization centers enabling aggregation of hydrophobic molecules up to a monolayer. This allows us to disregard the interaction realized in alcohol dimers, rather to take into consideration only the structures of the mixed dimers comprising one alcohol and one alkane molecule. In addition we consider two possible locations of the alkane molecules with respect to an alcohol molecule: 1) when the alkane molecule is shifted by an odd number of methylene units Δn=3 (cf. Fig. 1) with respect to the hydrophilic headgroup of the alcohol in the monolayer; 2) by an even number of Δn=2. Such an orientation of alkane molecules with respect to the surfactants correlates with small clusters that form 2D film 1 with single distribution of alcohol molecules with Δn=3 and Δn=2, respectively (cf. Figs. 3 and 4).

At the construction of the dimer structures (and larger structures as well) the fact has to be considered that these structures involve the ‘a’ type of intermolecular CH···HC interactions between the alkyl chains of the interacting molecules. This type of interactions is energetically most preferable, as shown in preceding papers. [41, 46] Note, that each alcohol molecule interacts with four alkane molecules at the formation of alkane monolayers in the presence of small quantities of alcohols at the water/alkane vapor interface. This means that four mixed dimers can be formed, namely two for each of the p and q propagation directions of the monolayer. These types of mixed dimers are marked with red dashed lines in Figure 5 and defined with the indices p and q in the propagation direction of the monolayer in which these mixed dimers are the basic units. In the same way the pure alkane dimers are defined as Dimer_CH_3,p and Dimer_CH_3,q, respectively (they are marked with dashed blue lines in Figure 5). It should be mentioned that the structures of pure alkane dimers are different for films with an odd value of Δn and the same for the film with even Δn (cf. Figs. 3 and 4). The thermodynamic parameters of dimerization of the dimer pairs Dimer 1,p and Dimer 4,p as well as Dimer 2,q and Dimer 3,q (comprising films with even Δn) are practically identical since these dimer pairs have the same number of intermolecular CH···HC interactions stipulated by their structural peculiarities. This was proved in a preceding paper dealing with the investigation of the incorporation possibility of alkanes into the surfactant monolayers. [54] Therefore, the Dimer 1,p and Dimer 2,q are taken as basic mixed small clusters in p and q propagation directions of the monolayer, respectively for the films with an even Δn value.

For the 2D films 1 with Δn=2 and 3 pure alkane dimers with alkyl chain lengths from 6 to 16 carbon atoms are built and mixed alcohol-alkane dimer series with alkyl chain length of alcohols from 8 to 16 carbon atoms, as well. For example, for octanol (n_{OH}=8) a number of mixed dimers with alkanes of different lengths from hexane (n_{CH_3}=6) to hexadecane (n_{CH_3}=16) are built, and so on up to hexadecanol. Thereby, 99 structures of mixed dimers of each type and 11 structures of pure alkane dimers (altogether 209 structures) are built for films with Δn=2, whereas for films with Δn=3 there are twice as many dimer structures as for the film with Δn=2.

The optimized structures of the regarded dimers are presented in Figures 3 and 4 for the structures of alcohol and alkane associates with 10 carbon atoms in the hydrocarbon chains. Enthalpy, entropy and Gibbs' energy of formation and clusterization are calculated for all dimer (and larger associates, as well) structures described above. Enthalpy, entropy and Gibbs' energy of clusterization are calculated according to the expressions: $\Delta H^{Cl}_{298,m} = \Delta H^{0}_{298} - \Delta H^{0}_{298,mon(OH)} - (\mathrm{m}-1)\,\Delta H^{0}_{298,mon(CH_3)}$; $\Delta S^{Cl}_{298,m} = S^{0}_{298} - S^{0}_{298,mon(OH)} - (\mathrm{m}-1)\,S^{0}_{298,mon(CH_3)}$; $\Delta G^{Cl}_{298,m} = \Delta H^{Cl}_{298,m} - \mathrm{T}\cdot\Delta S^{Cl}_{298,m}$, where ΔH^{0}_{298} and S^{0}_{298} are enthalpy and absolute entropy of the corresponding clusters, at 298 K; $\Delta H^{0}_{298,mon(OH)}$, $S^{0}_{298,mon(OH)}$ and $\Delta H^{0}_{298,mon(CH_3)}$, $S^{0}_{298,mon(CH_3)}$ are enthalpy and entropy of alcohol and alkane monomers, respectively at 298 K; *m* is the total monomer number in the cluster. The calculated thermodynamic parameters of dimerization of pure alkane and mixed alcohol-alkane dimers (for example with $n_{OH} = 12$ and $n_{CH_3} = 6-16$), that are the structural units of the 2D film 1 with even Δn=2, are listed in Table 3.

For all dimer series the correlation dependences of the thermodynamic dimerization parameters on the number of CH···HC interactions (K_a) realized in the associates are obtained. At first consider the dimers that are the basic units of the 2D film 1 with an even value of Δn=2. The increments of the intermolecular CH···HC interactions to the dimerization enthalpy for all regarded pure and mixed dimers vary from -10.03 to -11.87 kJ/mol, to the entropy from -17.53 to -24.24 J/(mol·K), and to Gibbs' energy from -3.09 to -6.57 kJ/mol. The free term characterizing the increments of the interactions between the terminal methyl units of alkanes for both dimer structures in p and q directions is -0.85 kJ/mol for enthalpy, 74.56 J/(mol·K) for entropy, and 21.37 kJ/mol for Gibbs' energy. The increments stipulated by the interactions between the terminal alcohol units (it includes the functional group and several methylene groups immersed in the water phase) and methyl fragments of alkane should be also taken into consideration. The values of these increments for the dimer series are calculated to vary from -3.86 to 1.44 kJ/mol for enthalpy, from -68.79 to -102.12 J/(mol·K) for entropy, and from 18.86 to 29.35 kJ/mol for Gibbs' energy. Note that for dimers belonging to the 2D film 1 with Δn=3 the values of the correlation parameters are somewhat different from those listed above, but the principal trend of the variation is the same. Therefore they are omitted here. In addition, there are only 1-3 points during building the correlation dependences of the thermodynamic dimerization parameters for mixed dimers with alcohols having less than 10 carbon atoms in their alkyl chains. In this connection the values of the corresponding partial regression coefficients are listed only for systems comprising alcohol monomers with more than 10 carbon atoms in their chains. However, the total correlation for all regarded dimer structures includes the data concerning also the dimers with alcohols possessing 8 and 9 carbon atoms in the chain.

As earlier, [54] the partial correlations for all dimers are generalized into one correlation in order to single out the increments of the intermolecular CH···HC interactions and the increments contributed by the interactions between the terminal surfactant units and the methyl groups of the alkanes:

- for dimers with even Δn=2:

$$\Delta H_{298}^{\dim} = -(10.10 \pm 0.07)\cdot K_a - (3.57 \pm 0.33)\cdot(n_{1,p} + n_{2,q}) - (1.71 \pm 0.54)\cdot(n_{CH_3,p} + n_{CH_3,q})$$

[N=209; R = 0.9997; S = 1.25 kJ/mol]; (1)

$$\Delta S_{298}^{\dim} = -(21.01 \pm 0.37)\cdot K_a - (83.35 \pm 1.70)\cdot(n_{1,p} + n_{2,q}) - (101.15 \pm 2.77)\cdot(n_{CH_3,p} + n_{CH_3,q})$$

[N=209; R = 0.9993; S = 6.49 J/(mol·K)]; (2)

$$\Delta G_{298}^{\dim} = -(3.84 \pm 0.12)\cdot K_a + (21.27 \pm 0.52)\cdot(n_{1,p} + n_{2,q}) + (28.44 \pm 0.86)\cdot(n_{CH_3,p} + n_{CH_3,q})$$

[N=209; R = 0.9575; S = 2.01 kJ/mol], (3)

- for dimers with odd Δn=3:

$$\Delta H_{298}^{\text{dim}} = -(10.11 \pm 0.04)\cdot \text{K}_\text{a} - (3.04 \pm 0.21)\cdot(\text{n}_{1,\text{p}} + \text{n}_{3,\text{q}}) - (4.12 \pm 0.22)\cdot(\text{n}_{2,\text{q}} + \text{n}_{4,\text{p}} + n_{CH_3,p}) -$$

$$-(1.64 \pm 0.42)\cdot n_{CH_3,q}$$

[N=418; R = 0.9997; S = 1.13 kJ/mol]; (4)

$$\Delta S_{298}^{\text{dim}} = -(20.97 \pm 0.37)\cdot \text{K}_\text{a} - (83.39 \pm 1.74)\cdot(\text{n}_{1,\text{p}} + \text{n}_{3,\text{q}}) - (70.74 \pm 1.77)\cdot(\text{n}_{2,\text{q}} + \text{n}_{4,\text{p}})$$

$$-(111.11 \pm 3.29)\cdot n_{CH_3,p} - (101.40 \pm 3.40)\cdot n_{CH_3,q}$$

[N=418; R = 0.9986; S = 9.20 J/(mol·K)]; (5)

$$\Delta G_{298}^{\text{dim}} = -(3.49 \pm 0.08)\cdot \text{K}_\text{a} + (20.46 \pm 0.39)\cdot(\text{n}_{1,\text{p}} + \text{n}_{2,\text{q}} + \text{n}_{3,\text{q}} + \text{n}_{4,\text{p}}) +$$

$$+(26.84 \pm 0.61)\cdot (n_{CH_3,p} + n_{CH_3,q})$$

[N=418; R = 0.9591; S = 2.07 kJ/mol], (6)

where K_a is the number of intermolecular CH···HC interactions realized in the regarded dimer. It can be defined using the next equations:

- for dimers with even Δn=2:

- for pure alkane dimers in both p and q directions $K_a = \left\{\frac{n_{CH_3}}{2}\right\}$ (7)

- for pairs of mixed alcohol and alkane dimers 1, p (3, q) and 4, p (2, q), respectively:

$$K_a = \min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\}-1\right] \text{ and } K_a = \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\}-1\right]; \qquad (8)$$

- for dimers with odd Δn=3:

- for pure alkane dimers in p and q directions $K_a = \left\{\frac{n_{CH_3}-1}{2}\right\}$ and $K_a = \left\{\frac{n_{CH_3}}{2}\right\}$, respectively (9)

- for pairs of mixed alcohol and alkane dimers 1, p (3, q) and 4, p (2, q), respectively:

$$K_a = \min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\}-1\right] \text{ and } K_a = \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\}-2\right]; \qquad (10)$$

where n_{OH} and n_{CH_3} are the numbers of carbon atoms in the alkyl chains of alcohol and alkane respectively; braces { ... } denote the integer part of the number; $\text{n}_{1,\text{p}}$, $\text{n}_{2,\text{q}}$, $\text{n}_{3,\text{q}}$, $\text{n}_{4,\text{p}}$ and $n_{CH_3,p}$ and $n_{CH_3,q}$ are the descriptors of the corresponding interactions between the terminal CH_3 fragment of the alkane molecule and the fatty alcohol chain in the structures of the mixed Dimers 1,p, Dimers 2,q, Dimers 3,q, Dimers 4,p, and the interactions between methyl groups in the pure alkane dimers in p and q directions, as well. If, for example, $\text{n}_{1,p}=1$ then this interaction is realized in the considered dimer structure. If the value of this descriptor is zero, then this interaction is absent. In eqs. (1)-(6) and below, N is the sampling amount, R is the regression coefficient, and S is the standard deviation.

The graphic dependencies of dimerization enthalpy and entropy for pure alkane dimers and mixed Dimers 1,p (they are analogous for mixed Dimers 2,q) on the alkyl chain lengths of the corresponding alkanes and alcohols are shown in Figures 6 and 7. The basic structures of the 2D film 1 with Δn=2 are taken as example. Here, the solid lines correspond to the values calculated according to the correlation equations (1) and (2), and the points stand for the results of the direct calculations. The color of the directly calculated points in the discussed figures corresponds to the color of the solid lines obtained using correlation equations. Meanwhile, the triangles indicate directly calculated data for the mixed dimers consisting of alkanes with odd number of carbon atoms in the alkyl chains, whereas the squares indicate the corresponding data obtained for systems with even number of carbon atoms in alkane chains. The data calculated in the framework of the PM3 method agree well with the predicted values.

Consider now the impact of the alkyl chain length of alcohols and alkanes in dimers on the dependences of the enthalpy, entropy and Gibbs' energy of dimerization. Thus, enthalpy and entropy of dimerization of the mixed dimers decrease with lengthening of the alkyl chains until a certain limit is reached. Then, a further alkyl chain elongation of the corresponding alcohol or alkane does not affect these parameters. This is stipulated by the structural features of the regarded mixed dimers that in turn define the maximum number of intermolecular CH···HC interactions realized between the alkyl chains of alcohol and alkane. For the series of the mixed dimers built on the basis of alcohols and alkanes with chain lengths n_{OH} and n_{CH_3} the maximum number of intermolecular CH···HC interactions is defined by the alcohol chain length, and it can be calculated according to the expression $\left\{\frac{n_{OH}}{2}\right\}-1$, that is equal to four, for example, for decanol $n_{OH}=10$ and alkanes $n_{CH_3}=6-16$. The same K_a corresponds with the mixed dimers built on the basis of undecanol. The maximum number of intermolecular CH···HC interactions for the dimer series, having alcohols with 12 and 13 carbon atoms in the alkyl chains, is 5 now, etc. At the same time before the maximum is reached the number of CH···HC interactions in mixed dimers depends also on the alkane chain length. It can be calculated using expression $\left\{\frac{n_{CH_3}+1}{2}\right\}$. So, the number of the intermolecular CH···HC interactions in the mixed Dimer 1,p increases stepwise until maximum is reached. Such dependence stipulates the values of the character of the dependences for the thermodynamic dimerization parameters.

The analysis of the graphical dependences presented in Figs. 6 and 7 and correlation equations (1)-(3) provide one with the following conclusions. It is clearly seen that in terms of dimerization enthalpy formation of the mixed alkane-alcohol dimers (with alkanes enabling the realization of the maximum number of CH···HC interactions) is more preferable as compared with the pure alkane dimers of the same chain length. The mixed dimers are typical of higher values (with respect to modulo) for dimerization entropy as compared with the pure alkane dimers of the same chain length for structures belonging to 2D film 1 with Δn=2, whereas for mixed dimers of 2D film 1 with Δn=3 the dimerization entropy is lower (with respect to modulo) in comparison with pure alkane dimers in q direction and higher in comparison with those in p direction. As a result in terms of the dimerization, Gibbs' energy formation of mixed dimers is more preferable than formation of the pure dimers if the alcohol chain length is equal or longer than the alkane chain length in the mixed dimer. For example, dimerization of pure alkanes is possible for compounds containing more than 16 carbon atoms in the chain, whereas collective dimerization of alkane with alcohol is possible for molecules with n_{OH}=14 and n_{CH_3}=11 carbon atoms for Dimers 1,p and n_{OH}=12 and n_{CH_3}=13 carbon atoms for Dimers 2,q with Δn=2.

Trimers, Tetramers and Hexamers. As in the case of dimers we follow the principle that there is only one alcohol molecule in the structures of the linear trimers and squared tetramers belonging to the 2D film 1 with single distribution of alcohols among alkanes. The optimized structures of pure and mixed clusters are presented in Fig. 3 and 4.

For all regarded associates the thermodynamic parameters of their formation and clusterization are calculated and listed in Table 2. Here, as in the case of mixed dimers, the calculated data for mixed trimers and tetramers are illustrated only on the example of clusters with alcohols having $n_{OH} = 12$ carbon atoms in the chain and alkanes with $n_{CH_3} = 6-16$. In case of the tetramer series with $n_{OH} = 12$, the data are listed only for structures with alkane chain length shorter than $n_{CH_3} = 13$, because tetramers with more long-chained alkanes have edge effects (the presence of other besides 'a' types of intermolecular CH···HC interactions between three alkane chains). Such structures are excluded from the partial and general correlations obtained later.

The correlation dependences of enthalpy, entropy and Gibbs' energy on the number of intermolecular CH···HC interactions (K_a) are obtained on the basis of directly calculated data. For small clusters of pure alkanes (belonging to 2D film 1 with Δn=2) the value of the slope standing for energetic contribution of the CH···HC interactions is –(10.27–10.35) kJ/mol for enthalpy, –(21.71–25.64) J/(mol·K) for entropy, and –(2.65–3.85) kJ/mol for Gibbs' energy. The free terms of the enthalpy dependences stipulated by the interaction of terminal methyl units of alkanes are –1.41, –2.88 and –4.40 kJ/mol for trimers, tetramers and hexamers, respectively. For entropy these values are –153.43, –284.93, –457.23 J/(mol·K), for Gibbs' energy 44.31, 82.03, 131.87 kJ/mol respectively.

Analogous correlation equations are obtained also for the pure small clusters of alkanes of 2D film 1 with Δn=3. The values of the increments of the CH···HC interactions for the mixed alkane-alcohol clusters are quite similar to the values mentioned above for pure alkane associates and are in the range of –(10.34–10.69) kJ/mol for enthalpy, –(16.32–21.12) J/(mol·K) for entropy, and –(4.34–5.61) kJ/mol for Gibbs' energy. The values of the free term to the enthalpy dependences for the series of mixed trimers and tetramers vary within the limits of –(0.22–1.97) and –(1.18–6.05) kJ/mol, respectively. For entropy they are –(164.72–186.12) and –(276.20–320.19) J/(mol·K), for Gibbs' energy: (48.86–54.69) and (81.33–92.17) kJ/mol, respectively. As in the case of mixed dimers, there are only 1-3 points while building the partial correlation dependencies of the thermodynamic parameters of clusterization for mixed clusters with alcohols having fewer than 10 carbon atoms in the alkyl chains (see Figs 6 and 7). Therefore, the values of the corresponding partial regression coefficients for the described structures of mixed clusters are omitted, whereas they are used for the building of the total correlation for all associates regarded.

Similar dependences of the thermodynamic clusterization parameters are typical for mixed alkane-alcohol clusters belonging to the 2D film 1 with odd value of Δn=3. The values of the regression coefficients are slightly different, so, they are not mentioned here.

It should be noted, that the values of the slope in the correlation dependences for the described small clusters are close to those obtained for alkane-alcohol dimers and other surfactant classes investigated earlier. [41-48] In this connection we combined the partial correlations to a general one and singled out the increments of the CH···HC interactions and interactions between the terminal surfactant parts and terminal methyl units of the alkane molecules:

- for associates with even Δn=2:

$$\Delta H_{298}^{Cl} = -(10.45 \pm 0.01)\cdot K_a - (1.51 \pm 0.19)\cdot n_{1,p} - (2.64 \pm 0.22)\cdot n_{2,q}$$

[N=415; R = 0.9998; S = 2.39 kJ/mol]; (11)

$$\Delta S_{298}^{Cl} = -(19.97 \pm 0.44)\cdot K_a - (77.42 \pm 2.30)\cdot (n_{1,p} + n_{CH_3,p} + n_{CH_3,q}) - (58.96 \pm 3.09)\cdot n_{2,q}$$

[N=415; R = 0.9975; S = 30.54 J/(mol·K)]; (12)

- for associates with odd Δn=3:

$$\Delta H_{298}^{Cl} = -(10.45 \pm 0.01)\cdot K_a - (1.42 \pm 0.12)\cdot n_{1,p} - (3.26 \pm 0.12)\cdot n_{2,q} - (2.75 \pm 0.15)\cdot n_{CH_3,p}$$

[N=429; R = 0.9999; S = 1.35 kJ/mol]; (13)

$$\Delta S_{298}^{Cl} = -(21.02 \pm 0.43)\cdot K_a - (69.85 \pm 2.60)\cdot (n_{1,p} + n_{CH_3,p}) - (57.82 \pm 2.90)\cdot n_{2,q} - (83.50 \pm 3.13)\cdot n_{CH_3,q}$$

[N=429; R = 0.9976; S = 28.87 J/(mol·K)]; (14)

where K_a is the number of intermolecular CH···HC interactions realized in the regarded associate and can be defined using eqs. (7)-(10); $n_{1,p}$, $n_{2,q}$, $n_{3,q}$, $n_{4,p}$ and $n_{CH_3,p}$ and $n_{CH_3,q}$ are the descriptors of the corresponding interactions between the CH_3 fragment of alkane molecule and terminal fragment of alcohol in the structures of the mixed Dimers 1,p, Dimers 2,q, Dimers 3,q, Dimers 4,p, and interactions between the CH_3 groups in the pure alkane dimers in p and q directions, as well. If these interactions are realized in the considered associate structure, then the value of the corresponding descriptor is equal to the number of the interactions of this type. If this interaction is absent, then the value of this descriptor is zero.

The standard deviations of the obtained correlation dependences for the description of clusterization enthalpy and entropy for mixed alkane-alcohol clusters do not exceed the corresponding values for the surfactant types investigated earlier. [41-48]

Large and infinite clusters. Prior to building the additive scheme enabling to calculate the values of the thermodynamic clusterization parameters of alkanes per one monomer of 2D films one has to regard the structural parameters of these monolayers. Figs. 3 and 4 list the optimized structures of mixed alkane-alcohol tetramers that can be considered as the unit cells of the corresponding monolayers. Thus, the calculated data using the PM3 method show that pure and mixed alkane tetramers have the following parameters (cf. Fig. 8,c): for 2D film 1 with even $\Delta n=3$ $a_1=4.20$ and $b_1=4.54$ Ǻ, $\theta_1=86°$, the molecular tilt angles with respect to the normal to the p and q directions of the monolayer spread are $\varphi_1=8°$ and $\delta_1=12°$, respectively, the molecular tilt angle with respect to the normal to the interface is $t_1=14°$ (the methodology of calculation of t is described in detail elsewhere [47]); for 2D film 1 with odd $\Delta n=2$ $a_2=4.47$ and $b_2=4.53$ Ǻ, $\theta_2=88°$, $\varphi_2=\delta_2=10°$, and $t_2=16°$. The 2D film 2 of the domain structure has the same geometrical parameters. These calculated data are in good agreement with experimental data: $a=4.26$ Ǻ, $b=4.81$ Ǻ, $\theta=86°$ and $t=22°$ for $C_{24}H_{50}$ multilayers [10] and X-ray powder diffraction patterns obtained for alkanes of different chain length. [55-57] It should be mentioned that the authors of ref. [10] indicated formation of multilayers comprising 2-20 monolayers for alkanes with 20-30 carbon atoms in the chain whereas monolayer formation is possible only for $C_{36}H_{74}$, and its unit cell is hexagonal with following parameters: a=5.0 Ǻ, b=7.4 Ǻ, θ=90°, t=0°. So, the chain length elongation of alkanes leads to change of the unit cell type from oblique to hexagonal and to upright position of the molecules with respect to the interface. The study [10] revealed that addition of aliphatic alcohols to alkanes having 23-24 or more carbon atoms in the chain results in formation of structurally different mono- and bilayers. Thus, the oblique unit cell is more preferable for alkane monolayers containing alcohols and for pure alkane multilayers, as well, whereas bilayers possess a hexagonal unit cell.

2D films 1 with single distribution of alcohols. Mixed 2D films of alkanes and alkohols comprise interactions that contribute to the values of thermodynamic clusterization parameters besides intermolecular CH···HC interactions. As seen in Fig. 5, they are six of them: interactions realized between the terminal part of alcohol molecule and the methyl fragment of alkane as in the Dimers 1, p and 4, p and as in Dimers 2, q and 3, q; interactions between the two terminal methyl groups of alkane molecules realized in the p and q propagation directions of the monolayer, respectively (they are marked with blue dashed lines). Let us remind that thermodynamic dimerization parameters for pairs of Dimers 1, p and 4, p and Dimers 2, q and 3, q nearly coincide. So, in further calculations of parameters for large and infinite clusters we use the increments contributed between the terminal part of alcohol molecule and CH_3 fragment of alkane as in Dimers 1, p and Dimers 2, q. The number of these interactions in p direction are defined as $n_{1,p}$, and in q direction as $n_{2,q}$. The number of interactions between the two CH_3 units of alkane molecules realized in p and q directions are designated as $n_{CH_3,p}$ and $n_{CH_3,q}$, respectively. The number of all interactions described above can be clearly defined from Fig. 5 regardless of the alcohol molecule position in the alkane monolayer (provided all alcohol molecules do not interact with each other and are enclosed by alkane molecules) as:

$$n_{1,p} = n_{2,q} = X \cdot pq\,, \qquad n_{CH_3,p} = q(p-1) - 2X \cdot pq\,, \qquad n_{CH_3,q} = p(q-1) - 2X \cdot pq\,, \tag{15}$$

where X is a molar fraction of alkanes in the mixed associates; p and q are the numbers of molecules in cluster in the corresponding directions.

The number of CH···HC interactions realized in the alkane clusters containing alcohol molecules depends on the chain length of these compounds and the immersion of the alcohol molecule into the water phase. Let us remind that the number of the CH···HC interactions K_a in the pairs alkane-alcohol increases stepwise until the maximum is reached. Then, the chain elongation does not affect K_a. For example, when short-chained alcohol is used for clusterization of long-chained alkanes, the length of alcohol is determinative in the corresponding pairs. And vice versa in pair short-chained alkane and long-chained alcohol the length of alkane is determinative. Accounting for eqs. (8) and (10), the number of CH···HC interactions in the large alkane-alcohol associates depends on their chain lengths as follows:

- for clusters with even Δn:

$$K_a = \left[\left(q(p-1) - 2X \cdot pq\right) + \left(p(q-1) - 2X \cdot pq\right)\right] \cdot \left\{\frac{n_{CH_3}}{2}\right\} + 2X \cdot pq \cdot \left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\} - \frac{\Delta n}{2}\right] + \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\} - \frac{\Delta n}{2}\right]\right], \tag{16}$$

- for clusters with odd Δn:

$$K_a = \left[q(p-1) - 2X \cdot pq\right] \cdot \left\{\frac{n_{CH_3}-1}{2}\right\} + \left[p(q-1) - 2X \cdot pq\right] \cdot \left\{\frac{n_{CH_3}}{2}\right\} + 2X \cdot pq \cdot \left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\} - \left\{\frac{\Delta n}{2}\right\}\right] + \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\} - \left\{\frac{\Delta n+1}{2}\right\}\right]\right], \tag{17}$$

where n_{CH_3} and n_{OH} are the number of carbon atoms in the alkyl chains of alkane and alcohol, respectively; the braces { ... } denote the integer part of the number; Δn is the number of methylene fragments of alcohol molecule by which the alkane molecule is shifted with respect to it during adsorption and clusterization (cf. Fig. 1).

To obtain the parameters per one monomer molecule for the 2D films one should divide the expressions of eqs. (15)-(17) by the number of monomers in the cluster $m = p \cdot q$, and calculate the limiting values of the resulting expressions at $p \to \infty$, $q \to \infty$. Then, for the infinite 2D cluster that involves all types of interactions between the methyl groups of alkanes and the terminal units of alcohols, eqs. (15)-(17) become:

$$n_{1,p}^{\infty}\big/m = n_{2,q}^{\infty}\big/m = X\ ,\ n_{CH_3,p}^{\infty}\big/m = n_{CH_3,q}^{\infty}\big/m = 1-2X\ , \tag{18}$$

- for the 2D film 1 with odd Δn:

$$K_{a}^{\infty}\big/m = (1-2X)\cdot\left(n_{CH_3}-1\right) + 2X\cdot\left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\}-\left\{\frac{\Delta n}{2}\right\}\right] + \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\}-\left\{\frac{\Delta n+1}{2}\right\}\right]\right], \tag{19}$$

- for the 2D film 1 with even Δn:

$$K_{a}^{\infty}\big/m = 2\cdot\left((1-2X)\cdot\left\{\frac{n_{CH_3}}{2}\right\} + X\cdot\left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_{OH}}{2}\right\}-\frac{\Delta n}{2}\right] + \min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_{OH}+1}{2}\right\}-\frac{\Delta n}{2}\right]\right]\right), \tag{20}$$

where n_{CH_3} and n_{OH} are the number of carbon atoms in the alkyl chains of alkane and alcohol, respectively; the braces { ... } denote the integer part of the number; Δn is the number of methylene fragments of alcohol molecule by which the alkane molecule is shifted with respect to it (cf. Fig. 1); X is the molar fraction of alcohols in the monolayer.

After introduction of eqs. (18)-(20) into the correlation equations for clusterization enthalpy (13) and entropy (14), one obtains the expressions for the calculation of the thermodynamic parameters of clusterization per one monomer for the mixed 2D films 1 depending of the alkyl chain length and on the molar fraction of alcohols. The obtained expressions take the form:

- for 2D film 1 with even Δn=2:

$$\Delta H_{298}^{Cl,\infty}\big/m = -10.45\cdot K_{a}^{\infty}\big/m - 8.24\cdot X\ , \tag{21}$$

$$\Delta S_{298}^{Cl,\infty}\big/m = -19.97\cdot K_{a}^{\infty}\big/m + 36.92\cdot X - 154.84\ , \tag{22}$$

$$\Delta G_{298}^{Cl,\infty}\big/m = -4.50\cdot K_{a}^{\infty}\big/m - 19.24\cdot X + 46.14\ ; \tag{23}$$

- for 2D film 1 with odd Δn=3:

$$\Delta H_{298}^{Cl,\infty}\big/m = -10.45\cdot K_{a}^{\infty}\big/m - 3.88\cdot X - 2.75\ , \tag{24}$$

$$\Delta S_{298}^{Cl,\infty}\big/m = -21.01\cdot K_{a}^{\infty}\big/m + 51.36\cdot X - 153.35\ , \tag{25}$$

$$\Delta G_{298}^{Cl,\infty}\big/m = -4.20\cdot K_{a}^{\infty}\big/m - 19.19\cdot X + 42.95\ , \tag{26}$$

where $K_{a}^{\infty}\big/m$ is the number of intermolecular CH···HC interactions per one monomer of the 2D films with odd and even Δn and can be defined using eqs. (19) and (20).

The dependences of the thermodynamic characteristics per one monomer molecule of the alkane monolayer on the alkyl chain length of alkanes and alcohols at 298 K are illustrated by the example of

Gibbs’ energy for alkane monolayer containing X=2, 8 and 10 molar % of alcohols. They are shown for mixed monolayers with odd and even values of Δn in Figs. 9 and 10, respectively. The set of colored lines refers to the dependences of clusterization Gibbs’ energy for alkanes in the presence of aliphatic alcohols with different chain length. The solid black line corresponds to the variation of Gibbs’ energy of clusterization per one alkane molecule of the pure alkane monolayer. As seen from Figs. 9 and 10, the increase of the alcohol content results in widening of the range for clusterization Gibbs’ energy of the color line set. However, in general, the impact of the alcohol molar fraction within the regarded limits of X=0-10% is quite weak for the alkane clusterization.

A number of experimental studies [31-38] shed the light on the adsorption of alkane vapor at the pure water surface and in presence of ionic and non-ionic surfactants. These studies deal with kinetics of the adsorption process. They revealed that the presence of surfactants at the water surface favors the process of alkane adsorption. It takes ~700 s for adsorption equilibrium to be reached. Whereas the time for reaching the adsorption equilibrium for alkanes at pure water surface is ~5000-8000 s. I.e. not each interaction of the hydrogens belonging to the alkane methyl groups with surface water molecules is effective and leads to the formation of the adsorption layer due to complete hydrophobicity of alkanes. In other words, there is a certain barrier for this process. But if the surface contain some amount of surfactants the vaporous alkanes interact with them, form adsorptive layer, which results in additional decrease of surface tension. So, in this case the barrier is significantly lower or almost absent.

The existing experimental data [10] suggest that alkanes with chain lengths no shorter than 23-24 carbon atoms are capable of mono- and multilayer formation at the water surface. The solid black lines in Figs. 9,a and 10,a correspond to this barrier mechanism of monolayer formation. To ensure the readability of the corresponding figures these lines are shown only in one from three graphs presented in Figs. 9 and 10. If the alkane adsorption takes place without barrier, the crystalline film formation at the water surface will be possible for compounds with 12 and more carbon atoms in the chain. This is depicted by the dashed black lines in Figs. 9 and 10. Note, that the clusterization Gibbs’ energy for pure alkane monolayers should not depend on Δn, because alcohol molecules are absent according to eqs. (23) and (26). The differences in $\Delta G_{298}^{Cl,\infty}/m$ are stipulated by another reason. In the section *Model* we specified that two possible structures of alkane monolayers are considered: one of them has the maximal number of intermolecular CH···HC interactions ($2\cdot\left\{\frac{n_{CH_3}}{2}\right\}$, where n_{CH_3} is the alkane chain length, and the other film has the number of intermolecular CH···HC interactions of $(n_{CH_3}-1)$, that is less than for the most favorable one. Despite this fact the values of the threshold chain length of spontaneous clusterization for theses monolayer structures are similar. We examined the influence of even Δn=2 on the thermodynamics of formation for the most energetically favorable film with maximal number of CH···HC interactions whereas for the second favorable alkane film structure we examined the influence of odd Δn=3. Such differences in the number of intermolecular CH···HC interactions for two alkane films stipulate the type of $\Delta G_{298}^{Cl,\infty}/m$ dependences: stepwise for the most preferable film with even Δn=2 and linear for the second favorable with odd Δn=3.

As it has been already mentioned, the studies [31-38] show that the vaporous hexane is possible to be adsorbed at the water surface even without any detected quantity of surfactants. However, it is impossible to claim that the obtained adsorptive film is monomolecular and crystalline. Investigations [4] using neutron and X-ray reflectivity methods have shown that the thickness of the octane adsorptive film at the water surface is 21 Å. This corresponds to the bilayer of upright standing molecules. Weinbach *et al* [10] found that the formation of the crystalline mono- and multilayers is possible for molecules having no less than 23-24 carbon atoms in the chain.

The surfactant additives to the water/vapor interface lead to the change from the barrier to non-barrier mechanism of the alkane adsorption. Such a change of the mechanism can be explained as follows. The amphiphilic nature of the surfactant molecule stipulates its possibility to exist at the water/alkane vapor interface, so that the functional group is in the water phase, whereas the remaining hydrocarbon part is in the vapor phase. So, the surfactant molecule acts as a 'float' for alkane molecules and makes their adsorption possible due to formation of intermolecular CH···HC interactions between the hydrophobic chains. As a result, the effectiveness of the interactions between the vaporous alkanes and the interface increases significantly resulting in a non-barrier adsorption mechanism. Such approach agrees with the results of the experimental studies [32, 33] of the adsorption of hexane vapor at the surface of the water drop containing either ionic or non-ionic surfactants of different concentration.

In present paper we describe the thermodynamics of monolayer formation of alkanes for the case when the barrier is absent (in presence of alcohols at the vapor/water interface). However, it is possible to assess the value of the energetic barrier for spontaneous clusterization of alkanes using the experimental [10] and calculated values of the threshold chain lengths of alkanes with (n_{CH_3}=12) and without (n_{CH_3}=24) surfactant additives:

$$\Delta\Delta G_{298,\infty}^{Cl,barr}/m = U_i \cdot \Delta K_a^{\infty}/m\,, \tag{27}$$

where $\Delta K_a^{\infty}/m$ is the number of intermolecular CH···HC interactions stipulated by the difference of the threshold chain lengths of alkanes for barrier and non-barrier mechanisms of clusterization; U_i are the increments of one CH···HC interaction of the 'a' type per one monomer molecule of the regarded 2D film 1 with odd and even Δn ($U_1^{odd} = -4.20$ and $U_1^{even} = -4.50$ kJ/mol).

The value of $\Delta K_a^\infty / m$ for pure alkane monolayers is possible to be calculated using eqs. (19) and (20) with account for the alcohol molar fraction in such monolayers equal to zero (X=0%). Then, the values of the energetic barriers are 50.4 and 54.0 kJ/mol for pure 2D film 1 with Δn=2 and 3, respectively.

As seen from the Figs. 9 and 10, the clusterization Gibbs' energy per one monomer of the 2D films 1 decreases with lengthening of the alkane and alcohol chains. The formation of the 2D film 1 with even Δn=2 is energetically more preferred than the formation of the analogous film but with odd Δn=3, because the first one contains the larger number of intermolecular CH···HC interactions per one monomer, than for the second one. This is caused by some differences of the structure of the pure alkane dimers, which are the units of the monolayers. In turn, this affects the dependences of the number of CH···HC interactions realized in these dimers (cf. eqs. (7) and (9)) and in corresponding monolayers, as well (cf. eqs. (19) and (20)). Therefore, the dependences of the thermodynamic clusterization parameters of alkanes are linear for the 2D film 1 with odd Δn value and stepwise for the film with even one.

Note, that the above described regularities of thermodynamic parameter variation for regarded films with Δn=2 and Δn=3 will be the same for monolayers with other Δn values. The corresponding dependencies for mixed alkane films with alcohols will be shifted along the abscissa axis to longer alkyl chain lengths of alkanes with the increase of Δn (Figs. 9 and 10).

The above described effect of the presence of alcohol on the alkane clusterization can be illustrated using hexadecane as an example. Fig. 11 lists the graphs of the dependences of the clusterization Gibbs' energy per one monomer of the 2D film 1 with Δn=2 for hexadecane on the molar fraction of alcohol. One can see that alcohols with chain lengths $n_{OH} \geq 16$ carbon atoms favor the process of hexadecane clusterization. At the same time the effect of alcohol additives is identical for surfactants starting from octadecanol up to pentacosanol. It is caused by the equal number of intermolecular CH···HC interactions realized in the mixed dimers of hexadecane and the mentioned alcohols. In turns, it stipulates the isoenergetic formation of these dimer structures and subsequently larger clusters up to monolayer. One should keep in mind that lengthening of the alkane chain and shortening of the alcohol chain provokes regression of the alcohol effectiveness on the alkane clusterization process. It is caused forth by the fact that mixed alkane-alcohol dimers have fewer numbers of intermolecular CH···HC interactions than the pure alkane dimers. The greater the difference between the considered alkane and alcohol and the higher alkane molecule is shifted with respect to alcohol molecule, the fewer numbers of CH···HC interactions are realized in the monolayer.

It is logically to presume that the increase of the alcohol concentration (close to CMC) at the water/alkane vapor interface leads to the competitive formation of pure alcohol monolayers along with the formation of mixed alkane-alcohol monolayers. Fig. 12 illustrates the variation of the clusterization Gibbs' energy per one monomer of the mixed 2D films 1 with Δn=2 and X=2% and the corresponding dependence for pure alcohol film. As seen in Fig. 12, shortening of the alkane chain and lengthening of the alcohol chain leads to more energetic preference of the formation of pure alcohol monolayers. This does not contradict the data, [31, 32] which show that the most effective coverage of the interface by the vaporous alkanes is typical for medium surfactant concentrations (0.1-1.0 mmol/l), since the further increase of the alcohol concentration results in the formation of pure alcohol monolayers and the decrease of free interface for alkane adsorption.

2D films 2 with domain distribution of alcohols. Such films consist of surfactant clusters enclosed by alkane molecules. The interactions realized between the hydrophilic parts of the surfactants have to be taken into account along with the interactions between the methyl units of the alkanes for such films. It should be noted that the limiting number of interactions between the alkane and alcohol molecules realized at the boundary of alcohol domains tends to zero during obtaining the thermodynamic clusterization parameters per one monomer of the film. Thus, the thermodynamic clusterization parameters for such films $A_{298,\infty}^{Cl,\infty,dom}/m$ can be calculated as weight-average sum of the corresponding clusterization parameters for pure alcohol $A_{298,\infty}^{Cl,\infty,OH}/m$ and alkane $A_{298,\infty}^{Cl,\infty,CH_3}/m$ monolayers. This means that $A_{298,\infty}^{Cl,\infty,dom}/m = X \cdot A_{298,\infty}^{Cl,\infty,OH}/m + (1-X) \cdot A_{298,\infty}^{Cl,\infty,CH_3}/m$, where X is the molar fraction of the alcohols in the alkane film. The increments of the interactions realized between the hydrophilic parts of alcohols to the thermodynamic clusterization parameters were estimated in a preceding study. [54] For the clusterization enthalpy they are -3.12 and -7.71 kJ/mol, for entropy -131.44 and -150.27 J/(mol·K), and for Gibbs' energy 36.50 and 37.07 kJ/mol for pure alcohol monolayers with even and odd Δn value, respectively. Then, the expressions of the thermodynamic clusterization parameters per one monomer of 2D film 2 with even and odd Δn value are as follows:

- for 2D films 2 with even Δn=2:

$$\Delta H_{298}^{Cl,\infty,dom}/m = -10.45 \cdot K_{a}^{\infty}/m - 3.12 \cdot X, \quad (28)$$

$$\Delta S_{298}^{Cl,\infty,dom}/m = -19.97 \cdot K_{a}^{\infty}/m + 23.4 \cdot X - 154.84, \quad (29)$$

$$\Delta G_{298}^{Cl,\infty,dom}/m = -4.50 \cdot K_{a}^{\infty}/m - 10.09 \cdot X + 46.14, \quad (30)$$

- for 2D films 2 with odd Δn=3:

$$\Delta H_{298}^{Cl,\infty,dom}/m = -10.45 \cdot K_{a}^{\infty}/m - 4.96 \cdot X - 2.75, \quad (31)$$

$$\Delta S_{298}^{Cl,\infty,dom}/m = -21.01 \cdot K_{a}^{\infty}/m + 3.08 \cdot X - 153.35, \quad (32)$$

$$\Delta G_{298}^{Cl,\infty,dom}/m = -4.20 \cdot K_{a}^{\infty}/m - 5.88 \cdot X + 42.95, \quad (33)$$

where X is the molar fraction of the alcohos in the alkane film; K_a^{∞}/m is the number of intermolecular CH···HC interactions per one monomer of pure alkane and alcohol 2D films and depend on the alkyl chain length (n) as $2\cdot\left\{\frac{n}{2}\right\}$ and $(n-1)$ for films with odd and even Δn value.

The analysis of eqs. (21)-(26) and (28)-(31) shows that, on the one side, the presence of the alcohol molecules is more effective for the formation of 2D film 1 with single distribution of alcohols among alkanes, than for the formation of 2D film 2 with alcohol domains. However, on the other side, 2D films 1 possess a fewer number of CH···HC interactions per one monomer of the film because of the partial loss of interactions between the alcohol and alkane molecules due to their different chain length and the shift of the alkane molecule with respect to the alcohol one by the value of Δn, whereas 2D films 2 with domain structure have the maximal number of CH···HC interactions K_a^{∞}/m for the clustering compounds.

The graphical dependence of the clusterization Gibbs' energy per one monomer of 2D film 2 is illustrated in Fig. 13 by the example of the energetically more preferred monolayer with even Δn=2. Here, as in Fig. 10 for 2D film 1 with single distribution of alcohol molecules the dashed line corresponds to $\Delta G_{298}^{Cl,\infty}/m$ for the pure alkane monolayer presuming non-barrier adsorption. The comparison of the obtained dependences of clusterization Gibbs' energy of 2D film 1 and 2 and taking into consideration the differences in eqs. (21)-(26) and (28)-(31) listed above indicate the competitive formation of these films. The preferable formation of 2D film with one or another structure depends on the chain length ratio for alkanes and alcohols participating into the clusterization process.

Conditions of competitive clusterization of alkanes from the vapor phase in presence of non-ionic surfactants. The thermodynamic condition for alkane clusterization from the vapor phase with alcohol additives is that the Gibbs' energy of monolayer formation with single alcohol molecules included in it $\Delta G_{298,\infty}^{Cl}/m$ has to be lower than the Gibbs' energy of clusterization for pure alkane $\Delta G_{298,\infty}^{Cl,CH_3}/m$ presuming the non-barrier mechanism of the film formation. That means

$$\Delta\Delta G_{298,\infty}^{Cl}/m = \left[\Delta G_{298,\infty}^{Cl}/m - \Delta G_{298,\infty}^{Cl,CH_3}/m\right] \le 0\,. \qquad (34)$$

It is obvious that at X=1 the monolayer consists completely of alcohol molecules. As said above, according to the scheme applied here, we single out the interactions between the terminal CH_3 units of alkanes and the interactions between the terminal CH_3 units of alkanes and terminal surfactant fragments partially immersed into the water phase. Then, using eqs. (23) and (26) obtained for 2D films 1 of alkanes with alcohols it is simple to obtain the expressions for $\Delta\Delta G_{298,\infty}^{Cl}/m$ of analogous films with any other surfactant:

$$\Delta\Delta G^{Cl}_{298,\infty}\big/m = \left[U_i \cdot \Delta K^{\infty}_{a}\big/m - 2\cdot V_i \cdot X + 2\cdot A_i \cdot X\right] \le 0\,, \tag{35}$$

where X is the surfactant molar fraction in the alkane film; V_i are the increments of the CH_3 group interactions in the clusterization Gibbs' energy per one monomer (for the alcohol 2D film 1 with odd and even Δn value: V^{odd} =42.95 and V^{even} =46.14 kJ/mol, as it follows from eqs. (23) and (26)); U_i are the increments of one CH···HC interaction of the 'a' type of the regarded 2D monolayers 1 and 2 (U^{odd}=-4.20 and U^{even}=-4.50 kJ/mol); A_i are the contributions of the interactions between hydrophobic alkyl chains of the amphiphile and the methyl fragment of alkanes in the clusterization Gibbs' energy per one monomer (A^{odd} =33.35 and A^{even} =36.50 kJ/mol for 2D films with odd and even value of Δn respectively); $\Delta K^{\infty}_{a}\big/m$ is the number of the intermolecular CH···HC interactions per monomer molecule of monolayers with even and odd Δn values lost owing to the presence of surfactant molecules into them. $\Delta K^{\infty}_{a}\big/m$ for monolayers with the presence of any amphiphilic compound depends on the chain length of the corresponding alkanes and surfactants and the surfactant molar fraction X in the 2D film 1 with odd and even Δn value. It can be calculated using eqs. (19) and (20):

- for 2D film 1 with odd Δn:

$$\Delta K^{\infty}_{a}\big/m = 2X\cdot\left(\left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_S}{2}\right\}-\left\{\frac{\Delta n}{2}\right\}\right]+\min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_S+1}{2}\right\}-\left\{\frac{\Delta n+1}{2}\right\}\right]\right]-\left(n_{CH_3}-1\right)\right), \tag{36}$$

- for 2D film 1 with even Δn:

$$\Delta K^{\infty}_{a}\big/m = 2X\cdot\left(\left[\min\left[\left\{\frac{n_{CH_3}+1}{2}\right\};\left\{\frac{n_S}{2}\right\}-\frac{\Delta n}{2}\right]+\min\left[\left\{\frac{n_{CH_3}}{2}\right\};\left\{\frac{n_S+1}{2}\right\}-\frac{\Delta n}{2}\right]\right]-2\cdot\left\{\frac{n_{CH_3}}{2}\right\}\right), \tag{37}$$

where n_{CH_3} and n_S are the numbers of carbon atoms in the hydrocarbon chain of alkane and surfactant, respectively, the braces denote the integer part of the number; Δn is the number of surfactant methylene units immersed into the water phase (cf. Fig. 1).

In eq. (35) for $\Delta\Delta G^{Cl}_{298,\infty}\big/m$, the first summand defines the positive contribution from the decrease of the number of the intermolecular CH···HC interactions between the amphiphilic molecules and alkanes. It is connected with the fact that the $\Delta K^{\infty}_{a}\big/m$ value is always negative because the alkane molecules are vertically shifted with respect to the surfactant molecules, which act as 'floats' during the non-barrier adsorption of alkanes from the vapor phase. The second summand describes the negative contribution from the decrease of the number of destabilizing interactions between the methyl groups of alkanes in the monolayer. The third summand defines the positive contribution of the interactions between hydrophobic alkyl chains of the amphiphiles and the methyl fragment of alkanes.

Eq. (35) gives an opportunity to define the ratio for the chain length of alcohols and alkanes capable of formation of mixed 2D films 1 at high surface concentration of alcohols (close to CMC) at the water/alkane vapor interface:

- for 2D film 1 with odd Δn:

$$n_{CH_3} - n_{OH} > \frac{V_{OH}^{odd} - V_{CH_3}^{odd} + 2X \cdot (V_{CH_3}^{odd} - A^{odd}) + 2X \cdot U^{odd}(\Delta n - 1)}{U^{odd} \cdot (1-2X)}, \qquad (38)$$

- for 2D film 1 with even Δn:

$$\left\{\frac{n_{CH_3}}{2}\right\}(1-2X) - \left[\left\{\frac{n_{OH}}{2}\right\} - X \cdot n_{OH}\right] > \frac{V_{OH}^{even} - V_{CH_3}^{even} + 2X \cdot (V_{CH_3}^{even} - A^{even}) + 2XU^{even} \cdot \Delta n}{2U^{even}}. \qquad (39)$$

It is obvious that the difference between the chain lengths of the regarded compounds can be only integer number. Therefore, the values obtained using eqs. (38) and (39) should be rounded to the integer number. Then, after introduction of the values of all required coefficients in eqs. (38) and (39), it follows that the difference between the chain lengths of alcohols and alkanes leading to the preferable formation of mixed 2D films 1 as compared with pure alcohol films increases with the increase of the alcohol molar fraction. *The alkane chain length should exceed the alcohol chain length by more than 2-3 carbon atoms in the range of the regarded alcohol molar fractions X=0-10% for the preferable formation of 2D films 1 with single distribution of alcohol molecules as against pure alcohol films.*

It is also necessary to consider one more possibility for collective clusterization of vaporous alkanes and alcohols at the water surface at low surface concentration of alcohols. In this case, two competitive processes are possible: formation of the monolayer with single distribution of alcohol molecules among alkanes (2D film 1) and formation of the monolayer consisting of separate alcohol domains distributed among alkanes (2D film 2). The thermodynamic condition for preferable formation of 2D film 1 as compared with 2D film 2 is that the clusterization Gibbs' energy for the first film $\Delta G_{298,\infty}^{Cl}/m$ (the first summand in eq. (40)) should be smaller than the clusterization Gibbs' energy for the second film with the same molar fraction of alcohols X (the second and third summands in eq. (40)):

$$\Delta\Delta G_{298,\infty}^{Cl}/m = \left[\Delta G_{298,\infty}^{Cl}/m - X \cdot \Delta G_{298,\infty}^{Cl,OH}/m - (1-X) \cdot \Delta G_{298,\infty}^{Cl,CH_3}/m\right] \le 0. \qquad (40)$$

Taking into account eq. (35) one obtains:

$$\Delta K_a^{\infty}/m - X \cdot \left(n_{OH} - n_{CH_3}\right) \le X \frac{V_i^{OH} + V_i^{CH_3} - 2A_i}{U_i}, \qquad (41)$$

where $\Delta K_a^{\infty}/m$ is the number of the intermolecular CH···HC interactions per monomer molecule of 2D films with even and odd Δn values lost owing to the shift of the alkane molecules with respect to the surfactant molecules (cf. eqs. (36) and (37)). Since all summands in inequality (41) are proportional to the molar fraction of alcohols in the monolayers X, and taking into account eqs. (36) and (37) for calculation of $\Delta K_a^{\infty}/m$, the previous inequality can be transformed as follows:

- for 2D film 1 with odd Δn:

$$\frac{V_{OH}^{odd}+V_{CH_3}^{odd}-2A^{odd}}{2U^{odd}}+\Delta n-1\le n_{OH}-n_{CH_3}\le 2-\frac{V_{OH}^{odd}+V_{CH_3}^{odd}-2A^{odd}}{U^{odd}}; \qquad (42)$$

- for 2D film 1 with even Δn:

$$\frac{V_{OH}^{even}+V_{CH_3}^{even}-2A^{even}}{2U^{even}}-\Delta n\le\left\{\frac{n_{OH}+1}{2}\right\}-\left\{\frac{n_{CH_3}}{2}\right\}\le\frac{V_{OH}^{even}+V_{CH_3}^{even}-2A^{even}}{2U^{even}}. \qquad (43)$$

As in the case of the use of eqs. (38) and (39), the results obtained according to eqs. (42) and (43) should be rounded to the integer number. Then, the formation of 2D film 1 with Δn=3 is possible when the difference between the alcohol and alkane chain lengths is between 1 and 5 carbon atoms. For 2D film 1 with Δn=2 this difference should be in range of 1-3 and 0-4 carbon atoms for surfactants with even and odd number of carbon atoms in their chains, respectively (cf. Fig. 14). Figure 14 does not present the points for $n_{OH}=8-11$ and $n_{CH_3}=10-11$ since the clusterization Gibbs' energy is positive for mixed films with such chain lengths, i.e. these monolayers do not exist.

The formation of the 2D film 2 with alcohol domains is preferred for the compounds long-chained alkane–short-chained alcohol and vice versa, as the number of intermolecular CH···HC interactions realized between the compounds of the same class is larger than those realized between dissimilar molecules. In total the gain in the number of CH···HC interactions exceeds the destabilizing contribution from the interaction of the alcohol headgroups to the clusterization Gibbs' energy. For example, it is possible to use dodecanol to form the 2D monolayers 1 of decane and undecane with single distribution of the alcohol (Δn=2), tridecanol to form the monolayers of alkanes from decane to tridecane, and so on. This means that the preferential formation of 2D films 1 of alkanes with alcohols is possible in the narrow range of the chain lengths for these compounds when the alkane chain length is almost equal or slightly shorter than the chain length of the corresponding alcohol. The same situation is also typical for the case of odd Δn=3. The only difference is that the region of preference for 2D films 1 has not stepwise, rather monotonous character. *In total, the formation of 2D films 1 with single distribution of alcohols among alkanes is possible when the difference between the alcohol and alkane chain lengths does not exceed 4 or 5 methylene units for Δn=2 and 3, respectively. Formation of 2D films 2 with alcohol domains among alkanes is typical for other differences in the chain lengths of the regarded compounds.*

It is interesting also to reveal the impact of the interactions between hydrophilic groups of different surfactants on the preference of formation of regarded types of 2D films 1 and 2. As can be seen from the analysis of eqs. (42) and (43), the more positive the contribution of the interactions between the surfactant headgroups into the clusterization Gibbs energy, the larger the range of possible differences between the surfactant and alkane chain lengths providing the formation of the 2D films 1 with single distribution of surfactant molecules among alkanes. In other words, the narrow region of the preference for 2D films 1 in Fig. 14 (blue dots) is widening. Consider now, for example, the aliphatic amides of carboxylic acids taken for the improvement of the alkane clusterization at water surface. In this case the formation of 2D films 1 with single distribution of surfactant molecule in the alkane monolayer is possible when $\left\{\frac{n_S+1}{2}\right\}-\left\{\frac{n_{CH_3}}{2}\right\}\geq 5$ or $\left\{\frac{n_{CH_3}}{2}\right\}-\left\{\frac{n_S+1}{2}\right\}\geq 3$. Note once more, that all terms in inequality (41) are proportional to the surfactant molar fraction X. Therefore, the preference of the film formation of one or another type does not depend on X according to eqs. (42) and (43).

Conclusion

In the framework of the semi-empirical quantum chemical PM3 method the impact of additives of aliphatic alcohols $C_nH_{2n+1}OH$ (n_{OH}=8-16) is studied on the process of spontaneous clusterization of alkanes C_nH_{2n+2} ($n_{CH_3}=6-16$) from the vapor phase on the water surface. The model, successfully exploited in preceding studies dealing with thermodynamics of 2D clusterization of substituted alkanes at the air/water interface, is used for the description of the structural and thermodynamic parameters of monolayer formation. [41-48] According to this model, the surfactant molecule orientates in such a way that the non-ionic functional group, are immersed into the water phase, whereas the hydrophobic chain is situated in the vaporous phase. The location of alkane molecule with respect to the interface is determined by realization of the maximal number of intermolecular CH···HC interactions between alkane and surfactant molecules and possible shift of the first one with respect to the second. During the adsorption of the vaporous alkanes the amphiphilic molecule acts as a ‘float’ leading to the change from barrier to non-barrier mechanism of the adsorption, due to its amphiphilic nature. This allows the consideration of the alcohol molecules as clusterization centers for vaporous alkanes at the water surface. The obtained results are in agreement with the existing experimental data. [32-38]

It is shown that the lengthening of the surfactant and alkane chain lengths favors the alkane clusterization at the water/vapor interface, whereas the surfactant concentration (within the scope of X=0-10%) slightly affects the clusterization process. The collective clusterization of alkanes with surfactant molecules is dealt with competitive formation of films of two types: 2D films 1 with single alcohol molecules distributed among alkane molecules, and 2D films 2 that contain alcohol domains enclosed by alkane molecules. In the case of low surface concentration of alcohols 2D films 1 with single distributed surfactant molecules among alkanes are more energetically preferred in comparison to 2D films 2, when the difference between the chain lengths of alkane and the corresponding alcohol does not exceed 5 carbon atoms. At the same time monolayer formation of alkanes in the presence of alcohols is possible for alkanes with chains longer than 10-12 carbon atoms. For other differences between the chain lengths of the regarded compounds clusterization will take place via preferential formation of mixed 2D films 2 that contain a mixture of alcohol domains surrounded by alkane molecules. The more destabilizing the increment of the interaction between the hydrophilic parts of surfactant to the clusterization Gibbs' energy, the larger the difference between the chain lengths of alkanes and surfactants when the formation of 2D films 1 is more favorable than 2D films 2. The conditions of the competitive clusterization are independent of the surfactant molar fraction at the interface.

References

1. Somasundaran, P. *Encyclopedia of Surface and Colloid Science.* Taylor & Francis: Pennsylvania, **2006**.
2. Gaines, G. L., Jr. *Insoluble Monolayers at Liquid - Gas Interfaces*; Interscience: New York, **1966**.
3. Aveyard, R., Binks, B.P., Fletcher, P.D.I., MacNab, J.R. Interaction of Alkanes with Monolayers of Nonionic Surfactants. *Langmuir*, **1995**, *11*, 2515-2524.
4. Kwon, O.-S., Jing, H., Shin, K., Wang, X., Satija, S. K. Formation of *n*-Alkane Layers at the Vapor/Water Interface *Langmuir*, **2007**, *23*, 12249-12253.
5. Hauxwell, F.; Ottewill, R. H. A Study of the Surface of Water by Hydrocarbon Adsorption *J. Colloid Interface Sci*. **1970**, *34*, 473-479.
6. Richmond, P.; Ninham, B. W.; Ottewill, R. H. A Theoretical Study of Hydrocarbon Adsorption on Water Surfaces Using Lifshitz Theory *J. Colloid Interface Sci*. **1973**, 45, 69-80.
7. Pfohl, T., Mohwald, H., Riegler, H. Ellipsometric Study of the Wetting of Air/Water Interfaces with Hexane, Heptane, and Octane from Saturated Alkane Vapors *Langmuir*, **1998**, *14*, 5285-5291.
8. Del Cerro, C.; Jameson, G. J. The Behavior of Pentane, Hexane, and Heptane on Water *J. Colloid Interface Sci*. **1980**, *78*, 362-375.
9. Pethica, B.A., Glasser, M. L. Lateral Intermolecular Forces in the Physisorbed State: Surface Field Polarization of Benzene and *n*-Hexane at the Water/ and Mercury/Vapor Interfaces. *Langmuir*, **2005**, *21*, 944-949.

10. Weinbach, S.P., Weissbuch, I., Kjaer, K., Bouwman, W.G., Als Nielsen, J., Lahav, M., Leiserowitz, L. Self-assembled Crystalline Monolayers and Multilayers of n-Alkanes on the Water Surface. *Adv. Mater.*, **1995**, *7*, 857-862.
11. Li, M., Acero, A.A., Huang, Zh., Rice, S.A. Formation of an Ordered Langmuir Monolayer by a Non-Polar Chain Molecule. *Nature*, **1994**, *367*, 151-153.
12. Broniatowski, M., Nieto-Squarez, M., Vila-Romeu, N., Hac-Wydro, K., Dynarowicz-Latka, P. Two-Dimensional Miscibility between Semifluorinated Hydrocarbon and Hydrogenated Alcohols. *Colloids and Surfaces A: Physicochem. Eng. Asp*., **2004**, *249*, 3-9.
13. Small, D.M. *The Physical Chemistry of lipids: Handbook of Lipid Research*, Vol. 4. Plenum Press: New York, **1986**.
14. Tabe, Y., Yamamoto, T., Nishiyama, I., Aoki, K. M., Yoneya, M., Yokoyama, H. Can Hydrophobic Oils Spread on Water as Condensed Langmuir Monolayers?. *J. Phys. Chem. B*, **2002**, *106*, 12089-12092.
15. Matta, C. F., Castillo, N., Boyd, R. J. Characterization of a Closed-Shell Fluorine−Fluorine Bonding Interaction in Aromatic Compounds on the Basis of the Electron Density. *J. Phys. Chem. A*, **2005**, *109*, 3669-3681.
16. Watkins, E. K., Jorgensen, W. L. Perfluoroalkanes: Conformational Analysis and Liquid-State Properties from *Ab Initio* and Monte Carlo Calculations. *J. Phys. Chem. A*, **2001**, *105*, 4118-4125.
17. Vysotsky, Yu. B.; Bryantsev, V. S.; Boldyreva, F. L.; Fainerman, V. B.; Vollhardt, D. Quantum Chemical Semiempirical Approach to the Structural and Thermodynamic Characteristics of Fluoroalkanols at the Air/Water Interface. *J. Phys. Chem. B*, **2005**, *109*, 454–462
18. Broniatowski, M.; Dynarowicz-Latka, P.; Camacho, L.; Romero, M.T.M.; Munoz, E. Semifluorinated thiols in Langmuir monolayer. *J. Colloid Int. Sci.* **2010**, *346*, 153-162.
19. Jacquemain, D., Wolf G. S., Leveiller, F., Frolow, F., Eisenstein, M., Lahav, M., Leiserowitz, L. Correlation Between Observed Crystalline Self-Assembly of Fluorocarbon and Hydrocarbon Amphiphiles at the Air-Water Interface and Calculated Lattice Energy. Determination of Electrostatic Properties of the CF2 Group From a Low-Temperature X-Ray Diffraction Study of Perfluoroglutaramide. *J. Am. Chem. Soc.*, **1992**, *114*, 9983-9989.
20. Eaton, D. F., Smart, B. E. Are Fluorocarbon Chains Stiffer Than Hydrocarbon Chains? Dynamics of End-to-End Cyclization in a C8F16 Segment Monitored by Fluorescence. *J. Am. Chem. Soc*., **1990**, *112*, 2821-2823.

21. Kuzmenko, I., Rapaport, H., Kjaer, K., Als-Nielsen, J., Weissbuch, I., Lahav, M., Leiserowitz, L. Design and Characterization of Crystalline Thin Film Architectures at the Air−Liquid Interface: Simplicity to Complexity. *Chem. Rev.*, **2001**, *101*, 1659-1696.
22. Kellay, H., Meunier, J., Binks, B. P. Wetting Properties of *N*-Alkanes on AOT Monolayers at the Brine-Air Interface. *Physical Rev. Lett.*, **1992**, *69*, 1220-1224.
23. Tikhonov, A. M., Schlossman, M. L. Vaporization and Layering of Alkanols at the Oil/Water Interface. *J. Phys.: Condens. Matter.*, **2007**, *19*, 375101.
24. Tikhonov, A. M., Pingali, S. V., Schlossman, M. L. Molecular Ordering and Phase Transitions in Alkanol Monolayers at the Water–Hexane Interface. *J. Chem. Phys.*, **2004**, *120*, 11822.
25. Zhang, Z., Mitrinovic, D. M., Williams, S. M., Huang, Z., Schlossman, M. L. X-Ray Scattering from Monolayers of $F(CF_2)_{10}(CH_2)_2OH$ at the Water–(Hexane Solution) and Water–Vapor Interfaces. *J. Chem. Phys.*, **1999**, *110*, 7421-7432.
26. Richmond, G. L. Peer Reviewed: Vibrational Spectroscopy of Molecules at Liquid/Liquid Interfaces. *Anal. Chem.* **1997**, *69*, 536A-543A.
27. Yue, B. Y., Jackson, C. M., Taylor, J. A. G., Mingins, J., Pethica, B. A. Phospholipid Monolayers at Non-Polar Oil/Water Interfaces. Part 1.—Phase Transitions in Distearoly-Lecithin Films at the N-Heptane Aqueous Sodium Chloride Interface. *J. Chem. Soc., Faraday Trans. 1*, **1976**, *72*, 2685-2693.
28. Messmer, M. C., Conboy, J. C., Richmond, G. L. Observation of Molecular Ordering at the Liquid-Liquid Interface by Resonant Sum Frequency Generation. *J. Am. Chem. Soc.*, **1995**, *117*, 8039-8040.
29. Thoma, M., Möhwald, H. Monolayers of Dipalmitoylphosphatidylcholine at the Oil-Water Interface. *Colloids & Surfaces A: Physicochemical and Engineering Aspects*, **1995**, *95*, 193-200.
30. Brezesinski, G., Thoma, M., Struth, B., Möhwald, H. Structural Changes of Monolayers at the Air/Water Interface Contacted with *n*-Alkanes. *J. Phys. Chem.*, **1996**, *100*, 3126-3130.
31. Javadi, A., Moradi, N., Möhwald, H., Miller, R. Adsorption of Alkanes from the Vapour Phase on Water Drops Measured by Drop Profile Analysis Tensiometry. *Soft Matter*, **2010**, *6*, 4710-4714.
32. Fainerman, V.B., Aksenenko, E.V., Kovalchuk, V.I., Javadi, A., Miller, R. Study of the Co-Adsorption of Hexane from the Gas Phase at the Surface of Aqueous $C_{10}EO_8$ Drops. *Soft Matter*, **2011**, *7*, 7860-7865.

33. Javadi, A., Moradi, N., Fainerman, V.B., Möhwald, H., Miller, R. Alkane Vapor and Surfactants Co-Adsorption on Aqueous Solution Interfaces. *Colloids and Surfaces A: Physicochem. Eng. Asp.*, **2011**, *391*, 19-24.
34. Fainerman, V.B.; Mucic, N.; Pradines, V.; Aksenenko, E.V.; Miller, R. Adsorption of Alkyltrimethylammonium Bromides at Wtare/Alkane Interfaces: Competitive Adsorption of Alkanes and surfactants. *Langmuir*, **2013**, *29*, 13783-13789.
35. Mucic, N.; Kovalchuk, N.M.; Aksenenko, E.V.; Fainerman, V.B.; Miller, R. Adsorption Layer Properties of Alkyltrimethylammonium Bromides at Interfaces between Water and Different Alkanes. *J. Colloid Int. Sci.*, **2013**, *410*, 181-187.
36. Fainerman, V.B.; Aksenenko, E.V.; Mucic, N.; Javadi, A.; Miller, R. Thermodynamics of Adsorption of Ionic Surfactants at Water/Alkane Interfaces. *Soft Matter*, **2014**, *10*, 6873-6887.
37. Mucic, N.; Moradi, N.; Javadi, A.; Aksenenko, E.V.; Fainerman, V.B.; Miller, R. Mixed Adsorption Layers at the Aqueous C_nTAB Solution/Hexane Vapour Interface. *Colloids Surf. A: Physicochem. Eng. Asp.*, **2014**, *442*, 50-55.
38. Mucic, N.; Moradi, N.; Javadi, A.; Aksenenko, E.V.; Fainerman, V.B.; Miller, R. Effect of Partial Vapor Pressure on The Co-Adsorption of Surfactants and Hexane at the Water/Hexane Interface. *Colloids Surf. A: Physicochem. Eng. Asp.*, **2015**, *480*, 79-84.
39. Stewart J. J. *MOPAC 2000.00 Manual*; Fujitsu Limited: Tokyo: Japan, **1999**.
40. Soloviov, M. E.; Soloviov, M. M. *Computational Chemistry*; SOLON-Press: Moscow, **2005** (in Russian).
41. Vysotsky, Yu. B., Bryantsev, V. S., Fainerman, V. B., Vollhardt, D. Quantum Chemical Analysis of the Thermodynamics of 2D Cluster Formation of Odd *n*-Alcohols at the Air/Water Interface. *J. Phys. Chem. B*, **2002**, *106*, 11285-11294.
42. Vysotsky, Yu. B., Bryantsev, V. S, Fainerman, V. B., Volhardt, D., Miller, R. Quantum Chemical Analysis of Thermodynamics of the Two-Dimensional Cluster Formation at the Air/Water Interface. *Phys. Chem. B*, **2002**, *106*, 121-131.
43. Vysotsky, Yu. B., Bryantsev, V.S., Fainerman, V.B., Vollhardt, D., Miller, R. Quantum Chemical Semi-Empirical Approach to the Thermodynamic Characteristics of Oligomers and Large Aggregates of Alcohols at the Water/Air Interface. *Colloids and Surfaces, A*, **2002**, *209*, 1-14.
44. Vysotsky, Y.B., Bryantsev, V.S., Fainerman, V.B. Thermodynamics of Two-Dimensional Cluster Formation at the Water/Air Interface. A Quantum Chemical Approach. *Progr. Colloid Polym. Sci.,* **2002**, *121*, 72-75.

45. Vysotsky, Yu. B., Muratov, D. V., Boldyreva, F. L., Fainerman, V.B., Vollhardt, D., Miller, R. Quantum Chemical Analysis of the Thermodynamics of 2D Cluster Formation of *n*-Carboxylic Acids at the Air/Water Interface. *J. Phys. Chem. B*, **2006**, *110*, 4717-4730.
46. Vysotsky, Yu. B.; Belyaeva, E. A.; Fainerman, V. B.; Aksenenko, E.V.; Vollhardt, D.; Miller, R. Quantum Chemical Analysis of the Thermodynamics of 2-Dimensional Cluster Formation of Alkylamines at the Air/Water Interface. *J. Phys. Chem. C*, **2007**, *111*, 15342 – 15349.
47. Vysotsky, Yu. B., Fomina, E. S., Belyaeva, E.A., Aksenenko, E. V., Vollhardt, D., Miller, R. Quantum-Chemical Analysis of Thermodynamics of Two-Dimensional Cluster Formation of α-Amino Acids at the Air/Water Interface. *J. Phys. Chem. B*, **2009,** *113*, 16557-16567.
48. Vysotsky, Yu. B., Fomina, E. S., Belyaeva, E.A., Aksenenko, E. V., Vollhardt, D., Miller, R. Quantum-Chemical Analysis of Thermodynamics of Two-Dimensional Cluster Formation of Racemic α-Amino Acids at the Air/Water Interface. *J. Phys. Chem. B*, **2011**, *115*, 2264-2281.
49. Thoma, M., Schwendler, M., Baltes, H., Helm, C. A., Pfohl, T., Riegler, H., Möhwald, H. Ellipsometry and X-ray Reflectivity Studies on Monolayers of Phosphatidylethanolamine and Phosphatidylcholine in Contact with *n*-Dodecane, *n*-Hexadecane, and Bicyclohexyl. *Langmuir*, **1996**, *12*, 1722-1728.
50. Knoble, C.M., Desai, R. C. Phase Transitions in Monolayers. *Annu. Rev. Phys. Chem.*, **1992**, *43*, 207-236.
51. Abranko-Rideg, N.; Darvas, M.; Horvai, G.; Jedlovszky, P. Immersion Depth of the Surfactants at the Free Water Surface: A Computer Simulation and ITIM Analysis Study. *J. Phys. Chem. B*, **2013**, *117*, 8733-8746.
52. Vysotsky, Yu.B.; Fomina, E. S.; Belyaeva, E.A.; Fainerman, V.B.; Vollhardt, D.; Miller, R. On the Temperature Effect in the Monolayer Formation of Substituted Alkanes at the Air/Water Interface. Quantum Chemical Approach. *J. Phys. Chem. B*, **2012**, *116*, 8996-9006.
53. Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, **1969**.
54. Vysotsky, Yu.B.; Fomina, E. S.; Belyaeva, E.A.; Fainerman, V.B.; Vollhardt, D.; Miller, R. On the Inclusion of Alkanes into the Monolayer of Aliphatic Alcohols at the Water/Vapor of Alkanes Interface. A Quantum-Chemical Approach. *Phys. Chem. Chem. Phys.*, **2013**, *15*, 2159-2176.
55. Gerson, R.; Roberts, K. J.; Sherwood, J. N. X-ray Powder Diffraction Studies of Alkanes: Unit-Cell Parameters of the Homologous Series $C_{18}H_{38}$ to $C_{28}H_{58}$. *Acta Cryst.*, **1991**, *B47*, 280-284.

56. Ocko, B. M.; Wu, X. Z.; Sirota, E. B.; Sinha, S. K.; Gang, O.; Deutsch, M. Surface Freezing in Chain Molecules: Normal Alkanes. *Phys. Rev. E*, **1997**, *55*, 3164-3182.

57. Gerson, A. R.; Roberts, K. J.; Sherwood, J. N. X-Ray Powder Diffraction Studies of N-Alkanes: A Re-examination of the Unit-Cell Parameters of $C_{24}H_{50}$ and $C_{26}H_{54}$. *Acta Cryst.*, **1992**, *B48*, 746.

Table 1. Correlation equations of type: y = (*a* ± Δ*a*)·n + (*b* ± Δ*b*) for alkane and alcohol monomers (sampling amount N=14), n is the number of the carbon atoms in the chain

System	Parameters	*a* ± *Δa*	*b* ± *Δb*	S
Alkanes	ΔH^0_{298}, kJ/mol	-22.68 ± 0.00	-30.84 ± 0.01	0.02
	S^0_{298}, J/(mol·K)	32.22 ± 0.04	181.65 ± 0.42	0.61
	ΔG^0_{298}, kJ/mol	8.32 ± 0.01	-46.08 ± 0.13	0.19
Alcohols	ΔH^0_{298}, kJ/mol	-22.67 ± 0.00	-199.92 ± 0.02	0.03
	S^0_{298}, J/(mol·K)	33.18 ± 0.12	201.74 ± 1.23	1.80
	ΔG^0_{298}, kJ/mol	7.95 ± 0.04	-190.59 ± 0.38	0.56

Table 2. Standard thermodynamic parameters of clusterization of pure and mixed alkane (n_{CH_3}=6–16) and alcohol (n_{OH}=12) associates in approximation of PM3 method for the structure of 2D film 1 with Δn=2

Alkane chain length	$\Delta H^{Cl}_{298,m}$, kJ/mol	$\Delta S^{Cl}_{298,m}$, J/(mol·K)	$\Delta G^{Cl}_{298,m}$, kJ/mol	$\Delta H^{Cl}_{298,m}$, kJ/mol	$\Delta S^{Cl}_{298,m}$, J/(mol·K)	$\Delta G^{Cl}_{298,m}$, kJ/mol
	Dimer CH_3, p (Dimer CH_3, q)			Trimer CH_3, p (Trimer CH_3, q)		
C_6H_{14}	-30.30	-145.25	12.99	-60.63	-292.34	26.49
C_7H_{16}	-32.71	-157.57	14.24	-65.16	-319.60	30.08
C_8H_{18}	-40.58	-173.16	11.02	-81.25	-347.11	22.19
C_9H_{20}	-43.11	-185.09	12.04	-85.98	-368.71	23.90
$C_{10}H_{22}$	-50.97	-200.93	8.90	-102.06	-402.00	17.73
$C_{11}H_{24}$	-53.50	-210.45	9.21	-106.80	-418.30	17.85
$C_{12}H_{26}$	-61.37	-228.42	6.70	-122.88	-459.43	14.03
$C_{13}H_{28}$	-63.91	-235.35	6.22	-127.64	-468.78	12.06
$C_{14}H_{30}$	-71.76	-254.69	4.13	-143.71	-510.62	8.45
$C_{15}H_{32}$	-74.30	-261.13	3.51	-148.44	-517.97	5.91
$C_{16}H_{34}$	-82.17	-279.63	1.16	-164.57	-556.94	1.40
	Tetramer CH_3			Hexamer CH_3		
C_6H_{14}	-121.56	-522.68	34.20	-212.97	-895.66	53.93
C_7H_{16}	-130.88	-558.53	35.56	-228.75	-972.29	60.99
C_8H_{18}	-162.93	-611.05	19.16	-285.55	-1049.64	27.25
C_9H_{20}	-172.66	-654.75	22.46	-302.05	-1128.58	34.27
$C_{10}H_{22}$	-204.69	-703.17	4.85	-358.79	-1212.34	2.48
$C_{11}H_{24}$	-214.44	-739.49	5.93	-375.36	-1275.86	4.85
$C_{12}H_{26}$	-246.47	-796.39	-9.15	-432.08	-1366.26	-24.94
$C_{13}H_{28}$	-256.26	-826.81	-9.87	-448.71	-1428.96	-22.88
$C_{14}H_{30}$	-288.27	-881.08	-25.71	-505.40	-1507.36	-56.21
$C_{15}H_{32}$	-298.10	-914.83	-25.48	-522.09	-1639.64	-33.47
$C_{16}H_{34}$	-330.09	-963.26	-43.04	-578.76	-1715.94	-67.41
	Dimer 1, p (mixed)			Dimer 2, q (mixed)		
C_6H_{14} (n_{OH}=12)	-33.42	-141.20	8.65	-33.06	-146.96	10.73
C_7H_{16} (n_{OH}=12)	-41.99	-162.78	6.52	-34.68	-145.60	8.71
C_8H_{18} (n_{OH}=12)	-43.30	-163.82	5.52	-43.45	-168.09	6.64

C_9H_{20} (n_{OH}=12)	-51.96	-191.19	5.02	-44.78	-156.52	1.86
$C_{10}H_{22}$ (n_{OH}=12)	-52.24	-188.95	4.07	-53.54	-186.57	2.05
$C_{11}H_{24}$ (n_{OH}=12)	-53.49	-191.84	3.68	-53.84	-187.48	2.03
$C_{12}H_{26}$ (n_{OH}=12)	-53.61	-190.17	3.06	-56.02	-182.43	-1.66
$C_{13}H_{28}$ (n_{OH}=12)	-53.63	-194.66	4.38	-56.19	-191.28	0.81
$C_{14}H_{30}$ (n_{OH}=12)	-53.63	-183.87	1.16	-56.48	-190.26	0.22
$C_{15}H_{32}$ (n_{OH}=12)	-53.64	-193.38	3.99	-56.53	-174.67	-4.48
$C_{16}H_{34}$ (n_{OH}=12)	-53.64	-188.60	2.56	-56.54	-184.56	-1.54
	Trimer 1, p (mixed)			Tetramer (mixed)		
C_6H_{14} (n_{OH}=12)	-63.37	-284.23	21.33	-127.27	-503.72	22.84
C_7H_{16} (n_{OH}=12)	-74.84	-319.06	20.24	-142.68	-521.96	12.86
C_8H_{18} (n_{OH}=12)	-83.82	-327.53	13.78	-168.75	-574.31	2.40
C_9H_{20} (n_{OH}=12)	-95.15	-361.34	12.53	-183.55	-589.05	-8.01
$C_{10}H_{22}$ (n_{OH}=12)	-103.32	-367.02	6.05	-208.70	-649.99	-15.01
$C_{11}H_{24}$ (n_{OH}=12)	-106.91	-370.19	3.40	-214.12	-656.50	-18.49
$C_{12}H_{26}$ (n_{OH}=12)	-115.03	-400.03	4.18	-233.37	-694.12	-26.52
$C_{13}H_{28}$ (n_{OH}=12)	-117.62	-389.09	-1.67	-237.89	-688.71	-32.66
$C_{14}H_{30}$ (n_{OH}=12)	-125.48	-419.04	-0.60	-	-	-
$C_{15}H_{32}$ (n_{OH}=12)	-128.06	-408.19	-6.42	-	-	-
$C_{16}H_{34}$ (n_{OH}=12)	-135.90	-416.97	-11.64	-	-	-

Figure captions

Figure 1. Orientation of the alkane molecule with respect to the alcohol molecule and interface

Figure 2. Torsion angles of the functional group of alcohols (R – hydrophobic chain)

Figure 3. Optimized geometrical structures of alcohol and alkane associates for 2D film1 with even $\Delta n=2$

Figure 4. Optimized geometrical structures of alcohol and alkane associates for 2D film1 with odd $\Delta n=3$

Figure 5. Fragment of the geometric structure of the infinite mixed 2D Cluster 1 with single distribution of alcohol molecules in alkanes. Denotation of the basic dimers: 1 – Dimer 1,p; 2 – Dimer 2,q; 3 – Dimer 3,q; 4 – Dimer 4,p; 5 – Dimer CH_3,p; 6 – Dimer CH_3,q;

Figure 6. Dependence of the variation of the dimerization enthalpy for mixed dimers 1,p (3,q) with $\Delta n=2$ on the alkane and alcohol chain length

Figure 7. Dependence of the variation of the dimerization entropy for mixed dimers 1,p (3,q) with $\Delta n=2$ on the alkane and alcohol chain length

Figure 8. The unit cell structure of the mixed infinite 2D cluster1 fragments: 1) with odd Δn and 2) with even Δn: (a) view along the q axis; (b) view along the p axis; (c) view along the molecular chain axis

Figure 9. Dependence of the clusterization Gibbs' energy per one monomer of alkane monolayer on the molar fraction of alcohol additives and chain lengths of alkanes and alcohols for 2D film 1 with $\Delta n=3$

Figure 10. Dependence of the clusterization Gibbs' energy per one monomer of alkane monolayer on the molar fraction of alcohol additives and chain lengths of alkanes and alcohols for 2D film 1 with $\Delta n=2$

Figure 11. Dependence of the clusterization Gibbs' energy per one monomer of hexadecane monolayer on the molar fraction of alcohols for 2D film 1 with $\Delta n=2$

Figure 12. Dependence of the clusterization Gibbs' energy per one monomer of 2D film 1 with $\Delta n=2$ for pure alcohol monolayers and mixed alkane-alcohol monolayers on the alcohol chain length

Figure 13. Dependence of the clusterization Gibbs' energy per one monomer of 2D film 2 with $\Delta n=2$ on the alcohol and alkane chain length

Figure 14. Phase diagram for mixed alkane-alcohol monolayers depending on the chain lengths for alcohol molar fraction X=8%: (●) 2D film 2 consisted of pure alcohol and alkane domains; (◆) 2D film 1 with single distribution of alcohol molecules in alkanes

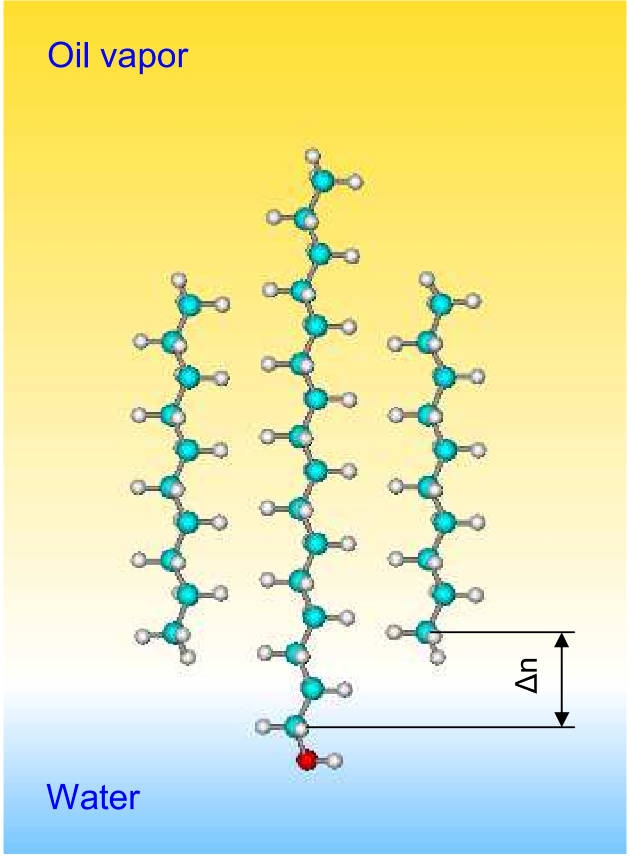


Fig. 1

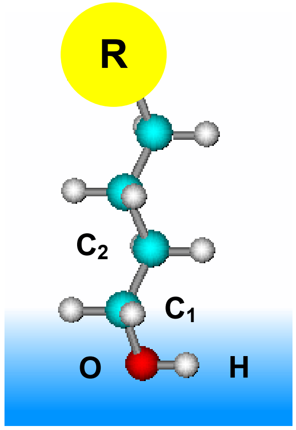
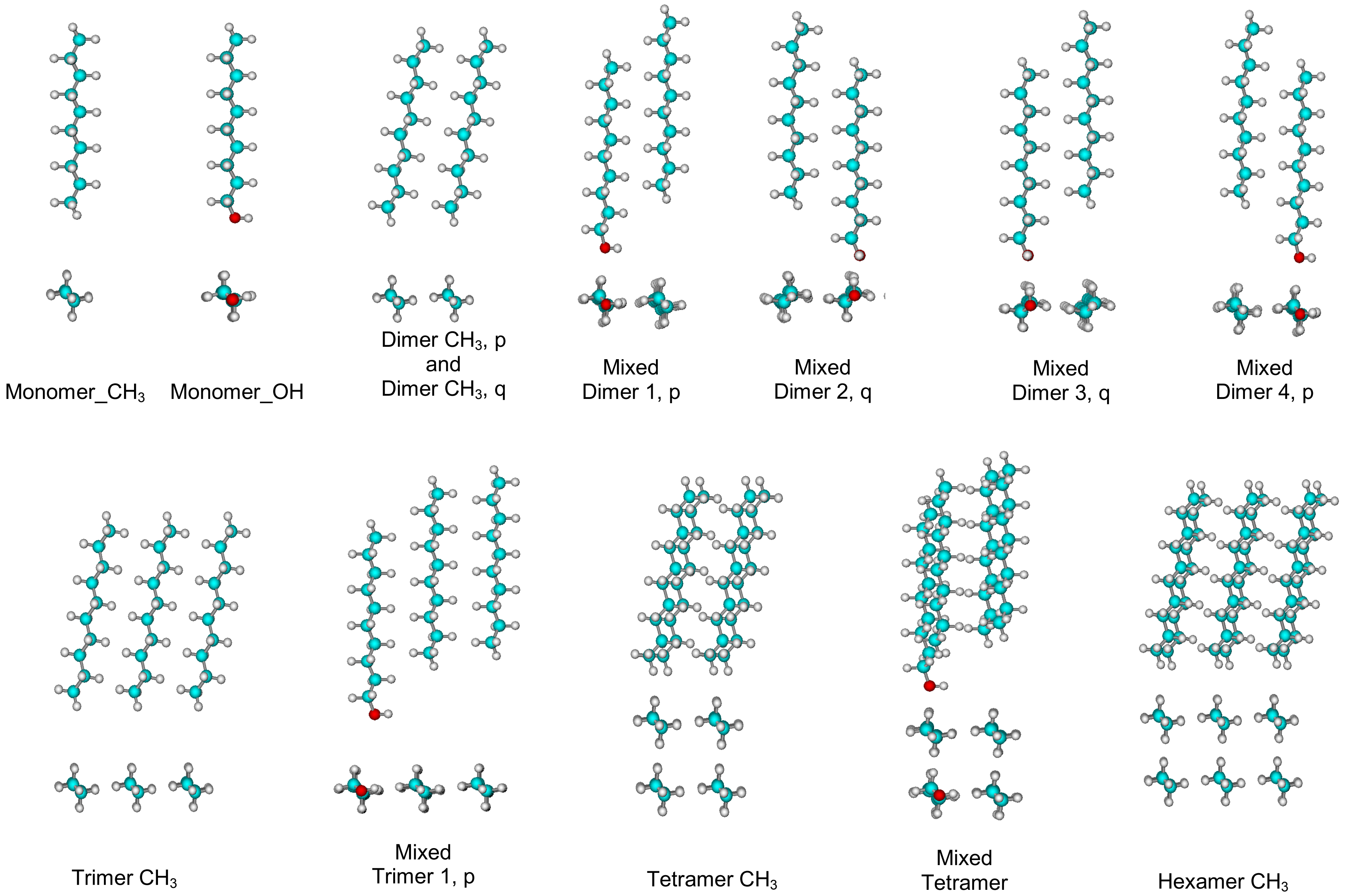


Fig. 2



Monomer_CH$_3$

Monomer_OH

Dimer CH$_3$, p
and
Dimer CH$_3$, q

Mixed
Dimer 1, p

Mixed
Dimer 2, q

Mixed
Dimer 3, q

Mixed
Dimer 4, p

Trimer CH$_3$

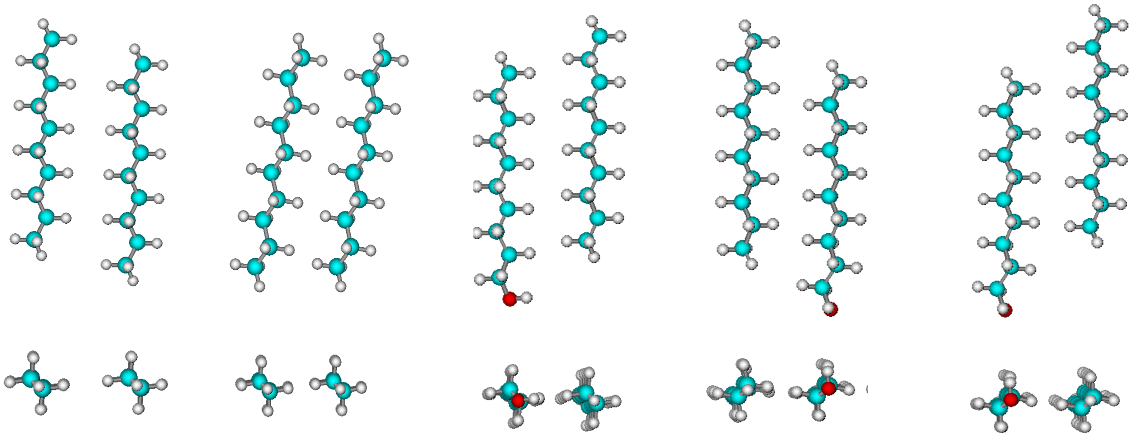
Mixed
Trimer 1, p

Tetramer CH$_3$

Mixed
Tetramer

Hexamer CH$_3$

Fig. 3



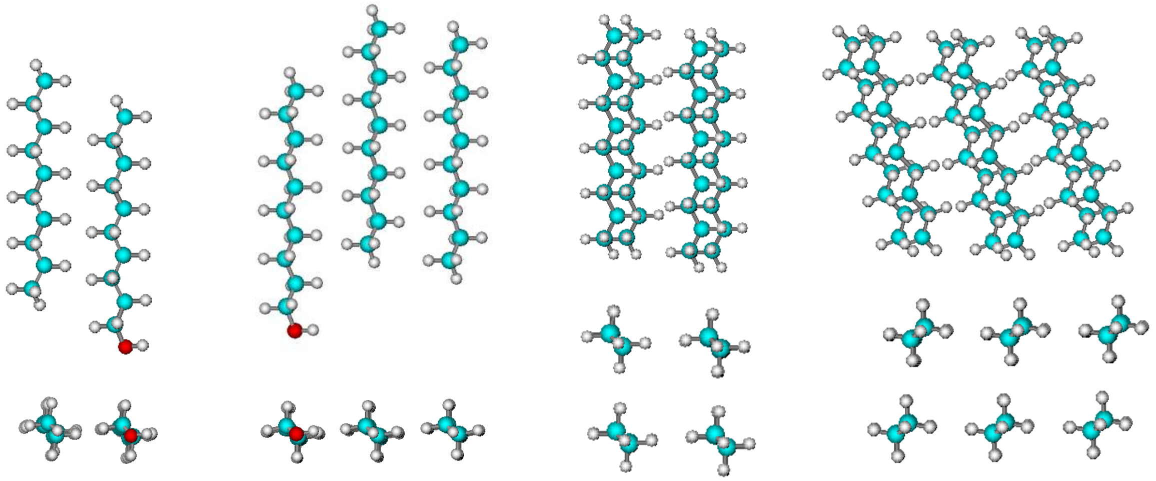
Dimer CH_3, p

Dimer CH_3, q

Mixed
Dimer 1, p

Mixed
Dimer 2, q

Mixed
Dimer 3, q



Mixed
Dimer 4, p

Mixed
Trimer 1, p

Tetramer CH_3

Hexamer CH_3

Fig. 4

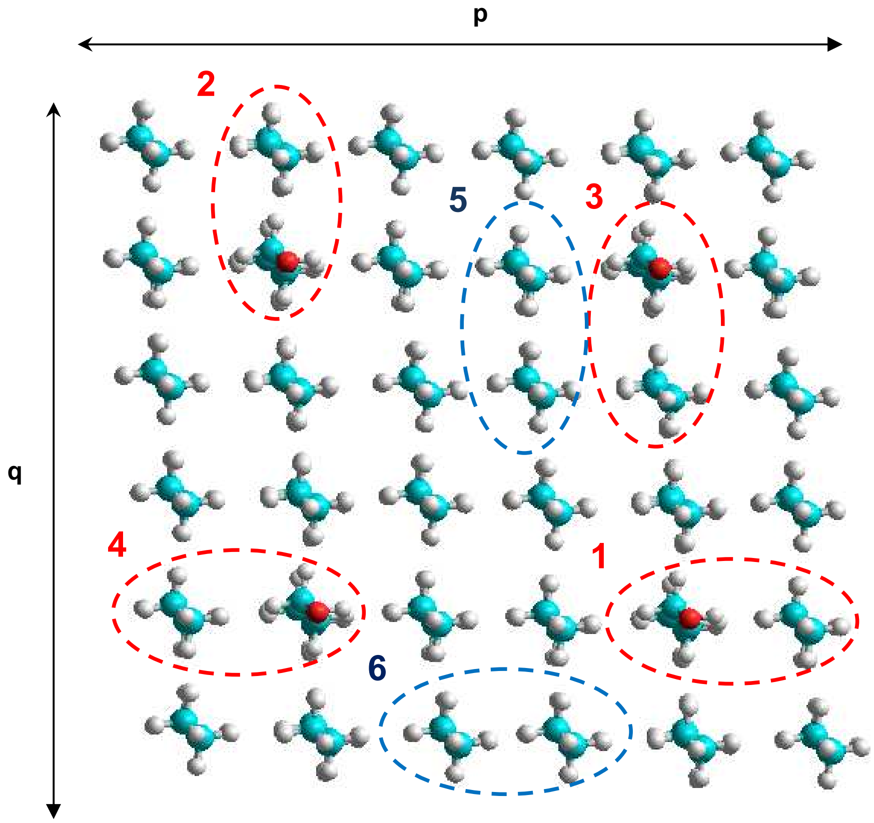


Fig. 5

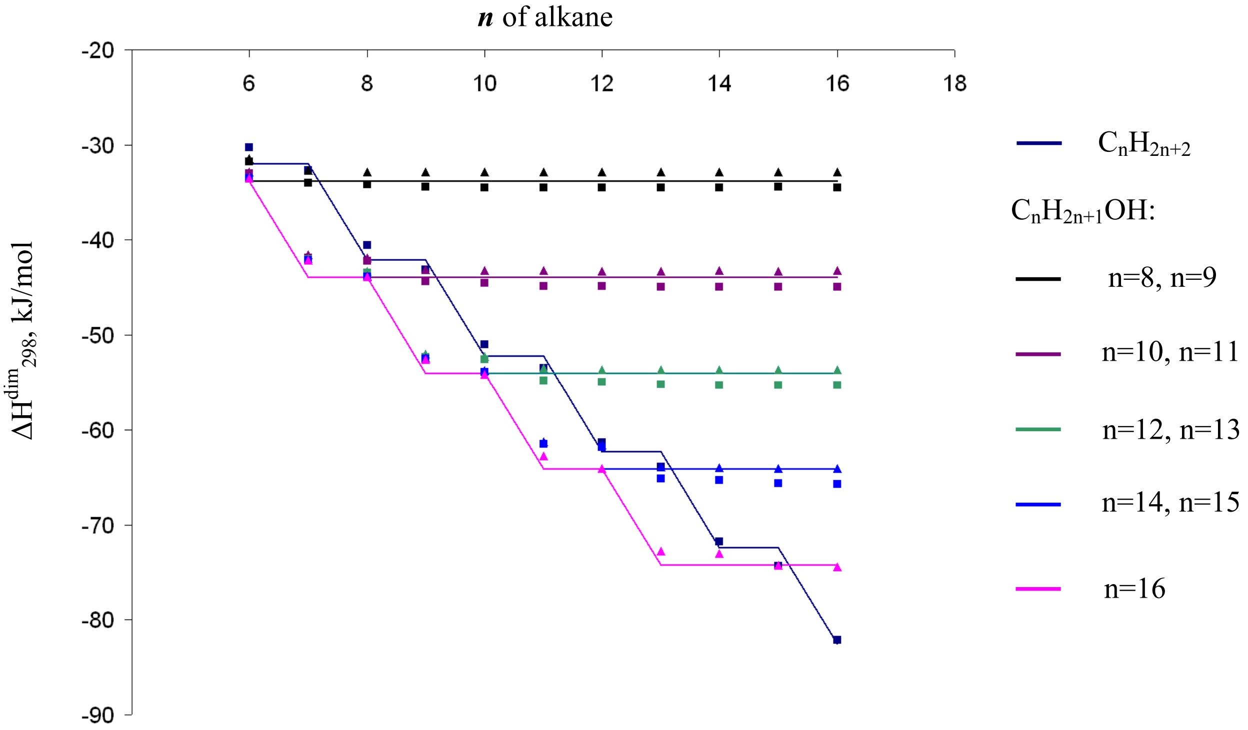

n of alkane
6
8
10
12
14
16
18
-20
-30
-40
-50
-60
-70
-80
-90
ΔH^{dim}_{298}, kJ/mol
C_nH_{2n+2}
$C_nH_{2n+1}OH$:
n=8, n=9
n=10, n=11
n=12, n=13
n=14, n=15
n=16

Fig. 6

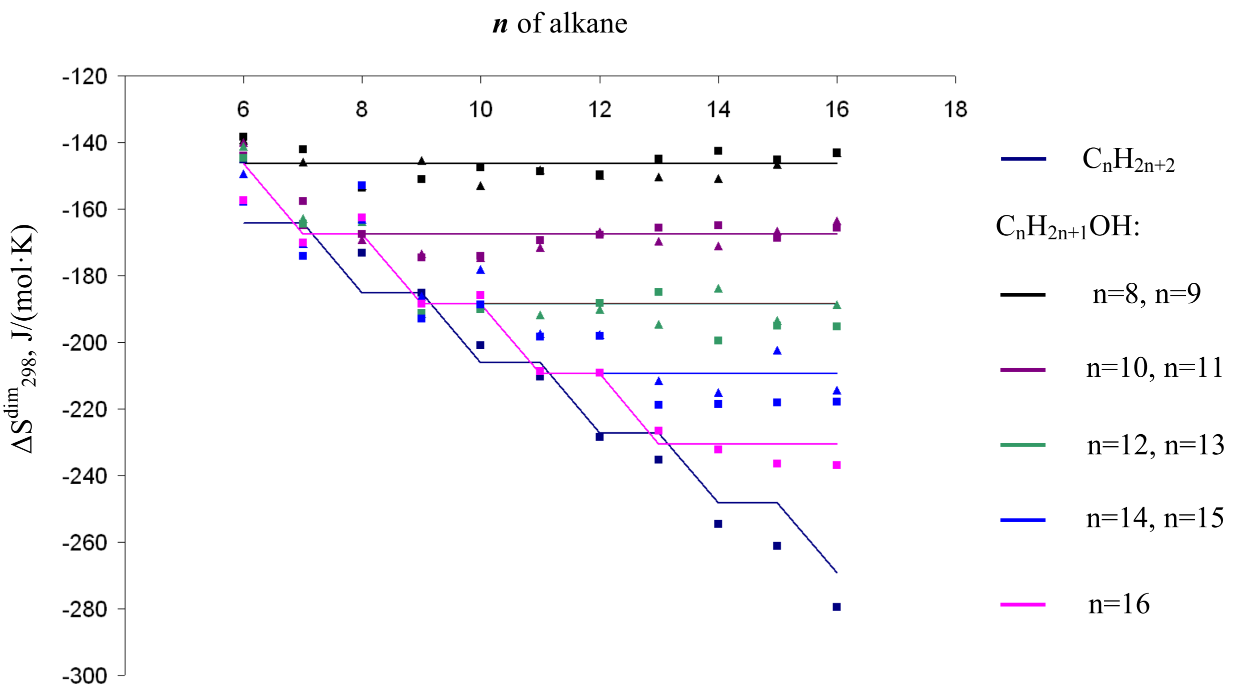
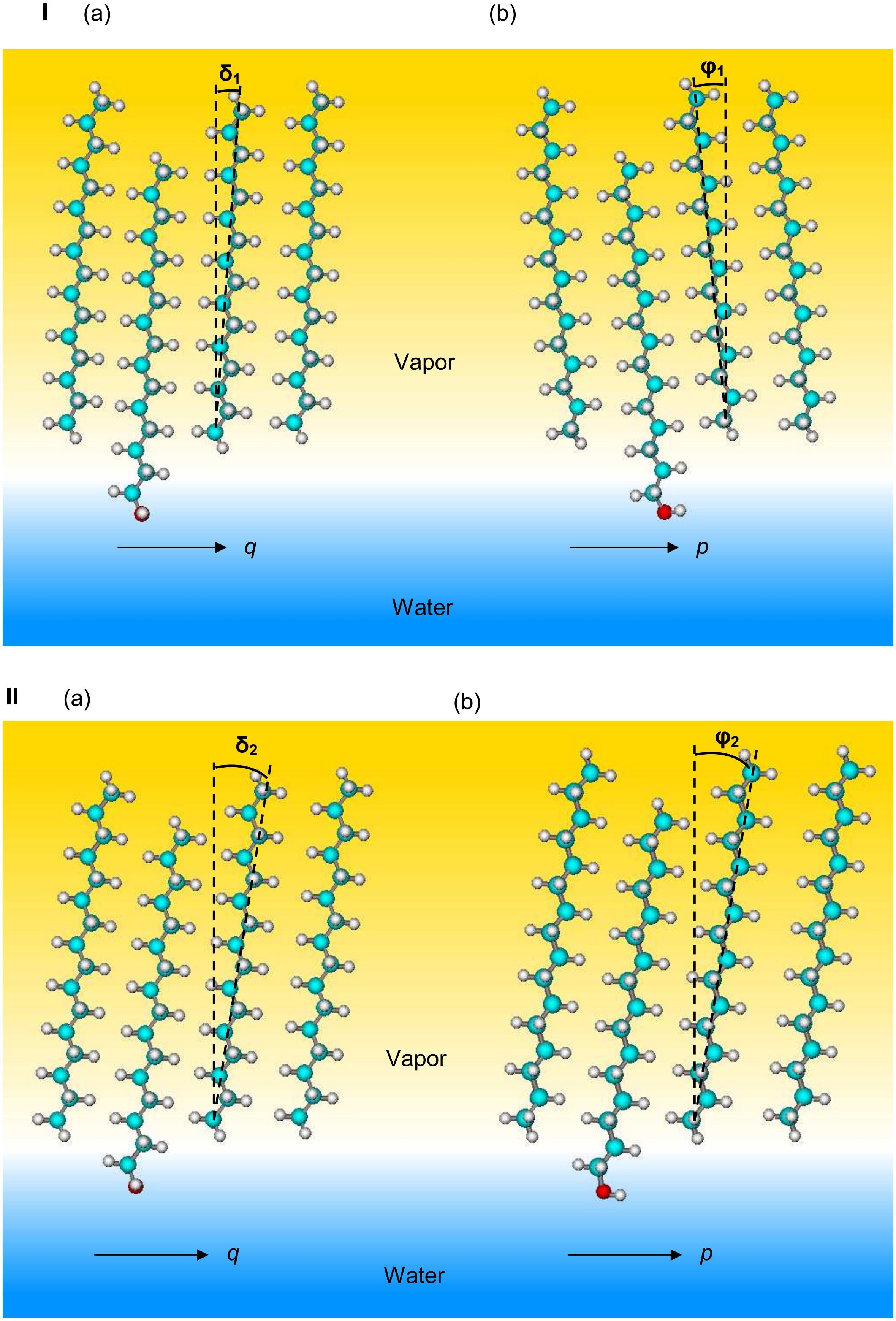

n of alkane
ΔS^{dim}_{298}, J/(mol·K)
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
6
8
10
12
14
16
18
C_nH_{2n+2}
$C_nH_{2n+1}OH$:
n=8, n=9
n=10, n=11
n=12, n=13
n=14, n=15
n=16

Fig. 7


I
(a)
(b)
δ₁
φ₁
Vapor
q
p
Water
II
(a)
(b)
δ₂
φ₂
Vapor
q
p
Water

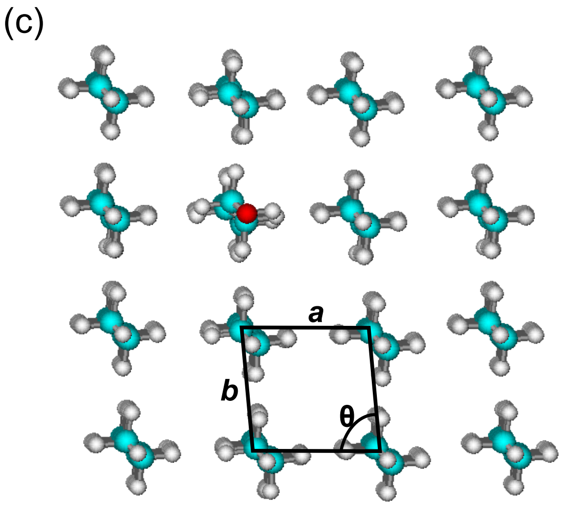


Fig. 8

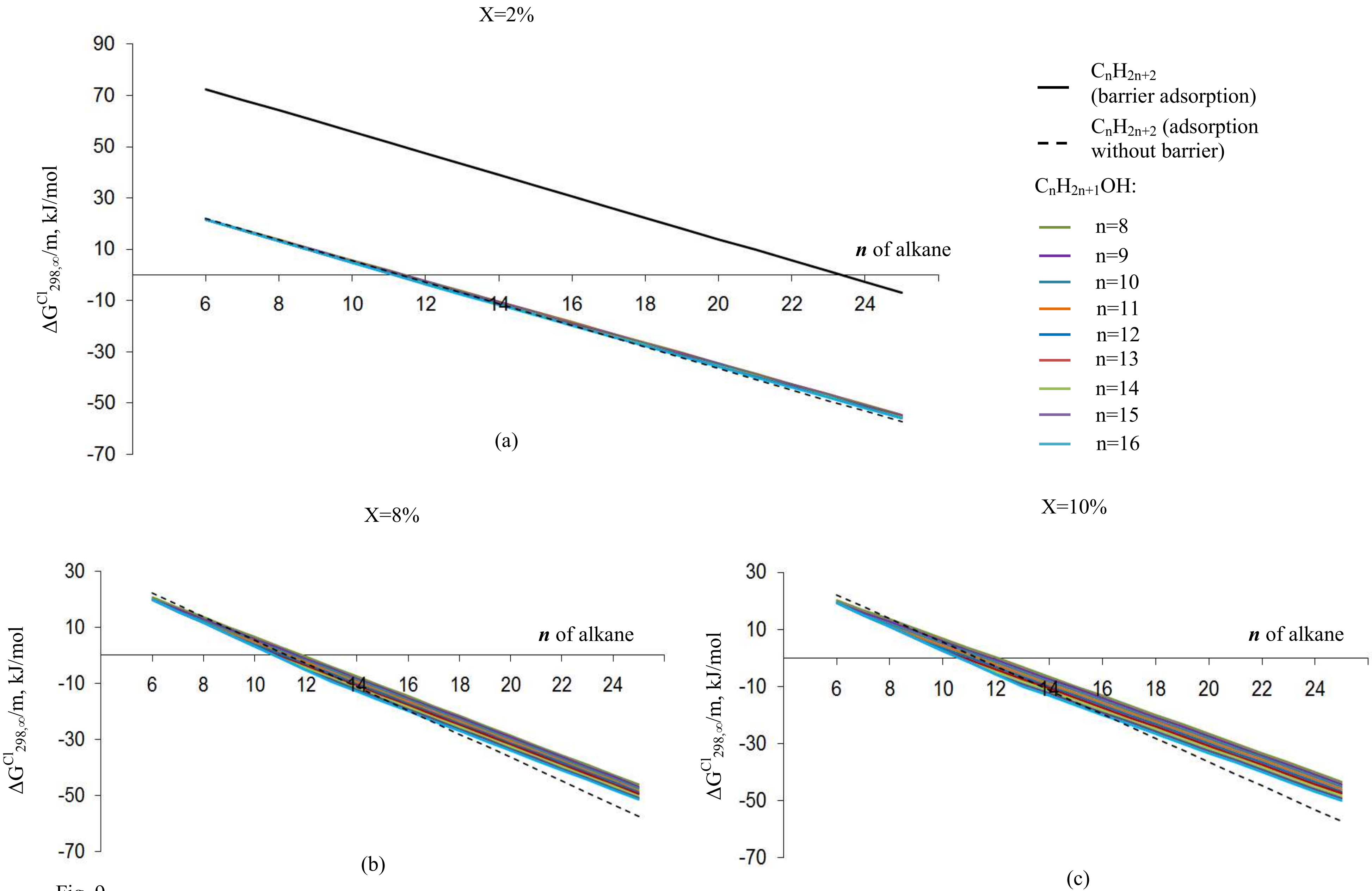
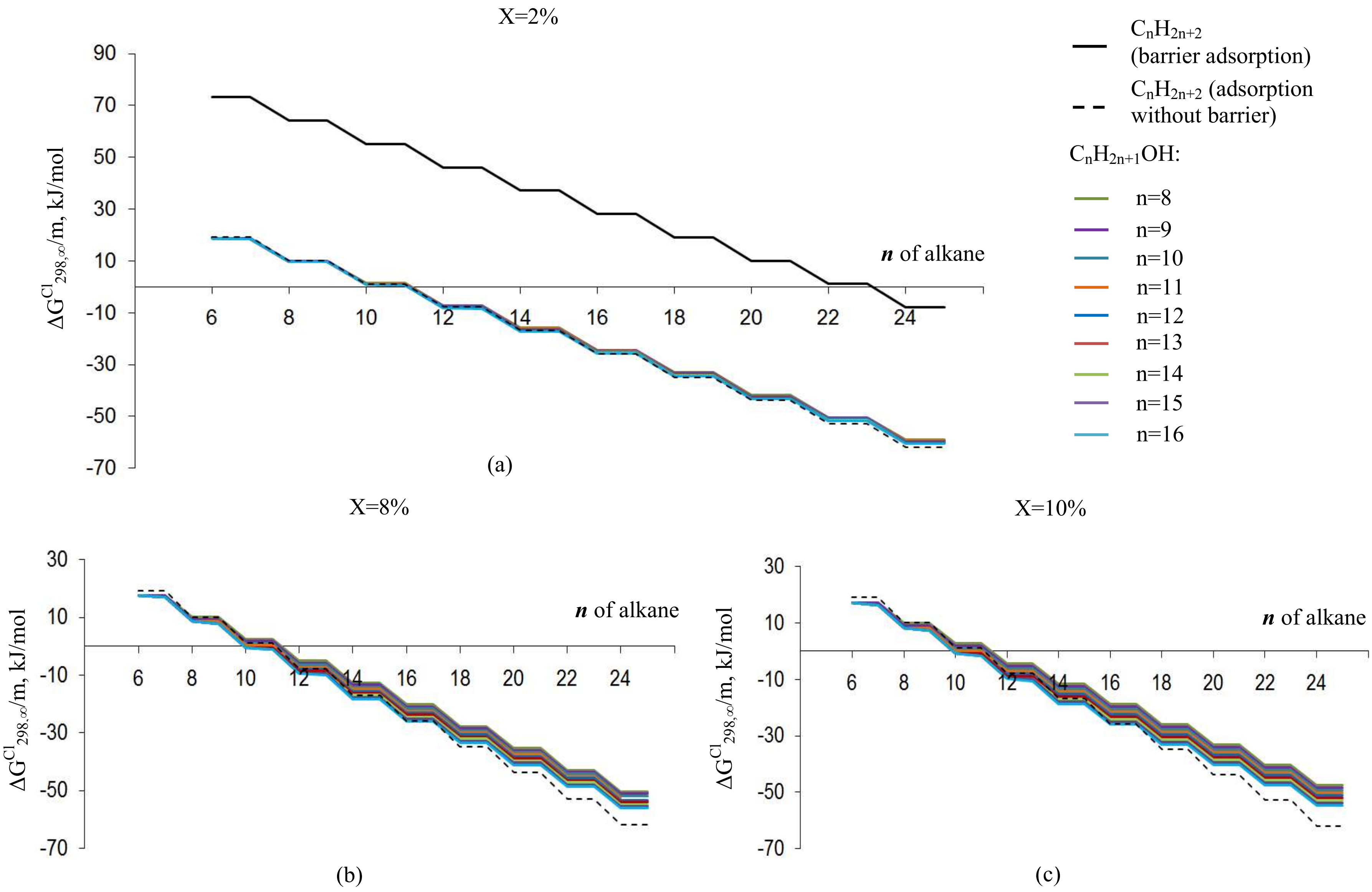

X=2%
90
70
50
30
10
-10
-30
-50
-70
ΔG^Cl_298,∞/m, kJ/mol
6
8
10
12
14
16
18
20
22
24
n of alkane
(a)
C_nH_2n+2 (barrier adsorption)
C_nH_2n+2 (adsorption without barrier)
C_nH_2n+1OH:
n=8
n=9
n=10
n=11
n=12
n=13
n=14
n=15
n=16
X=8%
30
10
-10
-30
-50
-70
ΔG^Cl_298,∞/m, kJ/mol
6
8
10
12
14
16
18
20
22
24
n of alkane
(b)
X=10%
30
10
-10
-30
-50
-70
ΔG^Cl_298,∞/m, kJ/mol
6
8
10
12
14
16
18
20
22
24
n of alkane
(c)

Fig. 9


X=2%
X=8%
X=10%
$\Delta G^{Cl}_{298,\infty}$/m, kJ/mol
n of alkane
90
70
50
30
10
-10
-30
-50
-70
6
8
10
12
14
16
18
20
22
24
C_nH_{2n+2} (barrier adsorption)
C_nH_{2n+2} (adsorption without barrier)
$C_nH_{2n+1}OH$:
n=8
n=9
n=10
n=11
n=12
n=13
n=14
n=15
n=16

(a)

(b)

(c)

Fig. 10

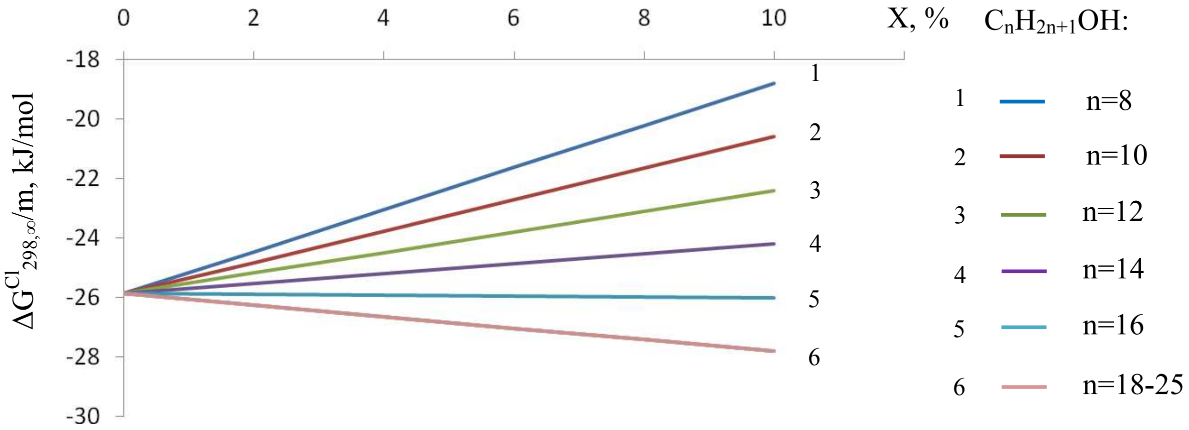

0
2
4
6
8
10
X, %
$C_nH_{2n+1}OH$:
-18
-20
-22
-24
-26
-28
-30
$\Delta G^{Cl}_{298,\infty}/m$, kJ/mol
1
2
3
4
5
6
1 n=8
2 n=10
3 n=12
4 n=14
5 n=16
6 n=18-25

Fig. 11

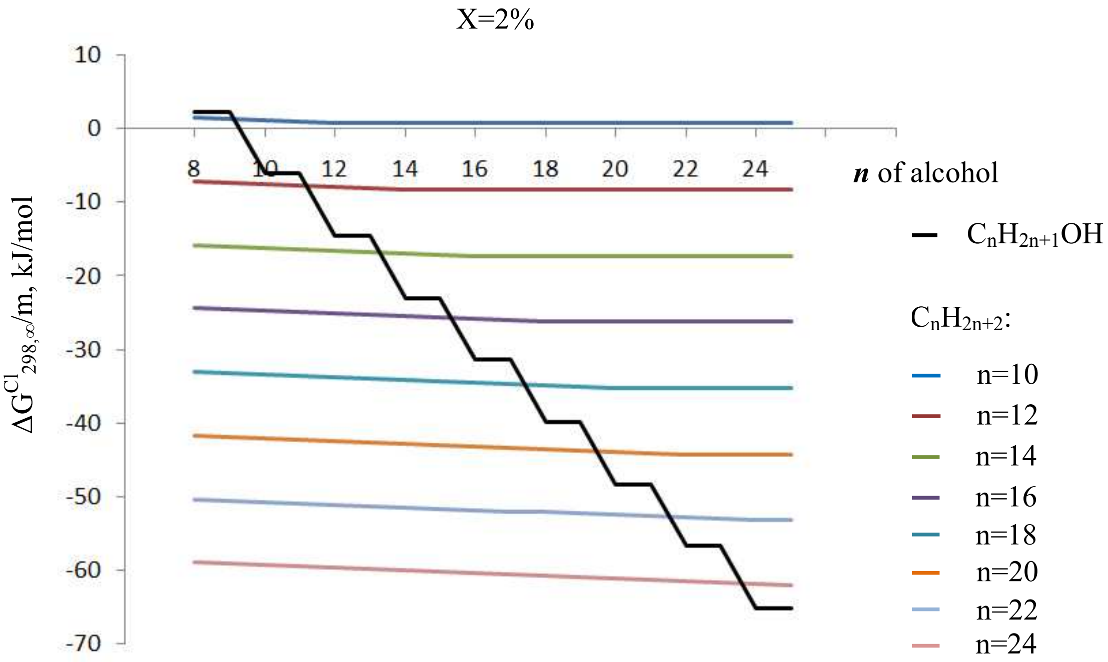

X=2%
10
0
-10
-20
-30
-40
-50
-60
-70
8
10
12
14
16
18
20
22
24
n of alcohol
$\Delta G^{Cl}_{298,\infty}$/m, kJ/mol
$C_nH_{2n+1}OH$
C_nH_{2n+2}:
n=10
n=12
n=14
n=16
n=18
n=20
n=22
n=24

Fig. 12

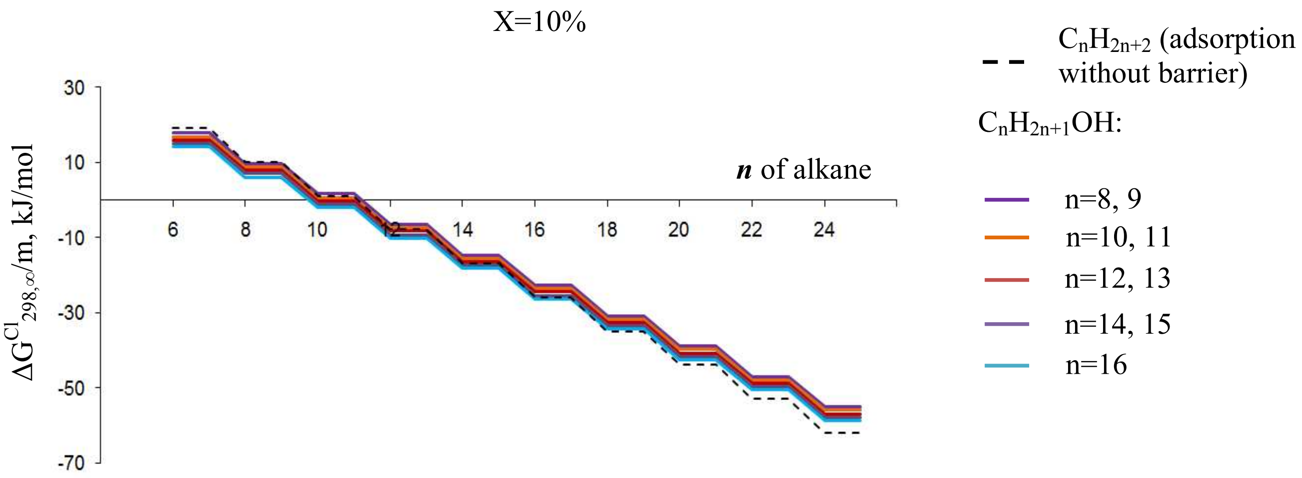

X=10%
$\Delta G^{Cl}_{298,\infty}$/m, kJ/mol
30
10
-10
-30
-50
-70
6
8
10
12
14
16
18
20
22
24
n of alkane
C_nH_{2n+2} (adsorption without barrier)
$C_nH_{2n+1}OH$:
n=8, 9
n=10, 11
n=12, 13
n=14, 15
n=16

Fig. 13

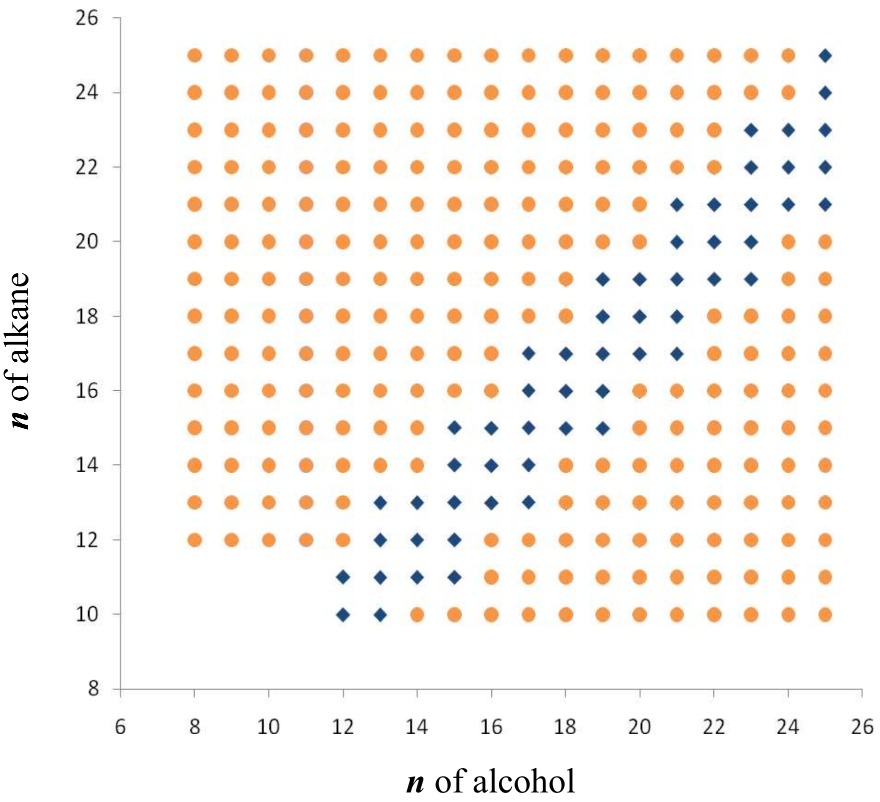
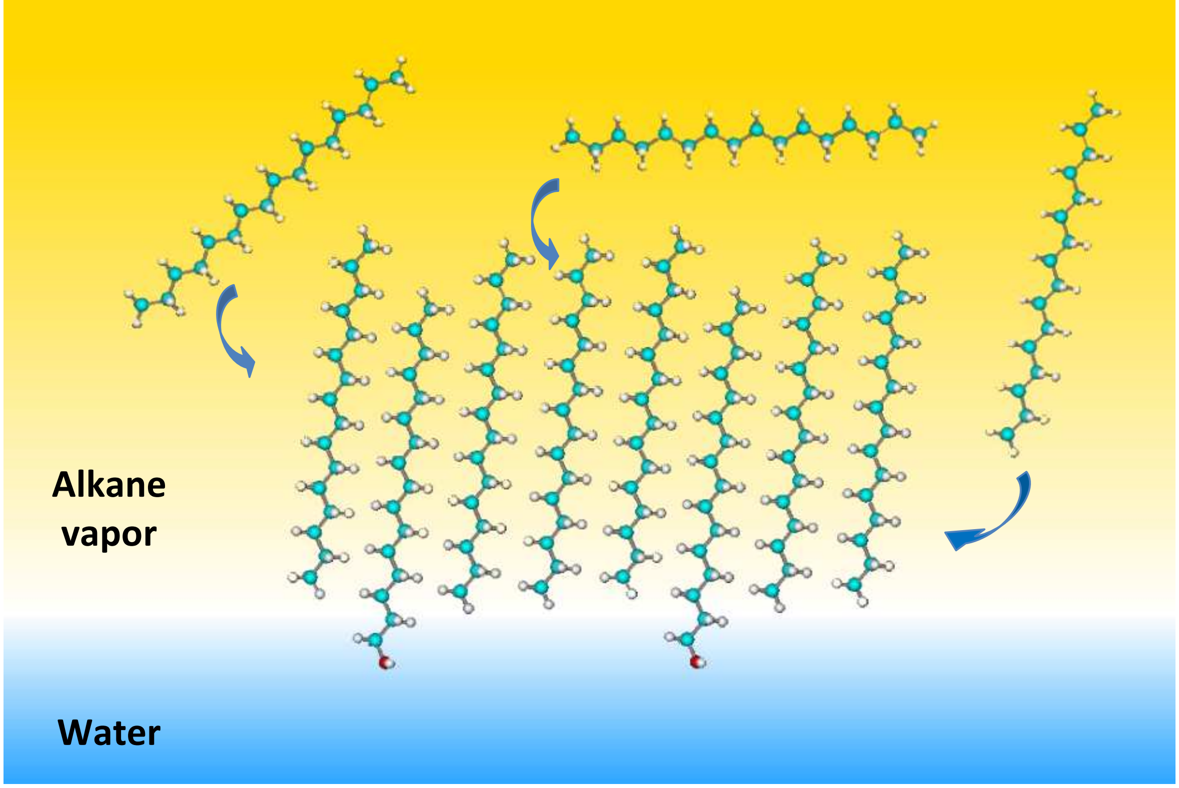

26
24
22
20
18
16
14
12
10
8
6
8
10
12
14
16
18
20
22
24
26
n of alkane
n of alcohol

Fig. 14



TOC

A quantum-chemical model for alkane monolayer formation is developed at the water/vapor interface containing non-ionic surfactants.