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QUANTUM CHEMICAL ANALYSIS OF THERMODYNAMIC PARAMETERS OF α-HYDROXY ACID DIMERIZATION AT THE AIR/WATER INTERFACE

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In the framework of quantum chemical semiempirical method PM3 the thermodynamic and structural parameters of formation and dimerization have been calculated for homochiral α-hydroxy acids with general formula $C_nH_{2n}OHCOOH$ (n = 6–16). On the basis of five optimized monomer structures, dimers with 'serial' and 'parallel' order of monomer functional groups were built. The tilt angles between hydrocarbon radical and normals to the p- and q-directions of the interface in regarded dimer structures have been shown to be $\delta = 8.9°–21.0°$ and $\varphi = 9.8°–20.9°$ dependently on the monomer structure of basic dimer. It has been shown that thermodynamic parameters of dimerization depend on the length of alkyl chain by stepwise and formation of 'parallel' dimers is more energetically preferred. Using dependencies of thermodynamic parameters of dimerization, it is possible to make an assumption about further path of the clusterization process of α-hydroxy acids via preferred formation of linear aggregates on the base of 'parallel' dimers.

INTRODUCTION

Surfactant monolayers have been successfully used as high-quality coatings for different surfaces including displays for electronic devices and hard disks [1, 2]. In addition, the ability of surfactants to form the films is used in modern systems of firefighting [3], particularly in the case of complex and valuable equipment which can be destroyed by water or CO_2. On the base of α-hydroxy acids, similarly to α-amino acids, it is possible to carry out controlled crystallization of chiral compounds and resolution of enantiomers [4, 5]. This amphiphilic compounds can be used for construction of Langmuir-Blodgett films widely used in electronics and optics while obtaining thing-layer coatings with predefined optical properties, and in biotechnology for construction of artificial biomembranes and biosensors [6]. Also α-hydroxy acids are used extensively in food industry (lactic and citric acids) [7, 8] and cosmetology (hydroxyacetic and α-hydroxy-octadecanoic acids) [9–11].

Investigation of surfactant monomolecular films is of interest from the theoretical point of view as well. Thus, development of the models capable of assessment of clusterization thermodynamic parameters of surfactants allows us to control the process of structure formation in the monolayer during the film growth. It should be noted that a lot of papers in recent decades are devoted to research of lipid properties [12–15]. Introduction of hydroxylic group into them could significantly modify the properties of the whole biomembrane which consists of these lipids [16]. α-Hydroxy acids are good objects for investigation of the influence of the second polar group of surfactant on their surface properties because it has the smallest cross-sectional area among all the functional groups. In addition, as it is noted in [17], new researches concerning the effect of branching of surfactant alkyl chain or introduction the second functional group in it are quite rare. Nevertheless, existing experimental data [16–21] reveal significant influence of the OH group position with respect to the alkyl chain of the acid molecules on the structural characteristics of obtained monolayers.

It should be also noted that α-hydroxy acids are chiral compounds. So, it is possible to get monolayers on their base with different optical and structural properties. Meanwhile, one can control the process of enantiomeric or racemic monolayer formation varying such factors as temperature, pH, and content of metal ions in the

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aqueous phase. For example, for the films of α-hydroxyhexadecanoic acid such a situation is typical: presence of Ca^{2+}, Zn^{2+} and Pb^{2+} cations in the aqueous phase results in compaction of homo- and heterochiral monolayers, while presence of Zn^{2+} cations causes preference of homochiral interactions in the monolayer, but presence of Pb^{2+} cations vice versa favors heterochiral interactions in the cluster [21]. Influence of the temperature on the clusterization of chiral compounds was defined by authors [22] for 9-hydroxypalmitic acids. They show that the temperature increase by 5° stipulates increase in the transition pressure of π-A isotherm on1.5–2.0 mN/m in average. Also it affects the domain shape of the monolayer which results in brunching of the aggregate structure.

All the mentioned above stipulates a necessity of further detailed research of structural and thermodynamic parameters of cluster formation of α-hydroxy acids at the air/water interface. Earlier in the frameworks of quantum chemical approach we described the process of cluster formation for ten classes of surfactants [23–33], particularly α-amino acids [31, 32]. Calculated values of the spontaneous clusterization threshold for α-amino acids and structural parameters of their films are in a good agreement with available experimental data [34]. That allows us to apply mentioned approach to description of behavior of other surfactant classes with several functional groups. This paper deals with quantum chemical investigation of structural and thermodynamic parameters of the dimerization process as the first stage of monolayer formation for α-hydroxy acids $C_nH_{2n}OHCOOH$ (n = 6–16) at the air/water interface.

METHODS

Calculations of structural and energy parameters of dimerization for α-hydroxy acids at the air/water interface were carried out using quantum chemical software package MOPAC 2000 in the framework of the semiempirical PM3 approximation [35]. This method is parameterized with respect to the heats of formation [36, 37]. It should be noted that despite some restrictions of this method (overestimation of CH···HC interaction force between hydrophobic chains of amphiphilic molecules) [38], only the PM3 method describes sufficiently the experimental data concerning the monolayer formation of different classes of surfactants, as shown in our previous works [23–33]. In addition, the papers [31, 32] showed that the geometry parameters of the unit cells of homo- and heterochiral α-amino acids monolayers evaluated by using the PM3 method well agreed with the experimental data [34]. Considering all the facts mentioned above, the quantum chemical semiempirical PM3 method proves its value in the works dealt with the investigations of the thermodynamic parameters of clusterization of substituted alkanes [23–33].

RESULTS AND DISCUSSION

Monomers. The first stage of this study was conformational analysis of monomers. The potential energy dependence of the monomer on the values of two torsion angles $\angle \alpha = C_2–C_3–C_4–O_2$ and $\angle \beta = C_2–C_3–O_1–H_1$ was calculated. These angles correspond to the carboxylic and hydroxylic group location with respect to the alkyl chain of α-hydroxy acid molecule (Fig. 1). Both of them were varied in the range 0 to 360° in steps of 15°. The potential energy dependence for monomer of α-hydroxytridecanoic acid on these torsion angles is shown in Fig. 2, *a*. There are 5 minima in this plot. Additional optimization of the monomer structures in the vicinity of these minima has confirmed that five stable conformations exist. They are characterized by the next values of α and β angles: (−96°, −60°); (80°, −54°); (67°, 29°); (−61°, −164°) and (−123°, 25°), respectively. It should be noted that the heats of formation for all five conformers are quite similar, but the most energetically advantageous is the second monomer (α = –96°, β = –60°) and the less preferable is the forth (α = –61°, β = –164°).

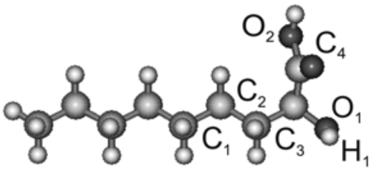
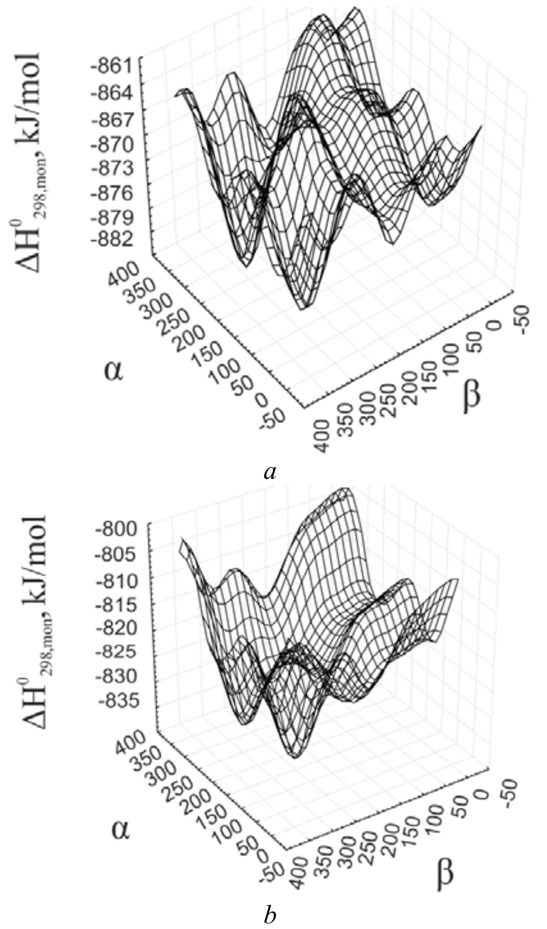


Fig. 1. Torsion angles of the functional groups of α-hydroxynonanoic acid

For the most energetically advantageous conformer of α-hydroxytridecanoic acid (α = –96°, β = –60°) a dependence of the monomer heat of formation on the value of torsion angle $\angle \gamma = C_1–C_2–C_3–C_4$ has been obtained. This angle γ defines the general location of the hydrophilic ‘head’ of acid molecule with respect to its alkyl chain (the 'head' of molecule includes both functional groups). As a result three minima were obtained with the next values of γ: 73°, 168° and −69° (Fig. 3). These γ values for α-hydroxy acids virtually coincide with those obtained for α-amino acids studied earlier [31] (74°, 166° and −67°). As in the case of α-amino acids, conformers of α-hydroxy acids with γ = 168° are slightly more energetically preferable. In spite of this fact, it will be shown below that dimerization of monomers with γ = 73° is characterized by much decrease in the dimerization Gibbs energy. It should be mentioned that two last conformers of α-hydroxy acids with γ = 73° described above have different values of α and β angles: (–176°, 171°) and (98°, –172°) for Monomer 4 and Monomer 5, respectively. The potential energy dependence for α-hydroxytridecanoic acid with γ = 73° is shown in Fig. 2, *b*.

Optimized geometric structures of obtained five conformers of α-hydroxy acids with γ = 73° are listed in Fig. 4. It can be seen that Monomers 1 and 4 are stabilized with the interactions realized between hydrogen atom of OH unit and hydroxylic oxygen of COOH unit. In addition in the Monomer 1 there is an interaction between carbonyl oxygen and α-hydrogen of the molecular alkyl chain. In the Monomer 4 this interaction involves carbonyl oxygen and γ-hydrogen of the molecular alkyl chain. The Monomer 2 has an intramolecular interaction between hydrogen atom of OH group and carbonyl oxygen of COOH group. The structure of the Monomer 3 has an intramolecular interaction between carbonyl oxygen and α-hydrogen of the molecular hydrophobic chain. The Monomer 5 is stabilized by the interaction between hydrogen and oxygen atoms of two OH units and by the intramolecular one between hydrogen atom of carboxylic group and γ-hydrogen of the molecular alkyl chain. It should be also noted that found values of the torsion angles of functional groups for four of five conformers of α-hydroxy acids (apart from the Monomer 4) coincide within the scope of 50° with corresponding values of structural parameters for α-amino acids described previously [31]. Table 1 contains the calculated thermodynamic parameters of formation (enthalpy, absolute entropy, Gibbs energy) for the most energetically preferred Monomer 2, as an example, at 298 K.



a

b

Fig. 2. Potential energy surfaces for monomer of α-hydroxytridecanoic acid: γ = 168°*(a)*, γ = 73°*(b)*

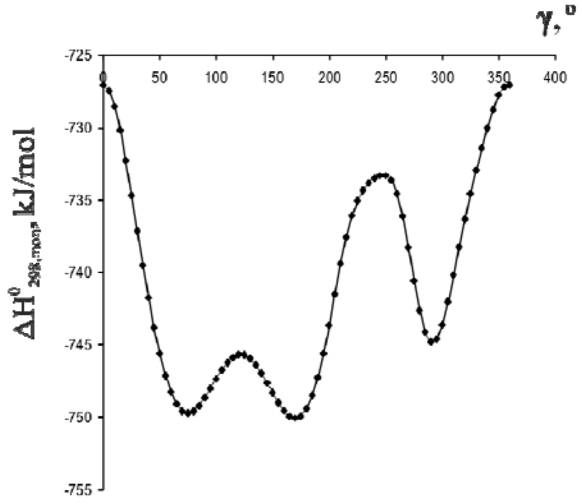


Fig. 3. Dependence of the monomer formation enthalpy of α-hydroxytridecanoic acid on the value of angle γ

It should be mentioned that experimental data regarding the standard thermodynamic characteristics of α-hydroxy acid formation are scarce. They concern only the crystalline phase of the first two members of the homologous series [39]. The standard enthalpy, entropy and Gibbs energy of formation of α-hydroxypropanoic acid are –694.1 kJ/mol, 142.3 J/(mol·K) and –522.9 kJ/mol. For α-hydroxybutanoic acid these data are available only for the enthalpy of formation –676.6 kJ/mol [39]. That is why it is impossible to compare obtained calculated data with experimental values.

On the basis of calculated data correlation dependences of the standard thermodynamic characteristics of α-hydroxy acids on alkyl chain length (n) were constructed at T = 298 K. These dependences are linear similarly to other classes of amphiphiless studied previously [23–33]. Their parameters and standard deviations are listed in Table 2. As the values of the slopes and absolute terms of the corresponding correlations are quite similar, it is possible to express these partial correlations in a general form:

$$\Delta H^{0}_{298,\,\mathrm{mon}} = -(22.68 \pm 0.21)\,n - (581.43 \pm 1.91)$$
$$[S = 7.86\ \mathrm{kJ/mol},\ N = 75], \qquad (1)$$

$$S^{0}_{298,\,\mathrm{mon}} = (31.41 \pm 0.27)\cdot n + (312.99 \pm 2.41)$$
$$[S = 9.92\ \mathrm{J/(mol\cdot K)};\ N = 75]. \qquad (2)$$

where S is the standard deviation, and N is the sampling amount.

The values of the slopes in eqs. (1), (2) which characterize the contributions from the methylene groups agree well with the values calculated earlier for other classes of amphiphilic compounds at 298 K [23–33]. The standard errors for the calculation of enthalpy, entropy and Gibbs energy of α-hydroxy acid formation do not exceed corresponding values of the amphiphile classes previously studied. The correlation coefficients exceed 0.997.

Table 1. Thermodynamic parameters of formation of the most energetically preferred Monomer 2 of α-hydroxy acids (γ = 73°) at 298 K

System	$\Delta H^{0}_{298,\,\mathrm{mon}}$, kJ/mol	$S^{0}_{298,\,\mathrm{mon}}$, J/(mol·K)	$\Delta G^{0}_{298,\,\mathrm{mon}}$, kJ/mol	System	$\Delta H^{0}_{298,\,\mathrm{mon}}$, kJ/mol	$S^{0}_{298,\,\mathrm{mon}}$, J/(mol·K)	$\Delta G^{0}_{298,\,\mathrm{mon}}$, kJ/mol
$C_3H_6O_3$	–618.19	334.21	–515.60	$C_{11}H_{22}O_3$	–798.66	578.35	–468.07
$C_4H_8O_3$	–637.45	363.72	–506.07	$C_{12}H_{24}O_3$	–821.73	608.43	–462.52
$C_5H_{10}O_3$	–660.40	394.33	–500.55	$C_{13}H_{26}O_3$	–844.80	638.10	–456.86
$C_6H_{12}O_3$	–683.37	425.52	–495.21	$C_{14}H_{28}O_3$	–867.87	668.56	–451.42
$C_7H_{14}O_3$	–706.42	456.27	–489.82	$C_{15}H_{30}O_3$	–890.95	698.47	–445.82
$C_8H_{16}O_3$	–729.46	487.16	–484.47	$C_{16}H_{32}O_3$	–914.02	727.65	–440.03
$C_9H_{18}O_3$	–752.53	517.35	–478.94	$C_{17}H_{34}O_3$	–937.10	757.83	–434.51
$C_{10}H_{20}O_3$	–775.59	547.85	–473.50				

Table 2. Correlation equations y=(a±Δa)·n+(b±Δb) for the α-hydroxy acid monomers (sampling amount is 15) where n is the number of methylene units

Monomer	Parameters	a ± Δa	b ± Δb	S
1	ΔH^{0}_{298}, kJ/mol	–22.57 ± 0.06	–590.53 ± 0.52	0.96
	S^{0}_{298}, J/(mol·K)	31.69 ± 0.06	310.24 ± 0.90	0.49
	ΔG^{0}_{298}, kJ/mol	8.55 ± 0.03	–511.60 ± 0.26	0.48
2	ΔH^{0}_{298}, kJ/mol	–22.50 ± 0.06	–587.92 ± 0.51	0.94
	S^{0}_{298}, J/(mol·K)	31.66 ± 0.06	309.86 ± 0.50	0.92
	ΔG^{0}_{298}, kJ/mol	8.55 ± 0.03	–508.88 ± 0.25	0.47
3	ΔH^{0}_{298}, kJ/mol	–22.66 ± 0.00	–574.51 ± 0.04	0.06
	S^{0}_{298}, J/(mol·K)	31.70 ± 0.05	317.69 ± 0.47	0.75
	ΔG^{0}_{298}, kJ/mol	8.50 ± 0.01	–498.34 ± 0.11	0.17
4	ΔH^{0}_{298}, kJ/mol	–22.54 ± 0.07	–577.97 ± 0.61	1.13
	S^{0}_{298}, J/(mol·K)	31.77 ± 0.06	314.05 ± 0.50	0.93
	ΔG^{0}_{298}, kJ/mol	8.55 ± 0.04	–500.17 ± 0.37	0.67
5	ΔH^{0}_{298}, kJ/mol	–22.67 ± 0.00	–574.51 ± 0.05	0.08
	S^{0}_{298}, J/(mol·K)	31.64 ± 0.05	319.04 ± 0.49	0.79
	ΔG^{0}_{298}, kJ/mol	8.51 ± 0.01	–498.74 ± 0.14	0.14

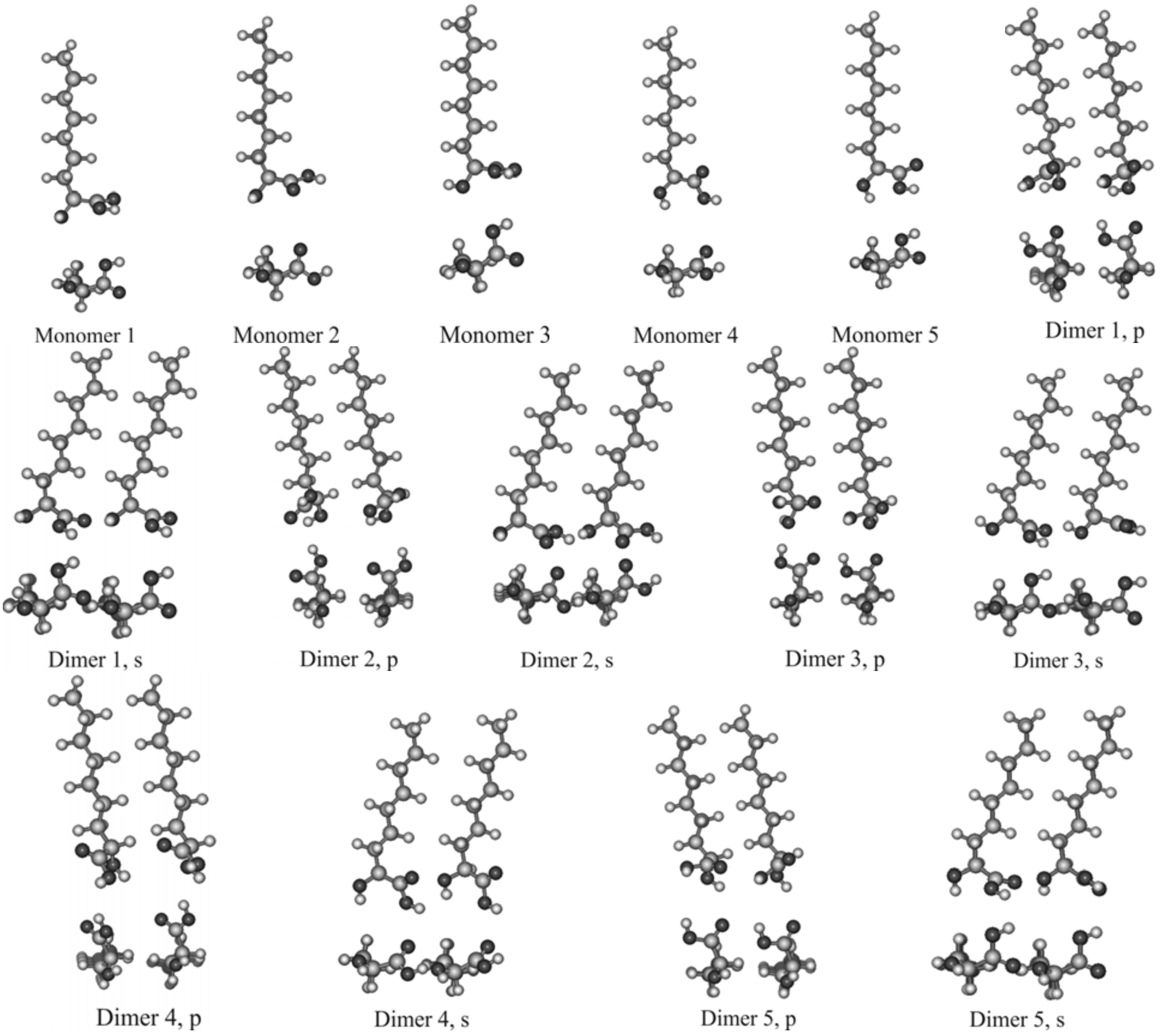


Fig. 4. Optimized geometrical structure of α-hydroxy acid aggregates

Dimers. The dimers were built from the monomer conformations thus obtained. The structures of these entities based on Monomer 2 are illustrated in Fig. 5. Here, the vector drawn through the centers of oxygen atoms of two OH groups was chosen as a direction of the orientation of the monomer 'heads' in the dimer. According to this definition, the structures of dimers were subdivided into two types, characterized by 'parallel' (*p*) and 'serial' (*s*) relative orientation of the 'heads'. For example, the definition 'Dimer 2, p' indicates that this dimer structure is built on the basis of Monomer 2, and the hydrophilic head groups of the monomers are oriented 'parallel' in it (Fig. 5, *a*).

Note, that it is possible to construct dimers with different tilt angles δ and φ of their molecular chains with respect to the normals to the p- and q-directions of the monolayer unit cell respectively (Fig. 6). On the basis of these δ and φ values, it is possible to construct larger clusters, tetramers in particular, which can be regarded as the units cells of corresponding monolayers, and thus define the general tilt angle *t* of the α-hydroxy acid molecules with respect to the normal to the air/water interface. As it is described elsewhere [32] the value of the general tilt angle *t* of the alkyl chain with respect to the normal to the interface can be calculated using the next equations:

$$t = \arcsin\left(\frac{\sin\delta}{\cos\theta_1}\right), \; \theta_1 = \mathrm{arctg}\left(\frac{\sin\varphi}{\sin\delta\cdot\sin\theta} - \mathrm{ctg}\theta\right), \qquad (3)$$

where δ is the tilt angle of surfactant molecules with respect to p-axis of the cluster unit cell, φ is the tilt angle of surfactant molecules with respect to the q-axis of the cluster unit cell, θ is the angle between the p and q directions of the cluster unit cell.

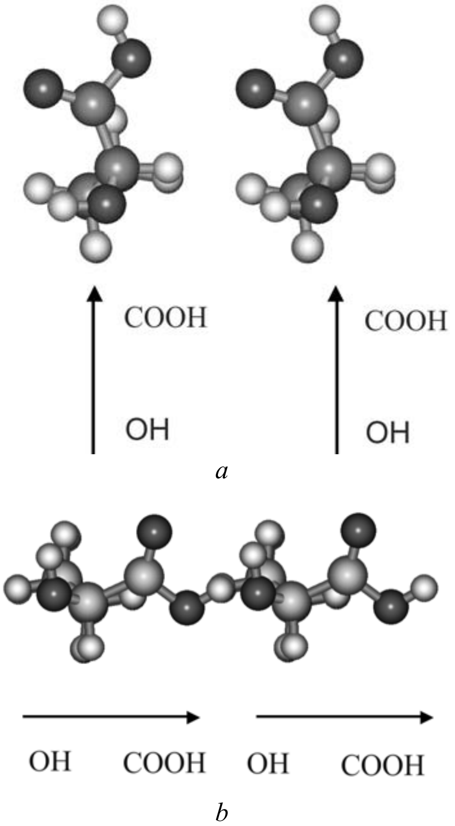


Fig. 5. Relative orientation of α-hydroxy acid monomers in the dimer: 'parallel' *(a)* and 'serial' *(b)*

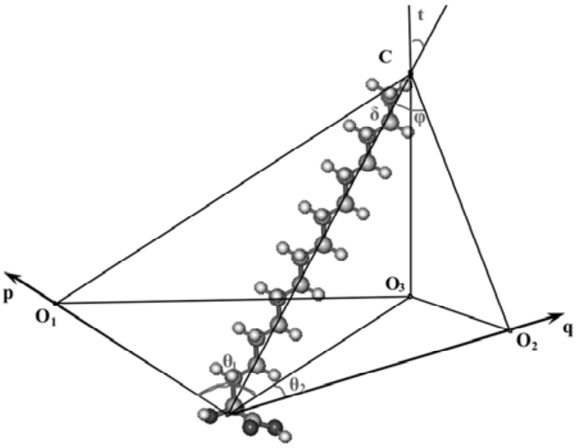


Fig. 6. Orientation of α-hydroxy acid molecule with respect to the air/water interface

To determine the tilt angles of α-hydroxy acid molecules with respect to the p and q directions of the cluster unit cell the 'parallel' and 'serial' types of dimers with the 'a' CH···HC interaction type (marked in Fig. 7 with thin arrows) have been constructed of two monomers. Applying the parallel shift of one molecule with respect to another in both of p and q directions, the dependencies of the dimerization Gibbs energy on the δ and φ angles were tabulated respectively. The minima of the dimerization Gibbs energy for these associates correspond to optimum δ and φ values.

Dependences of the Gibbs energy of dimerization for the structure of Dimer 2, p and Dimer 2, s on the values of tilt angles of the molecules with respect to the normals to p- and q-directions of the monolayer spread are listed in Table 3. These data show that minimum values of the Gibbs energy of dimerization correspond to the structures with following values of φ angle: 9.8°, 22.0° and 40.9°. Additional optimization of dimers with $\varphi = 9.8°$ and 22.0° reveals only existence of single stable structure with $\varphi = 9.8°$. Presence of the second minimum of the Gibbs energy of dimerization with $\varphi = 40.9°$ corresponds to the dimers which have one less CH···HC contact than dimer of α-hydroxy-tridecanoic acid shown in Fig. 7. The loss of this CH···HC interaction causes an increase in the dimerization Gibbs energy and a lower preference of such structures in comparison with those having the maximum number of CH···HC contacts.

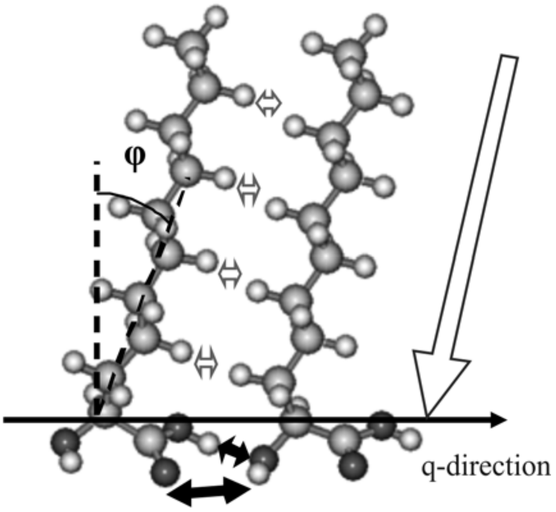


Fig. 7. Determination of the molecular tilt angle with respect to the normal to the q-direction

It should be noted that in the structure of Dimer 2, s there are two intermolecular interactions. The first is realized between hydrogen atom of the carboxylic group of one acid molecule and oxygen atom of the OH group of another. The second interaction takes place between oxygen atom of the carboxylic unit of one molecule and hydrogen atom of the OH unit of another. Mentioned interactions are marked in the Fig. 7 with double-edged solid black arrows. Presence of described interactions causes the dimer orientation with the angle $\varphi = 9.8°$ respectively to the normal to the q-direction.

For Dimers 2, p with ‘parallel’ orientation of the ‘heads’ minimum values of the dimerization Gibbs energy correspond to the values of δ angle equal to 10.2°, 21.0° and 36.6° (Table 3). After additional optimization of these structures, two minima were observed. The first corresponds to the structure with $\delta = 21.0°$ and the second – with $\delta = 36.6°$. The second structure of Dimer 2, p, as in the case of the second structure of the Dimer 2, s, has one less CH···HC contact than the dimer of α-hydroxytridecanoic acid with $\delta = 21.0°$.

Application of the described procedure to dimers built on the basis of other monomer conformations of α-hydroxy acids allows us determining the angles of molecular chains with respect to the normals to the directions of monolayer spread. Obtained values of δ and φ tilt angles for all the five monomer conformations were found to be (18.9°, 14.6°), (21.0°, 9.8°), (8.9°, 11.5°), (9.9°, 20.6°), (9.9°, 20.9°) respectively. Using found values of δ and φ angles, dimer structures with ‘parallel’ and ‘serial’ orientations of the ‘heads’ were constructed for all the five monomers (Fig. 4). Note that only in Dimer 5, p there is the interaction between hydrogen atom of the carboxylic group of one acid molecule and carbonyl oxygen atom of another. While Dimers 1, s, 2, s and 3, s have contacts between hydrogen atom of OH unit of one molecule and carbonyl oxygen atom of another. ‘Serial’ dimers formed using Monomer 5 possess another interaction between hydrogen atom of OH group of one molecule and the hydroxylic hydrogen atom belonging to COOH unit of the second monomer.

Thermodynamic parameters of formation and dimerization were calculated for all the dimer structures described above. Enthalpy, entropy and Gibbs energy of dimerization were calculated according to the next equations:

$$\Delta H_T^{\dim} = \Delta \mathrm{H}^0{}_T - 2\ H^0_{T,\mathrm{mon}};$$

$$\Delta S_T^{\dim} = \mathrm{S}^0{}_T - 2\cdot S^0_{T,\mathrm{mon}};$$

$$\Delta G_T^{\dim} = \Delta H_T^{\dim} - \mathrm{T}\cdot \Delta S_T^{\dim},$$

where $\Delta\mathrm{H}^0_\mathrm{T}$ and S^0_T are enthalpy and entropy of the dimers at a certain temperature T, $H^0_{T,\,mon}$ and $S^0_{T,\,mon}$ are enthalpy and entropy of respective monomers at the same temperature T. Corresponding values of the enthalpy, entropy and Gibbs energy of dimerization are listed in Table 4 for the dimers built on the base of Monomer 2, as an example. For all the homologous series of the calculated thermodynamic parameters of dimerization (enthalpy, entropy, and Gibbs energy) correlation dependences on the number of intermolecular CH···HC contacts K_a were built.

Table 3. Dependence of the dimerization Gibbs’ energy of α-hydroxy acids built on the basis of Monomer 2 (n=12) on the δ and φ values

Molecular tilt angle, φ, °	$\Delta H_{298}^{\dim}$, kJ/mol	$\Delta S_{298}^{\dim}$, J/(mol·K)	$\Delta G_{298}^{\dim}$, kJ/mol	Molecular tilt angle, δ, °	$\Delta H_{298}^{\dim}$, kJ/mol	$\Delta S_{298}^{\dim}$, J/(mol·K)	$\Delta G_{298}^{\dim}$, kJ/mol
53.7	–41.59	–221.81	24.51	54.3	–43.48	–201.21	16.49
51.1	–43.09	–231.26	25.83	51.1	–50.93	–253.50	24.61
40.9	–50.99	–226.12	16.40	36.6	–53.87	–224.40	13.00
35.7	–54.58	–265.73	24.61	34.0	–61.76	–284.91	23.14
22.0	–57.61	–245.97	15.69	21.0	–60.84	–235.28	9.27
11.5	–51.41	–242.15	20.75	10.2	–60.66	–233.64	8.96
9.8	–58.62	–260.34	18.96	9.8	–55.97	–238.86	15.21

Table 4. Thermodynamic parameters of α-hydroxy acid dimerization found within the PM3 method

System	$\Delta H^{\text{dim}}_{298,m}$, kJ/mol	$\Delta S^{\text{dim}}_{298,m}$, J/(mol·K)	$\Delta G^{\text{dim}}_{298,m}$, kJ/mol	System	$\Delta H^{\text{dim}}_{298,m}$, kJ/mol	$\Delta S^{\text{dim}}_{298,m}$, J/(mol·K)	$\Delta G^{\text{dim}}_{298,m}$, kJ/mol
Dimer 2, p				**Dimer 2, s**			
$C_7H_{14}O_3$	–29.74	–156.19	16.80	$C_7H_{14}O_3$	–30.67	–197.03	28.05
$C_8H_{16}O_3$	–32.00	–166.78	17.70	$C_8H_{16}O_3$	–36.06	–204.89	25.00
$C_9H_{18}O_3$	–39.90	–180.76	13.97	$C_9H_{18}O_3$	–39.20	–220.91	26.64
$C_{10}H_{20}O_3$	–42.40	–191.96	14.81	$C_{10}H_{20}O_3$	–45.81	–228.65	22.33
$C_{11}H_{22}O_3$	–50.27	–207.90	11.68	$C_{11}H_{22}O_3$	–48.64	–245.37	24.48
$C_{12}H_{24}O_3$	–52.75	–219.17	12.56	$C_{12}H_{24}O_3$	–56.06	–254.37	19.74
$C_{13}H_{26}O_3$	–60.66	–234.64	9.26	$C_{13}H_{26}O_3$	–58.62	–260.80	19.10
$C_{14}H_{28}O_3$	–63.15	–242.89	9.23	$C_{14}H_{28}O_3$	–66.42	–278.51	16.58
$C_{15}H_{30}O_3$	–71.05	–259.09	6.16	$C_{15}H_{30}O_3$	–68.97	–288.66	17.05
$C_{16}H_{32}O_3$	–73.56	–265.20	5.47	$C_{16}H_{32}O_3$	–76.79	–300.96	12.89
$C_{17}H_{34}O_3$	–81.44	–281.70	2.51	$C_{17}H_{34}O_3$	–79.36	–311.87	13.57

In this study, as in previous papers [23–33], we regard the amphiphile aggregates with regular structure of monomers entered in them. Therefore, the inclusion of data concerning small clusters with edge effects is unreasonable for further building of the additive scheme that allows calculation of thermodynamic parameters of clusterization for 2D films. The edge effects mean the appearance of such interactions between monomer molecules (both between their functional groups and alkyl chains) absent in 2D films. Note that they can be avoided in structures of larger rectangular clusters (tetramers, hexamers) as the increase in the monomer number in the cluster leads to a more ordered optimized structure because of the better regularity of interactions between the atom groups inside of this cluster. Therefore, the structures of Dimer 3, p are not included in the further construction of the general correlation for all dimer types. The corresponding energetic increments of the interactions realized between functional groups of the α-hydroxy acid molecules can be obtained further from the Tetramers 3 having these interactions without the edge effect distortion.

Parameters of correlation equations for enthalpy, entropy and Gibbs energy of dimerization are listed in Table 5. These data reveal that the values of the slope *a* which characterize the increment of the CH···HC interaction in the corresponding values of thermodynamic parameters of dimerization are virtually equal to corresponding values obtained for earlier studied surfactant classes (alcohols, saturated and unsaturated carboxylic acids, α-amino acids, amines, and thioalcohols). The contribution of interactions of α-hydroxy acid ‘heads’ with ‘serial’ orientation in the enthalpy of dimerization was negative for all the dimers apart from the Dimer 4, p structure. Possibly, it can be stipulated by the structural peculiarities of this dimer. Oxygen atom belonging to OH group of one monomer and carbonyl oxygen atom of another mutually repulse. By-turn this causes the less thermodynamical preference of formation of such dimers constructed from Monomer 4 comparatively to other ‘serial’ dimers of α-hydroxy acids. The contribution of interactions of ‘heads’ with ‘parallel’ orientation in to the enthalpy of dimerization was statistically insignificant. Therefore, there are dashes in the corresponding cells of the Table 5. For entropy of dimerization, the increment of the hydrophilic group interactions in ‘serial’ dimers was larger (by absolute value) than that for ‘parallel’ dimers. In addition, as it was noted above, the less number of intermolecular CH···HC contacts is realized in dimers with ‘serial’ orientation of the ‘heads’ than that in ‘parallel’ dimers (for the structures with odd number of carbon atoms in the alkyl chain). As a result, formation of ‘parallel’ dimers is more advantageous with respect to the Gibbs energy of dimerization.

Table 5. Parameters of correlation dependences of the thermodynamic characteristics of dimerization for α-hydroxy acids (sampling amount N=11)

System	$\Delta H_{298}^{\mathrm{dim}}$, kJ/mol			
	(a ± Δa)	(b ± Δb)	R	S
Dimer 1, p	–10.19±0.28	–	0.9967	1.48
Dimer 1, s	–10.24±0.14	–8.95±0.72	0.9991	0.76
Dimer 2, p	–10.25±0.25	–	0.9973	1.33
Dimer 2, s	–9.80±0.33	–8.82±1.63	0.9950	1.74
Dimer 3, s	–9.96±0.30	–11.09±1.48	0.9960	1.58
Dimer 4, p	–10.23±0.26	–	0.9970	1.41
Dimer 4, s	–10.21±0.16	21.33±0.77	0.9990	0.82
Dimer 5, p	–10.26±0.25	–5.20±1.39	0.9973	1.34
Dimer 5, s	–10.83±0.28	–	0.9971	1.46
		$\Delta S_{298}^{\mathrm{dim}}$, J/(mol·K)		
Dimer 1, p	–23.15±1.50	–99.39±8.29	0.9815	7.99
Dimer 1, s	–24.32±0.34	–123.73±1.73	0.9991	1.84
Dimer 2, p	–24.71±1.04	–88.47±5.72	0.9922	5.51
Dimer 2, s	–22.62±1.32	–146.87±6.63	0.9849	7.05
Dimer 3, s	–23.14±2.30	–132.35±11.46	0.9584	12.19
Dimer 4, p	–25.17±1.19	–90.38±6.54	0.9901	6.30
Dimer 4, s	–25.67±1.14	–105.18±5.70	0.9912	6.06
Dimer 5, p	–25.49±1.56	–105.53±8.57	0.9837	8.26
Dimer 5, s	–26.69±0.53	–102.60±2.62	0.9982	2.79
		$\Delta G_{298}^{\mathrm{dim}}$, kJ/mol		
Dimer 1, p	–3.30±0.19	27.48±1.07	0.9847	1.03
Dimer 1, s	–2.99±0.15	27.92±0.77	0.9883	0.81
Dimer 2, p	–2.88±0.10	26.13±0.56	0.9945	0.54
Dimer 2, s	–3.06±0.16	34.95±0.78	0.9885	0.83
Dimer 3, s	–3.06±0.42	28.35±2.07	0.9263	2.20
Dimer 4, p	–2.73±0.11	24.58±0.61	0.9928	0.58
Dimer 4, s	–2.56±0.34	52.69±1.67	0.9304	1.78
Dimer 5, p	–2.66±0.22	26.24±1.24	0.9693	1.19
Dimer 5, s	–2.87±0.38	33.19±1.88	0.9307	2.00

The slopes of the calculated regression coefficients of partial correlations for α-hydroxy acid dimers are quite similar. Therefore, the partial correlations for all dimers considered can be generalized into one correlation:

$$\Delta H_{298}^{\mathrm{dim}} = -(10.18 \pm 0.04)\cdot(K_a + n_{1,s} + n_{3,s}) - (2.43 \pm 0.0.35)\cdot(n_{1,p} + n_{4,p}) - (7.03 \pm 0.46)\cdot n_{2,s} +$$
$$+ (21.21 \pm 0.46)\cdot n_{4,s} - (5.61 \pm 0.46)\cdot n_{5,p}, \text{ [N=99; R = 0,9997; S = 1,40 kJ/mol];} \quad (4)$$

$$\Delta S_{298}^{\mathrm{dim}} = -(24.53 \pm 0.44)\cdot K_a - (91.74 \pm 2.62)\cdot(n_{1,p} + n_{2,p} + n_{4,p}) - (124.24 \pm 2.56)\cdot (n_{1,s} + n_{3,s}) -$$
$$- (111.30 \pm 2.48)\cdot(n_{4,s} + n_{5,p} + n_{5,s}) - (137.84 \pm 2.97)\cdot n_{2,s}, \text{ [N=99; R = 0.9996; S = 7.03 J/(mol·K)],} \quad (5)$$

$$\Delta G_{298}^{\mathrm{dim}} = -(2.91 \pm 0.08)\cdot K_a + (54.32 \pm 0.57)\cdot n_{4,s} + (25.70 \pm 0.50)\cdot(n_{1,p} + n_{2,p} + n_{4,p}) + (33.76 \pm 0.49)\cdot(n_{2,s} + n_{5,s}) +$$
$$+ (27.54 \pm 0.48)\cdot(n_{1,s} + n_{3,s} + n_{5,p}), \text{ [N=99; R = 0,9978; S = 1.34 kJ/mol],} \quad (6)$$

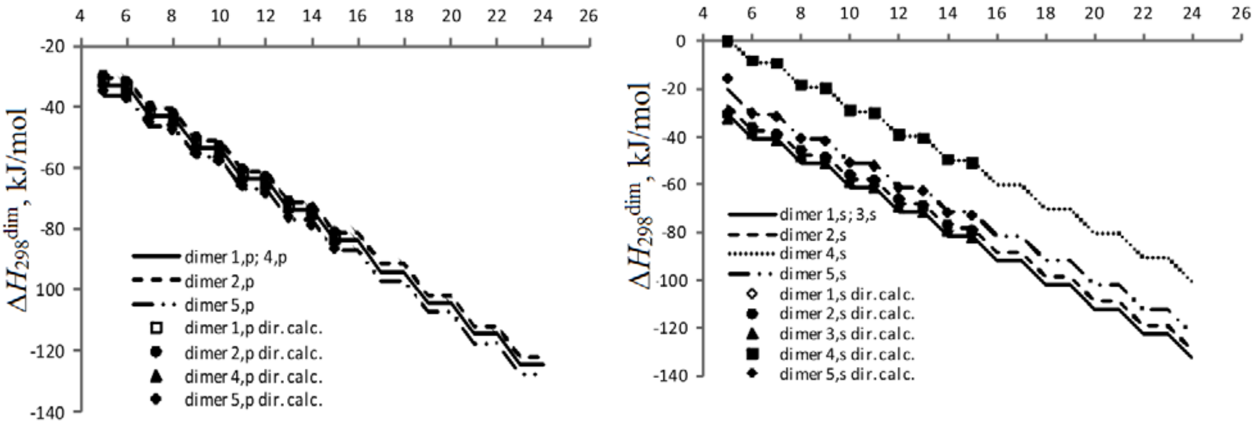
where K_a is the number of CH···HC contacts realized in the regarded dimer. It can be obtained for 'serial' and 'parallel' dimers as follows:

$$K_a = \left\{\frac{n-1}{2}\right\} \text{ and } K_a = \left\{\frac{n}{2}\right\}, \text{ respectively,} \quad (7)$$

where n is the number of methylene groups in the alkyl chain of α-hydroxy acids; braces denote the integer part of the number; $n_{i,p}$ and $n_{i,s}$ are the descriptors of 'parallel' (p) and 'serially' (s) oriented functional head groups in the structure, with *i* denoting the number of the corresponding monomer used for construction of regarded dimer. In the case when interaction between the functional groups of the head groups exists in the dimer structure then the value of corresponding descriptor is equal to unity. If this interaction is absent, this descriptor is zero.

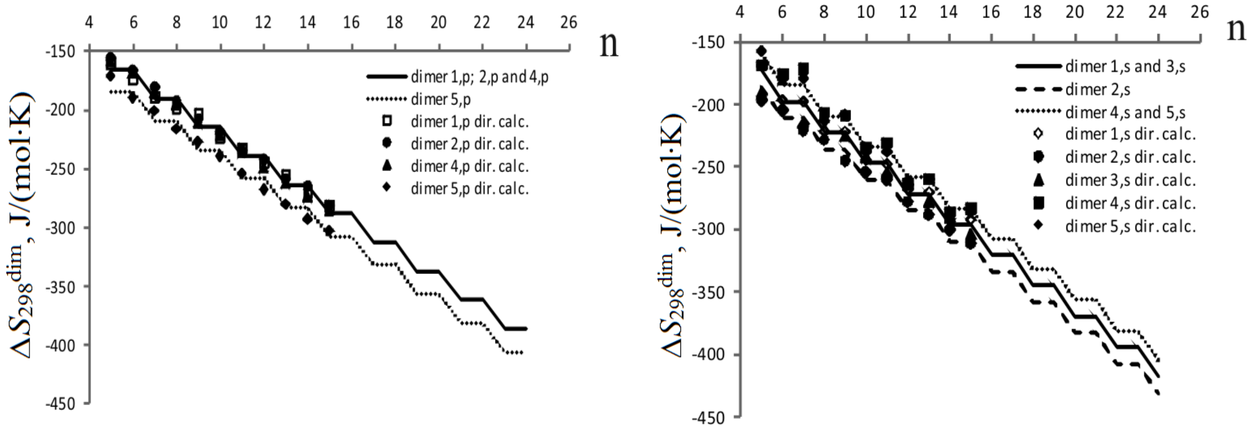
Note, that the values of the standard deviations for enthalpy, entropy and Gibbs' energy of dimerization for α-hydroxy acids do not exceed corresponding values for studied earlier surfactant classes [23–33].

The graphical dependences of the variation of the dimerization enthalpy, entropy, and Gibbs energy are shown in Figs. 8–10. Here the solid lines represent the dependencies calculated from eqs. (4)–(6), whereas the points correspond to the data obtained by direct quantum chemical calculations. It is seen that the results of direct calculation agree well with the values predicted by correlation dependences. Analysis of depicted data enables to make a prediction that the spontaneous dimerization threshold at 298 K for 'parallel' Dimers 1, p, Dimers 2, p, and Dimers 4, p is 17–18 carbon atoms in the aliphatic chain, while for Dimers 5, p it is 19–20 carbon atoms. For 'serial' dimers this threshold shifts to the region of compounds with longer alkyl chains: for Dimers 1, s and Dimers 3, s – 20–21 carbon atoms, for Dimers 2, s and Dimers 5, s – 24–25, for Dimers 4, s – 38–40. This is caused by the fact that in the dimer structures with 'serial' orientation of the 'heads' there are less number of intermolecular CH···HC interactions (for the structures with odd number of carbon atoms in the chain).



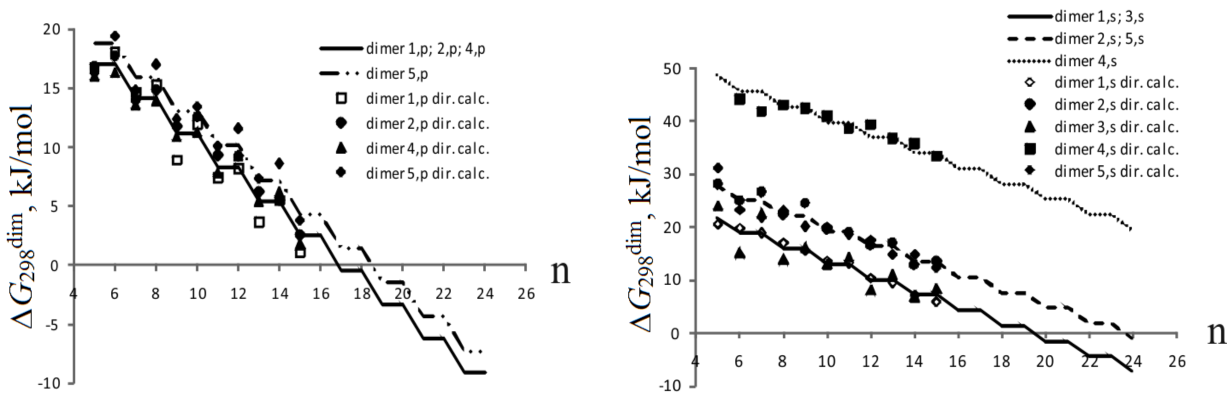
a *b*

Fig. 8. Dependence of the variation of dimerization enthalpy on the alkyl chain length for 'parallel' *(a)* and 'serial' *(b)* dimers



a *b*

Fig. 9. Dependence of the variation of dimerization entropy on the alkyl chain length for 'parallel' *(a)* and 'serial' *(b)* dimers



a *b*

Fig. 10. Dependence of the variation of dimerization Gibbs energy on the alkyl chain length for 'parallel' *(a)* and 'serial' *(b)* dimers

Obtained data are useful for the further construction of an additive scheme for calculation of the thermodynamic parameters of α-hydroxy acid clusterization up to 2D films. In addition, described graphs of the dimerization Gibbs' energy dependences for obtained α-hydroxy acid conformers enable to make an assumption about the further clusterization path and domain structure of these compounds. So, aggregation of α-hydroxy acids will take place via preferential formation of 'parallel' dimers, their further linkage in tetramers, hexamers, etc. possessing and less preferable interactions of the hydrophilic parts of molecules as in 'serial' dimers. That is the 2D film formation will progress via preferential formation of linear aggregates stipulated more friable, 'dendritic' structure of the monolayer.

CONCLUSIONS

The dimerization thermodynamics of unbranched α-hydroxy acids $C_nH_{2n}OHCOOH$ (n=6–16) at the air/water interface has been studied using semiempiric PM3 method. Five stable monomer structures were found. Monomer 2 is the most energetically advantageous structure with the values of torsion angles of carboxylic group (α) and hydroxylic group (β) –96° and –60° respectively, while the torsion angle of the hydrophilic 'head' which includes both functional groups of α-hydroxy acids was found to be 73°. The values of torsion angles of the functional groups for four of five α-hydroxy acid monomers agree reasonably with corresponding structural parameters of α-amino acid monomers described earlier [31]. It has been shown that dependences of the enthalpy, entropy and Gibbs energy of α-hydroxy acid formation on the alkyl chain length are linear; corresponding correlation coefficients exceed 0.997.

The dimers with 'serial' and 'parallel' orientation of monomer functional gropus were built on the basis of found monomer structures. The dependences of the dimerization enthalpy, entropy and Gibbs energy of α-hydroxy acids on the alkyl chain length are stepwise as in the case of previously studied surfactant classes [23–33]. Formation of the α-hydroxy acid dimers with 'parallel' orientation of the monomer 'heads' is more energetically preferred as compared to 'serial' orientation.

It has been found that spontaneous dimerization of the 'parallel' dimers built on the basis of Monomer 1, 2 and 4 is possible for structures which have 17–18 carbon atoms in their alkyl chains, while for other dimers this threshold is larger. Analysis of the graphs of the dimerization Gibbs energy dependences for considered α-hydroxy acid conformers allows one to make an assumption about the path of further domain growth. Aggregation of α-hydroxy acids can take place via preferential formation of 'parallel' dimers, their further linkage linear associates that causes more friable, 'dendritic' structure of the monolayer.

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Квантово-хімічний аналіз термодинамічних параметрів димеризації α-гідроксікислот на міжфазній поверхні повітря/вода

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В рамках квантово-хімічного напівемпіричного методу PM3 розраховані термодинамічні та структурні параметри утворення та димеризації гомохіральних α-гідроксікислот загальної формули $C_nH_{2n}OHCOOH$ *(n = 6–16). На основі отриманих п'яти конформацій мономерів були побудовані димери з «послідовним» та «паралельним» розташуванням функціональних груп мономерів в них. Знайдено, що гідрофобні ланцюги молекул α-гідроксікислот у досліджуваних типах димерів можуть розташовуватись під різними кутами нахилу відносно нормалей до p- і q-напрямків міжфазної поверхні –* $\delta = 8.9°–21.0°$ *і* $\varphi = 9.8°–20.9°$ *залежно від структурних особливостей мономерів, що формують димер. Показано, що ентальпія, ентропія та енергія Гіббса димеризації усіх досліджуваних структур димерів ступінчасто залежить від довжини вуглеводневого ланцюга, при цьому за енергією Гіббса димеризації вигідним є утворення димерів з «паралельним» розташуванням функціональних груп α-гідроксікислот у них. На основі залежностей термодинамічних параметрів димеризації зроблено припущення про подальший шлях перебігу самочинної кластеризації α-гідроксікислот через переважне утворення лінійних асоціатів з «паралельних» димерів.*

Квантово-химический анализ термодинамических параметров димеризации α-гидроксикислот на межфазной поверхности воздух/вода

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В рамках квантово-химического полуэмпирического метода PM3 рассчитаны термодинамические и структурные параметры образования и димеризации гомохиральных α-гидроксикислот с общей формулой $C_nH_{2n}OHCOOH$ *(n = 6–16). На основе полученных пяти оптимизированных структур мономеров были построены димеры с «последовательным» и «параллельным» расположением функциональных групп мономеров в них. Выявлено, что гидрофобные цепи молекул α-гидроксикислот в рассматриваемых типах димеров могут располагаться под различными углами наклона относительно нормалей к p- и q-направлениям межфазной поверхности –* $\delta = 8.9°–21.0°$ *и* $\varphi = 9.8°–20.9°$ *в зависимости от структурных особенностей мономеров, входящих в димер. Показано, что энтальпия, энтропия и энергия Гиббса димеризации всех рассмотренных структур димеров ступенчато зависят от длины углеводородной цепи, при этом по энергии Гиббса димеризации более предпочтительным является образование димеров с «параллельным» расположением функциональных групп α-гидроксикислот в них. На основе зависимостей термодинамических параметров димеризации сделано предположение о дальнейшем пути протекания самопроизвольной кластеризации α-гидроксикислот через преимущественное образование линейных ассоциатов из «параллельных» димеров.*