

Thermodynamics of the Clusterization Process of *trans*-Isomers of Unsaturated Fatty Acids at the Air/Water Interface

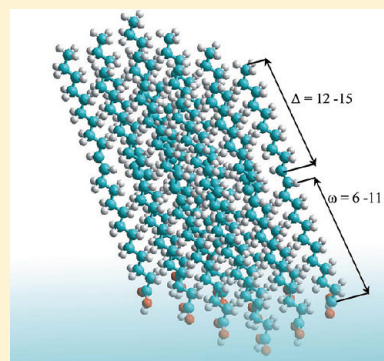
Yu. B. Vysotsky,[†] E. A. Belyaeva,[†] E. S. Fomina,[†] D. Vollhardt,^{*,‡} V. B. Fainerman,[§] and R. Miller[‡]

[†]Donetsk National Technical University, 58 Artema Strasse, 83000 Donetsk, Ukraine

[‡]Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam/Golm, Germany

[§]Medical Physicochemical Centre, Donetsk Medical University, 16 Ilych Avenue, Donetsk 83003, Ukraine

ABSTRACT: In the frameworks of the quantum-chemical semiempirical PM3 method, the thermodynamic parameters of *trans*-isomers of unsaturated carboxylic acids at the air/water interface were studied. Systems with 18–26 carbon atoms in the alkyl chain and different positions of the double bond are considered. Using quantum-chemical semiempirical PM3 method enthalpy, Gibbs' energy of monomers' formation from the elementary compounds and absolute entropy of *trans*-unsaturated carboxylic acids are calculated. It has been shown that thermodynamic parameters mentioned above for isomers with the same number of carbon atoms in the hydrocarbon chain but different position of double bond are practically the same within the margin of error. For dimers, trimers, and tetramers of the four *trans*-unsaturated carboxylic acids, the thermodynamic parameters of clusterization were calculated. It is shown that the position of double bond does not significantly affect the values of thermodynamic parameters of formation and clusterization of carboxylic acids with equal alkyl chain lengths. The only exception is the case that the double bond is in the ω -position (extremely distanced from the carboxylic group). In this case, the number of intermolecular interactions between alkyl chains is changed. Spontaneous clusterization of *trans*- in the standard conditions is possible for molecules that possess more than 16–17 carbon atoms in the alkyl chain. These threshold values exceed the corresponding values that were calculated previously using the quantum-chemical PM3 method for saturated carboxylic acids (12–13 carbon atoms in the alkyl chain) and are a little bit smaller than the corresponding parameters for *cis*-unsaturated carboxylic acids (18–19 carbon atoms). These values agree with experimental parameters. Also, the calculated structural parameters of *trans*-unsaturated carboxylic acids' monolayer for the unit cell with $a = 6.98$ Å, $b = 8.30$ Å, and for the molecular tilt angle with 64.95° agree with the experimental parameters.



INTRODUCTION

Unsaturated carboxylic acids are abundant in numerous biological systems and also are important constituents of biological membranes.^{1,2} The broad variation in the biological properties of lipids and the membrane characteristics is based on the fact that the unsaturated chains alter in type, number, position, and geometric configuration of unsaturated carbon–carbon bonds. Correspondingly, unsaturated fatty acids found wide interest in practical applications in the fields of food, pharmaceutical, and cosmetic industries. For understanding the role of unsaturated fatty acids in biological membrane systems, model studies with Langmuir monolayers have been performed focused on the effect of *cis*–*trans* isomerization, position, and the number of the double bonds.^{3–14} These studies have shown that the main characteristics of unsaturated carboxylic acid monolayers deviate considerably from those of the corresponding saturated fatty acids. Both the *cis*- and the *trans*-isomers of the unsaturated fatty acids unsaturation cause expansion of the monolayer in comparison to the saturated fatty acids at the same alkyl chain length, but the expansion of the *cis*-isomers is much larger than that of the *trans*-isomers because the *trans* double bond changes the configuration of a saturated alkyl chain much less than does a *cis* double bond.

Studies of the three-dimensional crystal structures of unsaturated fatty acids having different molecular conformations and polymorphism indicated that relations exist between the molecular structure (alkyl chain length, position of the double bond) and functionality.^{15–18}

Recent progress in the experimental characterization of unsaturated fatty acid monolayers was achieved by comparison of phase behavior, domain morphology, and two-dimensional lattice structure of the *cis*- and *trans*-isomers using surface pressure–molecular area (π – A) isotherms, Brewster angle microscopy (BAM), and grazing incidence X-ray diffraction (GIXD) techniques.^{19,20}

On the basis of the π – A isotherms, it was demonstrated by thermodynamic analysis that the introduction of unsaturation into the alkyl chain affects the thermodynamic characteristics of the monolayer in a similar way as shortening the alkyl chain length, and it is much larger for the *cis*-isomers rather than for the *trans*-isomers. It is of special interest that, completely different from the behavior of saturated fatty acid monolayers,

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for all *cis*- and *trans*-unsaturated fatty acids studied, only a centered rectangular lattice with alkyl chains tilted toward the nearest neighbor (NN) direction was found, and no indication for a phase transition between different condensed phases could be observed.²⁰ It was discussed that the conformity of the *cis*- and *trans*-unsaturated fatty acid monolayers to only one lattice type having a rectangular centered unit cell with alkyl chains tilted in the NN direction correlates obviously with the obstructive effect of the double bond in the alkyl chain on the molecular ordering.²⁰

It is interesting to note that at temperatures of 20–25 °C the formation of Langmuir monolayers, and thus the clusterization process of saturated carboxylic acids, occurs for alkyl chain lengths with 12–13 carbon atoms,^{13,14} whereas it needs for *cis*-unsaturated carboxylic acids with chain lengths of 18–19 carbon atoms.^{15–18}

In our previous papers, the quantum-chemical semiempirical PM3 method was used to calculate thermodynamic parameters of clusterization of saturated²¹ and *cis*-unsaturated²² carboxylic acids. The present work focuses on the calculation of the thermodynamic characteristics for the clusterization of *trans*-unsaturated carboxylic acids at the air/water interface and on the structural parameters of the unit cell of the corresponding monolayers within the framework of the semiempirical PM3 method.

METHODS

Optimization of geometrical parameters of monomers and clusters of *trans*-unsaturated carboxylic acids was carried out using the program complex Mopac2000 in the framework of quantum-chemical semiempirical PM3 method. There are two preconditions for choosing this method. First, the accuracy of the enthalpy calculation in this method is 40% higher than that in the previous semiempirical AM1 method.²³ Second, only this method describes correctly the intermolecular interactions between the alkyl chains of substituted alkanes at the air/water interface. In particular, the structure parameters of clusters (dimers, tetramers) of the surface-active compounds optimized with the PM3 method correspond to the structural parameters of the real monolayers.²⁴

In our calculations, the air/water interface was taken into account implicitly by its stretching and orienting action. The stretching action of interface consists of making the amphiphilic molecules take a linear conformation where all hydrogen atoms at the next carbon atoms are in *trans*-position to each other. It is known that the interface orients molecules of substituted alkanes to itself under some angle, usually under 60°–80°.²⁵ For the definition of values of this angle, one of the monomers in the dimer was moved along another, changing the conditional angle between the molecules and interface. For the given structures, the Gibbs energy of dimerization was calculated, and by its comparison the most energetically preferable structure was determined. This procedure is described in detail in ref 24.

The correlation analysis of the results of the direct calculations was carried out in the framework of the program package Microsoft Office Excel.

STRUCTURAL AND THERMODYNAMIC PARAMETERS OF MONOMERS

Before thermodynamic parameters for the monomer formation were calculated, the geometrical parameters of the most stable conformations were determined. Previously,²¹ the conformational analysis of monomers of saturated carboxylic acids was performed, and the values of the torsion angle $C_3C_2C_1O_1$ of

–92° and the angle $C_2C_1O_2H$ of 180° were determined (see Figure 1).

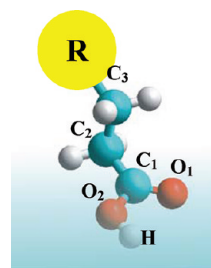


Figure 1. Mutual orientation of the atoms of the functional group and the hydrocarbon chain in the molecules of carboxylic acids (R: hydrocarbon chain).

The carboxylic group is far from the part of hydrocarbon chain that contains a double bond, and its presence does not affect the spatial orientation of the atoms of the functional group.²² That is why the values of the angles $C_3C_2C_1O_1$ and $C_2C_1O_2H$ calculated for saturated and *cis*-unsaturated carboxylic acids were used for constructing the structures of the *trans*-unsaturated carboxylic acids.

According to the generally accepted nomenclature² and in analogy to ref 22, the part of the hydrocarbon chain from the carboxylic group to the double bond was denoted as Δ , and the part from the double bond to the methyl group as ω (see Figure 2).

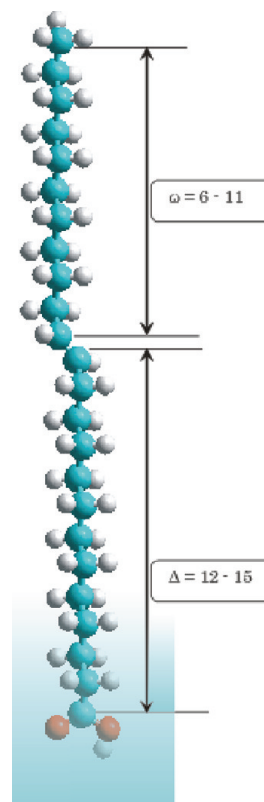


Figure 2. Optimized geometric structure of the monomer of *trans*-unsaturated carboxylic acid with $\Delta = 13$, $\omega = 11$ (in this Article, Δ was varied from 12 to 15, and ω for each Δ was varied from 6 to 11).

As in ref 22, the total length of the alkyl chain ($n = \Delta + \omega$) was varied from 18 to 26 carbon atoms, Δ has values of 12, 13,

14, and 15, and for each Δ of them ω varied from 6 to 11. Isomers with different positions of the double bond were chosen by varying the Δ and ω values, for example, $n = 22 = \Delta + \omega = 12 + 10 = 13 + 9 = 14 + 8 = 15 + 7$. All of these structures were optimized, and then the enthalpy of formation ($\Delta H^\circ_{298,\text{mon}}$), absolute entropy ($S^\circ_{298,\text{mon}}$), and Gibbs' energy of formation ($\Delta G^\circ_{298,\text{mon}}$) of monomers from elementary compounds were calculated within the framework of the program complex Mopac2000 (semiempirical method PM3). The results of the calculations are shown in Table 1.

Table 1. Thermodynamic Parameters of Monomers' *trans*-Unsaturated Carboxylic Acids Formation ($n = 18\text{--}26$)

ω	$\Delta = 12$	$\Delta = 13$	$\Delta = 14$	$\Delta = 15$
$\Delta H^\circ_{298,\text{mon}}$, kJ/mol				
6	−675.41	−698.10	−720.77	−743.46
7	−698.08	−720.78	−743.45	−766.14
8	−720.76	−743.46	−766.13	−788.82
9	−743.44	−766.14	−788.81	−811.51
10	−766.11	−788.83	−811.49	−834.19
11	−788.79	−811.51	−834.17	−856.87
$S^\circ_{298,\text{mon}}$, J/mol·K				
6	801.72	833.77	862.75	892.88
7	830.15	870.06	895.45	920.80
8	864.90	896.38	928.05	954.29
9	893.45	938.04	956.26	980.94
10	925.50	958.91	990.28	1016.39
11	954.24	996.55	1017.09	1041.50
$\Delta G^\circ_{298,\text{mon}}$, kJ/mol				
6	−181.74	−175.09	−167.50	−160.27
7	−172.28	−167.98	−159.32	−150.67
8	−164.71	−157.90	−151.11	−142.72
9	−155.29	−152.39	−141.59	−132.75
10	−146.91	−140.69	−133.80	−125.39
11	−137.54	−133.98	−123.86	−114.95

As demonstrated in ref 22, the position of the double bond in the hydrocarbon chain of *cis*-unsaturated carboxylic acids does not affect the values of enthalpy, entropy, and Gibbs' energy of the compounds with the same total alkyl chain length. This holds also for the *trans*-unsaturated carboxylic acids. As can be seen in Table 1, the thermodynamic parameter values of the monomeric *trans*-unsaturated acids of the same total alkyl chain length are positioned in diagonals. These parameter values are quite close to each other. The values of their derivation from the mean value are 0.013 kJ/mol for enthalpy of formation, 3.21 J/mol·K for absolute entropy, and 0.97 kJ/mol for Gibbs' energy of formation.

For each system of monomers of *trans*-unsaturated carboxylic acids ($\Delta = 12, 13, 14, 15$, whereas ω was varied from 6 to 11), the correlation dependence of enthalpy of formation and absolute entropy on the number of methylene fragments were obtained by: $y = (a \pm \Delta a) \cdot (n - 1) + (b \pm \Delta b)$, where y are the thermodynamic parameters (enthalpy of formation, absolute entropy, Gibbs' energy of formation) and $(n - 1)$ are the number of methylene fragments. Correlation parameters and standard derivations (S) are presented in Table 2.

The values of the slope, $a \pm \Delta a$, characterizing the increment of one methylene group in the thermodynamic parameters of the monomer formation, coincide within error limits. Also, these values coincide with the corresponding values calculated

earlier for saturated carboxylic acids,²¹ *cis*-unsaturated carboxylic acids,²² alcohols,^{26,27} thioalcohols,²⁸ amines,²⁹ and amino-acids.³⁰ The absolute term of the correlation, $b \pm \Delta b$, characterizes the increment from the functional group and two CH_2 -groups in the thermodynamic parameters. Regression coefficients are higher than 0.9997. In view of the similarity of the partial correlation parameters, it seems possible to join these correlations in general correlation dependencies of enthalpy of formation, $\Delta H^\circ_{298,\text{mon}}$ and absolute entropy, $S^\circ_{298,\text{mon}}$, on the number of methylene groups in the hydrocarbon chain:

$$\Delta H^\circ_{298,\text{mon}} = -(22.68 \pm 0.001) \cdot (n - 1) - (335.17 \pm 0.02), \text{ kJ/mol} (S = 0.01 \text{ J/mol} \cdot \text{K}, N = 24) \quad (1)$$

$$S^\circ_{298,\text{mon}} = (30.53 \pm 0.048) \cdot (n - 1) + (345.69 \pm 8.56), \text{ J/mol} \cdot \text{K} (S = 4.48 \text{ J/mol} \cdot \text{K}, N = 24) \quad (2)$$

Here and in the following, S is the standard derivation and N is the sampling amount.

These dependencies provide the opportunity to predict the values of these thermodynamic parameters for any *trans*-unsaturated carboxylic acids with nonbranched chain and one carboxylic group with high accuracy.

To define how the conformation of the molecule affects the value of the thermodynamic parameters of monomers of *trans*-unsaturated carboxylic acid, the parameters mentioned above (in Table 1) were compared to the corresponding parameters calculated for monomers of *cis*-unsaturated carboxylic acid²² with the same number of carbon atoms in the hydrocarbon chain. This comparison revealed systematic deviations of 2.56 kJ/mol for enthalpy of formation and 10.16 J/mol·K for absolute entropy. In case of enthalpy, it could be caused by the different character of the intermolecular interactions between the CH_2 -group and CH -group in the hydrocarbon chain and in case of absolute entropy by differences in the spatial orientation of hydrocarbon chains in the *cis*- and *trans*-isomers (see Figure 3).

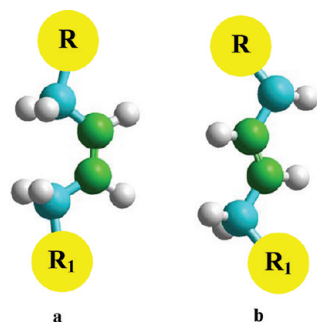
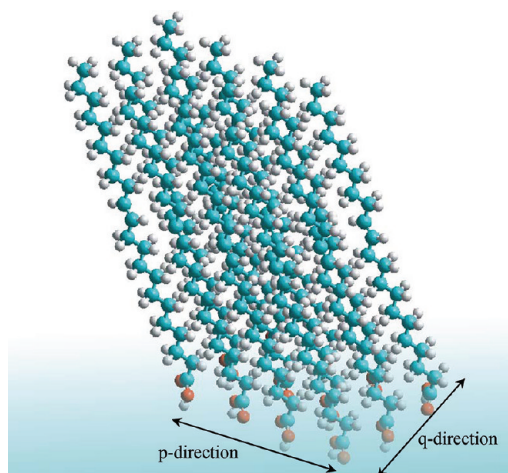
■ STRUCTURAL AND THERMODYNAMIC PARAMETERS OF DIMERS, TETRAMERS, AND INFINITE CLUSTERS

Dimers. In ref 22, it was shown that there are three types of mutual displacement of carboxylic groups in successive and anti-successive direction in the regular monolayer of *cis*-unsaturated acids. The vector drawn conditionally through the centers of the C_1 and O_1 atoms (see Figure 1) and directed from the carbon to the oxygen atom was chosen as a direction of the functional group orientation.

In our previous papers,^{21,22,26–31} we called the two dimensions of the monolayer expansion as p -direction and q -direction (see Figure 4). The number of monomers in the cluster in the p - and q -directions was designated as p and q , correspondingly. So, for example, for the cluster that is schematically shown in Figure 4, $p = 4$ and $q = 3$. It is obvious that the dimers are characterized with the values $p = 2$ and $q = 1$ or $p = 1$ and $q = 2$, dependent on the way of the orientation of their hydrocarbon chains. In each of such dimers, carboxylic groups can be oriented in the three different ways, as demonstrated in ref 22. In this and our previous papers, only

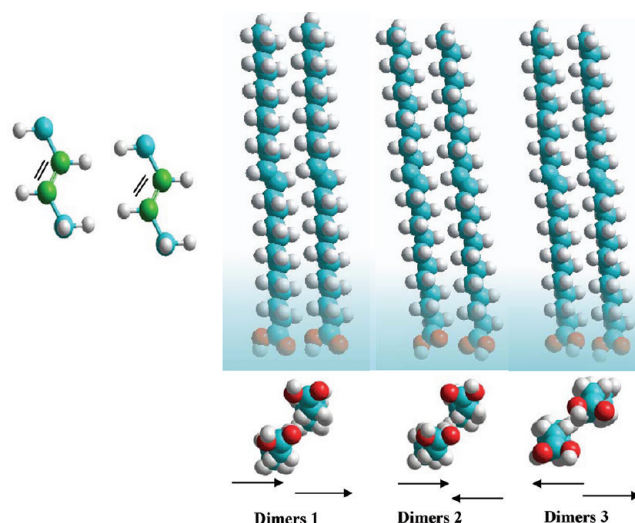
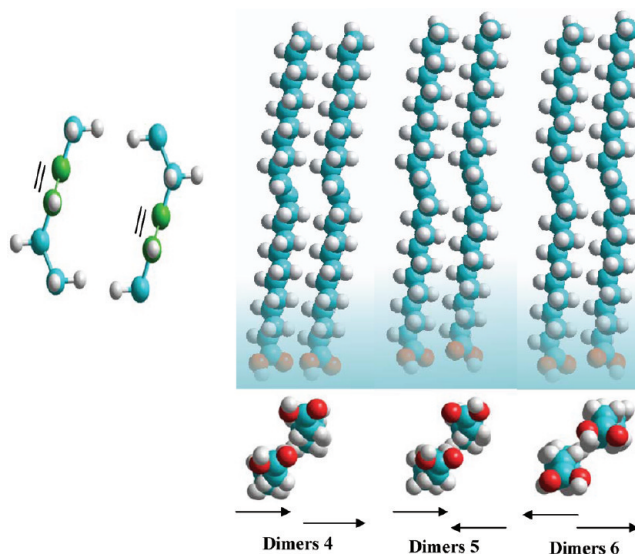
Table 2. Correlation Parameters of Dependence of Thermodynamic Parameters of Monomers' Formation on the Number of Methylene Fragments in the Hydrocarbon Chain

system	characteristics	$a \pm \Delta a$	$b \pm \Delta b$	S
$\Delta = 15, \omega = 6-11$	$\Delta H_{298, \text{mon}}^\circ$ kJ/mol	-335.17 ± 0.006	-22.68 ± 0.0003	0.001
	$S_{298, \text{mon}}^\circ$ J/mol·K	348.97 ± 11.95	30.19 ± 0.58	2.43
	$\Delta G_{298, \text{mon}}^\circ$ kJ/mol	-320.80 ± 3.56	8.93 ± 0.17	0.72
$\Delta = 14, \omega = 6-11$	$\Delta H_{298, \text{mon}}^\circ$ kJ/mol	-335.21 ± 0.015	-22.68 ± 0.0008	0.003
	$S_{298, \text{mon}}^\circ$ J/mol·K	337.51 ± 9.12	30.98 ± 0.47	1.95
	$\Delta G_{298, \text{mon}}^\circ$ kJ/mol	-315.71 ± 2.71	8.69 ± 0.14	0.58
$\Delta = 13, \omega = 6-11$	$\Delta H_{298, \text{mon}}^\circ$ kJ/mol	-335.18 ± 0.006	-22.68 ± 0.0003	0.001
	$S_{298, \text{mon}}^\circ$ J/mol·K	322.48 ± 20.36	32.06 ± 1.10	4.59
	$\Delta G_{298, \text{mon}}^\circ$ kJ/mol	-309.50 ± 6.06	8.37 ± 0.33	1.37
$\Delta = 12, \omega = 6-11$	$\Delta H_{298, \text{mon}}^\circ$ kJ/mol	-335.25 ± 0.016	-22.68 ± 0.0009	0.004
	$S_{298, \text{mon}}^\circ$ J/mol·K	339.72 ± 6.70	30.78 ± 0.38	1.59
	$\Delta G_{298, \text{mon}}^\circ$ kJ/mol	-312.99 ± 2.00	8.76 ± 0.11	0.48

**Figure 3.** Structure of the hydrocarbon chain fragment with the double bond in it: (a) *cis*-unsaturated carboxylic acids; (b) *trans*-unsaturated carboxylic acids (R and R_1 are hydrocarbon chains).**Figure 4.** Schematic illustration of the monolayer fragment of the *trans*-unsaturated carboxylic acid at the air/water interface ($p = 4$, $q = 3$).

the conformations energetically most preferable were investigated. So, for each Δ , there are six conformations of the dimer. These conformations for the dimers with $\Delta = 12$ and $\omega = 11$ with $p = 2$ and $q = 1$ or $p = 1$ and $q = 2$ are shown in Figures 5 and 6, respectively (there are fragments of the hydrocarbon chain containing the double bond at the left sides of Figures 5 and 6). The arrows represent the conditional orientation of the carboxylic group.

Enthalpy, entropy, and Gibbs' energy of dimerization for all conformations of the dimers with $n = 18-26$ were calculated.

**Figure 5.** Optimized geometric structures of the dimers of *trans*-unsaturated carboxylic acid ($p = 2$, $q = 1$).**Figure 6.** Optimized geometric structures of the dimers of *trans*-unsaturated carboxylic acid ($p = 1$, $q = 2$).

The thermodynamic parameters of clusterization (and for the particular case of dimerization) were calculated by the next formulas: $\Delta H_{298}^{\text{Cl}} = \Delta H_{m, 298}^\circ - m \cdot \Delta H_{298, \text{mon}}^\circ$, $\Delta S_{298}^{\text{Cl}} = S_{m, 298}^\circ$

$-m \cdot S_{298, \text{mon}}^{\circ}$, $\Delta G_{298}^{\text{Cl}} = \Delta H_{298}^{\text{Cl}} - T \cdot \Delta S_{298}^{\text{Cl}}$, where $\Delta H_{m, 298}^{\circ}$ is enthalpy of cluster formation, kJ/mol; $S_{m, 298}^{\circ}$ is absolute entropy of cluster, J/mol·K; T is absolute temperature, K; and m is the number of monomers in a cluster (so, for the monomer, $m = 1$, for the dimer, $m = 2$, for the tetramer, $m = 4$, and so on). The results of these calculations are demonstrated in Table 3 (as, for example, for the system with $\Delta = 14$).

Table 3. Thermodynamic Parameters of Formation and Dimerization of Dimers of *trans*-Unsaturated Carboxylic Acids ($\Delta = 14$)

n	$\Delta H_{m, 298}^{\circ}$ kJ/mol	$S_{m, 298}^{\circ}$ J/mol·K	$\Delta H_{298}^{\text{Cl}}$ kJ/mol	$\Delta S_{298}^{\text{Cl}}$ J/mol·K	$\Delta G_{298}^{\text{Cl}}$ kJ/mol
Dimers 1 ($p = 2, q = 1$)					
20	−1536.55	1392.32	−95.01	−333.18	4.28
21	−1589.72	1436.36	−102.81	−349.40	1.32
22	−1637.64	1494.60	−105.36	−347.00	−1.95
23	−1690.85	1539.37	−113.20	−369.20	−3.18
24	−1738.76	1598.81	−115.75	−363.07	−7.55
25	−1791.98	1640.70	−123.60	−392.08	−6.76
Dimers 2 ($p = 2, q = 1$)					
20	−1536.97	1394.68	−95.43	−330.83	3.15
21	−1590.13	1441.13	−103.21	−344.63	−0.51
22	−1638.05	1493.81	−105.77	−347.79	−2.13
23	−1691.24	1541.77	−113.60	−366.80	−4.29
24	−1739.17	1596.09	−116.16	−365.79	−7.15
25	−1792.37	1639.14	−123.99	−393.64	−6.69
Dimers 3 ($p = 2, q = 1$)					
20	−1535.46	1401.64	−93.92	−323.87	2.59
21	−1588.63	1447.65	−101.71	−338.10	−0.95
22	−1636.54	1499.09	−104.26	−342.52	−2.19
23	−1689.76	1546.73	−112.11	−361.84	−4.28
24	−1737.68	1598.35	−114.66	−363.53	−6.33
25	−1790.85	1648.05	−122.47	−384.73	−7.82
Dimers 4 ($p = 1, q = 2$)					
20	−1525.33	1408.29	−83.79	−317.22	10.74
21	−1578.58	1461.07	−91.66	−324.69	5.09
22	−1626.44	1507.09	−94.16	−334.52	5.53
23	−1679.68	1563.35	−102.04	−345.22	0.84
24	−1727.57	1606.95	−104.55	−354.93	1.22
25	−1780.78	1658.95	−112.40	−373.83	−1.00
Dimers 5 ($p = 1, q = 2$)					
20	−1526.68	1405.86	−85.14	−319.65	10.11
21	−1579.90	1458.47	−92.98	−327.29	4.55
22	−1627.82	1505.00	−95.54	−336.61	4.77
23	−1681.06	1565.73	−103.42	−342.84	−1.25
24	−1728.95	1606.01	−105.93	−355.87	0.11
25	−1782.14	1659.21	−113.76	−373.57	−2.43
Dimers 6 ($p = 1, q = 2$)					
20	−1525.21	1406.40	−83.67	−319.11	11.42
21	−1578.54	1458.14	−91.62	−327.62	6.01
22	−1626.32	1506.25	−94.04	−335.35	5.89
23	−1679.64	1557.39	−102.00	−351.18	2.66
24	−1727.46	1603.66	−104.45	−358.22	2.30
25	−1780.76	1655.34	−112.39	−377.45	0.09

After analysis of the values of the calculated parameters, it is obvious that the Gibbs' energies of dimerization of the dimers 1–3 (see Figure 5) are very similar, also for the dimers 4–6 (see Figure 6).

As was previously shown,^{21,22,26–31} the increment of the intermolecular CH \cdots HC interactions of the “a”-type³² in the

thermodynamic parameters of clusterization is equal for all types of substituted alkanes. However, in the case of *trans*-unsaturated carboxylic acids, there are intermolecular CH \cdots HC interactions not only between the CH₂-groups, but also intermolecular CH \cdots HC interactions between CH- and CH-group (one interaction in the dimers with an even number of Δ (see Figure 7a)) and intermolecular CH \cdots HC interactions

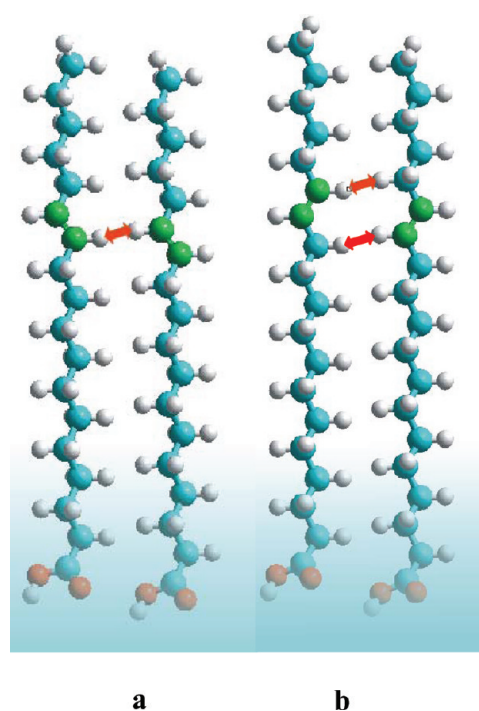


Figure 7. Optimized geometric structures of dimers: (a) *trans*-12-octadecenoic acid; (b) *trans*-13-nonadecenoic acid.

between CH- and CH₂-groups (two interactions in the dimers with an odd Δ) (see Figure 7b). These intermolecular interactions are illustrated by the red arrows in Figure 7.

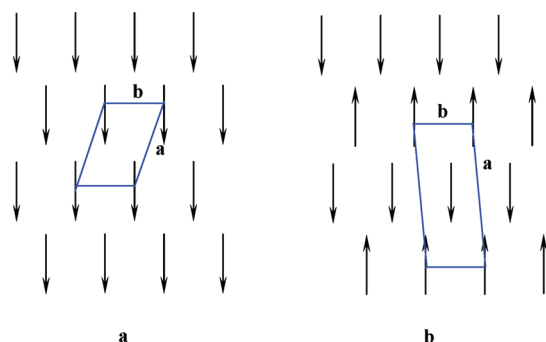
The thermodynamic characteristics of the dimer formation and dimerization coincide within the error limits for the structures with equal n and different location of the double bond in the hydrocarbon chain, as shown above for the thermodynamic parameters of monomers. For example, this fact is illustrated for dimers 3 with $\Delta = 12, 13, 14$, and 15 in Table 4. The divergence between calculated parameters for the dimers is quite higher than that of the corresponding value for the monomers. In this case, the deviation from the mean value of the thermodynamic parameters of the dimerization for dimers with the same number of CH₂-fragments in the hydrocarbon chain and different location of the double bond in it is 0.18 kJ/mol and 5.80 J/mol·K for enthalpy and the entropy, respectively.

For the correct description of the monolayer structure, it is necessary to take into account not only the mutual location of the hydrocarbon chains but also the mutual location of the functional groups. We defined three types of mutual orientation of the carboxylic groups in the dimers (see Figures 5 and 6, the orientation of the carboxylic groups is shown by the arrows). Resulting from these three variants of the location of functional groups (one is successive and two antisuccessive), one can propose two types of regular infinite monolayers with the maximum number of (most energetically preferable) intermolecular

Table 4. Comparative Analysis of Thermodynamic Parameters of Dimers' Formation and Dimerization of *trans*-Unsaturated Carboxylic Acids (for Dimers 3)

<i>n</i>	$\Delta H_{m,298}^{\circ}$ kJ/mol	$S_{m,298}^{\circ}$ J/mol·K	$\Delta H_{cl,298}^{\circ}$ kJ/mol	$\Delta S_{cl,298}^{\circ}$ J/mol·K	$\Delta G_{cl,298}^{\circ}$ kJ/mol
$\Delta = 12$					
18	−1434.35	1297.89	−83.53	−305.55	7.52
19	−1487.49	1348.99	−91.29	−318.54	3.64
20	−1535.42	1397.39	−93.88	−328.12	3.89
21	−1588.62	1458.90	−101.70	−326.86	−4.30
22	−1636.54	1494.86	−104.26	−346.75	−0.93
23	−1689.74	1554.69	−112.09	−353.88	−6.64
$\Delta = 13$					
19	−1487.87	1349.04	−91.67	−318.50	3.24
20	−1535.78	1398.97	−94.24	−326.53	3.07
21	−1588.99	1446.24	−102.07	−339.52	−0.89
22	−1636.89	1499.81	−104.60	−341.79	−2.75
23	−1690.10	1543.93	−112.46	−364.64	−3.80
24	−1738.00	1597.49	−114.99	−364.39	−6.40
$\Delta = 14$					
20	−1535.46	1401.64	−93.92	−323.87	2.59
21	−1588.63	1447.65	−101.71	−338.10	−0.95
22	−1636.54	1499.09	−104.26	−342.52	−2.19
23	−1689.76	1546.73	−112.11	−361.84	−4.28
24	−1737.68	1598.35	−114.66	−363.53	−6.33
25	−1790.85	1648.05	−122.47	−384.73	−7.82
$\Delta = 15$					
21	−1589.02	1450.52	−102.11	−335.23	−2.21
22	−1636.91	1495.49	−104.63	−346.12	−1.49
23	−1690.14	1548.64	−112.49	−359.93	−5.23
24	−1738.04	1595.19	−115.03	−366.69	−5.75
25	−1791.25	1649.57	−122.88	−383.21	−8.68
26	−1839.17	1693.99	−125.43	−389.02	−9.50

CH–HC interactions of the “a”-type. The first of them (see Figure 8a) will be formed only by dimers with successive

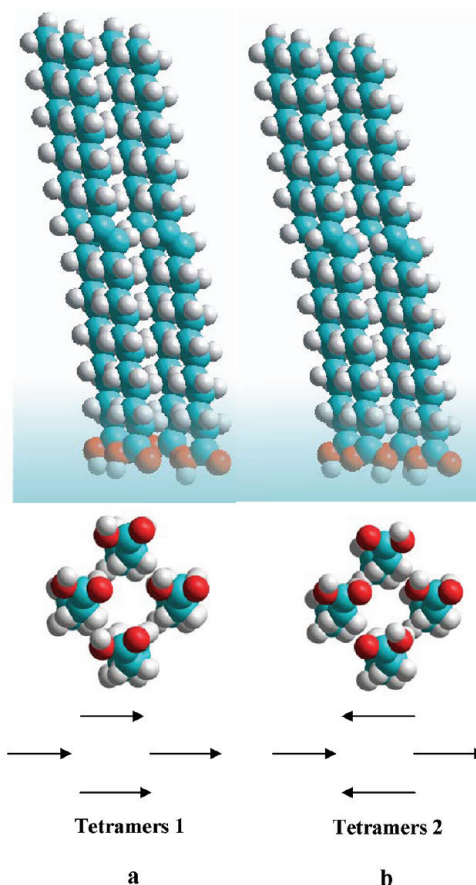
**Figure 8.** Schematic illustration of the two types of mutual orientation of the monomers of *trans*-unsaturated carboxylic acid monolayer at the interface (bottom view): (a) with successive; (b) with antisuccessive orientation of the functional groups.

orientation of the carboxylic groups (like in dimers 1 and dimers 4); the second type of monolayer (see Figure 8b) will be formed by alternation of the dimers with antisuccessive orientation of the carboxylic groups (like in dimers 2, dimers 5 and in dimers 3, dimers 6). In the case of *cis*-unsaturated carboxylic acids,²² it was demonstrated that the formation of monolayers of the second type (see Figure 8b) was

energetically more preferable than the formation of the monolayers of the first type (see Figure 8a). To draw such a conclusion for monolayers of the *trans*-unsaturated carboxylic acids, it is necessary to calculate the thermodynamic parameters of clusterization for the tetramers, which contain dimers with successive and antisuccessive orientation of the functional group, and to compare them.

The fragments marked in the blue parallelogram in Figure 8 correspond to the unit cell of the monolayer, and *a* and *b* are their sides. For the first monolayer, these values are 4.68 and 4.83 Å, respectively; and for the second one, they are 6.98 and 8.30 Å, respectively. The tilt angle between the hydrocarbon chain of the molecules of the monolayer and the water interface (*t*) is 70.97° for the first monolayer, and 64.95° and for the second one (the methodology of calculation of the *t* is described in ref 24). The parameters of the second monolayer agree quite well with the experimental values using grazing incidence X-ray diffraction (GIXD) for *trans*-13-docosenoic acid: *a* = 5.30 Å, *b* = 8.48 Å, *t* = 64.75°.²⁰

Tetramers. As mentioned above, there are two types of the regular monolayers in which intermolecular CH···CH interactions of “a”-type are realized and the tilt angle between the monolayer molecules and the water interface is 65–70°. Two tetramers are the basis of these unit cells: tetramers 1 are formed by dimers 1 and dimers 4 (see Figure 9a), and

**Figure 9.** Optimized geometric structures of the tetramers of *trans*-unsaturated carboxylic acids.

tetramers 2 are formed by dimers 2 and dimers 5 or dimers 3 and dimers 6 (see Figure 9b).

Table 5. Thermodynamic Parameters of Tetramers' Formation and Tetramerization of *trans*-Unsaturated Carboxylic Acids

<i>n</i>	$\Delta H_{m,298}^\circ$ kJ/mol	$S_{m,298}^\circ$ J/mol·K	ΔH_{298}^{Cl} kJ/mol	ΔS_{298}^{Cl} J/mol·K	ΔG_{298}^{Cl} kJ/mol	<i>n</i>	$\Delta H_{m,298}^\circ$ kJ/mol	$S_{m,298}^\circ$ J/mol·K	ΔH_{298}^{Cl} kJ/mol	ΔS_{298}^{Cl} J/mol·K	ΔG_{298}^{Cl} kJ/mol
$\Delta = 12$						$\Delta = 14$					
Tetramers 1						Tetramers 1					
18	−3016.55	2168.87	−314.93	−1038.01	−5.60	20	−3239.77	2275.03	−356.69	−1175.98	−6.25
19	−3138.70	2203.62	−346.30	−1131.45	−9.13	21	−3363.19	2344.32	−389.35	−1227.19	−23.65
20	−3236.89	2307.70	−353.81	−1143.31	−13.10	22	−3463.02	2441.06	−398.46	−1242.15	−28.30
21	−3361.86	2364.51	−388.02	−1207.00	−28.33	23	−3586.38	2509.44	−431.09	−1307.70	−41.40
22	−3460.09	2472.83	−395.53	−1210.38	−34.83	24	−3684.71	2625.24	−438.68	−1298.51	−51.72
23	−3585.10	2524.13	−429.81	−1293.01	−44.49	25	−3809.46	2670.66	−472.70	−1394.90	−57.02
Tetramers 2						Tetramers 2					
18	−3013.76	2211.28	−312.13	−995.59	−15.45	20	−3240.01	2287.35	−356.93	−1163.66	−10.16
19	−3138.54	2206.13	−346.14	−1128.94	−9.71	21	−3364.49	2334.44	−390.65	−1237.08	−22.00
20	−3236.78	2314.59	−353.71	−1136.43	−15.05	22	−3462.80	2454.39	−398.23	−1228.82	−32.04
21	−3361.74	2369.67	−387.90	−1201.85	−29.75	23	−3587.68	2497.06	−432.40	−1320.08	−39.01
22	−3459.98	2476.65	−395.42	−1206.56	−35.87	24	−3685.98	2615.70	−439.95	−1308.05	−50.15
23	−3584.99	2530.97	−429.70	−1286.17	−46.42	25	−3810.92	2665.04	−474.16	−1400.52	−56.81
$\Delta = 13$						$\Delta = 15$					
Tetramers 1						Tetramers 1					
19	−3127.60	2191.08	−335.20	−1143.99	5.71	21	−3350.06	2357.63	−376.23	−1213.89	−14.49
20	−3239.19	2267.08	−356.11	−1183.94	−3.30	22	−3459.43	2451.86	−394.87	−1231.36	−27.92
21	−3350.66	2350.63	−376.83	−1220.88	−13.01	23	−3573.32	2521.23	−418.03	−1295.91	−31.85
22	−3462.42	2434.88	−397.86	−1248.34	−25.86	24	−3682.67	2614.55	−436.64	−1309.20	−46.50
23	−3573.96	2519.13	−418.67	−1298.01	−31.86	25	−3796.61	2681.23	−459.85	−1384.33	−47.32
24	−3685.57	2597.58	−439.54	−1326.17	−44.34	26	−3905.92	2777.94	−478.44	−1388.08	−64.79
Tetramers 2						Tetramers 2					
19	−3127.61	2210.60	−335.21	−1124.47	−0.12	21	−3350.67	2353.16	−376.83	−1218.35	−13.76
20	−3239.19	2285.05	−356.12	−1165.96	−8.66	22	−3460.02	2441.94	−395.45	−1241.27	−25.56
21	−3350.81	2373.52	−376.97	−1197.99	−19.97	23	−3573.92	2513.70	−418.63	−1303.44	−30.21
22	−3462.34	2454.25	−397.77	−1228.96	−31.54	24	−3683.21	2605.61	−437.18	−1318.14	−44.37
23	−3574.01	2540.13	−418.72	−1277.02	−38.17	25	−3797.14	2674.82	−460.39	−1390.75	−45.94
24	−3685.59	2616.17	−439.56	−1307.58	−49.90	26	−3906.45	2772.56	−478.97	−1393.45	−63.72

The thermodynamic parameters of clusterization of tetramers 1 and tetramers 2 of *trans*-unsaturated carboxylic acids with $\Delta = 12$ –15 were calculated. Enthalpy of formation from the elementary substances of the tetramers and their absolute entropy were calculated as well. All results are demonstrated in Table 5.

It is seen that Gibbs' energies of tetramerization of tetramers 1 and tetramers 2 with equal Δ values are quite close to each other. Also, the thermodynamic parameters of clusterization of the tetramers with the same hydrocarbon chain length but different position of double bond are very similar. This is demonstrated by the thermodynamic parameters of clusterization for the tetramers with 21 carbon atom in the hydrocarbon chain and with the different positions of the double bond. The values of deviation of the calculated parameters from the mean value are 4.60 kJ/mol and 5.80 J/mol·K, respectively, for enthalpy and entropy of clusterization.

The correlation dependence of enthalpy and entropy of clusterization on the number of intermolecular CH \cdots HC interactions and interactions between carboxylic groups was obtained on the basis of the calculated thermodynamic parameters of clusterization of the dimers and tetramers of *trans*-unsaturated carboxylic acids. According to our previous papers,^{21,22,26–31} the number of intermolecular CH \cdots HC interactions of "a"-type in the clusters was indicated as K_a . The number of intermolecular CH \cdots HC interactions between the CH- and CH $_2$ -groups was indicated as K , and the number of intermolecular CH \cdots HC interactions between CH-groups as

K_1 . The number of intermolecular interactions between the carboxylic groups was indicated as $n_{\rightarrow\rightarrow}$, $n_{\rightarrow\leftarrow}$, $n_{\leftarrow\leftarrow}$ in dependence on their mutual orientation (see Figures 5, 6, 8, 9). As in refs 21 and 22, the increments related to the alcohol framework were used; that is, the increment of one CH \cdots HC interaction between two CH $_2$ -groups in the enthalpy of clusterization is equal to -9.20 kJ/mol, and in the entropy of clusterization is -18.40 J/mol·K.

$$\begin{aligned} \Delta H_{298}^{Cl} = & -(9.20 \pm 0.08) \cdot K_a - (10.52 \pm 0.34) \cdot K \\ & - (9.47 \pm 0.68) \cdot K_1 - (10.77 \pm 0.36) \cdot \\ & (n_{\rightarrow\rightarrow} + n_{\rightarrow\leftarrow} + n_{\leftarrow\leftarrow}) \\ R = & 0.997, S = 3.38 \text{ kJ/mol}, N = 156 \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta S_{298}^{Cl} = & -(18.40 \pm 0.60) \cdot K_a - (27.32 \pm 2.58) \cdot K \\ & - (25.90 \pm 5.16) \cdot K_1 - (130.69 \pm 2.70) \cdot \\ & (n_{\rightarrow\rightarrow} + n_{\rightarrow\leftarrow} + n_{\leftarrow\leftarrow}) \\ R = & 0.998, S = 25.37 \text{ J/mol·K}, N = 156 \end{aligned} \quad (4)$$

where R is the regression coefficient.

As seen from eqs 3 and 4, the values of the increments of the intermolecular CH \cdots HC interactions between two CH $_2$ -groups, between the CH- and CH $_2$ -groups, and between two CH- and CH-groups in the enthalpy of clusterization almost coincide

(see eq 3). Contributions to the entropy of clusterization are also very close for the CH \cdots HC interactions realized between the CH- and CH₂-groups and between two CH-groups (see eq 4). Besides, the correlation analysis shows that the increment of the intermolecular interactions between the carboxylic groups of the clusters in the thermodynamic parameters of the clusterization of *trans*-unsaturated carboxylic acids is equal.

Using the well-known equation $\Delta G_{298}^{\text{Cl}} = \Delta H_{298}^{\text{Cl}} - T \cdot \Delta S_{298}^{\text{Cl}}$, the correlation dependence of Gibbs' energy of clusterization of the *trans*-unsaturated carboxylic acids on the number of intermolecular CH \cdots HC interactions is obtained:

$$\Delta G_{298}^{\text{Cl}} = -(3.72 \pm 0.26) \cdot K_a - (2.38 \pm 1.11) \cdot K - (1.75 \pm 2.22) \cdot K_1 + (28.42 \pm 1.16) \cdot (n_{\rightarrow\rightarrow} + n_{\rightarrow\leftarrow} + n_{\leftarrow\leftarrow}) \quad (5)$$

It is seen from eq 5 that although intermolecular CH \cdots HC interactions between CH- and CH₂-groups, and between two CH-groups, result in negative increments in Gibbs' energy of clusterization, these increments are lower than the corresponding increment of the intermolecular CH \cdots HC interaction between two methylene groups. So this result shows again that, under the same conditions (temperature, pressure, interface, functional group), unsaturated fatty acids need a longer hydrocarbon chain length than do the saturated fatty acids to realize the spontaneous clusterization process and spontaneous monolayer formation.^{20,32,33}

Large and Infinite Clusters. Above, we have already defined the probable structures of the *trans*-unsaturated carboxylic acids monolayers (see Figure 8). Before calculating the thermodynamic parameters of their formation, we need to get the dependence of the enthalpy, entropy, and Gibbs' energy of clusterization on the number of intermolecular interactions of clusters of arbitrary dimension (and such clusters must have the same arrangement of the hydrocarbon chains and functional groups as the investigated ones).

To calculate the thermodynamic parameters of clusterization of cluster of arbitrary dimension, first, we need to define the wnumber of intermolecular CH \cdots HC interactions and the number of interactions between carboxylic groups in the cluster. Similar to what was done in the case of *cis*-unsaturated carboxylic acids,²² the number of intermolecular CH \cdots HC interactions in the clusters with even and odd Δ value is different, and was indexed as $K_a(\text{u})$ and $K_a(\text{g})$, respectively.

These values can be defined coming from the structure of the corresponding cluster:

$$K_a(\text{u}) = q \cdot (p - 1) \cdot \left\{ \frac{n - 3}{2} \right\} + p \cdot (q - 1) \cdot \left\{ \frac{n - 3}{2} \right\} \quad (6)$$

$$K_a(\text{g}) = q \cdot (p - 1) \cdot \left\{ \frac{n - 5}{2} \right\} + p \cdot (q - 1) \cdot \left\{ \frac{n - 4}{2} \right\} \quad (7)$$

where (u) and (g) refer to the values characteristic for the clusters with even and odd Δ values, respectively, and the braces {...} denote the integer part of a number.

The dependence of the number of intermolecular CH \cdots HC interactions between CH- and CH₂-groups, and between two

CH-groups on the cluster dimension (i.e., on the $p \cdot q$ value), can be described with eq 8:

$$K = 2q \cdot (p - 1); K_1 = q \cdot (p - 1) \quad (8)$$

The number of intermolecular interactions between carboxylic groups was calculated using eq 9:

$$n_{\rightarrow\rightarrow} = p \cdot (q - 1) + q \cdot (p - 1); n_{\rightarrow\leftarrow} = n_{\leftarrow\rightarrow} = 0.5 \cdot (p \cdot (q - 1) + q \cdot (p - 1)) \quad (9)$$

After the calculation of all intermolecular interactions in the cluster using eqs 6–9, the thermodynamic parameters of clusters of arbitrary dimension can be calculated by substituting the number of intermolecular interactions in eqs 3–5. Here, as above, p and q are the number of monomers in the cluster in p - and q -directions, respectively.

Now, to calculate the parameters of infinite clusters or monolayers, one needs to divide the number of intermolecular interactions, which were calculated according to eqs 6–9, by the number of monomers in the cluster $m = p \cdot q$ and to calculate the limit of this value where m is tending to infinity. So, we obtain

$$K_{a\infty}(\text{u})/m = 2 \cdot \left\{ \frac{n - 3}{2} \right\} \quad (10)$$

$$K_{a\infty}(\text{g})/m = n - 5 \quad (11)$$

$$K_{\infty}/m = 2; K_1_{\infty}/m = 1 \quad (12)$$

$$n_{\rightarrow\rightarrow}/m = 2; n_{\rightarrow\leftarrow}/m = n_{\leftarrow\rightarrow}/m = 1 \quad (13)$$

Substitution of the values, calculated by eqs 10–13, in eqs 3–5 leads to

$$\begin{aligned} \Delta H(\text{u})_{\infty}^{\text{Cl}}/m &= -18.40 \cdot \left\{ \frac{n - 3}{2} \right\} - 31.01, \text{ kJ/mol} \\ \Delta S(\text{u})_{\infty}^{\text{Cl}}/m &= -36.80 \cdot \left\{ \frac{n - 3}{2} \right\} - 287.28, \text{ J/mol} \cdot \text{K} \\ \Delta G(\text{u})_{\infty}^{\text{Cl}}/m &= -7.44 \cdot \left\{ \frac{n - 3}{2} \right\} + 54.59, \text{ kJ/mol} \end{aligned} \quad (14)$$

$$\begin{aligned} \Delta H(\text{g})_{\infty}^{\text{Cl}}/m &= -9.22 \cdot (n - 5) - 42.58, \text{ kJ/mol} \\ \Delta S(\text{g})_{\infty}^{\text{Cl}}/m &= -18.40 \cdot (n - 5) - 316.02, \text{ J/mol} \cdot \text{K} \\ \Delta G(\text{g})_{\infty}^{\text{Cl}}/m &= -3.72 \cdot (n - 5) + 51.59, \text{ kJ/mol} \end{aligned} \quad (15)$$

Equation 14 allows one to calculate the thermodynamic parameters of clusterization of monolayers of *trans*-unsaturated carboxylic acids with even Δ , and eq 15 with odd Δ . The increments in the thermodynamic parameters of interactions between carboxylic groups for the three types of their mutual orientation (see Figures 5 and 6) coincide with the error limit (see eqs 3–5). That is why the thermodynamic parameters of clusterization of monolayers with successive and antisuccessive orientation between the functional groups (see Figure 9) are equal.

Consider now infinite linear clusters. The number of intermolecular CH \cdots HC interactions is $\{(n - 3)/2\}$ for such clusters with an even Δ value and $\{(n - 5)/2\}$ for clusters with an odd Δ value. The increments of the intermolecular

interactions between the methylene groups in enthalpy, entropy, and Gibbs' energy of clusterization are: -9.20 kJ/mol, -18.40 J/mol·K, and -3.72 kJ/mol, respectively. The increments from the interactions between carboxylic groups per one monomer in the cluster to the thermodynamic parameters of clusterization are illustrated in Table 6.

Table 6. Increments from the Interactions of Carboxylic Groups in the Thermodynamic Parameters of Clusterization of Linear Clusters of *trans*-Unsaturated Carboxylic Acids

Δ		$\Delta H_{\infty}^{\text{Cl}}/m$, kJ/mol	$\Delta S_{\infty}^{\text{Cl}}/m$, J/mol·K	$\Delta G_{\infty}^{\text{Cl}}/m$, kJ/mol
even	$q = 1, p = \infty$	-20.24	-156.59	26.42
	$q = \infty, p = 1$	-10.77	-130.69	28.42
odd	$q = 1, p = \infty$	-31.81	-185.33	23.42
	$q = \infty, p = 1$	-10.77	-130.69	28.42

The dependencies of enthalpy, entropy, and Gibbs' energy of clusterization per one monomer of the cluster on ω can be obtained taking into account eqs 14,15 and the coefficients from Table 6. The dependence of $\Delta H_{\infty}^{\text{Cl}}/m$ and $\Delta G_{\infty}^{\text{Cl}}/m$ on the ω is presented for acids with $\Delta = 12$ in Figures 10a and 11a

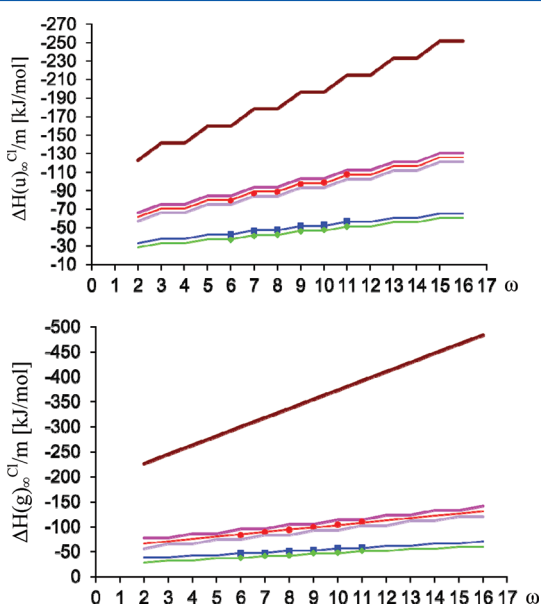


Figure 10. Dependence of the clusterization enthalpy of *trans*-unsaturated carboxylic acids per one monomer of the cluster on ω for structures with even (a) and odd (b) Δ : 1, $p = \infty, q = \infty$; 2, $p = \infty, q = 1$; 3, $p = 2, q = 2$; 4, $p = 1, q = \infty$; 5, $p = 2, q = 1$; 6, $p = 2, q = 1$.

and for acids with $\Delta = 13$ in Figures 10b and 11b. The results of the direct calculation are presented by points, and those of the correlation analysis are presented by lines.

Figure 11 illustrates the fact that spontaneous clusterization of *trans*-unsaturated carboxylic acids on the water surface under standard conditions is practicable when the hydrocarbon chain consists of more than 16 carbon atoms ($\omega > 4$) for the acids with even Δ (see Figure 11a) and when the hydrocarbon chain consists of more than 18 carbon atoms ($\omega > 5$) for the acids with odd Δ (see Figure 11b). These results correspond to the available experimental data.^{9–12,20} It is also seen in Figure 11b that the dependencies of $\Delta G_{\infty}^{\text{Cl}}/m$ on ω for the clusters with $p = 2, q = 1$; $p = 2, q = 2$; $p = \infty, q = 1$; and $p = \infty, q = \infty$ have

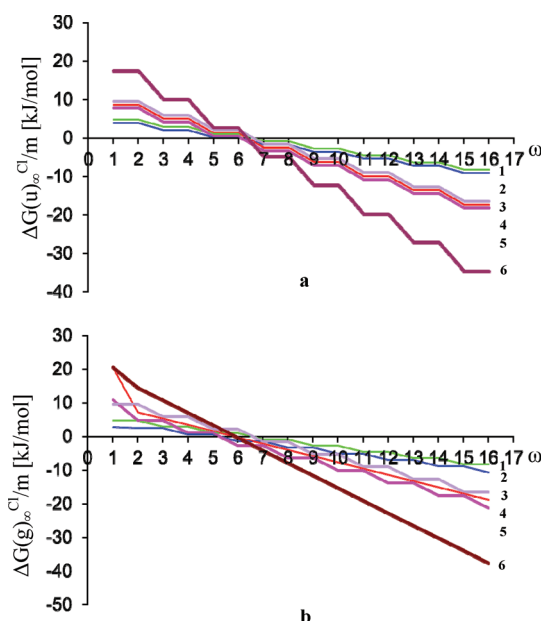


Figure 11. Dependence of the Gibbs' energy of clusterization of *trans*-unsaturated carboxylic acids per one monomer of the cluster on ω for structures with even (a) and odd (b) Δ : 1, $p = 1, q = 2$; 2, $p = 2, q = 1$; 3, $p = 1, q = \infty$; 4, $p = 2, q = 2$; 5, $p = \infty, q = 1$; 6, $p = \infty, q = \infty$.

sharp upper extreme values when $\omega = 1$. This can be explained by the position of the double bond. In the case that it is near the last carbon atom of the hydrocarbon chain so there is one interaction less between CH- and CH₂-groups, that is, there is one such interaction, not two, in dimers ($p = 2, q = 1$), two interactions, not four, in tetramers ($p = 2, q = 2$), and so on. For the calculation of the number of interactions in such clusters ($\omega = 1$), the value of the absolute term of correlation should be replaced with -32.06 kJ/mol, -288.70 J/mol·K, and 53.97 kJ/mol for enthalpy, entropy, and Gibbs' energy of clusterization, respectively, in eq 15.

CONCLUSIONS

In the framework of a quantum-chemical approach, the thermodynamic parameters of monomers of *trans*-unsaturated carboxylic acids with 18–26 carbon atoms in the alkyl chain and different positions of the double bond were calculated. It was shown that, at the same hydrocarbon chain length, the position of the double bond in the chain does not influence the values of the calculated parameters. This is in agreement with the results obtained for the monomers of *cis*-unsaturated carboxylic acids.³⁰

Six conformations of dimers were defined, and all structures were optimized with the quantum-chemical Mopac2000 complex, and their enthalpy, entropy, and Gibbs' energy of dimerization were calculated. Two regular structures of tetramers were constructed using optimized geometrical structures of the dimers. After their optimization, the thermodynamic parameters of tetramerization were calculated. The results of these calculations indicate that the position of the double bond in the hydrocarbon chain does not influence essentially the values of the thermodynamic parameters of clusterization except for the case in which the double bond is in the ω -position (at the end of the alkyl chain). The additive scheme was constructed using the calculated thermodynamic parameters of clusterization. This scheme provides the opportunity to calculate thermodynamic

parameters (enthalpy, entropy, and Gibbs' energy) of clusterization of clusters of any dimension, including the monolayer, without using any quantum-chemical software.

The quantum-chemical calculations have shown that spontaneous clusterization of *trans*-unsaturated carboxylic acid is practicable under standard conditions when the hydrocarbon chain consists of more than 16 carbon atoms for acids with even Δ , and when the hydrocarbon chain consists of more than 18 carbon atoms for acids with odd Δ . The structural parameters of the unit cell of the monolayer of *trans*-unsaturated carboxylic acids determined as $a = 6.98 \text{ \AA}$, $b = 8.30 \text{ \AA}$, and the tilt angle between the molecules of the monolayer and the air/water interface of 64.95° correspond with the experimental data.

Generally, the presence of a double bond in the hydrocarbon chain of the amphiphiles shifts the spontaneous clusterization threshold to longer alkyl chain lengths in comparison with the saturated carboxylic acids. This fact corresponds to the experimental data.^{1,2,9–12,20} Correspondingly, the increment from intermolecular $\text{CH}\cdots\text{HC}$ interaction between CH-groups in the Gibbs' energy of clusterization is smaller by absolute value than the increment from the intermolecular $\text{CH}\cdots\text{HC}$ interaction of the methylene fragments. That means that the more unsaturated bonds are in the amphiphile, the higher is its Gibbs' energy of clusterization, and, therefore, a longer hydrocarbon chain is needed to start spontaneous monolayer formation.³⁴

In comparison with the *cis*-unsaturated carboxylic acids, the *trans*-unsaturated acids start to form spontaneous clusters, and thus monolayers with shorter hydrocarbon chains of 16–18 carbon atoms, whereas the corresponding threshold for *cis*-unsaturated carboxylic acids was found for 18–19 carbon atoms in the alkyl chain. These data are in agreement with experimental data.²⁰

AUTHOR INFORMATION

Corresponding Author

*Phone: 49-(0)331-567-9258. E-mail: dieter.vollhardt@mpikg.mpg.de.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Birdi, K. S. *Self-Assembly Monolayer Structures of Lipids and Macromolecules at Interfaces*; Kluwer Academic/Plenum Publishers: New York, 1999; Chapter 4.
- (2) Hann, R. A. In *Langmuir–Blodgett Films*; Roberts, G., Ed.; Plenum Press: New York, 1990; Chapter 2.
- (3) Hughes, A. H.; Rideal, E. K. *Proc. R. Soc. London* **1933**, A140, 253.
- (4) Marsden, J.; Rideal, E. K. *J. Chem. Soc.* **1938**, 1163.
- (5) Schneider, V. L.; Holman, R. T.; Burr, G. O. *J. Phys. Chem.* **1949**, 53, 1016.
- (6) Glazer, J.; Goddard, E. D. *J. Chem. Soc.* **1950**, 3406.
- (7) Goddard, E. D.; Alexander, A. E. *Biochem. J.* **1951**, 47, 331.
- (8) Welles, H. L.; Zografi, G.; Scrimgeour, C. M.; Gunstone, F. D. In *Monolayers*; Goddard, E. D., Ed.; Advances in Chemistry Series 144; American Chemical Society: Washington, DC, 1975; Chapter 10.
- (9) O'Brien, K. C.; Rogers, C. E.; Lando, J. B. *Thin Solid Films* **1983**, 102, 131.
- (10) Bishop, D. G.; Kenrick, J. R.; Bayston, J. H.; Macpherson, A. S.; Johns, S. R. *Biochim. Biophys. Acta* **1980**, 602, 248.
- (11) Tomoasia-Cotisel, M.; Zsako, J.; Mocanu, A.; Lupea, M.; Chifu, E. *J. Colloid Interface Sci.* **1987**, 117, 464.
- (12) Peltonen, J. P.; Rosenholm, J. B. *Thin Solid Films* **1989**, 179, 543.
- (13) Sato, K.; Yoshimoto, N.; Suzuki, M.; Kobayashi, M.; Kaneko, F. *J. Phys. Chem.* **1990**, 94, 3180.
- (14) Agrowal, M. L.; Neuman, R. D. *J. Colloid Interface Sci.* **1990**, 121, 355.
- (15) Kaneko, F.; Kobayashi, M.; Kitagawa, Y.; Matsuura, Y.; Sato, K.; Suzuki, M. *Acta Crystallogr.* **1992**, C48, 1060.
- (16) Kaneko, F.; Yamazaki, K.; Kobayashi, M.; Kitagawa, Y.; Matsuura, Y.; Sato, K.; Suzuki, M. *Acta Crystallogr.* **1993**, C49, 1232.
- (17) Hiramatsu, N.; Inoue, T.; Sato, T.; Suzuki, M.; Sato, K. *Chem. Phys. Lipids* **1992**, 61, 283.
- (18) Kaneko, F.; Yamazaki, K.; Kobayashi, M.; Kitagawa, Y.; Matsuura, Y.; Sato, K.; Suzuki, M. *J. Phys. Chem.* **1996**, 100, 9138.
- (19) Iimura, K.; Yamauchi, Y.; Tsuchiya, Y.; Kato, T. *Langmuir* **2001**, 17, 4602.
- (20) Vollhardt, D. *J. Phys. Chem. C* **2007**, 111, 6805.
- (21) Vysotsky, Yu. B.; Muratov, D. V.; Boldyreva, F. L.; Fainerman, V. B.; Vollhardt, D.; Miller, R. *J. Phys. Chem. B* **2006**, 110, 4717.
- (22) Vysotsky, Yu. B.; Belyaeva, E. A.; Fainerman, V. B.; Vollhardt, D.; Aksenenko, E. V.; Miller, R. *J. Phys. Chem. B* **2009**, 113, 4347.
- (23) Stewart, J. J. P. *MOPAC 2000 MANUAL*; Fujitsu Ltd.: Tokyo, Japan, 1999.
- (24) Kaganer, V. M.; Möhwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, 71, 779.
- (25) Vysotsky, Yu. B.; Fomina, E. S.; Belyaeva, E. A.; Aksenenko, E. V.; Vollhardt, D.; Miller, R. *J. Phys. Chem. B* **2011**, 115, 2264.
- (26) Vysotsky, Yu. B.; Bryantsev, V. S.; Fainerman, V. B.; Vollhardt, D. *J. Phys. Chem. B* **2002**, 106, 11285.
- (27) Vysotsky, Yu. B.; Bryantsev, V. S.; Fainerman, V. B.; Vollhardt, D.; Miller, R. *J. Phys. Chem. B* **2002**, 106, 121.
- (28) Vysotsky, Yu. B.; Belyaeva, E. A.; Fainerman, V. B.; Vollhardt, D.; Miller, R. *J. Phys. Chem. C* **2007**, 111, 5374.
- (29) Vysotsky, Yu. B.; Belyaeva, E. A.; Fainerman, V. B.; Aksenenko, E. V.; Vollhardt, D.; Miller, R. *J. Phys. Chem. C* **2007**, 111, 15342.
- (30) Vysotsky, Yu. B.; Fomina, E. S.; Belyaeva, E. A.; Fainerman, V. B.; Aksenenko, E. V.; Vollhardt, D.; Miller, R. *J. Phys. Chem. B* **2009**, 113, 16557.
- (31) Vysotsky, Yu. B.; Belyaeva, E. A.; Vollhardt, D.; Aksenenko, E. V.; Miller, R. *Colloid Interface Sci.* **2008**, 326, 339.
- (32) Feng, S.; MacDonald, R. C. *Biol. J.* **1995**, 69, 460.
- (33) Peltonen, L.; Hirvonen, J.; Yliruusi, J. *J. Colloid Interface Sci.* **2001**, 239, 134.
- (34) Vysotsky, Yu. B.; Fomina, E. S.; Belyaeva, E. A.; Aksenenko, E. V.; Vollhardt, D.; Miller, R. *Phys. Chem. Chem. Phys.* **2011**, 13, 20927–20932.