

spectra - clearly separated signals with different chemical shifts, corresponding to fluorine atoms in different chemical environments.

Value of integrated intensities signal gives a reason to expect that in case of strontium fluoride, in which the Sr-F bond is more ionic than in case of other fluorinating agents, fluoride ion is a part of copper based structure fragments. The fact of chemical shift to the strong field in the spectra of samples indicates the increasing shielding of the ^{19}F nuclei, accompanied by the occurrence of fluoride ions in the extended fragments in the structure as possible bridges between copper atoms and increase symmetry close to them.

Chemical shift at 140 ppm corresponds to fluorine atoms that are associated with atoms of copper. This fact shows that, the fluorine atoms are situated in chains CuO_2 , and the substitution may significantly affect the electrophysical parameters of the Bi-containing ceramics.

Key words: cuprates, superconductors, synthesis, heterovalent substitution, fluoride ion, the properties.

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ON THE CALCULATION OF THE TILT ANGLE OF SUBSTITUTED ALKANES WITH RESPECT TO THE AIR/WATER INTERFACE IN FRAMEWORK OF PM3 APPROXIMATION

In the framework of quantum chemical semiempiric PM3 method the procedure for estimation of the geometric parameters of 2D unit cells of substituted alkane monolayers at the air/water interface is proposed. Its application is illustrated on the examples of four surfactant classes with different size of their hydrophilic parts. It was shown that inclination of surfactant molecules with respect to the interface is determined by orientation and volume of the hydrophilic parts of molecules and $\text{CH}\cdots\text{HC}$ interactions realized between their hydrophobic chains.

Key words: surfactant, tilt angle, unit cell, $\text{CH}\cdots\text{HC}$ interactions, Gibbs' energy of clusterization, hydrophilic part of molecule, molecular orientation, interface.

Introduction

Development of the modern instrumental research methods enables investigation the structure of Langmuir monolayers. Structural peculiarities of surfactant monolayers are determined mainly by conformational flexibility, length, structure of alkyl chain of the surfactant molecule and type and location of the functional groups in the molecule as well [1]. Commonly surfactant molecules orientate almost up-right with respect to the interface. In our previous papers [2-10] in was shown on the examples of alcohols, thioalcohols, amines, nitriles, and carboxylic acids that thermodynamic parameters of clusterization for these monolayers with tilt

angle of molecular chains equal to $\sim 9\text{-}10^\circ$ with respect to the normal to the air/water interface well agree with experimental data [11-15].

However, it should be noted that other molecular orientations with respect to the interface, besides up-right, are possible. Thus, GIXD analysis reveals that α -amino acid molecules orientate with the tilt angle of 36° with respect to the normal to the air/water interface [16]. Authors [17], who investigated α -amino acid derivatives, revealed that these surfactants could locate with the different tilt angles in the range of $18^\circ\text{-}40^\circ$ up to 49° for N-acylsubstituted α -amino acids [18].

Mentioned facts stipulate the necessity to summarize used previously [2-10, 19, 20] stages for determining the orientation of the surfactant molecules with respect to the interface into the orderly built procedure. This is the aim of the present work. This procedure enables one to estimate the geometric parameters of 2D unit cells of surfactant monolayers at the air/water interface and tilt angle of molecular chains with respect to the interface in particular. The application of this procedure is illustrated on the example of several surfactant classes with different types of functional groups of different volume of their 'heads'.

Description of exploited procedure and calculation method

Estimation of the geometric parameters of the 2D unit cells of substituted alkanes is based on the calculation of thermodynamic parameters of clusterization for small surfactant aggregates (dimers and tetramers). It is carried out according to the next procedure:

1. The conformational analysis that include the plotting of the potential energy surface of monomer molecule depending on the values of the dihedral angles between the functional groups of hydrophilic 'head' of molecule and hydrophobic chain; calculation of the thermodynamic parameters of formation of found conformers;

2. Constructing of two types of dimers with the 'a' $\text{CH}\cdots\text{HC}$ interactions type on the base of found conformers. These dimers are the base units of the 2D cluster in p and q directions at the interface;

3. Determination of the tilt angles δ and φ of the molecular chains of the surfactant with respect to the normal to the p and q directions respectively. Applying the parallel shift to one molecule with respect to the other one in the dimers, the dependence of the Gibbs' energy of dimerization on the δ and φ angles should be tabulated. Then, the values of δ and φ angles that respond to the minimum of the Gibbs' energy of dimerization of corresponding dimers should be used in the further calculations;

4. Calculation of the general tilt angle t of the molecular chains of the surfactant with respect to the normal to the interface;

5. Constructing of the 2D unit cell (tetramers or larger clusters) on the base of the dimer structures in order to estimate necessary geometric parameters.

Calculations of structural and energetical parameters of aggregates for substituted alkanes at the air/water interface were carried out using quantum chemical software package MOPAC 2000 in the framework of the semiempirical PM3 approximation [21]. This method is parameterized with respect to the heats of formation [22, 23]. It should be noted that despite some restrictions of this method (overestimation of $\text{CH}\cdots\text{HC}$ interaction force between hydrophobic chains of amphiphilic molecules) [24], only the PM3 method describes sufficiently the experimental data concerning the monolayer formation of different classes of surfactants, as shown in our previous works [2-10, 19, 20].

Results and discussion

Application of described procedure is illustrated on the example of aliphatic alcohols. Conformational analysis of the surfactant monomers was carried out previously [2]. Here we regard the surfactant aggregates built on the base of the most energetically preferred monomer structures found [2, 19, 20, 25]. Note that the quantum chemical calculation yields the tilt angles of the molecule with respect to the axes p and q of the unit cell, rather than the tilt angle of the molecules with respect to the interface. Figure 1 illustrates schematically the orientation of the alcohol molecule axis (CO) with respect to the interface plane (pOq). Here the CO_3 segment is perpendicular to the interface pOq , and the CO_1 and CO_2 segments are perpendicular to the axes p and q , respectively. In Figure 1, t denotes the tilt angle of the molecule with respect to the normal to the interface, δ and φ are the tilt angles of the molecule with respect to the normal within the O_1OC plane and the O_2OC plane, respectively.

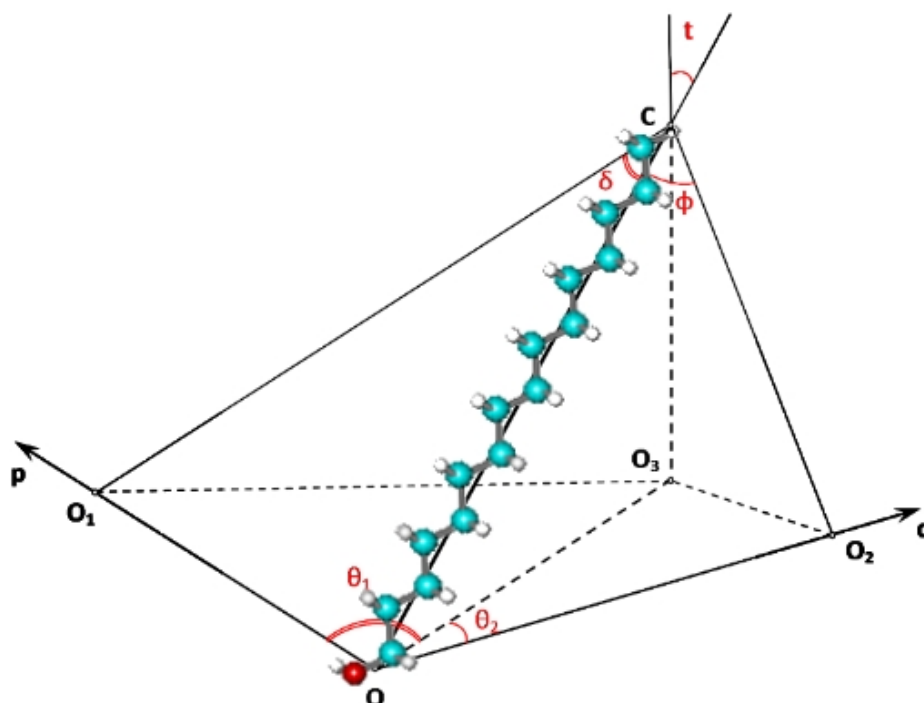


Fig. 1. Orientation of alcohol molecule with respect to the air/water interface

It follows from the theorem of the three perpendiculars that O_3O_2O and O_3O_1O are the right angles. Then, according to the right-angle triangles O_3CO , O_3CO_1 , O_3CO_2 , O_1CO , O_2CO , O_1OO_3 and O_2OO_3 (here the first listed vertex of the triangle corresponds to the right angle) it is straightforward to show that:

$$\frac{\sin \varphi}{\cos \theta_2} = \sin t, \quad \frac{\sin \delta}{\cos \theta_1} = \sin t, \quad \theta_1 + \theta_2 = \theta. \quad (1)$$

The solution of the set (1) with respect to θ_1 , θ_2 and t is:

$$\theta_1 = \arctg\left(\frac{\sin \varphi}{\sin \delta \cdot \sin \theta} - \text{ctg} \theta\right), \quad \theta_2 = \theta - \theta_1, \quad t = \arcsin\left(\frac{\sin \delta}{\cos \theta_1}\right). \quad (2)$$

To determine the tilt angles of surfactant 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 \cdots HC interaction type (marked in Fig. 2 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.

Dependencies of the Gibbs' energy of alcohol dimerization for the structures of 'parallel' and 'serial' dimers on the values of the tilt angles of the molecules with respect to the normals to p- and q-directions of the monolayer spread are listed in Table 1. These data shows that minimal value of the Gibbs' energy of alcohol dimerization correspond to the dimer structures with the next values of φ angle: 9.8°, 10.2° and 20.6°. Additional optimization of these dimers reveals the only existence of one stable structure with $\varphi=9.8^\circ$. Other 'parallel' dimers with φ equal to 36.3° and 52.6° corresponds to the dimers which have less by one and two CH \cdots HC interaction than in dimer of dodecanol shown in Fig. 2, a respectively. The loss of this CH \cdots HC interaction causes increase of dimerization Gibbs' energy and a lower preference of such structures in comparison with those having the maximal number of CH \cdots HC interaction.

Table 1. Dependence of the dimerization Gibbs' energy of substituted alkanes built on the basis of monomers with 12 carbon atoms in their chain on the δ and φ values

Molecular tilt angle, φ , °	$\Delta H_{298}^{\text{dim}}$, kJ/mol	$\Delta S_{298}^{\text{dim}}$, J/(mol·K)	$\Delta G_{298}^{\text{dim}}$, kJ/mol	Molecular tilt angle, δ , °	$\Delta H_{298}^{\text{dim}}$, kJ/mol	$\Delta S_{298}^{\text{dim}}$, J/(mol·K)	$\Delta G_{298}^{\text{dim}}$, kJ/mol
Alcohols							
52,6	-43,82	-164,22	5,11	52,6	-42,84	-163,75	5,96
36,3	-54,67	-192,76	2,77	38,9	-52,55	-185,70	2,79
20,6	-62,66	-198,18	-3,60	36,3	-52,54	-182,99	1,99
10,2	-61,26	-202,08	-1,04	20,6	-60,06	-191,67	-2,94
9,8	-62,97	-204,38	-2,06	10,4	-60,09	-193,01	-2,57
α -Hydroxy acids							
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
N-acylalanine							
55,3	-49,93	-213,29	13,63	62,7	-33,20	-186,06	22,25
52,7	-51,70	-223,55	14,92	51,6	-49,97	-238,17	21,01
50,8	-53,36	-280,19	30,14	35,5	-63,55	-269,94	16,89
50,0	-65,95	-290,15	20,52	21,3	-63,45	-295,36	24,56
42,8	-66,54	-261,32	11,33	10,6	-71,17	-296,32	17,13

For alcohol dimers with 'serial' orientation of the 'heads' minimal values of the dimerization Gibbs' energy correspond to the values of δ angle equal to 10.4° and 20.6°. After additional optimization of these structures one minimum was observed. It corresponds to the structure with $\delta=10.4^\circ$. Other dimer structures listed in the Table 1 with $\delta=38.9^\circ$ and 52.6°, as in the case of the 'parallel' dimers described above, have less by one and two CH \cdots HC interaction than the 'serial' dimer of dodecanol with $\delta=10.4^\circ$ correspondingly (see Fig. 2, b).

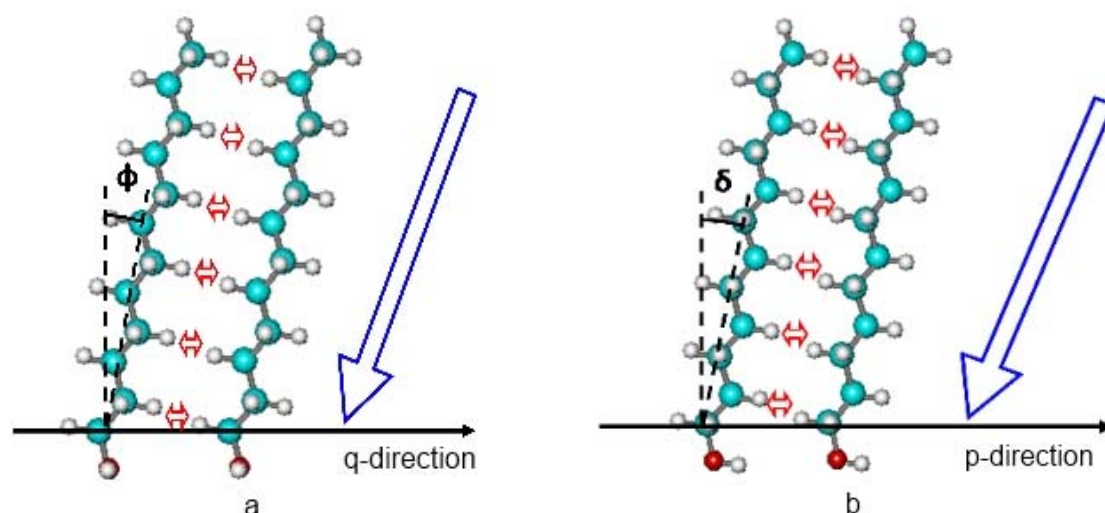


Fig. 2. Determination of the molecular tilt angle with respect to the normal to the monolayer directions

Using described dimers tetramer was built. On the basis of its optimized structure it is possible to get the value of the θ angle realized between p and q directions of the monolayer unit cell and its dimensions. Then according to the eqs.(2) one can easily obtain the value of the general tilt angle t of the surfactants with respect to the normal to the interface.

Described procedure was applied also to α -hydroxy acids, homo- and heterochiral α -amino acids and N -acylsubstituted alanine. Obtained geometrical parameters for mentioned surfactants of the unit cells are listed in Table 2. Here a and b are the dimensions of corresponding tetramers as the unit cells, θ is the angle between them and t is tilt angle of molecular chain with respect to the normal to the air/water interface.

Table 2. Geometric parameters of the 2D unit cells of substituted alkanes

Surfactant	Unit cell parameters							
	a, Å		b, Å		θ , °		t, °	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Alcohol [15]	4.49	5.0	4.29	7.5	94	-	14	9
α -Hydroxy acids [26] homochiral	4.77	4.79*	4.23	4.89*	89	123*	21	21.5*
α -Amino acids [16] homochiral heterochiral	4.71	4.91	5.67	5.25	103	112	31	36
	4.62	4.80	10.70	9.67	90	90	35	36
N -acylalanine [18]	4.53	4.91	6.06	5.64	100	105	54	46

* the GIXD results correspond to the monolayers of 11-hydroxyoctadecanoic acid

From the data listed in the Table 2 one can see the more voluminous 'head' surfactant has the less tilt angle with respect to the interface corresponds to the molecules in regarded monolayer. This statement correlate well with available experimental data listed in the Table 3. These data reveal that nearly up-right orientation with respect to air/water interface is typical for alcohols and carboxylic acids. While surfactants possessing more voluminous hydrophilic part orientate with larger values of tilt angles. Authors [27], who investigated the structure of chiral surfactants, claimed that the value of the tilt angle of molecules in the monolayer depended mainly on the size of functional groups located near the chiral center. It could vary in the range from 15° to 45° . Some authors [28, 29] consider that inclined

position with respect to the interface is typical of such surfactants which have bigger cross-sectional area of the hydrophilic part than the cross-sectional area of their hydrophobic chain. From our point of view location of surfactant molecules with respect to the interface is determined by orientation and volume of hydrophilic parts of molecules and CH \cdots HC interactions realized between their hydrophobic chains [30].

Table 3. Geometric parameters of the unit cells of surfactant monolayers at the air/water interface

System	T, °C	a, Å	b, Å	θ , °	t, °
C _n H _{2n+1} OH (n=23, 30, 31) [15]	5	5,0	7,5	90	9
C ₁₉ H ₃₉ O ₂ (CH ₂) _n OH (n=9, 10) [15]	5	5,7	7,5	90	29
C _n H _{2n+1} CONH ₂ (n=18) [31]	5-12	4,5	8,5	90	18
C _n H _{2n+1} COOH (n=20) [32]	5	5,0	7,5	90	15
S-C _n H _{2n+1} CHNH ₂ COOH (n=16) [16]	5	4,9	5,25	112	36
RS-C _n H _{2n+1} CHNH ₂ COOH (n=16) [16]	5	4,8	9,67	90	37
N-hexadecylalanine (R) [18]	20	4,9	5,7	105	46
N-hexadecylalanine (RS) [18]	20	4,9	5,6	105	45
N-hexadecylserine methyl ether (S) [18]	20	4,9	5,9	105	46
N-hexadecylserine methyl ether (RS) [18]	18	4,9	5,9	105	47
N-hexadecylasparagine acid (S) [18]	20	5,0	5,2	116	31
N-hexadecylasparagine acid (RS) [18]	20	5,0	5,2	116	30

Conclusion

In the present work the procedure for estimation of the geometric parameters of the 2D unit cells of surfactant monolayers at the air/water interface is summarized and described. It includes formation of the small clusters (dimers and tetramers) on the basis of the most energetically preferred monomer conformation of regarded surfactant. Construction of dimers allows obtaining the tilt angles δ and φ of the molecular chains of the surfactant with respect to the normals to the directions of the monolayer propagation using dimerization Gibbs' energy as a criterion. While construction of the tetramers enables one to get the value of the angle θ between the directions monolayer spread and the unit cell dimensions. Using mentioned parameters it is possible to obtain the general tilt angle of the surfactant chains with respect to the normal to the interface.

Implementation of described procedure shows, that the structural parameters of the unit cell of the 2D clusters of different surfactant classes are determined by the 'a' type of the CH \cdots HC interactions [2], whereas the tilt angle of the molecules in monolayer with respect to the interface depends on the volume and the structure of the functional groups involved in the hydrophilic part of the molecule. The more voluminous 'head' part is the larger inclination of the molecular chains with respect to the normal to the interface is.

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Е.С. Фомина К ВОПРОСУ ОБ ОПРЕДЕЛЕНИИ УГЛА НАКЛОНА ЗАМЕЩЕННЫХ АЛКАНОВ ОТНОСИТЕЛЬНО МЕЖФАЗНОЙ ПОВЕРХНОСТИ ВОДА/ВОЗДУХ В ПРИБЛИЖЕНИИ МЕТОДА РМЗ

В рамках квантово-химического полуэмпирического метода РМЗ предложена процедура оценки геометрических параметров 2D элементарных ячеек монослоев ПАВ на межфазной поверхности вода/воздух. Применение данной процедуры проиллюстрировано на примере четырех классов дифильных соединений с различным размером гидрофильных частей. Показано, что наклон молекул ПАВ относительно межфазной поверхности определяется ориентацией и объемом их гидрофильных частей, а также $\text{CH}\cdots\text{HC}$ -взаимодействиями, реализующимися между их гидрофобными цепями.

Ключевые слова: ПАВ, угол наклона, элементарная ячейка, $\text{CH}\cdots\text{HC}$ -взаимодействия, энергия Гиббса кластеризации, гидрофильная часть молекулы, ориентирование молекулы, межфазная поверхность.

О.С. Фоміна ЩОДО ПИТАННЯ ПРО ВИЗНАЧЕННЯ КУТА НАХИЛУ ЗАМІЩЕНИХ АЛКАНІВ ВІДНОСНО МІЖФАЗНОЇ ПОВЕРХНІ ВОДА/ПОВІТРЯ У НАБЛИЖЕННІ МЕТОДА РМЗ

У рамках квантово-хімічного напівемпіричного метода РМЗ запропонована процедура оцінки геометричних параметрів 2D елементарних комірок моношарів ПАВ на міжфазній поверхні вода/повітря. Застосування даної процедури проілюстровано на прикладі чотирьох класів дифільних сполук з різним розміром гідрофільних частей. Показано, що нахил молекул ПАВ відносно міжфазної поверхні визначається орієнтацією та об'ємом їх гідрофільних частей, а також $\text{CH}\cdots\text{HC}$ -взаємодіями, реалізованими між їх гідрофобними ланцюгами.

Ключові слова: ПАВ, кут нахилу, елементарна комірка, $\text{CH}\cdots\text{HC}$ -взаємодії, енергія Гіббса кластеризації, гідрофільна частина молекули, орієнтування молекули, міжфазна поверхня.

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